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REDUCTION OF NITRO COMPOUNDS USING *3d*-NON-NOBLE METAL CATALYSTS

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Dedicated to Dr. Michelangelo Scalone, F. Hoffmann-La Roche, for his important contributions to catalysis.

ABSTRACT. The reduction of nitro compounds to the corresponding amines is one of the most utilized catalytic processes in the fine and bulk chemical industry. The latest development of catalysts with cheap metals like Fe, Co, Ni and Cu has led to their tremendous achievements over the last years prompting to their greater application as "standard" catalysts. In this review we will comprehensively discuss the use of homogeneous and heterogeneous catalysts based on non-noble *3d*-metals for the reduction of nitro compounds using various reductants. The different systems will be revised considering both the catalytic performances and synthetic aspects highlighting also their advantages and disadvantages.

Contents

1. Introduction: setting the scene

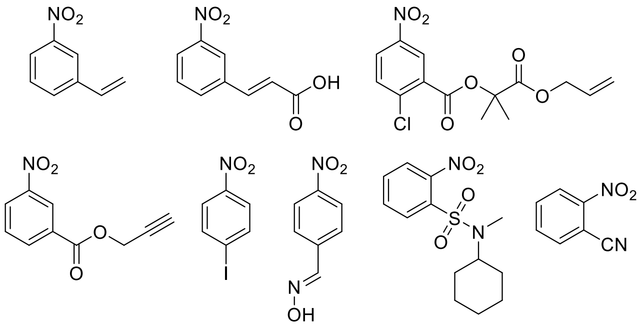
Amines, and specifically aniline and its derivatives, represent (and surely will hold in the future) a huge market portion in the organic chemical industry.[1,2] Aniline was isolated for the first time as product of the dry distillation of indigo by the German chemist Otto Unverdorben almost 200 years ago (1826). Fifteen years later, the Russian chemist Nikolay N. Zinin prepared for the first time aniline by reduction of nitrobenzene using sodium sulfides as the stoichiometric reductants (this transformation is generally known as Zinin reaction).[3] Few years later (1851), Piria reported a two-step procedure for the synthesis of anilines from nitroarenes: the nitro group is converted in the first step into an aminosulfonic acid which is then transformed into the final product by hydrolysis with mineral acids in the second step.[4] Later on (1854), the French chemist Pierre J. A. Béchamp demonstrated the use of metallic iron in acidic media as reducing agent for the production of aniline from nitrobenzene.[5] For a long time, this method was the main manufacturing process for a large number of aniline-based molecules at reasonable costs. The success of dyestuff production from aniline has been used by one of the largest chemical supplier in the world and adapted in its acronym, BASF (Badische Anilin- und Soda-Fabrik). Nowadays, industrial potential of the Béchamp reduction is decreasing since the iron oxides obtained as by-products and their market demand (mostly for pigments) does not require such amounts. Hence, this classic stoichiometric process is economically less attractive and does not fulfill the principles of green and sustainable chemistry. For these reasons, many efforts have been spent on the development of efficient methodologies for production of amines from the corresponding nitro compounds. In this respect, catalysis and related technologies represent the cornerstone for efficient production of such molecules. Hence, most of the primary anilines are currently produced *via* hydrogenation of the corresponding nitrobenzenes. During the last century, various catalytic systems (especially heterogeneous) have been developed by many chemical companies. They differ not only in the active metal, but also on the reaction conditions and the reactor configuration (gas or liquid phase reactions). Unfortunately, each of these catalytic systems is covered by industrial trade secrets that generally do not allow for a detailed description of them. Selected important processes for the title reaction are reported in Table 1.[6,7] Most of these catalysts offer a good combination of activity and reusability; however, in some cases reactivation is required. The hydrogenation of nitrobenzene does not imply significant selectivity problems since the possible side processes do not easily occur under operative conditions. For instance, hydrogenation of the aromatic ring or hydrodenitration extensively occurs only when Ru- or Rh-based catalysts under relatively harsh conditions are used. However, the situation is different for advanced functionalized nitro compounds containing carbon-carbon or carbon-heteroatoms multiple bonds, halogen atoms, carboxylic acid derivatives or heterocycles. Unfortunately, for such substrates standard catalytic systems relying on Ni-Raney® and especially noble metals such as Pd and Pt (Adams' catalyst, PtO_2) do not show sufficient selectivities.[8-11] Examples of critical substrates are reported in

Scheme 1.

Table 1 Industrially applied processes for the reduction of nitrobenzene to aniline.

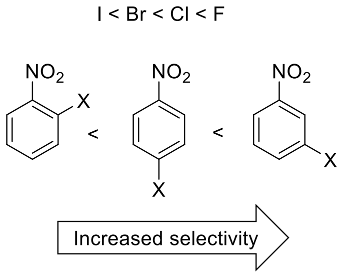
Catalyst	**Company**	**Reaction conditions**
Ni sulphides	Bayer, Allied	300-475 °C
Cu, Mn, Fe	ICI	300-475 °C
Pd/Al_2O_3	Bayer	250-350 °C; 7 bar
Cu/SiO_2 (Cr, Ba and Zn as promoters)	BASF, Cynamide, Lonza	270-290 °C; 5 bar
Pd-Pt/C (Fe as modifier)	DuPont (Dow Chemicals)	90-200 °C; 6 bar

Scheme 1 Selected examples of industrially important nitro compounds whose hydrogenation might give selectivity problems.



In order to avoid these issues, modifications of existing catalysts or their tailor made versions were reported. For instance, bimetallic catalysts (*e.g.* $Pt\text{-}Fe/TiO_2$, Rh-Fe/C, $Pb\text{-}Pd/CaCO_3$ or Pt colloids doped with Ni, Ce or Fe) are able to selectively reduce nitro compounds containing C=C, C≡C, C=O, BnO, C=N or C≡N functionalities.[12,13] In general, halogen-substituted nitroarenes represent challenging substrates since hydrodehalogenation of C-I and C-Br occurs particularly easy as undesired pathway during the nitro reduction. However, they are very important and versatile compounds since the presence of the C-X moiety allows for further functionalization through cross-coupling and related chemistry. Many industrial companies were involved in the development of selective processes dealing with the reduction of halide-substituted nitro compounds highlighting the significance of this transformation. Both the nature of the halogen and its position on the aromatic ring have a substantial influence on the reaction outcome. Iodo-substituted nitroarenes are considerably much prone to be hydrodehalogenated compared to Br, Cl or the less reactive F. *Meta*-substituted nitrocompounds are more resilient to this side-reaction than the *para*- or *ortho*- isomers (Scheme 2). For a comprehensive report concerning the selective reduction of halogenated nitro compounds, the reader is referred to the specific review of M. Pietrowski.[14]

Scheme 2 Reactivity trends towards hydrodehalogenation pathway.



Reaction conditions, in particular temperature, hydrogen pressure and solvent, have a remarkable influence on the selectivity. However, most of the efforts focused on the development of selective catalysts that are intrinsically able to suppress the undesired side reaction path. For instance, Pt/C or Pd/C catalysts modified with metallic additives (Zn, Pb, Bi, Sn, Ge or Ag) or with basic/acidic additives (*e.g.* morpholine, phosphorous acid) often display high selectivities in the case of simple halogenated (mainly for Cl, Br) nitroarenes. Iodo-substituted nitro compounds represent one of the most demanding (but at the same time stimulating) substrates since the hydrogenolysis of the C-I bond is relatively easy. Nevertheless, selective catalysts in this case are known such as Pt/$CaCO_3$ modified with Pb or Pt/C modified with phosphorous acids.[12,14,15]

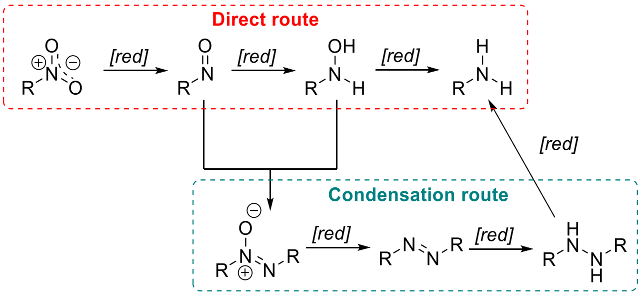
After decades of research in the area of selective catalytic nitro reductions, a breakthrough was reported by A. Corma and co-workers in 2006.[16-18] They described Au NPs supported on TiO_2 as an efficient catalyst for the reduction of nitroarenes showing excellent selectivities rarely reported for other noble-metal catalysts. Later on, the authors explained the success of their catalyst by the preferential adsorption of the nitro group rather than other moieties at the interface between the support and the Au NPs.[18] Along with Au, also Ag-based catalysts have been found to be active in this reaction by the group of J. Qui in 2005.[19]

All the catalytic systems described above suffer from the high metal price and in some cases are environmentally less acceptable. Here, the toxicity of some of the additives applied in Pt- and Pd-based (such as Pb and Zn salts, Ph_2S or H_3PO_2) systems has to be mentioned. In the last years, the use of transition *3d*-metals in catalysis has become one of the frontiers in synthetic chemistry. Owing to their abundance on the Earth´s upper crust, their price (and as a consequence its fluctuation over the time) is considerably lower than that of noble metals. Many of them have acceptable environmental impact and are involved in biochemical processes. For this reason they are sometimes also called *biocompatible* metals. However, the toxicity of a metal is not absolute since it depends from many factors such as solubility, bioavailability, oxidation state and counterion or coordinated ligand.[20] For this reason it is not possible to assign a definite order of toxicity and in some cases non-noble metal complexes are more toxic than noble-metal ones.

The use of heterogeneous catalytic systems especially based on Fe or Co at high temperature has been already known for more than 100 years and is well represented by the Haber-Bosch and Fischer-Tropsch processes. However, due to their poor activity compared to the noble counterparts, other possible catalytic applications especially for fine chemical synthesis were scarcely explored. Starting from the late 90's, the scientific community paid more and more attention in developing homogeneous and heterogeneous catalytic systems based on *3d*-metals. In homogeneous catalysis, specific ligands were tailored, which are able to tune the electronic properties of the complex through the so-called metal-ligand cooperation. Ligands of this type have been named *(redox)non-innocent* (in contrast to ancillary) since they play a direct role in the reaction mechanism. In the field of heterogeneous catalysis, the use of heteroatom-doped carbonaceous material has paved the way for new reactivity patterns using non-noble catalysts. Several notable reviews either on the general use of non-noble metals,[21-24] or of specific non-noble metals (Fe,[25-28] Mn,[29-32], Co[33,34]) in catalysis were published during the last 10 years.

The mechanism of the nitrobenzene reduction to aniline follows the model developed by Haber already in 1898 based on electrochemical experiments. In this reaction scheme, two different pathways can be proposed. In the first one (*direct route*), the nitro compound is reduced to the corresponding nitroso, aryl/alkyl hydroxylamine, and finally aniline. The *condensation route* involved the condensation of nitroso with *N*-aryl/alkyl hydroxylamine species giving rise to the corresponding azoxy- intermediate. Further on, the latter is converted into azo-, hydrazo- and finally aniline (Scheme 3).

Scheme 3 Proposed mechanism by Haber and co-workers. *[red]* = reduction



In many of the studied catalytic experiments, *N*-phenylhydroxylamine is detected and in some cases (especially when Pt-based catalysts were used) accumulation of it was described.[35,36] This indicates the conversion of *N*-phenylhydroxylamine to aniline as a rate-determining step (direct reduction pathway). However, although less usual, the condensation route generally occurs when the reduction reactions are conducted in the presence of strong bases (mainly inorganic). In this case, it is possible to selectively stop the reaction at the azoxyarene stage.[37-41]

Despite the relevance of the reduction of nitro compounds, only few studies on the reaction mechanism were published during the years and the majority of them dealt with heterogeneous noble metal catalysts (mainly based on Pd, Pt, Au and Rh).[17,42-44] As a consequence, the mechanism reported by Haber still continues to represent the main reference for describing the possible reaction pathways, even in the case of non-noble metal catalysts. An exception is represented by Ni-based heterogeneous catalysts, for which two studies were very recently reported and will be discussed in the dedicated chapter.

In the last years, reviews on the topic of nitro compounds reduction appeared in the literature.[45-50] However, many of them deal exclusively with noble-metal catalysts,[51,52] specific substrates[53] or reducing agents,[54] or focus on synthetic methodologies.[55] Complementary, herein the progress of nitro compounds reduction using non-noble metal catalysts is comprehensively reviewed focusing our attention from 2000 on. In fact, many breakthroughs in this area were recently made, spurring the research in assessing non-noble metals for this pivotal transformation. Most of these works deal with heterogeneous catalysts and only a limited number of examples for the homogeneous counterparts were published.

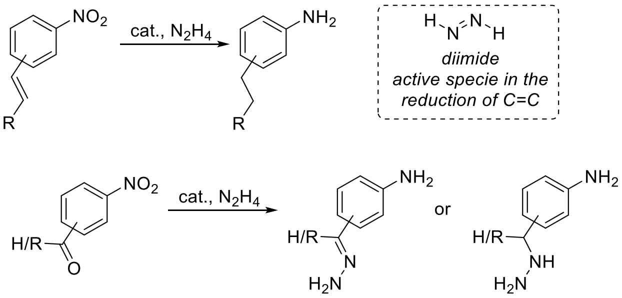
To better understand the developments, this manuscript is divided into chapters according to the metal used (in the following order: Fe, Co, Ni, Cu). Two final chapters deal with heterogeneous multimetallic catalysts and homogeneous systems. Each section examines the catalytic reaction based on the type of reductant. For this reason, a brief introduction on the employed reducing agents is preliminary discussed in the next chapter. Electrocatalytic and photocatalytic methods will be not taken into account and the reader is referred to specific works.[45]

2. Survey of reducing agents employed in the reduction of nitro compounds

A wide range of reducing agents has been used for the catalytic transformation of nitroarenes to amines. Each of them possesses advantages and disadvantages with respect to their handling, cost and environmental impact as well as hazardousness. Industrial reduction processes for the production of bulk chemicals are commonly conducted using molecular hydrogen, which is atom-efficient and inexpensive. Commonly, direct catalytic hydrogenations of nitroarenes are conducted under relatively high pressure and temperatures. In addition, the industrial reduction of nitrobenzene to aniline (*vide supra*) is done with molecular hydrogen under these conditions. However, as a result of the intense research in this area, catalytic systems able to work at low pressure and temperature (1 bar H_2, 40 °C) were recently developed. Another alternative gaseous reducing system is based on water gas shift reaction (WGSR) employing a combination of CO and water. Despite the lower price of CO compared to H_2, it is very toxic and requires special handling and safety equipment. Therefore, alternative processes have been designed using so-called CO-surrogates that enable the avoidance of gaseous CO.[56-58] However, only limited examples include the reduction of nitroarenes so far.[59] In addition to the conversion of nitro compounds to amines, catalytic reduction of nitroarenes using CO can be selectively directed to other important bulk (carbamates or isocyanates)[60,61] or fine chemicals (mainly nitrogen-containing heterocycles).[62-64] These reactions, conducted in the absence of water, are generally catalyzed by homogeneous Pd and Ru metal complexes and thus they are not included in this review. Within this topic, is worth to mention that a homogeneous Fe-catalyzed allylic amination of olefins with nitroarenes was reported by Nicholas before 2000.[65]

Typically, on small scale, the reductions of nitro compounds are performed using different non-gaseous reducing agents, sometimes under non-catalytic conditions. For instance, hydrazine is an often used alternative, which formally decomposes to dihydrogen and dinitrogen under catalytic conditions. Pure hydrazine is very toxic and hazardous, therefore its less harmful hydrated form ($N_2H_4·H_2O$) is preferably applied. The processes using $N_2H_4·H_2O$ are operationally simple and can be carried out using standard glassware. A disadvantage for nitroarenes bearing C=C or C=O bonds is the competitive reduction to alkanes or hydrazones formation, respectively. In this respect, diazene (diimide), an intermediate of the hydrazine dehydrogenation, is known to reduce carbon-carbon double bonds in a non-catalytic way (Scheme 4).[66]

Scheme 4 Main side-reactions using N_2H_4 as reductant.



Reactions employing hydrazine hydrate as reducing agent take place at low temperature and a large array of catalytic systems (especially based on Fe) were successfully employed. It is noteworthy that simple commercially available metal oxides were active which makes this reactant appealing for laboratory scale preparations.

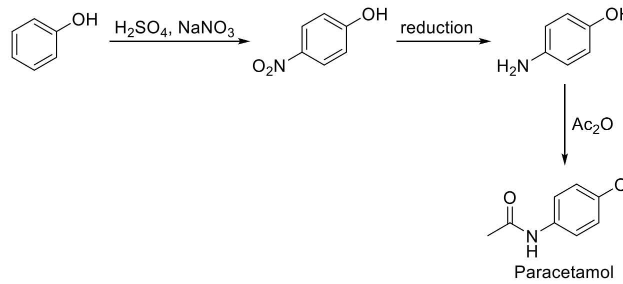
Alcohols, often in combination with basic media (especially methanol, ethanol, isopropanol and glycerol), represent cheap reducing agents. However, commonly added inorganic bases need to be used in significant amounts (often >1 equivalent with respect to the nitro compound). As a consequence, large quantities of salts are present and corrosion might be an issue. Under specific reaction conditions, alkali/alcohol couples are able to smoothly reduce nitroarenes to anilines in the absence of a catalyst along with variable amounts of azo- and azoxyarenes.[67,68] Another disadvantage of reduction of nitro compounds carried out with metal alkali/alcohols might be the hydrolysis or transesterification of carboxylic acid derivatives.

Sodium borohydride is widely used as reducing agent in organic chemistry. Indeed, the textbook reduction of ketones and aldehydes to alcohols is a great example for this relatively cheap and easy-to-use reagent. Under aqueous or protic solvent conditions it is (slowly) hydrolysed to give H_2 according to the following equation.

$$NaBH_{4(s)} + 2H(R)OH_{(l)} \longrightarrow 4H_{2(g)} + NaBO_{2(aq)}$$

However, transition metal based catalysts are able to remarkably accelerate this reaction paving the way for the use of $NaBH_4$ in the catalytic reduction of nitro compounds. In fact, a multitude of catalysts based on coinage (Au, Ag, Cu), noble (mostly Pd and Pt) and non-noble (Ni, Co, Fe) metals can catalyze this reaction.[69] Nevertheless, the price of the reductant as well as the formation of salts as by-products prevent, in most cases, larger scale applications. In addition, most of the papers dealing with this transformation use the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) as benchmark reaction. The latter is considered to be a useful transformation both in the pharmaceutical industry and in the pollutant-remediation field. Indeed, 4-NP is a toxic compound that derives as a by-product of the manufacture of pesticides and synthetic dyes. In addition, 4-AP is used as intermediate in the pharmaceutical industry in the original processes for the production of Paracetamol (*N*-acetyl-4-aminophenol, Scheme 5) and as a starting material in the preparation of developing agent for other applications.

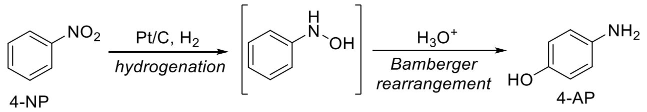
Scheme 5 Original method for the preparation of Paracetamol.



The catalytic reduction of 4-NP to 4-AP generally shows good rates at room temperature and the experimental protocol is simple. Moreover, the transformation can be easily followed by spectrophotometric methods such as UV-Vis. Nonetheless, the reagent is too expensive for this transformation and produces large amount of salts (sodium metaborate). Thus, the actual industrial approach for the production of 4-AP is based on the stoichiometric reduction of 4-NP by Fe/HCl (Béchamp method) or catalytic hydrogenation using Raney®-Ni or supported noble metals. Another important method for the preparation of 4-AP is the direct conversion of nitrobenzene to 4-AP *via* a two-steps one-pot reduction/Bamberger rearrangement process. The reaction takes place under acidic conditions since the rearrangement occurs at the stage of *N*-

hydroxylamine (Scheme 6). The industrial acid-resistant catalyst for this transformation is based on carbon-supported Pt.[70]

Scheme 6 Synthesis of 4-aminophenol from nitrobenzene through reduction/Bamberger rearrangement sequence.



It should be highlighted that many of the papers dealing with the specific reduction of 4-NP to 4-AP use this transformation only as a model reaction for testing the capability of the prepared materials. Here, often the substrate/metal molar ratio either approaches or is lower than 1. Most commonly, the weight of the catalyst exceeds that of the substrate by 10 to >100 times. For this reasons, we limit our discussion of such “catalytic” systems dealing mainly with the reduction of 4-NP as a model reaction.

Formic acid is widely recognized as a promising and sustainable reducing agent since it can be produced from biomass or CO_2 hydrogenation.[71] Additionally, it is cheap and shows low toxicity in diluted solutions. However, it is corrosive with respect to metals and skin, requiring also resistant reaction vessels. Formic acid is used as reductant often combined with bases (*e.g.* triethylamine) and only few reports showed a base-free protocol. Obviously, the latter are strongly favored since separation of unreacted triethylamine or triethylammonium formate salts is avoided. Because of the corrosive effects of HCOOH, it is clear that the employed catalysts have to be acid resistant. Especially in heterogeneous catalysis, this constitutes a challenging task since many nanostructured catalysts are degraded by HCOOH.

Finally, hydrosilanes are worth mentioning as selective reducing agents for organic synthesis.[72] The possibility to change the substituents bound to silicon allows controlling the reactivity pattern of multi-functional substrates towards the desired product. Several hydrosilanes are commercially available at a reasonable price and they do not require high-pressure equipment for their use. Hence, the reduction of nitroarenes in combination with a metal catalyst was reported by few groups. For a recent review describing hydrosilanes for the synthesis of amines, the reader is referred to the work of C. Darcel and co-workers.[54]

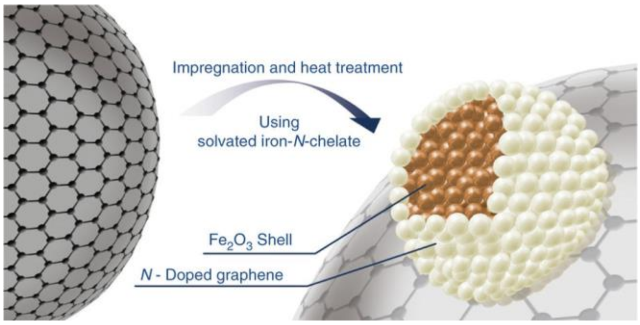
3. Heterogeneous iron-based catalysts

The use of iron in the stoichiometric reduction of nitro compounds is known for more than one century. In the introduction we have already provided a brief discussion of the Béchamp process as one of the first and still, although marginally, used method for the reduction of nitro compounds. Apart from this, some attention is paid to the development of simpler stoichiometric methods for the title reaction.[73-76] However, the generated wastes limit such protocols to laboratory preparation purposes. On the other hand, because of the low price and eco-compatibility of this metal, the development of Fe-based catalytic reductions of nitro compounds represents an ongoing goal for organic synthesis and catalysis.

3.1. Reductions with molecular H_2

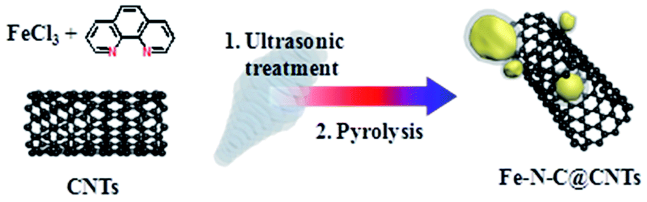
In recent years, the combination of Fe-based metal/metal oxides NPs and nitrogen-doped carbonaceous supports has been shown to be promising for various reductive transformations. The first report on the use of heterogeneous Fe-based catalysts for nitroarene hydrogenation using molecular hydrogen was published in 2013 by the group of Beller.[77,78] Catalysts were prepared by pyrolysis of iron/phenanthroline complexes supported onto carbon. The most active material (pyrolyzed at 800 °C) is composed by Fe_2O_3 NPs of different sizes surrounded by nitrogen-doped graphene layers (Figure 1).

Figure 1 Representative picture of Fe_2O_3/NGr@C developed by the group of Beller. (Reproduced with permission from Ref. 78. Copyright 2015, Macmillan Publishers Limited, part of Springer Nature)



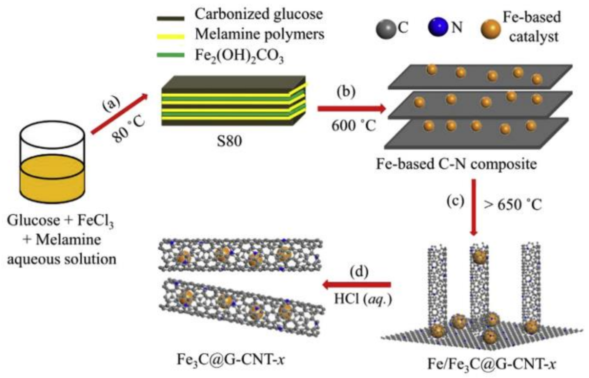
Higher or lower pyrolysis temperatures led to the formation of inactive/less active materials due to the formation of larger and not covered particles (1000 °C) or not properly grown Fe species (400 °C). The catalyst was applied to the hydrogenation of nitroarenes to anilines at 120-140 °C with full chemoselectivity in the desired products. Structurally diverse (hetero)aromatic nitro compounds, including complex molecules containing numerous functional groups, were successfully hydrogenated to the corresponding amines. Sensitive substrates including 4-nitrophenylacetylene and 3-nitrostyrene were hydrogenated affording the corresponding products in 75% and 96% yield, respectively. Moreover, nitro-containing pharmaceuticals were converted to the respective amines in high yields. The same material was found to be active in the reductive amination of nitro compounds with aldehydes to give secondary amines.[79] Despite the high temperature employed (170 °C), the corresponding amines (even from aliphatic nitro compounds and aliphatic aldehydes) were produced in moderate to good yields. Later on, the group of Q. Yang reported a similar material using CNTs as support instead of carbon (Figure 2).[80]

Figure 2 Preparation of Fe-N-C@CNTs developed by Q. Yang and co-workers. (Reproduced with permission from Ref. 80. Copyright 2016, The Royal Society of Chemistry)



The as-obtained material displayed a slightly different morphology and composition with respect to the catalyst reported by Beller, leading the authors to propose a pivotal role of both iron nitride (Fe_3N) and iron carbide (Fe_3C) in the reaction mechanism. Notably, it was found to be highly active in the hydrogenation of nitrobenzene to aniline. The successful combination of iron carbide and CNTs has been further demonstrated by Z. Hou and co-workers in 2016 (Figure 3).[81]

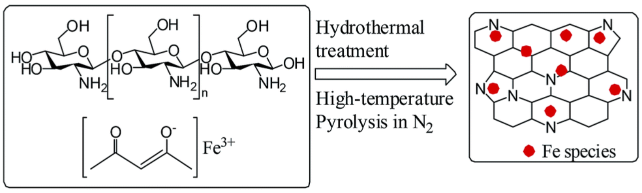
Figure 3 Preparation of Fe_3C@G-CNT-x developed by Z. Hou and co-workers. (Reproduced with permission from Ref. 81. Copyright 2016, Elsevier)



The procedure was similar to one previously reported by the group of Y. Wang using Co (see Chapter 4).[82] However, in the work of Z. Hou only a single thermal treatment was applied followed by a final acid leaching (aq. HCl) to remove unstable and redundant Fe NPs. The material prepared at 700 °C showed the exclusive presence of Fe_3C reflections (XPRD) along with the lowest I_d/I_g ratio (Raman spectroscopy). Electron microscopy demonstrated that the Fe_3C particles are covered by few layers of doped graphene that show cracks allowing for the reactant to reach the active site. In addition, EDS and XPS analyses confirmed the confinement of the particles within the N-doped carbon nanotubes (N-CNTs). This specific material showed a notable activity in the hydrogenation of nitrobenzene to aniline under mild conditions (40 °C, 20 bar H_2, 4.5 h, 1 mol% Fe). The results are remarkable, taking into account the low activity of Fe catalysts. The protocol was applied to some substituted nitroarenes with few substituents (Cl, Br, CH_3, OCH_3). It should be emphasized that this catalyst is able to reduce olefins under similar reaction conditions.

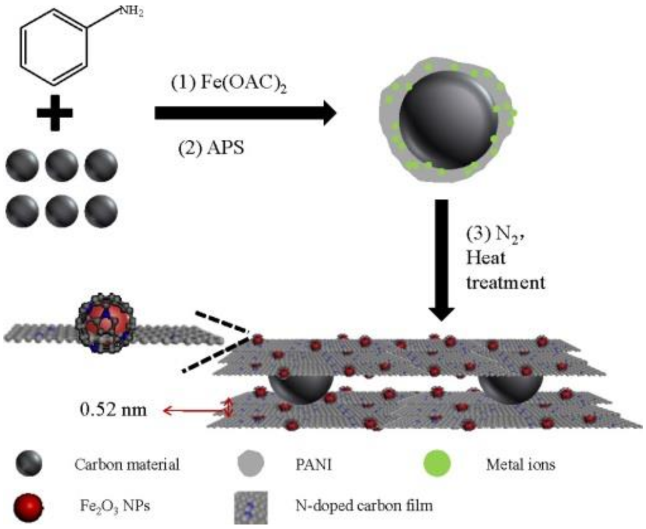
The use of biomass-derived precursors for the synthesis of nitrogen-doped carbon (NC) was evaluated by Xu, Sheng and co-workers in 2016.[83] Similar to a work with Co-based catalysts reported by the group of Beller (see Chapter 4),[84] chitosan was employed as concomitant source of carbon and nitrogen. The active catalyst was prepared in a two-step procedure: first, the Fe(II)/chitosan chelate was hydrothermally treated at 200 °C for 12 h and then the so-obtained solid pyrolyzed under nitrogen atmosphere for 4 h (Figure 4).

Figure 4 Preparation of Fe/N-C-x catalyst developed by S. Xu, H. Shen and co-workers. (Reproduced with permission from Ref. 83. Copyright 2016, The Royal Society of Chemistry)



The prepared materials showed the presence of Fe-based NPs mainly in the form of Fe_2O_3 or Fe_3O_4. Interaction of Fe with nitrogen and carbon was proposed due to the presence of FeN_x and FeC_x patterns at XPRD. The catalyst pyrolyzed at 500 °C was the most active for the hydrogenation of nitrobenzene and showed the highest content of FeN_x and FeC_x species that were previously found to be active sites.[80] Later on, the preparation of a similar catalyst was reported by Z. Hou and co-workers in 2017.[85] However, in this case a four step method involving the synthesis of polyaniline (PANI), subsequent adsorption of Fe(II) ions followed by solvothermal treatment and pyrolysis under inert conditions was employed (Figure 5).

Figure 5 Preparation of Fe_2O_3@G-C-T by the group of Z. Hou. (Reproduced with permission from Ref. 85. Copyright 2017, Elsevier)

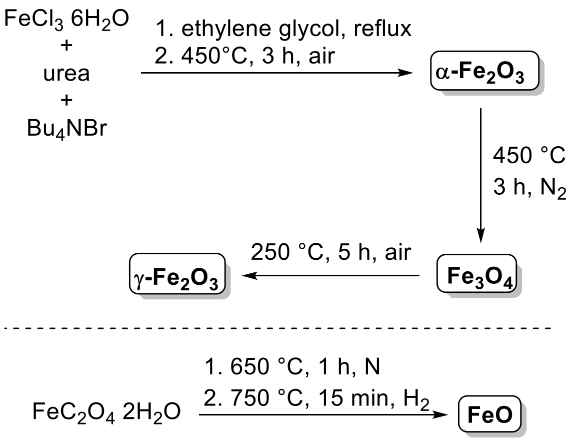


The authors demonstrated that the pyrolysis temperature has a significant influence on the chemical and physical properties of the materials. In agreement with previous work,[77] high pyrolysis temperatures led to larger particles (agglomeration) and to a decreasing of both surface area and superficial nitrogen content. The material pyrolyzed at 900 °C showed the largest surface area and pore volume and the smallest particles. This material was an efficient catalyst for the hydrogenation of nitrobenzene to aniline under mild conditions (70 °C, 20 bar H_2, 2 h). In addition, as already demonstrated in the seminal works of Beller and co-workers, it should be mentioned that the use of oxidic supports (SiO_2, Al_2O_3) led to poor or negligible activity indicating the positive effect of carbon as support.

Apart from iron catalysts activated by nitrogen-doped carbon, X. Tong, X. Guo and co-workers reported the capability of FeS_2 NPs to mediate the hydrogenation of nitrobenzene using molecular hydrogen.[86] The active catalyst was prepared through a solvothermal method starting from Fe(II) chloride and elemental sulfur yielding FeS_2 NPs with minor components such as iron (hydroxy)oxides, mixed sulfides and elemental sulfur (in the form of S_8) present. One year later, Schaak and co-workers demonstrated the activity of bulk pyrite FeS_2 in the hydrogenation of nitroarenes.[87] As in the previous case, XPS revealed the presence of iron oxides on the surface of the material raising a question on which phase is actually the active catalyst. Regardless the advantages of iron pyrite (availability, good biocompatibility, low price), the reported activity was poor. In fact, only substoichiometric reactions were performed. Worth of note is the chemoselectivity of these FeS_2-based systems in the presence of carbon-carbon double and triple bonds, which were unreactive. In fact, 3-nitrostyrene and 4-nitrophenylacetylene were hydrogenated to the corresponding amines with full selectivity at complete conversion. Conversely, 4-iodonitrobenzene showed full selectivity only at ≤75% conversion, which indicates the possibility of dehalogenation side-reactions at higher conversions. Despite the good selectivities obtained, the use of FeS_2 as catalyst does not bring any actual advantage over carbon-based systems (*vide supra*) since the reported activities are very poor.

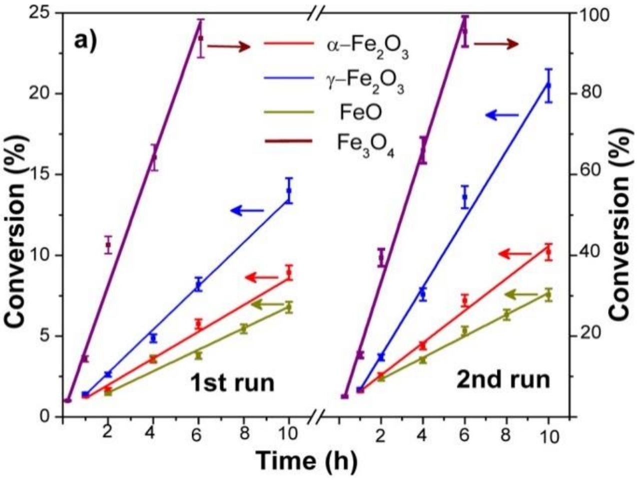
Furthermore, J.-J. Zou and co-workers reported a comprehensive study using unsupported bulk iron oxides in the hydrogenation of nitrobenzene.[88] As shown in Scheme 7, the materials were simply prepared through solvothermal and calcination/pyrolysis procedures.

Scheme 7 Preparation of various Fe-based oxides employed in the work of J.-J. Zou and co-workers.



During the reaction the catalysts were converted into other more active species due to the formation of oxygen vacancies on the surface which are considered to be important for the activation of the H-H bond. Notably, all the catalysts showed enhanced performances in the second run. This effect was pronounced in the case of α-Fe_2O_3 and γ-Fe_2O_3, which showed the appearance of an Fe(II) peak in the XPS spectra. The reactivity order was found to be the following: Fe_3O_4 >> γ-Fe_2O_3 > α-Fe_2O_3 > FeO both in the first and the second run (Figure 6).

Figure 6 Catalytic performances of Fe_3O_4, γ-Fe_2O_3, α-Fe_2O_3 and FeO in the reduction of nitrobenzene at 150 °C under hydrogen pressure (30 bar H_2): comparison of 1st *vs.* 2nd catalytic run. (Reproduced with permission from Ref. 88. Copyright 2016, American Chemical Society)



In this report, in addition to relatively harsh conditions (150 °C, 30 bar H_2, 15 h), the Fe/$PhNO_2$ molar ratio approaches the value of 1, making the reaction almost stoichiometric in Fe. Nevertheless, the simplicity, cheapness and availability of the presented catalysts make it appealing for further studies aimed to improve the activity.

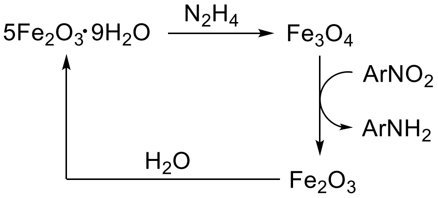
Among all the presented Fe-based catalytic systems, only the ones based on Fe-N-C materials (Fe-based nitrogen-doped carbons) seem to be competitive and working under "real" catalytic conditions. Furthermore, some of them are active even at low temperature and pressure (up to 40 °C and 20 bar H_2), which makes them comparable to catalysts of less abundant Co or Ni.

3.2. Transfer hydrogenations

3.2.1. Reductions with N_2H_4

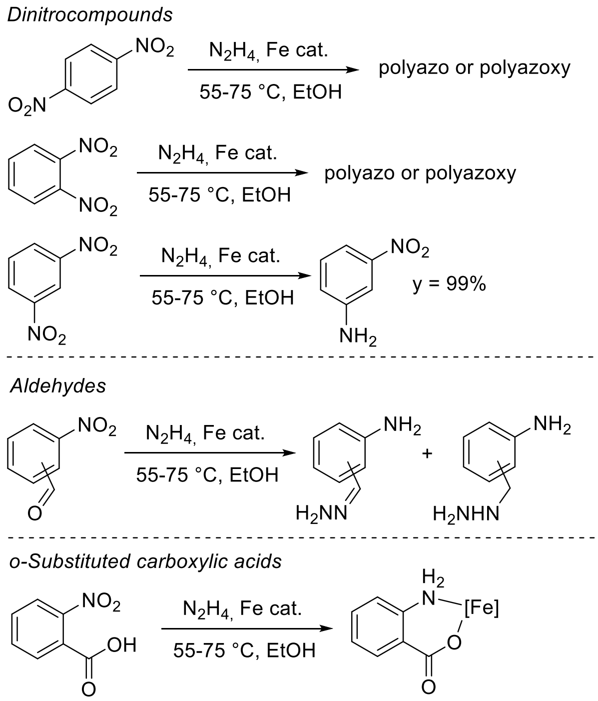
Due to its easy activation, the use of hydrazine (in its hydrated form) as reducing agent was extensively studied using heterogeneous Fe-based catalysts. A seminal work on this topic was published by T. Hirashima and co-workers already in 1975 assuming that $FeCl_3$ in combination with active carbon is able to produce iron oxyhydroxyde that acts as the real catalyst.[89] Based on this working hypothesis, the same authors later synthesized Fe(III) oxyhydroxyde and subsequently used this in catalysis.[90] The catalyst, composed of β-FeO(OH) (or β-$Fe_2O_3 \cdot H_2O$), was able to reduce a few number of nitroarenes and it was recycled up to 8 times maintaining its activity after being converted into the less active α-Fe_2O_3. The successful use of Fe(III) oxides was later on confirmed by N. R. Ayyangar and co-workers.[91] In a series of papers appeared in the late 90's, the groups of P. Rys and R. Prins investigated systematically the catalytic system based on Fe(III) oxide hydroxide both from a mechanistic and synthetic point of view. Mössbauer spectroscopy and XPRD analysis of the catalyst evidenced that the material is better classified as ferrihydrate.[92,93] The latter is a Fe(III)-based mineral with the general formula $5Fe_2O_3 \cdot 9H_2O$.[94] Compared to other iron oxides, the produced ferrihydrate exhibited a relatively large surface area (up to 300 m^2 g^{-1}). Mechanistic insights (*in-situ* XPRD and Mössbauer spectroscopy) revealed the presence of a superficial Fe(II)/Fe(III) redox cycle that might be responsible for the catalytic activity (Scheme 8).

Scheme 8 Schematic representation of the Fe(II)/Fe(III) redox cycle proposed to take place in the catalytic system developed by the groups of P. Rys and R. Prins.



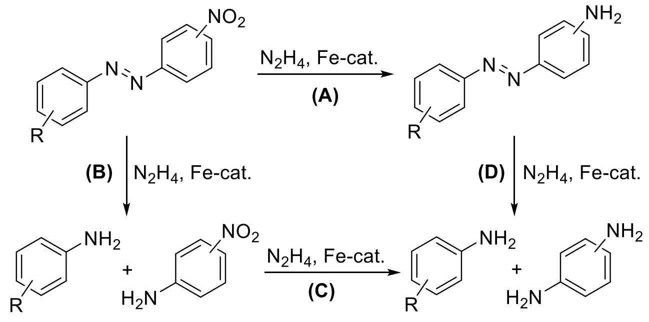
The catalyst was pre-activated by little amounts of water and above 70 °C the material was slowly converted into hematite that showed a sharply decreased activity. Following papers by the same authors focused on the synthetic applicability of this catalyst.[95] The scope of the reaction included nitroarenes substituted with halogens (except I-substituted nitro compounds), carboxylic acid derivatives, sulfonic acids and other functional groups. The yields are influenced by both steric and electronic factors. Indeed, a Hammett correlation revealed that EWG-substituted nitroarenes undergo reduction more rapidly than EDG. Limitations of the protocol were carefully studied and explained (Scheme 9).

Scheme 9 Limitations to the reaction scope using ferrihydrate as catalyst and hydrazine hydrate as reductant.



Dinitroarenes substituted in positions 1,2 and 1,4 were transformed into the corresponding polyazo and polyazoxy compounds whereas 1,3-dinitrobenzene was quantitatively converted into the corresponding 3-nitroaniline. As mentioned in the introduction, aldehydes are often not suitable substrates in the presence of hydrazine due to rapid formation of the corresponding hydrazones. Finally, the authors concluded that anthranilic acid derived from 2-nitrobenzoic acid poisons the catalyst. In subsequent works they focused their attention on the reduction of nitroazo compounds (Scheme 10).[96] The resulting products are of interest as starting materials for the preparation of dyes and related molecules.[97]

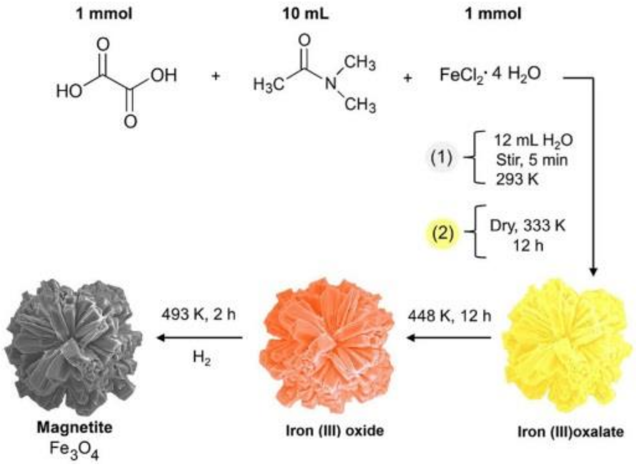
Scheme 10 Reduction of nitroazoarenes: desired (A) and undesired side-reactions' pathways (B, C, D).



Interestingly, a ferrihydrate catalyst in the presence of hydrazine as reductant can catalyze this reaction achieving yields up to 99% with azoarenes bearing EWG groups. Modifications of this method were performed by the groups of R. Lu[98] and R. S. Varma[99] supporting hydrazine onto polymers and alumina. The purpose of such modification was to overcome environmental issues concerning the disposal of toxic hydrazine. However, the absolute amount of supported hydrazine needed is relatively high (up to 2 g per mmol of nitroarenes) and the overall activity is slower if compared to the original protocol. Unfortunately, no information about recyclability and leaching was provided. Based on the work of R. Prins and P. Rys the activity of catalysts was later enhanced by F. Figueras and co-workers.[100,101] They prepared Fe(III) oxide/MgO from thermal treatment (450 °C, under nitrogen atmosphere) of a Mg-Fe hydrotalcite obtained by co-precipitation of $Mg(NO_3)_2$ and $Fe(NO_3)_3$ in basic aqueous media. The material is composed of a solid solution of Fe(III) oxide in MgO. In more detail, Mg-Fe hydrotalcite was converted into γ-Fe_2O_3 that exhibits the same Fe(II)/Fe(III) redox behavior reported for Fe ferrihydrate. Moreover, the presence of MgO enables a high dispersion of the active phase on the support. Owing to this increased activity, accumulation of hazardous intermediate species *N*-phenylhydroxylamine was never detected.

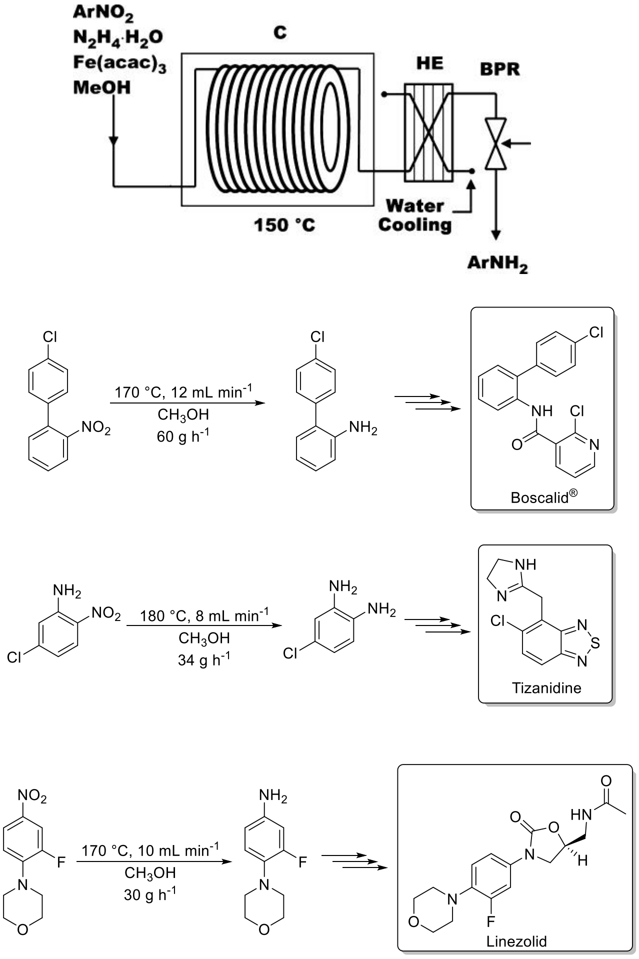
Simple magnetite (Fe_3O_4) has also been assessed as catalyst for the reduction of nitroarenes with hydrazine hydrate as the reductant. Magnetite is commercially available at a low price and exhibits a ferromagnetic behavior that makes it magnetically recyclable. B. M. Kim and co-workers showed for the first time the use Fe_3O_4 in the reduction of nitroarenes.[102] Commercially available Fe_3O_4 NPs (average size <50 nm) catalyzed this reaction, albeit relatively high catalyst loadings (up to 20 mol% Fe_3O_4) were required. Along with non-reducible moieties, the functional group tolerance comprises halogens (including iodine) and carboxylic acid derivatives. Conversely, carbon-carbon double bonds were not completely retained due to their reduction by diimide (*i.e.* the monodehydrogenated intermediate of hydrazine). Interestingly, aliphatic nitro compounds showed a poisoning effect towards the catalysts. The Fe_3O_4 NPs were easily recycled by magnetic separation, however the recyclability was not complete, requiring elongation of the reaction times or addition of fresh portion of catalyst in order to restore the original activity. Further studies on this topic were done by R. Zboril and M. B. Gawande, who prepared magnetite microspheres from iron(III) oxalate (Figure 7).[103]

Figure 7 Preparation of the Fe-based materials reported in the work of R. Zboril, M. B. Gawande and co-workers. (Reproduced with permission from Ref. 87. Copyright 2017, Nature Publishing Group)



The metal precursor was first converted into iron(III) oxide and then to magnetite under air and hydrogen. SEM and TEM images showed the flower-like structure of the obtained magnetite whose chemical composition was established by XPRD and Mössbauer spectroscopy. The catalytic activity is comparable to the one achieved by B. M. Kim under similar reaction conditions.[102] Nevertheless, higher efficiency can be achieved using microwave irradiation that allowed to significantly reduce the reaction times (from 180 to 15 minutes). Under these conditions, the authors showed a good functional group tolerance using differently substituted nitroarenes. However, substrates carrying carbon-carbon double bonds or carbonyl compounds were not included in their studies. Notably, homogeneous Fe(III) species are known to catalyze the reaction in liquid phase. Thus, as a general remark the possible leaching of iron species from the catalyst can be partially responsible for the observed catalytic activity (for the discussion of the use of soluble Fe catalyst the reader is referred to chapter 8). The same heterogeneous catalyst was shown to be active in related transformations using HCOOH as the reductant (*vide infra*). In 2013, two independent works on the use of graphene oxide and graphene as supports for Fe_3O_4 NPs, respectively, were reported by the groups of Q. Chen[104] and C. Wang[105] . In both cases, the supports were prepared through multi-step modified Hummers' method (oxidative conversion of graphite using potassium permanganate under acidic media) and the Fe-based catalysts through a co-precipitation of Fe(II) and Fe(III) precursors. In the case of graphene-supported catalysts, Fe_3O_4 NPs have a size ranging from 25 to 50 nm, whereas in the graphene-oxide supported one a narrow and decreased average size of 12 nm. This difference was imputed to a confinement effect provided by the oxygenated groups present on the surface of GO. The GO-supported Fe_3O_4-based catalysts exhibited an increased activity with respect to both the graphene-supported and the unsupported ones. Most probably, this result is due to the smaller NPs size in GO-supported Fe_3O_4. It should be underlined that even carbonaceous materials alone can act as catalysts for this reaction. In fact, r-GO, graphite and carbon in some case were found to promote such reductions also at room temperature.[106-108] Although Q. Chen and co-workers did not provide the control experiments, C. Wang stated that the reaction conducted with the pristine graphene furnished the desired product in 86% yield, only 8% less than the reaction conducted with the Fe-based catalyst. For this reasons, metal catalysts supported onto carbonaceous materials in combination with hydrazine should be always corroborated by control experiments devoted to clarify if the support alone could play any role in the stated transformation. In a first communication[109] and in a subsequent full paper[110], C. O. Kappe used Fe_3O_4 in continuous flow for the reduction of nitroarenes. Since hydrazine can be utilized for both producing Fe_2O_3 and as a reducing agent for the nitro compound, an *in-situ* protocol was developed. Here, Fe_3O_4 NPs were formed from Fe(III) or Fe(II) precursors, which then catalyzed the reduction of nitroarenes with high selectivity including challenging substrates (for instance, 4-iodoaniline was obtained in 98% yield). An impressive activity (TOF up to 12000 h^{-1}) was achieved under microwave irradiation at 150 °C in the presence of only 0.25 mol% of Fe. Under these conditions, various nitroarenes were converted into the corresponding anilines with full selectivity. Using the same catalyst under normal heating (80 °C), the reaction was completed in 60 minutes. In order to overcome the well-known issues due to exothermicity in microwave-induced reactions, the protocol was transferred to a continuous-flow setup. Since the Fe_3O_4 NPs are initially colloidal, the reaction mixture remained (quasi)homogeneous within the first minutes. Various amines were synthetized with productivity up to 60 g h^{-1}. In particular, three industrially relevant pharmaceutical intermediates were efficiently produced using this technology (Scheme 11).

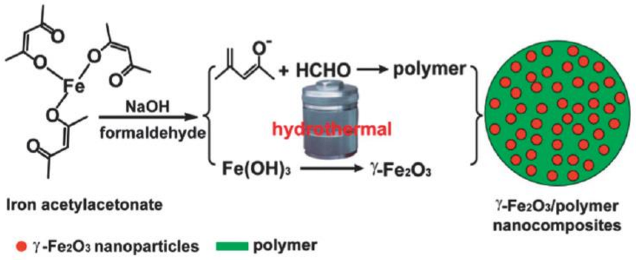
Scheme 11 Flow reactor setup for the reduction of nitroarenes and selected synthesis of pharmaceutical substrates used in the group of O. Kappe.



The main disadvantage of the two latter approaches is the poor recyclability of the catalyst. In order to overcome this drawback, the same group reported on the use of basic alumina as support and stabilizer for the colloidal produced Fe_3O_4.[111] Using this technology, full recyclability under microwave conditions (up to 10 runs) was achieved. Moreover, a flow protocol using a heated and pressure-stable cartridge was established.

In other works, bulk maghemite (γ-Fe_2O_3) was evaluated as catalyst for the title reaction.[90,92] However, it was found to be less active than Fe(III) oxide hydroxide employed in the work of Hirashima and Prins (*vide supra*). The reason for that was essentially ascribed to the low surface area of this material. Nonetheless, in 2013 Z. Su, X. Xu, D. Su and co-workers developed a γ-Fe_2O_3-based catalyst that worked well in the reduction of nitro compounds to anilines.[112] Following a hydrothermal approach, they prepared a polymer-embedded γ-Fe_2O_3 from $Fe(acac)_3$. The preparation strategy involved the formation of polymers derived from the reaction between formaldehyde and acetylacetonate under basic conditions (Figure 8).

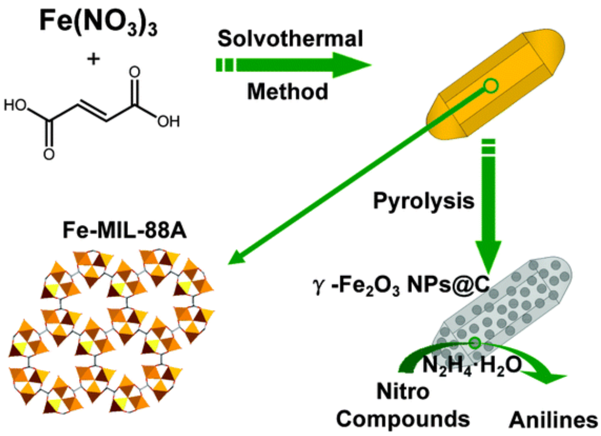
Figure 8 Preparation of γ-Fe_2O_3–polymer porous composites. (Reproduced with permission from Ref. 112. Copyright 2013, The Royal Society of Chemistry)



The final material is composed by γ-Fe_2O_3 NPs (average size of 3.5 nm) uniformly embedded into a polymeric matrix that prevents them against agglomeration. This catalyst was able to reduce nitrobenzene to aniline at 85 °C in only 20 minutes further showing a complete recyclability over six runs. A useful comparison with commercially available γ-Fe_2O_3 demonstrated both the vital role played by the polymer and the formation of γ-Fe_2O_3 as active phase. In fact, magnetite (Fe_3O_4) and hematite (α-Fe_2O_3) showed a significant decrease in activity. A similar preparation of the catalyst was very recently reported by H.-B. Sun, Q. Liang and co-workers.[113] Differently from the previous work, the γ-Fe_2O_3-embedded polymer was pyrolyzed instead of hydrothermally treated, furnishing NPs with increased size (20 nm average) embedded into porous carbon. It should be noticed that despite the high temperature reached during the pyrolysis treatment, γ-Fe_2O_3 was neither converted into hematite (α-Fe_2O_3), nor magnetite (Fe_3O_4) demonstrating the beneficial protection of the carbonaceous shells. The main differences between the two materials were the surface area and the porosity. Indeed, the hydrothermal treatment furnished a microporous material whereas pyrolysis caused a collapse of the polymeric structure giving rise to a mesoporous solid. The material pyrolyzed at 800 °C showed the highest activity in the reduction of 4-NP to 4-AP along with other substituted nitroarenes. Worth of note is the use of a labile 1,3-dioxolane-protected nitro compound as substrate that afforded the corresponding product in 90% yield without affecting the protective group. 4-nitrobenzamide was reported by R. Zboril and M. B. Gawande as a problematic substrate.[103] However, under similar reaction conditions the protocol proposed by H.-B. Sun, Q. Liang and co-workers provided in this case the desired product in almost quantitative yield.

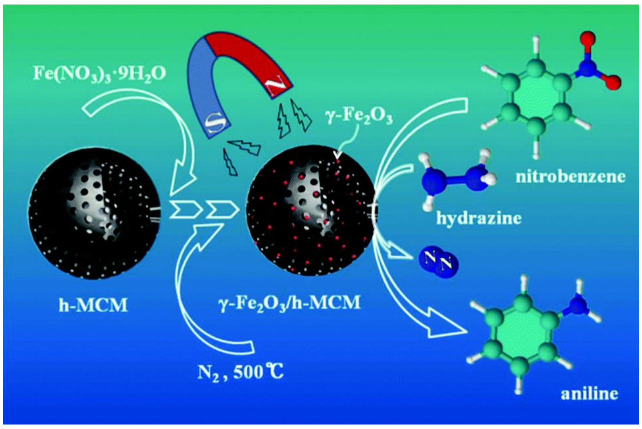
A γ-Fe_2O_3-based MOF-derived catalyst was proposed by H.-L. Jiang in 2016 (Figure 9).[114]

Figure 9 Preparation of γ-Fe_2O_3 NPs@C by the group of H.-L. Jiang. (Reproduced with permission from Ref. 114. Copyright 2016, The Royal Society of Chemistry)



As previously observed for a Co-based catalysts derived from MOF (see chapter 4), the pyrolysis temperature affects the composition and the morphological features of the material and thus the catalytic performances. In particular, higher pyrolysis temperatures produced materials mainly composed of metallic α-Fe and Fe_3C that showed decreased activity compared to the material prepared at 500 °C, which was found to be mainly composed by γ-Fe_2O_3. This catalytic protocol was exploited for the reduction of various nitroarenes, even containing sensitive functional groups like ketones and aldehydes. Here, the use of a polar aprotic solvent (DMF) instead of a polar protic one (EtOH) ensured the selective reduction of 4-nitrobenzaldehyde without the formation of the corresponding hydrazone. Moreover, simple alkyl nitro compounds were reduced to the corresponding primary amines. Similarly to the approach described by H.-L. Jiang, the group of Z. Dong prepared a catalyst based on γ-Fe_2O_3 NPs supported onto carbon by the pyrolysis of a Fe(III)/1,4-naphthalenedicarboxylic acid chelate.[115] As previously noticed in the work of H.-L. Jiang, pyrolysis temperatures >500 °C resulted in the formation of Fe(0) NPs which displayed a drastically lower activity than the material pyrolysed at 500 °C that contained exclusively γ-Fe_2O_3 NPs. The performances of such materials were explored in the reduction of halogenated nitroarenes showing complete selectivity to the corresponding haloanilines even in the case of 4-iodonitrobenzene (conversion and selectivity >99%). Another carbon-encapsulated γ-Fe_2O_3-based catalyst was proposed by Z. Dong and co-workers.[116] The material was prepared by high-temperature thermal treatment of a Fe(III) precursor and hollow-mesoporous carbon microspheres (h-MCM) (Figure 10). Interestingly, using a short (15 minutes) pyrolysis process, mesoporous γ-Fe_2O_3 NPs embedded into spherical h-MCM were formed with average size dependent on the pyrolysis temperature which greatly affected the catalytic activity.

Figure 10 Preparation of γ-Fe_2O_3/h-MCM. (Reproduced with permission from Ref. 116. Copyright 2016, The Royal Society of Chemistry)

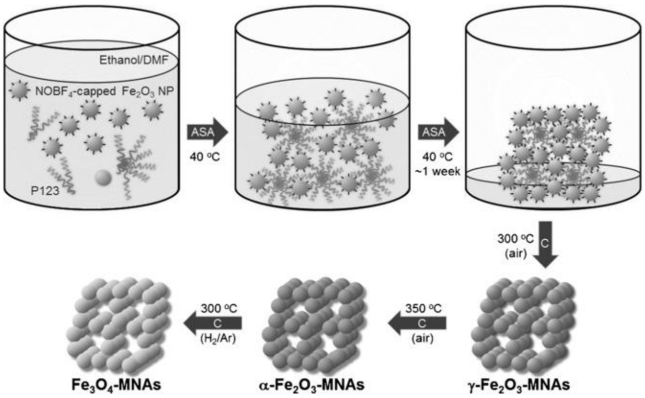


The use of NC as support for γ-Fe_2O_3 was reported by M. Beller and co-workers in 2011.[117] The catalyst was prepared through the thermal decomposition of a mixture of Fe(II) salts and phenathroline (Phen) adsorbed onto Vulcan® XC72R carbon. The full characterization of the catalyst was provided two years later when the same material was found to be active in the reduction of nitro compounds using molecular hydrogen.[77] The nano-structured iron-supported composite catalyzed the reduction of more than 40 nitroarenes carrying various labile functional groups such as halogens (excluding I-substituted), carbon-heteroatom multiple bonds and nitro-substituted heterocycles. Moreover, dinitro compounds were selectively reduced to the corresponding nitroaniline or diamine depending on the amount of catalyst employed. A similar approach for the preparation of γ-Fe_2O_3 NPs supported onto NC was subsequently reported by Z. Dong and co-workers.[118] The material was prepared from the pyrolysis of an iron precursor with polyacrylonitrile and melamine (Figure 11).

Figure 11 Schematic representation for the preparation of γ-Fe_2O_3/mCN-900-20 developed by Z. Dong and co-workers. (Reproduced with permission from Ref. 118. Copyright 2017, The Royal Society of Chemistry)

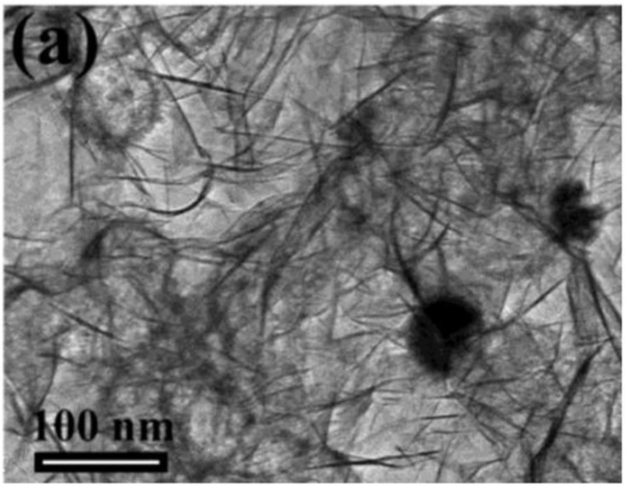
Here, the pyrolysis temperature seemed to have an opposite effect since the material prepared at 900 °C was the only one showing the formation of γ-Fe_2O_3 NPs and a suitable porous structure. Materials prepared at lower temperatures or with lower amount of melamine (<800 °C) neither show porous structure nor the complete formation of NPs. For these reasons, the catalyst prepared at 900 °C (γ-Fe_2O_3/mCN-900-20) showed the best activity with a TOF of 312 h^{-1}. Other undoped carbonaceous materials or common metal oxides as supports, as well as unsupported γ-Fe_2O_3 provided lower or negligible activity. Further works showed the use of unsupported γ-Fe_2O_3 NPs in the catalytic reduction of nitroaromatics. In a first paper by I. N. Lykakis, G. S. Armatas and co-workers[119] γ-Fe_2O_3 NPs were prepared through a polymer-assisted ligand-stripped method. Briefly, the original oleyl alcohol-capped γ-Fe_2O_3 NPs were stripped with $NOBF_4$ in order to remove the protecting agent and stabilized into a DMF solution of a nonionic surfactant (Pluronic®P-123). Then, after very slow evaporation of the solvent (7 days), the latter was completely removed upon thermal degradation at 300 °C under air, thus furnishing the desired mesoporous γ-Fe_2O_3 NPs (γ-Fe_2O_3-MNAs). Using this approach, solid-state transformations of γ-Fe_2O_3 into hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) were feasible (Figure 12).

Figure 12 Schematic representation for the preparation of γ-Fe2O3-MNAs and further transformation into α-Fe2O3-MNAs and Fe_3O_4-MNAs. (Reproduced with permission from Ref. 119. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)



This oxides exhibited the following activity order in the reduction of 4-nitroaniline to 1,4-phenylenediamine: γ-Fe_2O_3>α-Fe_2O_3>Fe_3O_4. From a synthetic perspective, worth of note is the ability of this catalyst to convert aliphatic nitro compounds to *N*-hydroxylamines instead of the fully-reduced product. Moreover, the double bond in 3-nitrostyrene was retained affording the desired product in 94% yield. The addition of water dramatically improved the activity of the reaction due to a possible interaction of the nitro group. Superficial modification of the catalyst could also be a possible reason, since iron oxides can undergo drastic alteration of their chemical structure upon water contact, which most commonly comprises the formation of hydroxyl groups.[120-122] In fact, materials similar to the ones reported by the groups of I. N. Lykakis and G. S. Armatas, were found to be active in the same transformation previous activation by water as demonstrated by the pioneering work of R. Prins and P. Rys.[92,93] In a recent paper, Z. Dong and co-workers prepared ultrathin γ-Fe_2O_3 nanosheets (γ-Fe_2O_3-UNSs) through a simple reduction method under air (Figure 13).[123]

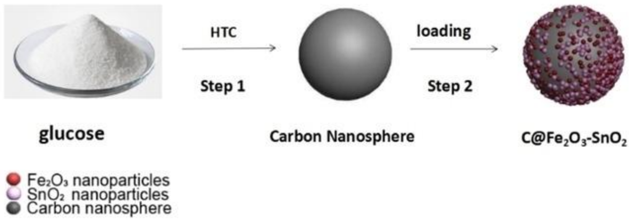
Figure 13 TEM image of γ-Fe_2O_3 nanosheets developed by Z. Dong and co-workers. (Reproduced with permission from Ref. 123. Copyright 2018, Elsevier)



The catalyst was then used for the reduction of various nitro compounds, among which 4-iodonitrobenzene and 4-nitrobenzaldehyde stand out since they were selectively converted into the corresponding amines without dehalogenation or hydrazone formation, respectively. Activated carbon fibers supported Fe_2O_3 NPs were as well reported by L. Kiwi-Minsker.[124] They were prepared in three steps: activated carbon fibers were wet impregnated with the Fe(III) precursor and then pyrolyzed at 350 °C followed by passivation under air/Ar. The as-obtained material showed microporosity with tiny pore diameter (<2 nm) and a large surface area (2140 m^2g^{-1}) compared to the other carbon-support Fe-based catalysts. The latter was found to be active in the reduction of various nitroarenes, and in particular 4-iodonitrobenzene and 3-nitrostyrene were obtained with a selectivity of 95% and 75% at 95% conversion of the starting material. The result obtained with 3-nitrostyrene is worth of note due to the capability of diazine in reducing carbon-carbon double bonds without the necessity of a metal catalyst. Unfortunately, the catalyst tends to leach little amount of Fe and this has an obvious negative impact on the recyclability. The same group published a similar catalyst based on Ni[125] and Co[126] which are described in the dedicated chapters.

Maghemite-bismuth bimetallic oxides were evaluated as catalysts in the reduction of nitrocompounds to aniline. In a first work, H.-B. Sun, Q. Liang and co-workers prepared the mixed oxide (Fe/Bi mol. ratio 18.5) by co-precipitation and then impregnation onto graphene oxide (GO).[127] The catalyst was used both in batch and in flow conditions. Using the latter technology, the mechanic robustness of the catalyst has been improved through calcination under air allowing for producing the desired amines in relatively large amount (>30 mmol scale). A similar approach proposed by the same authors, for the preparation of bimetallic Fe/Bi catalyst, consisted in the functionalization of carbon nanotubes with chitosan followed by cross-linking with glutaraldehyde and addition of Fe(III) and Bi(III) precursors.[128] Then, after the co-precipitation by means of aqueous NH_3, the solid was calcined at 250 °C to finally obtain the γ-Fe_2O_3/Bi_2O_3 NPs anchored onto chitosan-functionalized carbon nanotubes. The as-prepared catalyst showed catalytic activity comparable to the previously discussed one, but it can be directly used under continuous flow conditions without any pre-treatment. Despite photocatalytic methods are out of the aim of this review, the presence in the literature of a work dealing with the preparation of α-Fe_2O_3/Bi_2S_3 heterojunction for the catalytic transfer hydrogenation of nitroarenes should be mentioned.[129] H. Sun, D. Niu and co-workers prepared a glucose-derived carbon-coated Fe_2O_3/SnO_2 NPs through precipitation method (Figure 14).[130]

Figure 14 Preparation of C@Fe_2O_3-SnO_2 developed by H. Sun, D. Niu and co-workers. (Reproduced with permission from Ref. 130 Copyright 2018, Elsevier)



The synergistic effect of Sn was ascribed to its ability to promote the oxidation of Fe^{2+} to Fe^{3+}. It should be noticed that hematite (α-Fe_2O_3) never showed better catalytic activity than maghemite (γ-Fe_2O_3) or magnetite (Fe_3O_4) using hydrazine as reductant. However, the combination of SnO_2 with α-Fe_2O_3 resulted in enhanced activity.

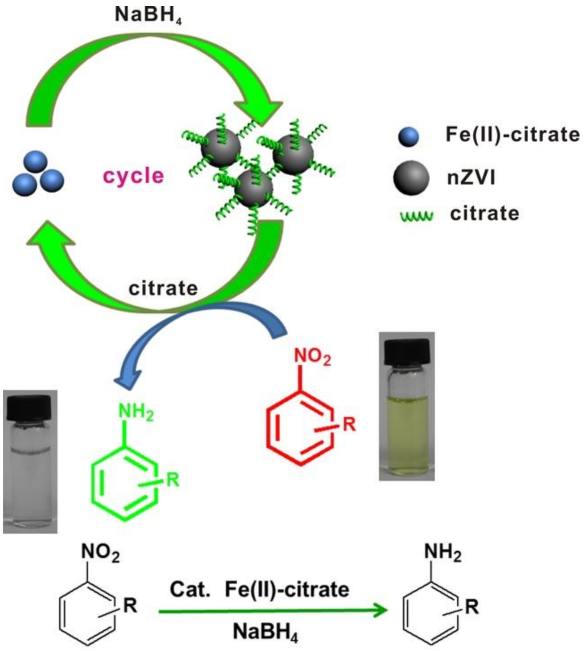
3.2.2.Reductions with alkali/alcohols

In the early 2000's, P. Selvam and co-workers studied the preparation and use of Fe(III) substituted hexagonal mesoporous aluminum phosphate as catalyst for various organic reactions, especially oxidative and reductive transformations. In particular, this catalyst was applied in combination with *i*PrOH/KOH for the reduction of nitro compounds[131] and azoarenes.[132] The combination of both acidic and basic Lewis sites in the catalyst, formed after the calcination step, was supposed to participate in the reaction mechanism. A range of substituted aromatic nitro and azo compounds was reduced to the corresponding amines. Worth of note is the preservation of the carbonyl group in ketones and aldehydes that are known to be reduced to the corresponding alcohols even in the absence of catalyst.[67,133,134] Moreover, unlike many other reports, the recyclability was proven to be effective for each substrate up to six runs. P. Veerakumar, S.-B. Lui and co-workers reported the preparation of Fe_3O_4 NPs embedded into biowastes-derived carbon.[135] A two-step protocol was employed for the preparation of the active material. Firstly, micro-mesoporous carbon was prepared by thermal treatment (600-900 °C) of beetroot-derived wastes with $ZnCl_2$ as an activating agent. Then, the as-obtained material was impregnated with $Fe(acac)_3$ and pyrolyzed at 900 °C affording the composite material constituted by Fe_3O_4 NPs (average size of 3.8 nm) incorporated into nitrogen-doped carbon. The reduction of nitro compounds was performed under microwave conditions showing good selectivity with many nitroarenes. Fe-impregnated SBA-15 was prepared by S. Velmathi and co-workers using tetraethyl orthosilicate (TEOS), Pluronic® P-123 and $Fe(NO_3)_3$ as SiO_2 precursor, surfactant and Fe source, respectively.[136] The catalytic activity of this material was comparable to other previous works in the field[131] with the disadvantage to have only a partial recyclability even after reactivation of the catalyst. The use of perovskite-type catalysts was evaluated by R. V. Jayaram and co-workers in 2003[137] and S. Farhadi and co-workers in 2011.[138] In the former work the authors proposed a successful microwave-assisted method for the production of bulk perovskite-type mixed oxides ($LaMO_3$ with M=Al, Fe, Cr, Co, Mn), whereas in the latter $LaFeO_3$ NPs were produced by pyrolysis of $La[Fe(CN)_6]\cdot 5H_2O$ at 700 °C. Both catalysts reduced nitro compounds using *i*PrOH/KOH. Unfortunately, since the reactions in the S. Farhadi work were performed under microwave irradiation, a direct comparison is not possible. However, under microwave irradiation, the nanosized $LaFeO_3$ catalyst showed five-fold activity than the bulk $LaFeO_3$. The reaction scope of both papers included many nitroarenes bearing various functional groups among which aldehydes and ketones were completely unaffected allowing for a complete selectivity towards the desired aniline.

3.2.3. Reductions with $NaBH_4$

During the last years, various Fe-based catalysts were proposed for this transformation. Bulk and supported iron oxides, Fe(0) NPs, and anchored defined complexes have been applied as catalytic systems. Metallic iron nanoparticles were proposed by the groups of K. Hanna[139] and Y. Cai.[140] In the former case, Fe(0) NPs were produced through the reduction of $FeCl_2$ by $NaBH_4$. For maintaining Fe in zero oxidation state, an excess of $NaBH_4$ is necessary during the catalyst storage. Recycling experiments *via* magnetic separation revealed leaching of Fe since the first recycled run which led to decreased activity. Y. Cai and co-workers developed an operationally-simple protocol for the one-pot preparation of citrate-coated Fe(0) NPs, which allow for nitro reductions. A complex of Fe(II) and citrate was *in-situ* prepared and reduced with $NaBH_4$ in the same vessel containing the nitro substrate (Figure 15).[140]

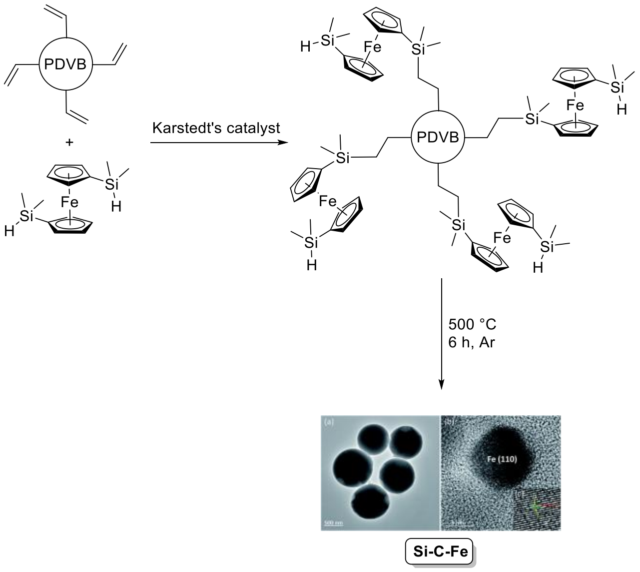
Figure 15 Mode of action of the catalytic system developed by Y. Cai and co-workers. (Reproduced with permission from Ref. 140. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)



The reaction proceeded efficiently with a good activity allowing the reduction of substituted nitroarenes beside 4-NP, such as 4-nitrobenzonitrile and 4-nitrostyrene. Even in this case the recyclability was not efficient since the original activity was maintained only for five runs.

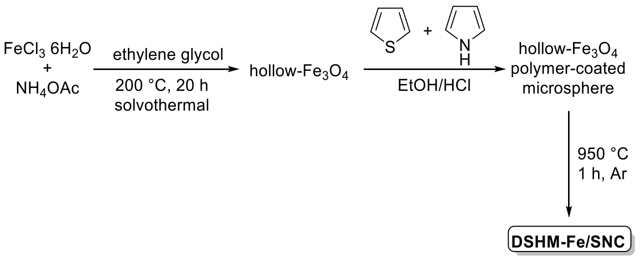
Moreover, various Fe-based supported catalysts were proposed for the titled reaction in recent years. In this respect, X. Wang, J. Kong and co-workers described Fe(0) NPs coated with Fe(II) oxides embedded into a carbonaceous matrix, which were produced through the pyrolysis of ferrocenyl-functionalized polydivinylbenzene particles (Scheme 12).[141]

Scheme 12 Preparation of Si-C-Fe. (Reproduced with permission from Ref. 141. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)



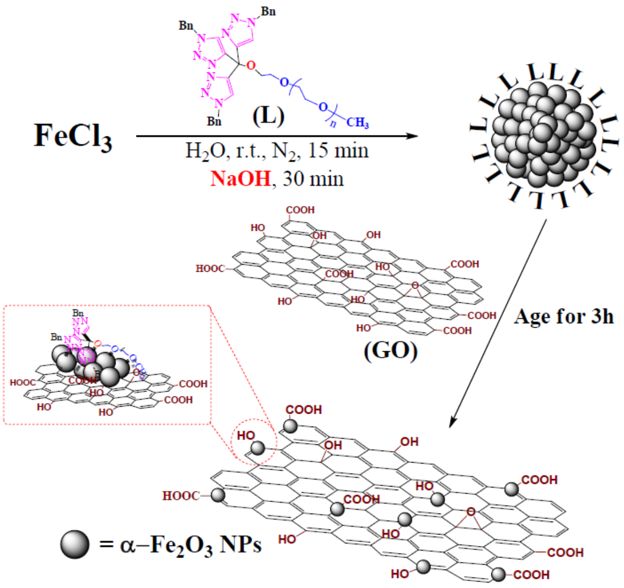
Very recently, S. Song and co-workers developed Fe-N-S-C materials prepared *via* a three-step methodology involving the production of Fe_3O_4 microspheres, subsequent Fe^{3+}-induced polymerization of pyrrole/thiophene on the surface and finally annealing treatment (Scheme 13).[142]

Scheme 13 Preparation of DSHM-Fe/SNC catalyst.



The synergistic interaction of both N and S in the carbon network was found to be crucial for achieving catalytic activity. Finally, D. Astruc and co-workers reported on the preparation and use of α-Fe_2O_3 NPs supported onto GO (Figure 16).[143] Apart from the application of this catalyst in the Suzuki-Miyaura cross-coupling, a good activity was shown for 4-NP reduction.

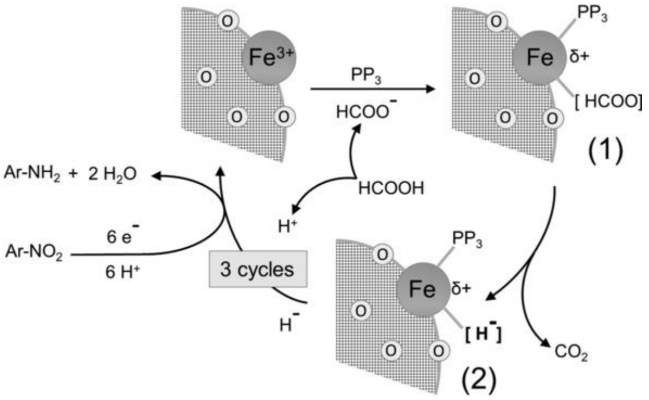
Figure 16 Preparation of α-Fe_2O_3 NPs supported onto GO. (Reproduced with permission from Ref. 143. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)



3.2.4.Other reductants

In addition to the aforementioned reducing agents, also formic acid (HCOOH) and paraformaldehyde were employed. The group of M. B. Gawande and R. Zboril reported the preparation and use of a flower-like magnetite (Fe_3O_4) nano-assembly for the reduction of nitroarenes using HCOOH in combination with tris[2-(diphenylphosphino)ethyl]phosphine (Tetraphos) as additive.[144] The same group used also hydrazine hydrate under microwave conditions in this transformation.[103] In case of formic acid, the authors proposed an iron hydride surface species, which is related to a previously published molecular-defined Fe-Tetraphos complex (Figure 17, see also Chapter 8.2).[145]

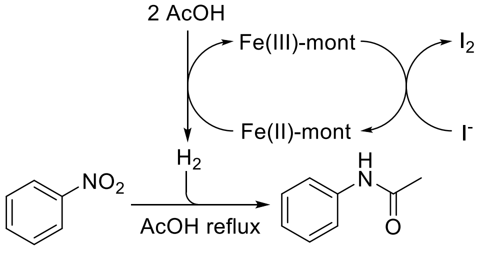
Figure 17 Proposed catalytic cycle the reduction of $ArNO_2$ to $ArNH_2$: coordination of both tetraphos (PP_3) and anion $HCOO^-$ and the subsequent formation of a superficial hydride species. (Reproduced with permission from Ref. 145. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)



Because of the similarity between these works, leaching of the heterogeneous catalyst might occur under operative conditions and the leached species could be the "real" active species. Unfortunately, the possible leaching of Fe species (either active or not) was not investigated and therefore cannot be ruled out. Comparing the two protocols by the groups of M. B. Gawande and R. Zboril (the one based on HCOOH and the one based on N_2H_4) the latter system has the intrinsic advantage of short reaction times (15-25 min). The first protocol based on HCOOH showed a similar efficiency at lower reaction temperature (70 °C) and does not require for special reactor apparatus. Regarding the reaction scope, the main difference can be found in the possibility of the HCOOH-based procedure in selectively reducing nitroarenes carrying carbonyl groups and carbon-carbon double bonds which are both known to be problematic if $N_2H_4 \cdot H_2O$ is used.

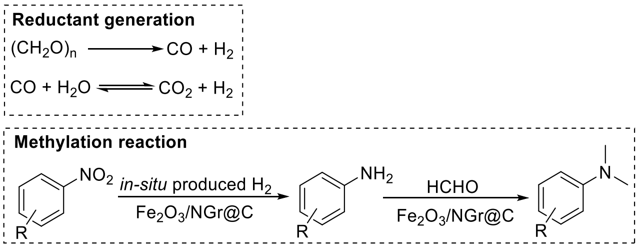
In 2005, B. M. Choudary developed a hydrogen evolving system from proton reduction with iodide anions as electron donor catalyzed by Fe(III)-exchanged montmorillonite (indicated as Fe(III)-mont in Scheme 14).[146] The system was applied for the reductive acylation of nitrobenzene to the corresponding acetanilide.

Scheme 14 Fe(II)/Fe(III)-based redox cycle in the production and consumption of hydrogen and related reduction of nitroarenes.



Finally, M. Beller, R. V. Jagadeesh and co-workers developed a Fe-based catalytic method for the dimethylamination of nitroarenes.[147] Using the Fe_2O_3/NGr@C catalyst developed in 2013,[77] paraformaldehyde was employed both as a reductant and a methylating agent (Scheme 15).

Scheme 15 Fe_2O_3/NGr@C catalyzed reductive methylation of nitroarenes without gaseous hydrogen.



Aromatic and heteroaromatic nitro compounds carrying different functional groups were selectively dimethylated. Functional groups like –OH, -SH, -$CONH_2$ and heterocycles were not affected in this protocol, which was applied to diverse life science molecules including the preparation of existing drug molecules. By careful variation of both the amount of paraformaldehyde and the reaction time, monomethylation of nitro compounds was also feasible.

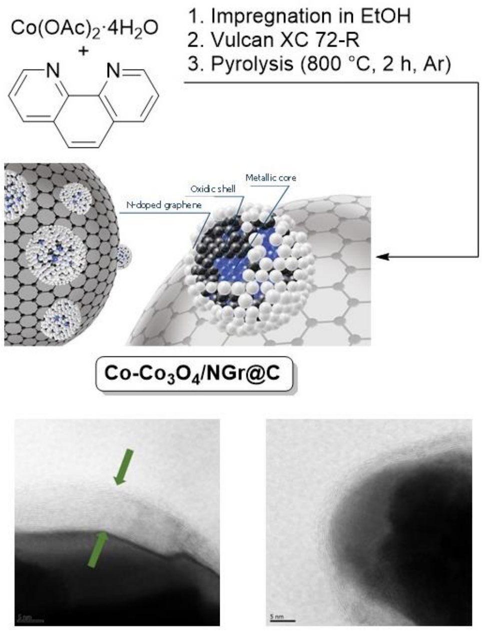
4. Heterogeneous cobalt-based catalysts

4.1. Reductions with molecular H_2

Seminal works reporting on the catalytic activity of Co using H_2 as reductant were first published in 1921[148] and 1937[149] by O. W. Brown and later on, in 1975, in a patent by Bayer AG.[150] In all cases, the active catalyst was claimed to be cobalt sulfide produced by treating Co oxides under a H_2S stream. Further publications regarding the use of homogeneous Co-based catalysts were then published and they will be discussed in chapter 8. In 2005, R. Raja and co-workers published one of the first modern reports in this area using heterogeneous catalysts.[151] The authors prepared metallic Co NPs supported onto commercially available mesoporous SiO_2 through an inverse-micelle method. Along with bimetallic Ni-Pd NPs, the supported Co NPs were able to efficiently catalyze the hydrogenation of nitroarenes to the related anilines with very high TOF (up to 23000 h^{-1} at almost complete conversion) at 80 °C and 25 bar H_2. The achieved efficiency of the catalyst is until now one of the highest ever reported, although the recycling turned out to be incomplete. After this important report, in 2013, the group of Beller developed a novel heterogeneous catalyst based on Co nanoparticles supported onto nitrogen-doped carbon (called Co-Co_3O_4/NGr@C).[152,153] The synergistic and complementary combination of both the Co-based NPs and the nitrogen-doped carbon seems to be crucial for the peculiar reactivity of this class of materials. The catalysts were prepared by pyrolysis of a Co(II)/N-ligand complex impregnated onto Vulcan® XC72-R carbon. Upon thermal treatment

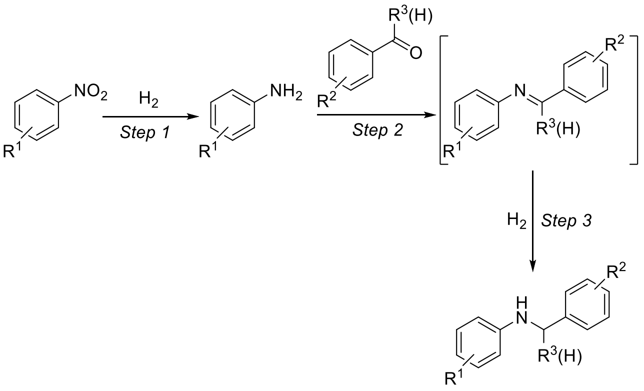
(800 °C for 2 h under Ar atmosphere) ordered nitrogen-doped carbon layers along with core-shell NPs are formed. The architecture of the materials is composed of an inner core of metallic Co and an external layer of Co_3O_4 (Figure 18). Interestingly, the nitrogen-donor is able to indirectly tune the activity of the final material. Among the investigated ligands, 1,10-phenanthroline (Phen) afforded the catalyst that provided the best activity in the hydrogenation of nitrobenzene to aniline.

Figure 18 Preparation of the Co-Co_3O_4/NGr@C catalyst developed by the group of Beller in 2013 and relative TEM images (green arrows highlight the graphene layers around the NPs).



Furthermore, the catalytic activity of the prepared material has been evaluated in the hydrogenation of substituted nitroarenes demonstrating excellent chemoselectivities. Aromatic nitro compounds bearing reducing-labile groups (*e.g.* carbon-carbon and carbon-heteroatom multiple bonds, halogens, carboxylic acid derivatives) were smoothly converted into the corresponding anilines without affecting the residual moieties. Later on, the performance of this catalytic system was enhanced through carefully assessing the composition of the reaction media (alcoholic solvents in combination with small portion of water) and the use of basic additives (such as triethylamine).[154] Even under those improved conditions, the selectivity in the case of substituted nitroarenes was maintained. Subsequently, the Co-Co_3O_4/NGr@C was used in the reductive amination of nitro compounds for the synthesis of secondary amines.[155] As general concept, this reaction occurs in three stages: reduction of the nitro compound to aniline, condensation of the latter giving the imine and then finally its hydrogenation (Scheme 16).

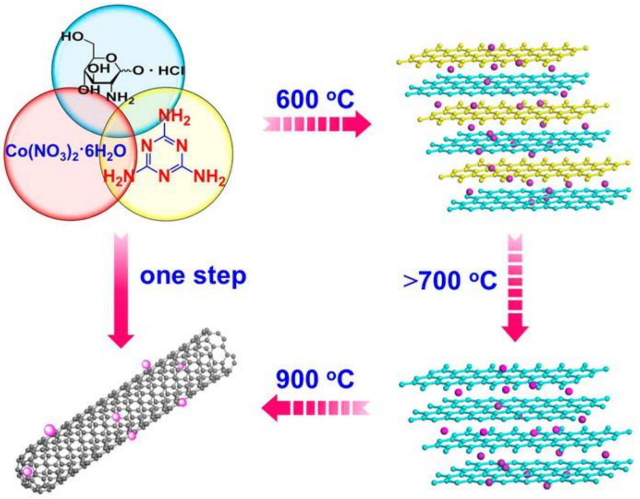
Scheme 16 Reductive amination of carbonyl compounds from nitroarenes.



Commonly, in this sequential process the rate determining step is the hydrogenation of the imine over the nitro group. For this reason, the overall transformation has to be conducted under harsher conditions than those used in the reduction of nitro to primary amine. The authors reported good yields only in the case of both nitroarenes and aldehydes bearing electron-donating groups (EDG). Other kind of substrates provided lower yields because of the presence of residual imine in the reaction mixture. This protocol also allowed for the synthesis of secondary amines from more challenging aliphatic nitro compounds and aldehydes. Finally, because of combined steric and electronic factors, ketones can be employed only if carbonyl activators (acids) and water scavengers (molecular sieves) are employed.

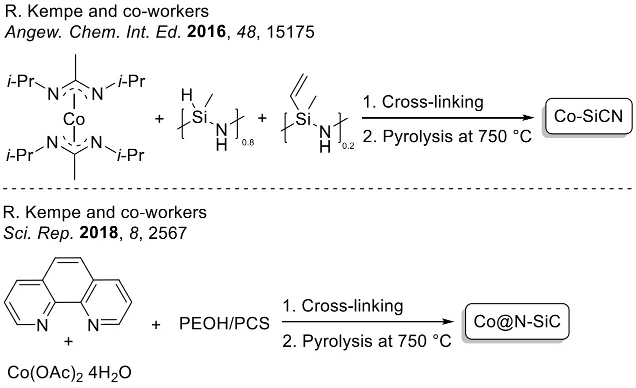
Starting from these works, a large number of reports dealing with the preparation and use of this kind of materials for reduction of nitroarenes were published. Various parameters such as nitrogen-donor, cobalt precursor, type of support, pyrolysis protocol and so on have been explored. In this context, in 2015 the group of Y. Wang prepared N-CNTs through a solvent-free method involving the use of cheap carbon precursors (D-glucosamine and melamine) and $Co(NO_3)_2 \cdot 6H_2O$ as the Co source in a two-temperature step pyrolysis procedure (Figure 19).[82] Similar to Co-Co_3O_4/NGr@C, this material is composed by Co(0) and Co_3O_4 NPs embedded in N-doped matrix onto CNTs. The as-obtained catalytic material exhibited a high productivity in the hydrogenation of nitrobenzene.

Figure 19 Preparation of CoO_x@N-CNTs. (Reproduced with permission from Ref. 82. Copyright 2015, American Chemical Society)



The authors claimed that the catalyst is reduced *in situ* to CoO and Co(0) and the latter species is supposed to be mainly responsible for the catalytic activity. The scope of the reaction was established using 20 nitroarenes substituted with various functional groups demonstrating high chemoselectivity. In 2014, the group of W. Xia reported an interesting study about the role of nitrogen atoms in the support.[156] They produced Co-based N-CNTs (produced through annealing of CNT at high temperature under NH_3 stream) *via* wet impregnation and applied them in the gas-phase hydrogenation of nitrobenzene. Using various techniques (XPRD, TPR-H_2 and XPS) they demonstrated that the presence of nitrogen atoms in the N-CNTs (1) promoted both the decomposition of the Co precursors and the reducibility of Co oxides thus forming active sites in the final catalyst, (2) improved the resistance of Co(0) to oxidation under exposition to air and (3) reduced the size distribution of the formed NPs. All these features led to an increased activity by at least two-fold with respect to the nitrogen-free catalyst. The importance and role of the nitrogen doping was also demonstrated by Ragaini, Beller and co-workers (*vide infra*).[68] In 2016, R. Kempe and co-workers developed a cobalt-based silicon carbonitride catalyst (Co-SiCN) from a defined cobalt amidinato complex (Scheme 17, upper part).[157] The prepared material was composed of small cobalt-based NPs (average of 1.7 nm) including both metallic Co and CoO_x. The oxidic nature of the material was confirmed by both XPS and TPR-H_2 analysis. The catalyst was not fully recyclable, in fact after the second run a decreased yield was notice. This fact was mainly attributed to oxidation of the Co(0) and in a small extent to metal leaching. Indeed, activity could be gained again by subjecting the catalyst to TPR-H_2, thus restoring Co in its low oxidation state. All these evidences point out to the role of Co(0) as active phase of the catalyst. The selectivity of the proposed transformation was then demonstrated using a number of nitro compounds containing reducible functional groups. For example, both 3-nitrostyrene and 4-iodonitrobenzene can be converted into the corresponding anilines with 82 and 76% yield, respectively. Furthermore, the same catalyst was applied in the reductive amination of nitro compounds with both aldehydes and ketones. Here again, the reductive amination of ketones required harsher condition and a higher catalyst loading along with carbonyl activators (Amberlyst® 15 and molecular sieves). Afterwards, the same authors reported the preparation of a catalyst using a similar approach (Scheme 17, lower part).[158] A block copolymer was firstly prepared from polycarbosilanes and hydroxyl-terminated polyethylene and then a Co(II)/Phen chelate was added and the material subjected to pyrolysis. The resulting mesoporous material was found to be composed of metallic cobalt Co NPs (average size 5 nm). The activity of this catalyst in the hydrogenation of nitrobenzene to aniline was conducted under reaction conditions similar to those reported for the Co-SiNC (*vide supra*), although with a decreased catalyst loading. The catalytic system was then applied to some other nitro derivatives showing complete selectivity even when challenging substrates like 4-iodonitrobenzene or 3-nitrostyrene were used (99% yield in both cases). Moreover, the new material showed an improved recyclability, unlike in the Co-SiNC.

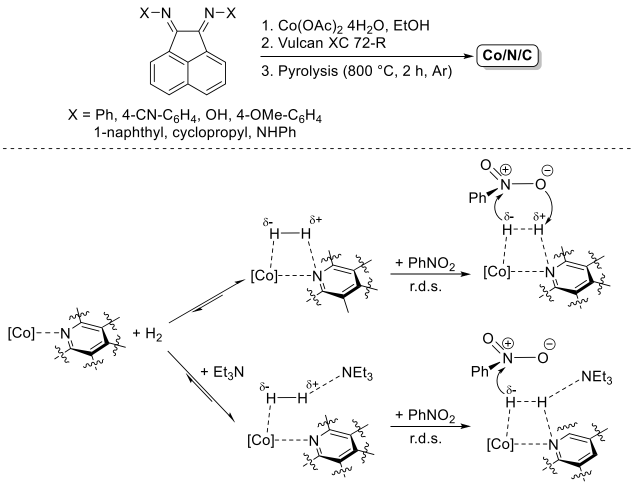
Scheme 17 Preparation protocols for Co-SiCN and Co@N-SiC developed by the group of R. Kempe.



Dong and co-workers developed a Co-N-C material produced from polyacrylonitrile and melamine coupled with an inorganic Co source *via* pyrolysis.[159] They found that 700 °C was the best pyrolysis temperature concerning both activity and selectivity in the hydrogenation of nitrobenzene. The thermal treatment at this specific temperature provided small (average size of 6 nm) and dispersed Co NPs onto mesoporous N-doped carbon along with the highest BET surface area and pore volume. Lower or higher temperatures did not provide proper growing of NPs and the formation of the mesoporous structure. The material mainly consists of metallic Co, even though some oxidic patterns cannot be ruled out. The catalyst demonstrated a good activity in the hydrogenation of nitrobenzene to aniline at relatively low H_2 pressure (10 bar). Nevertheless, some limitations are observed when carbonyl compounds or iodo-substituted nitroarenes were employed. In particular, nitroarenes substituted in 4-position with iodo, ketones, aldehydes and sulfonamides showed complete selectivity only at low conversion values, especially in the case of 4-iodonitrobenzene (24% conversion with 99% selectivity). The same catalyst was also applied in the reductive amination of nitroarenes with aldehydes under harsher conditions, showing good yields towards the desired products. However, aromatic aldehydes containing OH groups afforded the corresponding imines as major product without proceeding further towards the secondary amine.

In 2017, Ragaini, Beller and co-workers prepared a series of cobalt heterogeneous catalysts using α-diimine instead of Phen as nitrogen donor ligand, following the protocol established in 2013 (Scheme 18).[68]

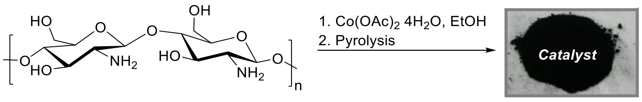
Scheme 18 Preparation of the catalyst developed from α-diimines by Beller and Ragaini (upper part) and proposed reaction mechanism (lower part): evidences for an heterolytic activation of the dihydrogen molecule. (Partially reproduced with permission from Ref. 68. Copyright 2017, Elsevier)



The materials showed a core-shell structure composed of an inner metallic and an outer oxidic layer with N-doped shells around the NPs. All the prepared materials showed activity in the hydrogenation of nitrobenzene to aniline. Kinetic studies revealed that the catalytic activity is directly correlated to the amount and configuration of the nitrogen species present in the carbonaceous matrix. On the basis of this experimental proofs, and supported by previous evidences,[154] the authors proposed a reaction mechanism in which the active site is composed of Co species (both in the form of NPs or isolated atoms) in contact with nitrogen atoms incorporated into the support. This specific conformation could allow for a heterolytic cleavage of the dihydrogen molecule. With the best catalyst, the reaction scope was demonstrated. It should be pointed out that the case-study 4-iodonitrobenzene did not provide the corresponding aniline at all, since complete hydrodehalogenation occurs under reaction conditions.

In most of the presented papers dealing with Co-N-C catalysts, the materials were prepared using a nitrogen-donor and a pre-formed carbonaceous support. In 2017, Beller and co-workers demonstrated that it is possible to use a unique and cheap molecule that combines these two features. Chitosan, a biopolymer derived from shrimp-shells bio-waste, contains -NH_2 and -OH moieties capable to coordinate metal ions and a carbon-based skeleton that is able to produce carbonaceous materials upon pyrolysis (Scheme 19).

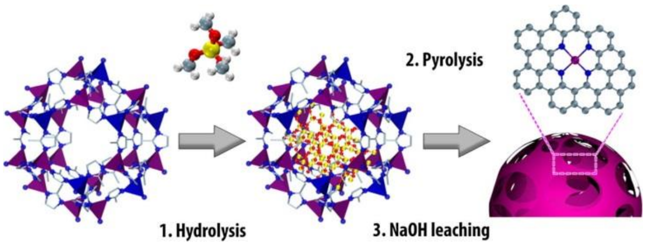
Scheme 19 Preparation of Co-based catalysts derived from chitosan.



This material was firstly presented as active catalyst in hydrodehalogenation reactions[160] and afterwards used in the hydrogenation of nitroarenes.[84] As in the previous cases, the material showed the concurrent presence of N-doped graphitic layers embedded Co(0) and core-shell Co_3O_4/Co(0) NPs. After an optimization of the reaction that confirmed the beneficial use of organic bases, a series of substituted nitroarenes were evaluated as substrates. Hydrogenation of halogen-containing nitroarenes proceeded smoothly resulting in obtaining the corresponding haloanilines with full selectivity, even if the same catalyst was used in the hydrodehalogenation reactions of $C_{sp2/sp3}$-X (X = Cl, Br, I) bonds. This evidence suggests a higher reaction rate for the nitro reduction over the hydrodehalogenation. The established protocol allowed for the synthesis of amine-containing intermediates involved in the preparation life-science molecules.

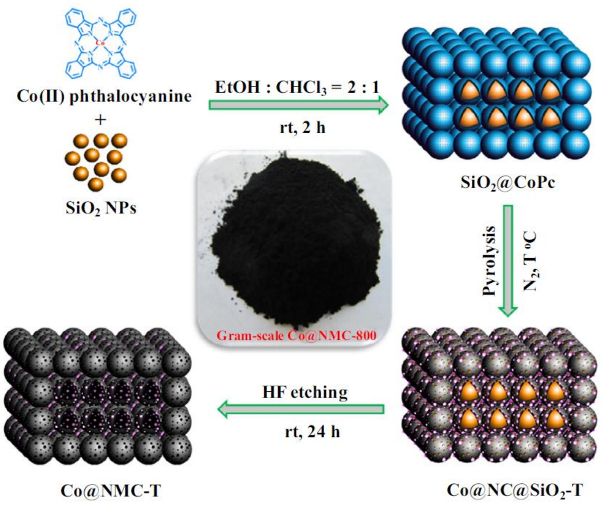
Y. Li and co-workers prepared an active Co-N-C material by the pyrolysis of well-defined Co-MOF (ZIF-67).[161] The preparation of the catalyst involved the synthesis of ZIF-67 and then its thermal treatment at various temperatures using both long pyrolysis times (10 h) and heating rates (1 °C min^{-1}). The material prepared at 600 °C was found to be the most active and selective one, achieving 97% selectivity in 3-nitrostyrene hydrogenation at full conversion. The presence of nitrogen species and in particular Co-N configurations in the catalyst is proposed as the reason for the high selectivity. This evidence is supported by a correlation between the conversion and the N content in the catalyst. Even if the authors have not proven it, this correlation was further observed by Ragaini and Beller (*vide infra*).[68] Moreover, *in-situ* ATR investigations revealed how the styrenic double bond is not adsorbed on the catalyst surface thus leading to a complete selectivity towards the aminostyrene without formation of side products. Various nitroarenes and heteronitroarenes with different reducible functional groups (including 4-iodonitrobenzene) were efficiently reduced to the corresponding anilines. As a consequence of the complete enveloping of the Co-based NPs into the carbonaceous matrix (which prevents them from agglomeration and overoxidation), recyclability of the catalyst was found to be complete over five reaction runs. The effective use of MOF as sacrificial starting materials for the preparation of Co-N-C catalysts was further demonstrated by Gascon and co-workers in two interconnected papers. In a first work,[162] the authors prepared the ZIF-67 MOF and afterwards direct pyrolysis led to the formation of the Co@NC catalyst. The preparation was similar to that previously reported by Y. Li and co-workers,[161] except for a passivation step that involved a post-treatment of the pyrolyzed material under an oxidative stream (5 vol% O_2 in N_2 for 2 hours). Comparing the preparation of the catalysts by J. Gascon and Y. Li, it turned out that the material prepared with passivation step still contains metallic Co NPs embedded into nitrogen-doped graphitic carbon structures. J. Gascon proved the presence of isolated CoN_x centers along with NPs through HCl leaching, poisoning test and HAADF-EDX techniques. The acid leached catalyst still showed activity indicating that both Co NPs and CoN_x centers play a role in the catalytic event. Acid leaching experiments were also performed by Y. Li and co-workers. However, the authors used *aqua regia* instead of hydrochloric acid, which resulted in the removal of every Co species leading to complete loss of activity. Indeed, the treatment with hydrochloric acid is known to be milder and thus more selective resulting in the removal of only uncovered Co NPs.[163] In a further work published in the same year, Gascon and co-workers studied a Co catalyst supported onto mesoporous N-doped carbon (Co@mesoNC), which was prepared following a sacrificial template approach.[164] Here, a silica precursor (tetramethyl orthosilicate, TMOS) was hydrolyzed inside the micropores of a Zn/Co-based MOF (BIMZIF(Co, Zn)) followed by pyrolysis (900 °C) and basic leaching of the obtained SiO_2 (Figure 20).

Figure 20 Preparation of Co@mesoNC. (Reproduced with permission from Ref. 164. Copyright 2017, Elsevier)



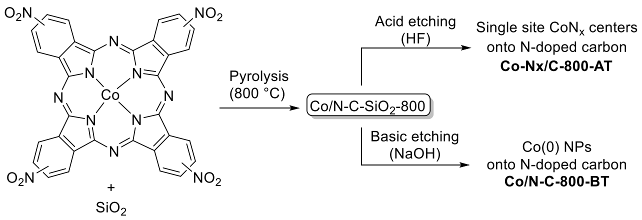
The material shows exclusively the presence of single CoN_x centers at a remarkable loading of 3.5 wt% Co without the formation of NPs as verified by various complementary analytical techniques (TEM, EDX, XPRD, XPS and XAS). Crucial for the formation of such isolated centers was the presence of Zn atoms in the original MOF which spatially separate Co centers preventing them from agglomeration into NPs. In addition, Zn evaporates during the high temperature treating process generating vacant sites in the carbonaceous matrix. Finally, the controlled synthesis of SiO_2 NPs and its removal created a mesoporous material network with 4-fold increased BET area. Hence, improved activity was achieved. Moreover, in contrast to the previous example, Co@mesoNC is able to reduce 3-nitrostyrene with full selectivity highlighting the importance of single CoN_x centers. Even though the preparation of Co@mesoN needs many steps, its performance is among the best for the hydrogenation of nitroaromatics. Following a similar procedure, F. Zhang, X.-M. Zhang, H. Yang and co-workers prepared a mesoporous Co-based catalyst using Co(II)/phthalocyanine as molecular precursor and SiO_2 as sacrificial templating agent (Figure 21).[165] In contrast to the Gascon work, they did not use a soluble molecular precursor of SiO_2 but the Co complex and the solid template were directly mixed together.

Figure 21 Preparation of Co@NMC-T (Reproduced with permission from Ref. 165. Copyright 2017, Elsevier)



The composition and architecture of the catalysts were found to be strictly dependent on the pyrolysis temperature. More specifically, the formation of NPs occurred only for pyrolysis temperature >600 °C and the material prepared at 800 °C showed the best activity in the benchmark hydrogenation of nitrobenzene to aniline. Again, here the pivotal role of Co(0) as dominant active species was established as shown by other precedent works. Worth of note are the mild reaction conditions (10 bar H_2, 80 °C, 1.2 h) and the ability to hydrogenate 4-iodonitrobenzene with full selectivity at 97% conversion. Within the same year, the group of Z. Zhang prepared a very active catalyst using a Co(II)/phthalocyanine complex and colloidal SiO_2 as sacrificial templating agent (Figure 22).[166]

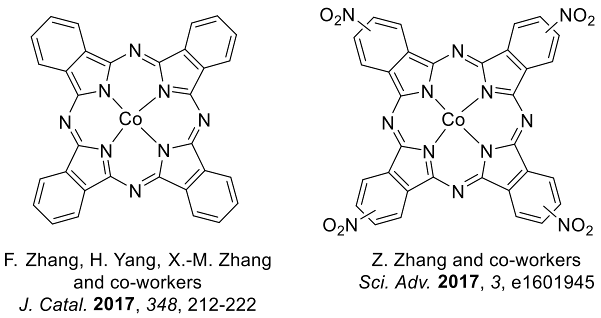
Figure 22 Preparation of the catalyst developed by Z. Zhang and co-workers.



They demonstrated that acidic treatment (aqueous HF) is favorable over the basic one (aqueous NaOH) because HF simultaneously removed both SiO_2 and redundant/unstable Co NPs. Thus, after the acidic etching only individual single CoN_x centers were left. Despite the low metal loading (0.25 wt% of Co) the material pyrolyzed at 800 °C and afterwards treated with HF was found to be active in the hydrogenation of nitrobenzene under mild conditions (1 bar H_2, 40 °C in water). Moreover, under more severe conditions (3.5 bar H_2, 110 °C in EtOH), the catalyst exhibited a productivity that outperforms the previously reported systems. Regarding the substrate scope, in addition to various nitroaromatics, the catalyst is also able to reduce more challenging aliphatic (both linear and cyclic) nitro compounds.

At a first glance, the works of Z. Zhang and co-workers[166] and F. Zhang, X.-M. Zhang and H. Yang and co-workers[165] may appear very similar. However, some key variations can be found that might explain the very different activity and morphology of the obtained materials. In the work of F. Zhang, X.-M. Zhang, H. Yang and co-workers, after the first pyrolysis a non-specified chemical leaching was performed followed by a second pyrolysis. This might explain the formation of NPs instead of single centers due to thermally-driven agglomeration. Unfortunately, the authors did not provide any information about the morphology and/or composition of the material obtained after the first pyrolysis step. Furthermore, the two employed Co(II) precursors differ in the ligand structure (Scheme 20). Though, according to TGA measurements it seems that the -NO_2 moieties were lost during the pyrolysis process questioning their actual role.

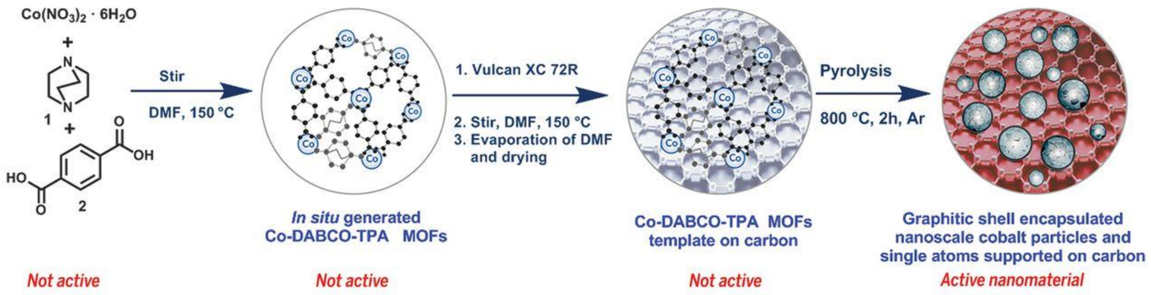
Scheme 20 Comparison between the two cobalt phthalocyanine precursors used in the works of F. Zhang, H. Yang, X.-M. Zhang and co-workers and Z. Zhang and co-workers.



The catalyst produced by Z. Zhang and co-workers was further employed in the reductive amination of nitro compounds under H_2.[167] In accordance with the results described by Beller and co-workers (*vide supra*), the authors reported that the use of protic solvents and high reaction temperatures (>130 °C) accelerate the conversion of the imine into the secondary amine. The broad reaction scope included various substituted nitroarenes and aryl aldehydes that were transformed into the corresponding secondary amines with good to excellent yields. However, in some cases (especially if one or both of the two reactants are sterically hindered) residual imine can be still detected limiting this protocol. Notably, the reductive amination of ketones (cyclic or acyclic) is possible by increasing the temperature (130 °C), avoiding the use of acids or molecular sieves. The catalyst reported by Z. Zhang and co-workers was found to be more active than Co-Co_3O_4/NGr@C.

In the field of Co-N-C catalysts derived from MOF´s, very recently the group of Beller reported the pyrolysis of a Co-MOF prepared from $Co(NO_3)_2$, DABCO and terephthalic acid deposited onto carbon (Figure 23).[168]

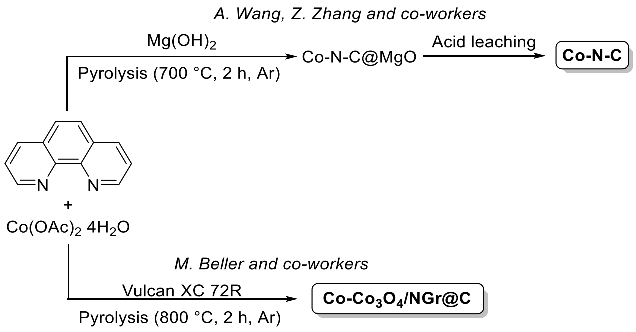
Figure 23 Preparation of the catalyst developed by Beller and co-workers in 2017. (Reproduced with permission from Ref. 168. Copyright 2017, American Association for the Advancement of Science)



The final material contained various Co species such as metallic Co NPs, core-shell Co/CoO_x NPs and single Co atoms. Along with reductive aminations from carbonyl compounds and amines (both aldehydes and ketones), this catalyst was applied in the synthesis of tertiary amines from nitroarenes. Both transformations provided the desired compounds in high yields even using substrates with multi-functionalized scaffolds.

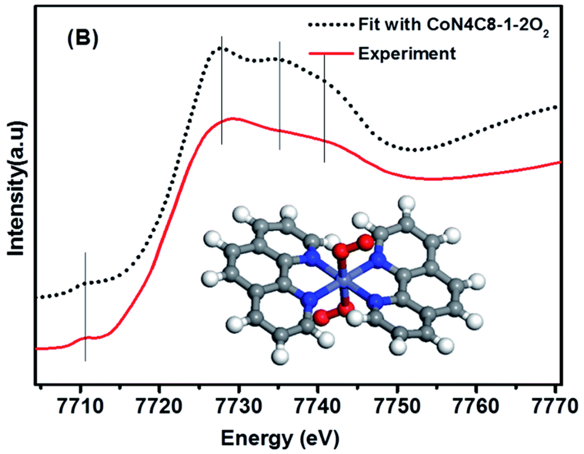
Finally, the group of T. Zhang and A. Wang demonstrated that the original system proposed by Beller in 2013 can be tuned to produce a single-atom catalyst.[169] The key-point was the use of $Mg(OH)_2$ as sacrificial template agent and a Co(II)/Phen chelate as the molecular-defined precursor (Scheme 21).

Scheme 21 Preparation of the catalysts developed by Beller and co-workers and A. Wang, Z. Zhang and co-workers.



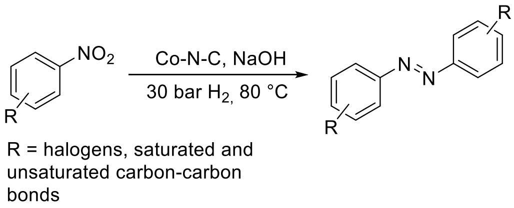
It was demonstrated that $Mg(OH)_2$ guarantees the proper dispersion of the Co(II)/Phen chelate and moreover it is converted into MgO which was subsequently acid-leached. Thanks to this approach, Co(II) single sites were unequivocally detected by HAADF-STEM and XANES in the sample pyrolyzed at 700 °C. Additionally, DFT calculations in combination with EXAFS depicted the possible configuration of the active species as a Co(II) atom coordinated to four pyridinic-configurated N atoms (Figure 24).

Figure 24 Comparison between the K-edge XANES experimental spectrum of Co–N–C (solid red line) and the theoretical spectrum (black dotted line) calculated with the inset structure. (Reproduced with permission from Ref. 169. Copyright 2016, The Royal Society of Chemistry)



The catalyst was employed in the base-promoted reductive coupling of nitroarenes for the synthesis of symmetric azo compounds (Scheme 22).

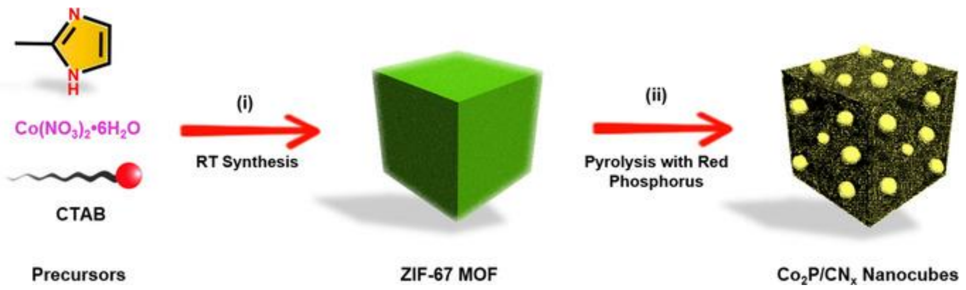
Scheme 22 Co-N-C catalyzed reduction of nitroarenes to azocompounds in the presence of NaOH.



The catalyst remains rather stable over the recycling runs, even if the reaction was conducted under basic conditions. This was due to the stability of the CoN_x centers embedded into the doped carbonaceous network that are prevented from leaching. This work constitutes a rare example of the direct reduction of nitroarenes to azoarenes using a Co-based catalyst. Apart from stoichiometric methods, this transformation still relies on noble-metal based catalytic systems.[97,170]

Very recently the group of W. L. Queen, broadened the use of Co-N-C catalyst demonstrating that Co_2P supported onto NC are good catalysts for the hydrogenation of nitrobenzene.[171] The active materials were prepared from the pyrolysis of ZIF-67 along with red phosphorous (Scheme 23).

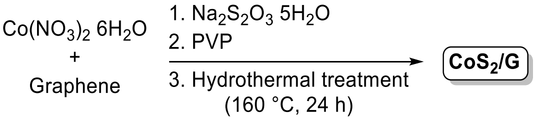
Scheme 23 Preparation of Co_2P/CN_x nanocubes. (Reproduced with permission from Ref. 171. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)



After the thermal treatment, Co_2P phosphides NPs with an average size of 5 nm supported onto nitrogen and phosphorous doped nanocubes were formed. Interestingly, the nanocubic structure was maintained after the thermal process. Despite the relatively mild conditions employed, the activity of such material is comparable to that obtained using the P-free catalyst.

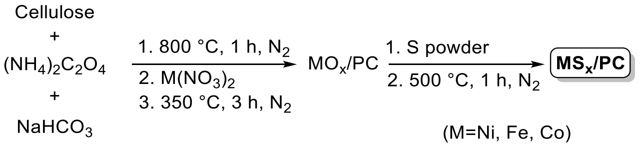
As demonstrated in the case of Fe (*vide supra*) cobalt sulfides act as catalysts in the hydrogenation of nitro compounds. In 2017, X. Guo and Y. Wang reported on the preparation of CoS_2 particles supported onto graphene produced through a hydrothermal method. $Co(NO_3)_2·6H_2O$ and $Na_2S_2O_3·5H_2O$ were used as inorganic precursors while graphene and polyvinylpyrrolidone carbonaceous ones (Scheme 24).[172]

Scheme 24 Preparation of CoS_2/G.



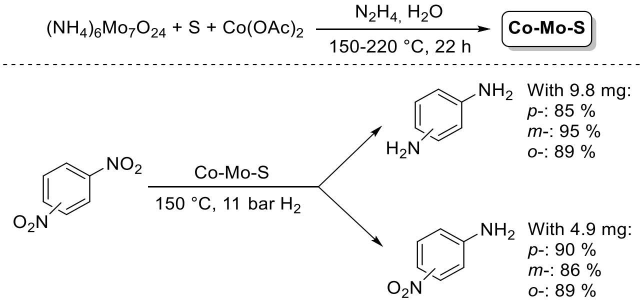
The material is composed by large CoS_2 particles (average size of 300 nm) distributed onto graphene. Initially, it was tested in the photocatalytic hydrogenation of nitrobenzene. Even though the reaction was performed in the dark, activity was still detected (nitrobenzene conversion <23% with full aniline selectivity). Both the inclusion of CoS_2 particles onto graphene and irradiation with visible light (300 W Xe lamp, 400-800 nm) enhanced the activity under mild conditions (30 °C, 2.5 bar H_2, 1.5 h). However, catalyst loadings were high (30 mol% based on CoS_2 using the graphene supported catalyst) and the provided information does not allow for a rigorous comparison with other materials. Few months later, Y. Wang reported a similar material for the hydrogenation of 3-nitrostyrene in the absence of light.[173] Various metal disulfides based on Fe, Co and Ni were prepared following the so-called *oxide-to-sulfide* method and then supported onto porous carbon (PC in Scheme 25).

Scheme 25 Preparation of MS_x/PC following the oxide-to-sulfide method.



Both CoS_2/PC and FeS_2/PC provided the desired 3-aminostyrene with complete conversion and selectivity. However, the Co catalyst showed an improved activity with respect to the Fe one. It should be noted that two more works regarding these FeS_2-based materials were recently published (*vide supra*). Combining theoretical (DFT) and experimental (EXAFS) studies the presence of two distinct cobalt sites was proposed for the H_2 activation and substrate adsorption. As straightforwardly demonstrated in previous works (especially from the group of A. Corma), the preferential adsorption of the NO_2 moiety instead of the C=C bond is the essential point for the observed selectivity in this specific transformation.[18,174] Moreover, the group of Corma group presented a very interesting work in the field of transition-metal sulfur-containing catalysts by developing a nanolayered unsupported Co-Mo-S material showing very good catalytic activity in the hydrogenation of nitro compounds. The catalyst was prepared through a simple hydrothermal method starting from inorganic precursors (Scheme 26).[175]

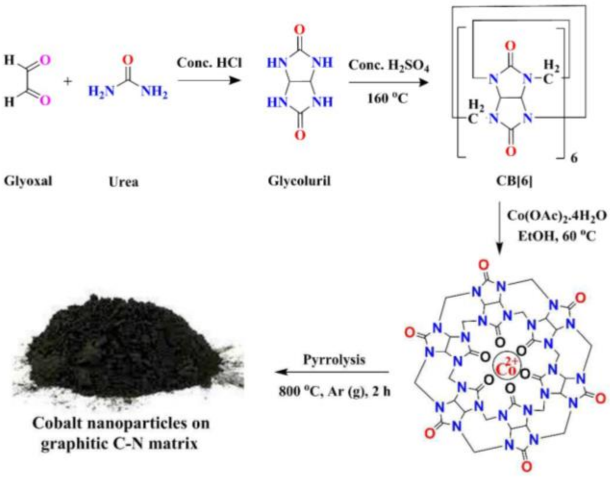
Scheme 26 Preparation of Co-Mo-S and selected application in the reduction of dinitrobenzenes reported by the group of A. Corma.



Through careful optimization of both temperature and amount of cobalt, the authors were able to prepare ordered layers of MoS_2 with Co atoms included in the structure. This resulted in the formation of active Co-Mo-S assemblies with minor amount of isolated CoS_2. Both MoS_2 and CoS_2 showed negligible activity in the hydrogenation of 3-nitrostyrene to 3-aminostyrene, chosen as case-study benchmark reaction. The Co-promoted Mo-S catalyst prepared at 180 °C with a precise Co/Mo ratio indicated highest activity that was ascribed to the presence of isolated Co atoms into the MoS_2 layers. In fact, catalysts rich of CoS_2 were found to be less active. It should be noticed that in all the catalytic experiments complete selectivity towards the desired 3-aminostyrene was observed as previously reported by Y. Wang and co-workers[173] highlighting the importance of the presence of metal-sulfur interactions. Following the catalytic protocol developed by Corma and co-workers it is possible to hydrogenate substituted nitro compounds with full selectivity in the presence of many labile groups such as halogens (despite 4-iodonitrobenzene was not included, 3-iodonitrobenzene was hydrogenated with full selectivity), carbon-carbon multiple bonds, carbonyls and carboxylic acid derivatives. Remarkably, dinitro compounds were successfully hydrogenated to the corresponding diamine or nitroanilines simply by varying the amount of catalyst. Finally, the catalyst showed a reduced activity over the recycling runs due to the deterioration of the ordered Co-Mo-S structures and the concomitant formation of agglomerated phases of CoS_2 thus still ensure the desired selectivity but lowers the conversion.[173]

In general, the use of pristine transition metal-based MOF´s in reduction reactions is limited. In this respect, only few examples for reduction of nitro compounds have been reported in the open literature. For example, in 2017 W. Lin and co-workers prepared a Zr/Co-based MOF. The authors claimed that differently configured OH groups created binding sites for Co(II) ions, which were reduced with $NaBH_4$ immediately before the catalytic experiments.[176] Despite the tedious preparation of the catalyst, the activity was low under rather severe conditions (40 bar H_2, 110 °C, 42 h). In addition, the material was not selective for nitroarenes having reducible functional groups such as polar or non-polar double bonds and C-I moieties. Most recently, the group of N. H. Khan proposed a new nitrogen-rich starting material (Cucurbit[6]uril) for the preparation of the Co-N-C catalysts active in nitro reductions (Figure 25).[177]

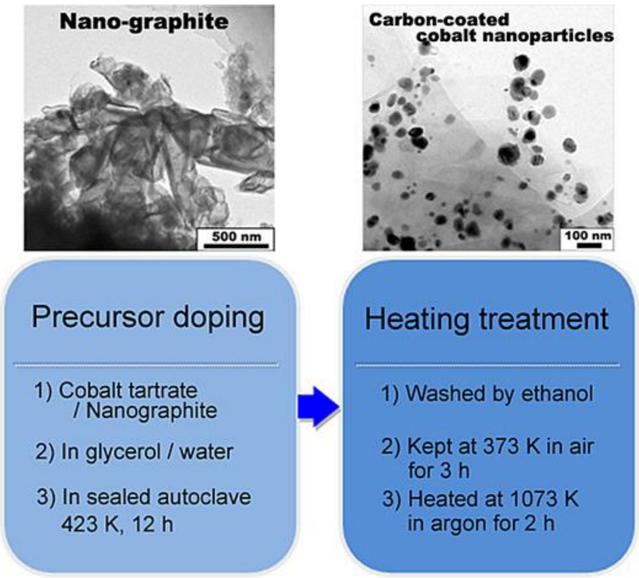
Figure 25 Preparation scheme for Co@g-C/N-T. (Reproduced with permission from Ref. 177. Copyright 2018, Royal Society of Chemistry)



In agreement to the report by Beller, Ragaini and co-workers higher N-content in the final material led to increased activity.[68] The pyrolysis of the Co(II)/cucurbit[6]uril complex generate a mesoporous material that showed a relatively high N concentration (8.54 wt%). As observed in many other cases, both Co(0) and Co oxides structures were detected by XPRD and XPS, respectively. The as-obtained material was active in the hydrogenation of nitrobenzene under mild conditions using low catalyst loading (*ca.* 0.02 mol% Co) exhibiting outstanding TOF (up to 14000 h^{-1}). The impressive activity outperformed the one obtained by Z. Zhang in 2017.[166] The reported reaction scope included dinitro compounds and substituted nitroarenes, but only few challenging substrates. Unfortunately, the catalyst is not well recyclable due to metal leaching after the second run. Notably, the organic precursor adopted in this work was also employed by the group of W. Ding for the preparation of an acid-resistant Ni-based nitrogen-doped carbon catalyst for the selective conversion of nitrobenzene to 4-AP under molecular hydrogen.[178]

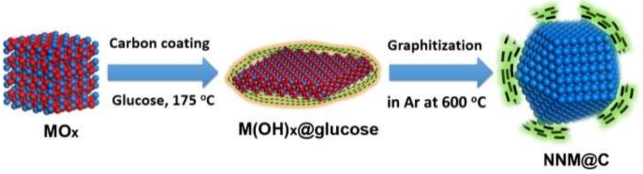
In all the aforementioned studies, the materials prepared without the addition of the nitrogen precursor are not active in the hydrogenation of nitro compounds. Accordingly, the synergistic combination of Co/Co oxide with the nitrogen atoms included in the carbon matrix is crucial for the reactivity. However, in 2016 F. Li and G. Yuan demonstrated that Co NPs embedded in ordered undoped carbon are equally active catalysts for the hydrogenation of nitro compounds.[179] The material was prepared by a two-step method: a first solvothermal treatment of a mixture of Co tartrate, glycerol, water and nanographite was followed by drying in the air and pyrolysis at 800 °C under Ar atmosphere (Figure 26). Unfortunately, the authors did not provide any characterization data for the material prepared through the solvothermal method.

Figure 26 Preparation of Co/CoO@Carbon. (Reproduced with permission from Ref. 179. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)



It might be supposed that both the glycerol and the nanographite could act as the reductant towards the Co(II) salt forming unsupported or capped Co(0) NPs that, upon exposure to air, were superficially oxidized to Co(II)/Co(III) oxides. Subsequently, the pyrolysis treatment might create graphene layers around such particles and again the Co(II)/Co(III) oxides could be reduced to Co(0). The authors clearly demonstrated that the generation of Co(0) during the pyrolysis process is correlated with its temperature, thus the catalyst prepared at 800 °C showed the highest activity. The reaction scope embraces many substrates bearing diverse functional groups including 4-iodonitrobenzene that was converted into the corresponding aniline in 80% yield. The recyclability test showed that after the 9th recycle the yield decreased dramatically, ascribing this behavior to the physical abrasion of the graphene shells that readily expose the Co(0) centers to oxidation. The key role of Co(0) NPs in the hydrogenation of nitro compounds was extensively studied by Corma and co-workers. In 2016, they reported an easy way to prepare metal-rich Co(0) NPs covered by graphenic layers following a two-step protocol.[174] A Co(II) precursor (in the specific case Co(II)-EDTA) was solvothermally treated in MeOH and then reduced under H_2 atmosphere at 450 °C. The as-prepared Co@C material displays a core-shell structure in which Co in zero oxidation state is surrounded by CoO_x (mainly in the form of Co_3O_4) covered by few graphenic layers that present cracks. It should be noticed that, even if EDTA was used, the final material does not contain nitrogen. Through the use of *in-situ* XPS the authors proved that under reaction conditions CoO_x species are completely converted into metallic Co without affecting the morphology of the material. The material prepared under air at lower temperature (250 °C) is composed by both Co(0) and CoO_x showing a decreased activity in the hydrogenation on 3-nitrostyrene. However, the material prepared under air at 450 °C displayed only Co_3O_4 and was not active in the hydrogenation of nitroarenes. Under optimized conditions hydrogenation of 3-nitrostyrene proceeded with 93% selectivity and 95% conversion. In a further work by the same group, a similar strategy was followed to produce Co(0) NPs embedded in glucose-derived carbon (Figure 27).[180] Nevertheless, a pyrolysis step was necessary for achieving the graphitization of carbon.

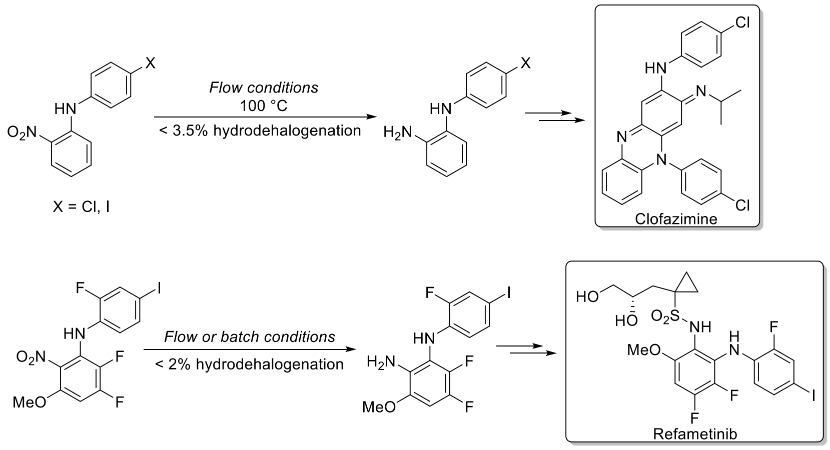
Figure 27 Preparation of Co@C NPs (Reproduced with permission from Ref. 180. Copyright 2017, Elsevier)



Despite the formation of protective carbon shells around the Co(0) NPs their exposure to air creates an oxidic layer that can be converted back to the pristine Co(0) by pre-treating the catalyst under H_2 before the catalytic reaction. Moreover, the use of glucose as carbon source provides a higher number of exposed active sites (Co(0) atoms) with respect to the previously discussed catalyst prepared from Co(II)/EDTA (*vide supra*). The two latter features ensure an increased catalytic activity in the selective hydrogenation of 3-nitrostyrene (selectivity up to 97% at conversion >95%). In order to enhance the formation of Co(0), a bimetallic Ni/Co catalyst was then developed which showed further improved activity (for an exhaustive discussion the reader is referred to chapter 7).

In the last years, a series of dedicated papers dealing with the specific transformation of 4-iodonitrobenzene to 4-iodoaniline was published. It should be noted that all of them include some authors from chemical industry highlighting the importance of this specific transformation. In 2016, Hassfeld, Roggan and co-workers prepared Co_3O_4-NPs encapsulated into nitrogen-doped graphene shells deposited onto CNTs through pyrolysis of $Co(OAc)_2$, Phen and carbon nanotubes.[181] The prepared material displayed an architecture similar to that observed in the material prepared by Beller and co-workers in 2013. Metal NPs composed of both Co(0) (detected from XPRD) and Co_3O_4 (detected from XPS) are incorporated into layers of graphene doped with nitrogen atoms and supported onto CNTs. The Co-Co_3O_4/NGr@CNTs catalyst efficiently catalyzed the hydrogenation of 4-iodonitrobenzene to 4-iodoaniline with complete conversion and 93% selectivity in the desired product under batch conditions. After a careful evaluation of its mechanical stability, the catalyst was employed in flow process. Interestingly, despite many structural and chemical parallels, the congener Co-Co_3O_4/NGr@C provides only the hydrodeiodinated product. In further series of papers by S. Roggan, N. Steinfeldt and P. Loos a careful evaluation of various catalysts and reaction parameters were examined in the hydrogenation of 4-iodonitrobenzene. In a first report,[182] among various commercially available noble-metal based heterogeneous catalysts (mainly Pt or Pd), Raney®-Co was found to provide superior selectivity with hydrodehalogenation <1%. However, complete conversion was never reached since upon full conversion the hydrodehalogenation rate became significant and thus leading to a rapid decrease of the selectivity. Although the use of Raney®-Co is worthwhile from a selectivity point of view, it showed less activity and for this reason high catalytic loadings were required (15 mol%). Good performances were achieved under continuous flow conditions, in which Raney®-Co displayed remarkable high-term stability over the standard Pt-V/C catalyst normally used in this specific reaction. Raney®-Co was applied as catalyst for the reduction of nitroarenes containing a halogen group in their structure. In particular, intermerdiates of Clofazimine (used against dermatological diseases) and Refametinib (selective MEK1/2 inhibitor) were prepared with remarkable selectivity (Scheme 27).[183]

Scheme 27 Synthesis of Clofazimine and Refametinib using Raney®-Co.



Later on, the performances of another family of commercially available catalysts (namely CoEnCat™) were studied.[183] The latter are composed by a Co/Al (Co/Al up to 21 wt%) alloy with minor amount of Ni (<6 wt%) and traces of Cr and Fe encapsulated into a polymeric network. As stated in the paper, the preparation of the same was not explained due to intellectual property reasons. However, characterization techniques revealed the formation of Al/Co and Al/Ni alloys (specifically Al_5Co_2 and Al_3Ni_2). Thanks to the significant mechanical stability, CoEnCat™ were successfully employed in continuous flow conditions showing high chemoselectivity in the desired 4-iodoaniline (<1% hydrodeiodination). Moreover, CoEnCat™ catalysts generally showed higher activity than Raney®-Co and more importantly they do not suffer of hazardous pyrophoricity. However, a comparison of the three reported systems revealed how the Co-Co_3O_4/NGr@CNTs provided greater productivity and selectivity with respect to both Raney®-Co and CoEnCat™.

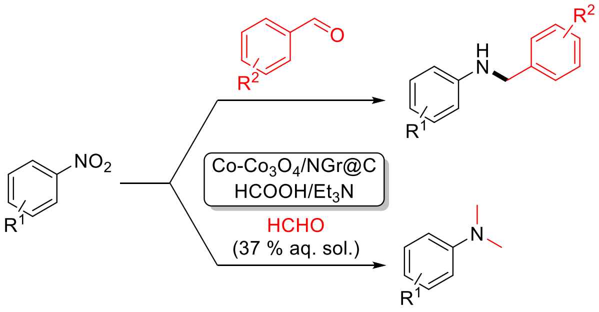
In conclusion, catalysts developed by the groups of Z. Zhang[166] and N. H. Khan[177] represent state-of-the-art in terms of activity. The first material can be effectively recycled, a crucial factor for a potential application. However, the availability of the starting material for the preparation of the catalyst is scarce since most of the common chemical suppliers do not provide that specific molecule (Scheme 11). On the other hand, the N-containing precursor proposed by N. H. Khan has to be preliminarily prepared (the synthetic pathway is rather simple – and involves commercially available chemicals - but concentrated acids need to be used). In this respect, the use of commercially available starting materials is advantageous. For instance, catalysts described by the groups Beller, F. Zhang, and A. Corma employed phenanthroline, chitosan, phthalocyanine, glucose and simple inorganic Co-precursors, thus making them more appealing.

4.2. Transfer hydrogenations

4.2.1. Formic acid and CO/H_2O as reductants

In addition to catalytic hydrogenations, the Co-Co_3O_4/NGr@C catalyst described by Beller in 2013 was used in the transfer hydrogenation of nitro compounds using formic acid and trimethylamine.[184] It turned out that the reduction of the nitro moiety proceeded with a very high chemoselectivity towards the desired product, especially in the case of nitroheterocycles. The same group demonstrated the use of CO/H_2O as reducing couple in the reduction of aromatic nitro compounds showing selectivities comparable to the two latter systems, which is another alternative to molecular hydrogen.[185] However, the efficiency of the catalyst is lower along with the necessity of higher operative temperature and pressure. In contrast to the previous systems, the catalyst was not recyclable. In fact, after the second, run both conversion and selectivity gradually decreased. The reason for that was ascribed to cobalt leaching, most probably in the form of carbonyl complexes. Recently, Jagadeesh and co-workers employed the Co-Co_3O_4/NGr@C catalyst in the reductive methylation of nitro compounds using aqueous formaldehyde as methyl source.[186] In addition, reductive amination of aryl aldehydes was also described by the authors. The transformations were conducted under transfer hydrogenation conditions using HCOOH/Et_3N (Scheme 28).

Scheme 28 Co-Co_3O_4/NGr@C-catalyzed reductive amination and dimethyamination of nitroarenes using HCOOH/Et_3N as reducing agent.



Both the reactions were applicable to many substrates. Along with structurally-simple nitroarenes, various bio-active molecules were converted into the corresponding secondary or tertiary amines with very high chemoselectivity. Furthermore, upscaling (up to 3 g) and recyclability were successfully demonstrated.

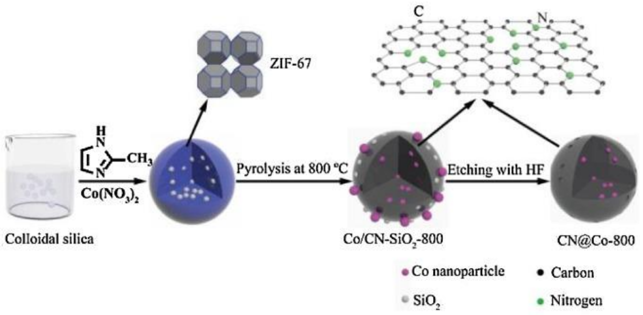
After reporting the production of an active Co-N-C catalyst using a template approach,[166] the group of Z. Zhang described the use of the same and related materials in the catalytic transfer hydrogenation of nitro compounds to substituted amines. Since the catalyst was prepared using hydrofluoric acid as leaching agent, it turned out to be intrinsically acid-resistant. This allowed for the successful application of the same in the reductive amination using an appealing base-free protocol in which only formic acid is employed as reductant.[187] The reaction was conducted at relatively high temperature (T>150 °C) in order to accelerate the imine hydrogenation found as the rate determining step. Consequently, at lower temperature, mixtures of imine and amine were always detected. The reaction scope included various amines prepared from nitro compounds and aldehydes bearing electronically-diverse functional groups. Later on, the transfer hydrogenation of nitroarenes was combined with the well-known Pall-Knorr synthesis for the production of *N*-substituted pyrroles in a one-pot fashion (Scheme 29).[188]

Scheme 29 Synthesis of pyrroles from nitroarenes and 2,5-hexadione with HCOOH as reductant using Co-N_x/C-800-AT catalyst developed by Z. Zhang group.

The transformation proceeded well with both aromatic and aliphatic nitro compounds leading to the corresponding *N*-substituted-2,5-dimethylpyrroles in high yields. However, at present the reaction is restricted to 2,5-dimethylpyrroles which limits its general applicability.

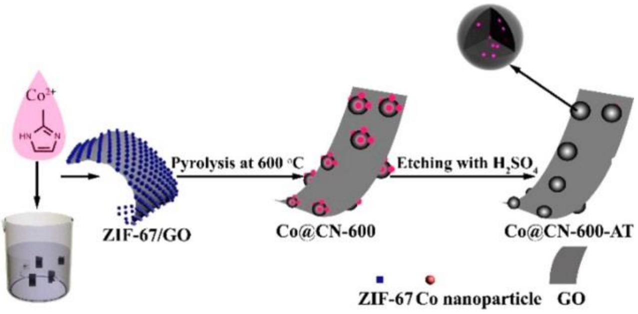
Shortly after, the same group prepared and evaluated the use of a Co-N-C catalyst produced from ZIF-67 and SiO_2 following the previously reported acid-mediated template approach (Figure 28).[189] Within the procedure, hydrofluoric acid was employed to simultaneously remove both silica and the excess of Co NPs leading to a mesoporous structure of the material with average particle size dependent on the pyrolysis temperature.

Figure 28 Preparation scheme for Co@CN-800 developed by the group of Z. Zhang. (Reproduced with permission from Ref. 189. Copyright 2017, Elsevier)



The latter is a phenomena previously observed with catalysts belonging to the Co-N-C family. Compared to similar works, XPS analysis showed the presence of both Co(0) and Co(II) oxide and XPRD only displayed the presence of Co(0). This evidence indicates the formation of oxidic layers on the surface that might be derived from the exposition of the material to air. Even in this case, a large number of nitro compounds, ketones and aldehydes were converted into the corresponding secondary amines. The use of Co-N-C catalysts in the reductive amination of nitro compounds was further studied by the same group using a material derived from ZIF-67 (Figure 29).[190] In addition to MOF, a carbonaceous support (graphene oxide; GO) was employed.

Figure 29 Preparation scheme for Co@NC-600-AT developed by the group of Z. Zhang. (Reproduced with permission from Ref. 190. Copyright 2017, American Chemical Society)

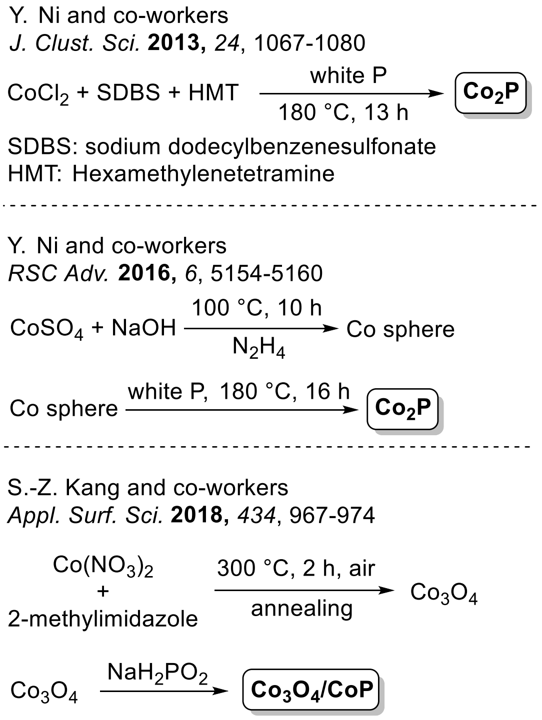


This material showed a micro-mesoporous support with Co(0)/Co(II) oxide NPs. Interestingly, the Co content decreases with the rising of the pyrolysis temperature. In fact, when ZIF-67 is directly pyrolyzed without any additional support, an opposite trend is observed. With respect to other systems using formic acid and Co-N-C as catalyst, the achieved efficiency was lower. Even if the reaction requires high temperatures (190 °C), many secondary amines can be produced with high selectivity. However, challenging substrates such as 4-iodonitrobenzene as well as furfural were converted to the corresponding amine with partial hydrodeiodination (<30%) and decomposition, respectively. Moreover, both aliphatic nitro and carbonyl compounds were successfully transformed. In the case of ketones, a decreased reactivity was found due to steric and electronic reasons. In the same year, Z. Zhang and co-workers published the same reaction using a Co-N-C catalyst under water-gas shift conditions. The catalytic material was produced through the direct pyrolysis of ZIF-67.[191] The structure and composition of the obtained material are in accordance to previously published works.[161,162,192] The microporous structure of ZIF-67 was converted into a carbonaceous mesoporous material upon pyrolysis. With the increased pyrolysis temperature the Co content rose, whereas the N content showed an opposite trend. The material is mainly composed of Co(0) NPs along with Co(II) oxides on the surface and with increasing the pyrolysis temperature the activity is lower. As a consequence, both high temperatures and high CO pressures were crucial for achieving high selectivity towards the desired secondary amine without the detection of the intermediate aniline and imine.

4.2.2. Reductions with $NaBH_4$

Numerous Co-based catalysts were explored for the reduction of nitroarenes to anilines using $NaBH_4$ as reductant, especially in the reduction of 4-NP to 4-AP as model system. Both bulk catalysts, supported and unsupported Co-based NPs were found to be active, leading to a large amount of reports on this topic. For instance, commercially available bulk Co_3O_4 was demonstrated to be very effective in this transformation as reported in 2011 by Gopal and co-workers.[193] In a following study, Meijboom and co-workers showed that mesoporous Co_3O_4 prepared by an inverse surfactant micelle method are more active than the commercial one.[194] The observed enhanced activity could be ascribed to a plethora of factors, namely high surface area, low pore and crystallite sizes. An improved activity was further reported by the same authors demonstrating that small amount of alkali- or alkaline earth metals are beneficial for the reaction rate.[195] In particular, electronic effects rather than morphological and/or structural changes are responsible for the observed outcome. Furthermore, M. Yang and G. Chen proved the formation of oxygen vacancies through a partial reduction of Co(III) to Co(II) by pre-reducing Co_3O_4 with $NaBH_4$.[196] The catalytic activity of this material was found to be higher than the pristine Co_3O_4. This fact could have a general implication for the reaction mechanism in other Co_3O_4-based catalysts since pre-reduction steps occur *in-situ* prior or in concomitance of the catalytic event. Co_3O_4 NPs were subsequently supported onto carbonaceous materials (reduced graphene oxide; r-GO)[197] or silica,[198] however without a significant improvement of the catalytic performances. In 2017, H. Song and co-workers reported that the pyrolysis of commercially available Co_3O_4 adsorbed onto melamine generated a Co-N-C catalyst showing higher activity than the pristine Co_3O_4.[199] Finally, S.-Z. Kang and co-workers reported a Co_3O_4/CoP composite that was produced through a two-step method,[200] which resulted in hollow polyhedrons of Co_3O_4 and CoP. The authors claimed that the catalytic activity of this material increased with the CoP content. It should be noted that the use of cobalt phosphides was already known before. Indeed, in 2013, Y. Ni and co-workers published rod-like Co_2P nanostructures produced *via* solvothermal method from cobalt(II) chloride, hexamethylenetetramine and white phosphorous (Scheme 30, upper part).[201] In another work, Co_2P structures were obtained using a similar approach (Scheme 30, central part).[202]

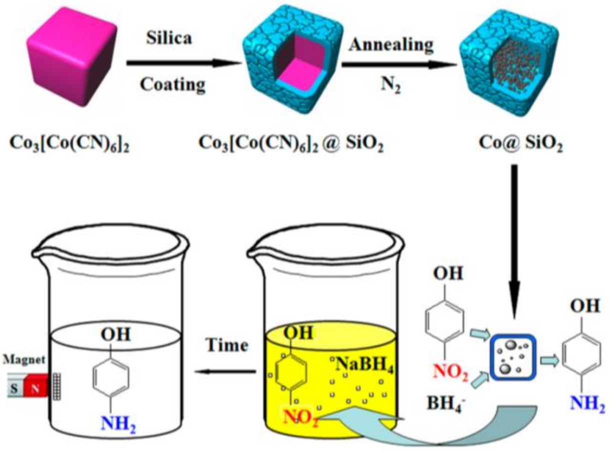
Scheme 30 Summary of Co_xP-based catalyst and related SEM/TEM images developed by the groups of Y. Ni and S.-Z. Kang.



J. J. Gutierrez and co-workers documented the use of Co_3S_4 as catalysts for the reduction of nitroarenes with $NaBH_4$.[203] In their work, the authors prepared various transition metal sulfides (NiS, Co_3S_4, CuS, ZnS and Fe_3S_4) and evaluated them in the benchmark reduction of nitrobenzene to aniline showing that Co_3S_4 is the most active. Subsequently, the catalytic protocol was extended to nitroarenes substituted with simple functional groups such as halogens, ethers and hydroxyl groups.

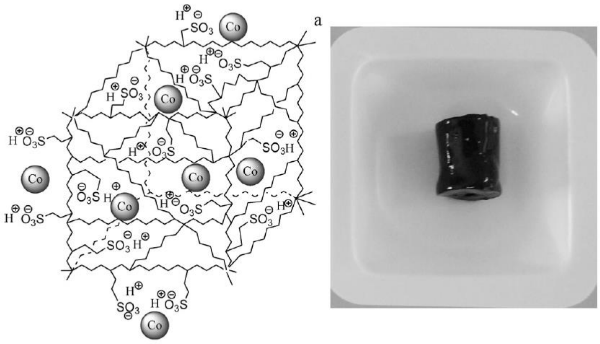
Supported metallic Co NPs were as well evaluated in this transformation. Q. Chen and co-workers prepared a catalyst through annealing under inert atmosphere of $Co_3[Co(CN)_6]_2$ with SiO_2 using a sol-gel method (Figure 30).[204]

Figure 30 Preparation of $Co@SiO_2$ developed by Q. Chen and co-workers. (Reproduced with permission from Ref. 204. Copyright 2014, American Chemical Society)



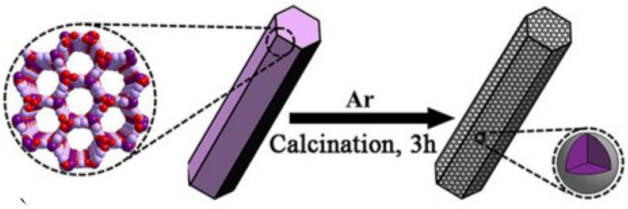
The material is solely composed by small and well dispersed metallic Co(0) NPs onto silica. Furthermore, N. Sahiner and co-workers prepared metallic Co NPs caged into a sulfonated hydrogel structure (Figure 31).[205]

Figure 31 Schematic representation of the Co NPs incarcerated into the sulfonated hydrogel polymer (left) and its appearance (right). (Reproduced with permission from Ref. 205. Copyright 2010, Elsevier)



Co-based catalytic materials derived from MOF were tested with $NaBH_4$ as reductant, as in the case of reduction with molecular hydrogen. In 2016, J. Wang and co-workers used Co-MOF-74 (based on 2,5-dihydroterephtahalic acid) as starting material for the preparation of Co@C catalyst (Figure 32).[206]

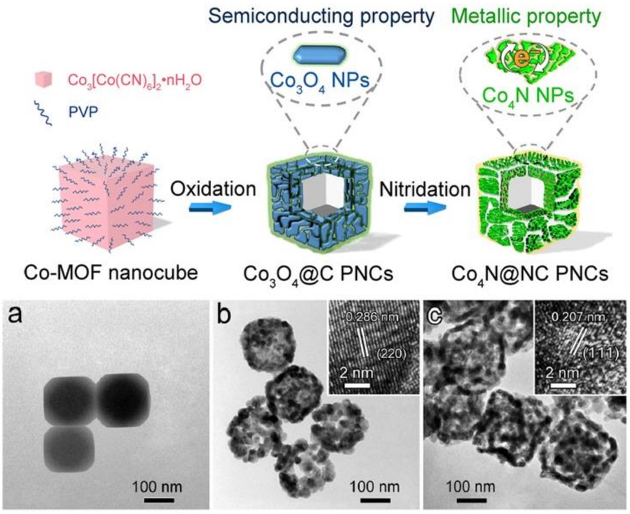
Figure 32 Preparation of Co@C hexagonal-shaped prisms developed by J. Wang and co-workers. (Reproduced with permission from Ref. 206. Copyright 2014, Materials Research Society)



The Co@C was composed of metallic Co NPs covered by cobalt oxide with an average size of 5-7 nm. The catalytic activities of the materials prepared by J. Wang and co-workers, and Q. Chen and co-workers were similar (kinetic constant value of approximately 10^{-2} s^{-1} for a pseudo-first order reaction). However, the catalyst prepared by N. Sahiner and co-workers showed an activity lower by one order of magnitude. This might be ascribed to the larger size of the NPs and mass transfer limitations inside the hydrogel that could limit the accessibility of the reactants.

The use of Co-N-C materials as catalysts in the reduction of nitroarenes (and in particular 4-NP) with $NaBH_4$ has been extensively studied. The methods for the preparation of these catalysts are similar to those already discussed which comprise the pyrolysis of mixtures of Co/N-ligands complexes (or soluble metal chelates with or without the addition of supports) or the thermal treatment of coordination polymers (including MOF). For example in a recent paper, Z. Wu and co-workers developed Co-N-C material supported onto SiO_2.[207] In particular, the material was prepared following a solvent-free mechanochemical method including coating of mesoporous silica (SBA-15) with a Co(II)/Histidine complex. The solid was then pyrolyzed at high temperature (600-1000 °C) leading to the formation of an interesting composite constituted by tiny metallic Co nanoclusters (average size <1 nm) dispersed into nitrogen-doped carbon present in the mesoporous channels of silica. The catalyst displays an impressive activity towards the reduction of nitrobenzene to aniline using $NaBH_4$ as reducing agent. Furthermore, as previously discussed, MOFs were successfully used as sources of Co-N-C catalysts. For instance, in 2016 H. Song and co-workers[208] as well as J. Jiang and co-workers[209] independently reported on the use of ZIF-67 for the preparation of active Co-N-C catalysts. The textural, morphological and chemical properties of the obtained materials are comparable to those reported by other authors.[161,162,192] The porous materials are both composed of metallic Co NPs covered by layers of Co(II) oxides enveloped into the doped carbon matrix. As a result, the two catalysts showed similar activity in the reduction of 4-NP. In a following work, L. Zhao and co-workers reported on the preparation of a Co-N-C catalyst from Co-MOF using a two-step protocol.[210] After the synthesis of ZIF-67, a post-nitrogenation step with urea and thioacetamide was performed. Using this catalyst, the reduction of 4-NP with $NaBH_4$ was completed after only 80 s with a remarkable pseudo-first order kinetic constant of $6\cdot10^{-2}$ s^{-1} higher than the one achieved with the catalyst prepared by the pyrolysis of untreated ZIF-67. In 2016, A. Choudhury and co-workers used a 1D coordination polymer made from Co(II) precursor and two organic components (a dicarboxylic acid and methylimidazole) for the reduction of 4-NP.[211] After pyrolysis the obtained material displays a mesoporous structure with relatively low surface area. The chemical composition was comparable to the one obtained in the case of ZIF-67 with a cobalt particle size distribution from 20 to 100 nm. However, the activity was found to be of one order of magnitude lower than that obtained applying 3D-coordination polymer-derived catalysts (MOF or ZIF). Finally, a very recent report by Y.-N. Liu, L. Deng and co-workers described the preparation of Co_4N nitride supported onto nitrogen-doped carbon porous nanocages (Figure 33).[212]

Figure 33 Preparation (upper part) and corresponding TEM images of: (a) Co-MOF nanocubes; (b) Co_3O_4@C PNCs; (c) Co_4N@NC PNCs reported by Y.-N. Liu, L. Deng and co-workers. (PNCs: porous nanocages). (Reproduced with permission from Ref. 212. Copyright 2018, American Chemical Society)



The preparation of this material was carried out *via* a two-step transformation involving the synthesis of Co-MOF nanocubes ($Co_3[Co(CN)_6]_2$) followed by pyrolysis and high temperature nitridation using gaseous NH_3 as nitrogen source. After the first pyrolysis step formation of Co_3O_4 NPs occurred, which were transformed into Co_4N phases after nitridation. The temperature of this latter step plays a key role since it was shown that below 300 °C only CoO oxides are obtained without incorporation of nitrogen atoms. Among all the prepared materials, the one treated at 500 °C (Co_4N@NC PNCs-500) was the most active. The reason for this was imputed to the higher concentration of Co_4N phases and the maximum pore volume.

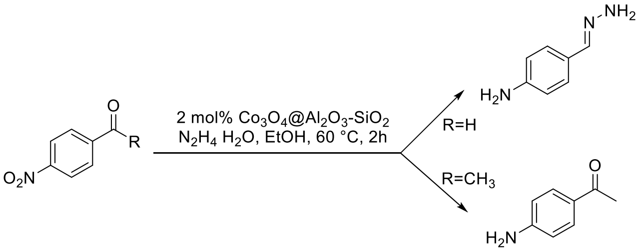
4.2.3.Reductions with N_2H_4 and other reducing agents

In this section, other reducing agents will be discussed focusing our attention on the use of hydrazine. Compared with Fe *vide supra* only few reports using heterogeneous Co-based catalysts for the reduction of nitro compounds were published with N_2H_4. In a work of D. S. Rawat and co-workers, a catalyst composed of Co_3O_4 supported onto SiO_2/Al_2O_3-mixed oxide was prepared by an impregnation method (Figure 34).[213]

Figure 34 Preparation of $Co_3O_4@Al_2O_3/SiO_2$ developed by D. S. Rawat and co-workers. (Reproduced with permission from Ref. 213. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

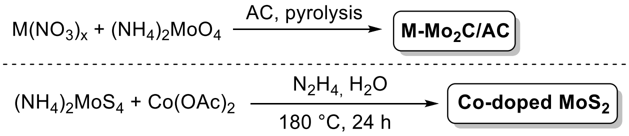
The material displays a microporous-mesoporous structure in which Co_3O_4 NPs of narrow size (2-3.5 nm) are present. This catalyst showed good activity in the reduction of substituted nitro compounds at 60 °C. In addition, the protocol tolerates typical functional groups including nitrile and other carboxylic acid derivatives, avoiding any hydrodehalogenation pathway while using Cl- and Br-substituted nitro derivatives. However, the authors did not test any more demanding iodo-substituted nitroarenes as starting materials. Noteworthy is the reduction of nitroarenes containing carbonyl moieties and carbon-carbon double bonds. In the case of 4-nitrobenzaldehyde the corresponding aminohydrazone formed, whereas 4-nitroacetophenone was selectively converted into the corresponding amine (Scheme 31).

Scheme 31 Side-reactions for the reduction of 4-nitrobezaldehyde and 4-nitroacetophenone using $Co_3O_4@Al_2O_3/SiO_2$ as catalyst.



As mentioned in the introduction, C=C bonds are easily reduced in the presence of hydrazine. Interestingly, in this work both conjugated and isolated double bonds were completely retained. The specific role of the mixed oxidic support was not investigated by additional control experiments. Although the authors claimed the full recyclability, a continuous decrease of the yields was detected after each run. In a related work, X. Wang,X. Lu and co-workers reported on the preparation and use of a mesoporous γ-Al_2O_3-supported Co catalyst.[214] The material was obtained through a co-precipitation/impregnation technique followed by calcination in the air at 450 °C. At this stage, Co_3O_4 NPs along with mixed oxides and Co/Al/O spinels were formed, which did not display any activity in the reduction of 2-chloronitrobenzene using hydrazine hydrate as reducing agent. However, if the so-obtained material was treated with Phen and then pyrolyzed at 700 °C, it showed good activity. So far, the necessity of this two-step procedure remains unclear. Characterization of the active material suggested the formation of metallic Co NPs (average size of 10-20 nm) and Co-N_x species. The reaction scope included 35 substrates carrying various functional groups. In general, EWG groups (halogens, trifluoromethyl) caused shorter reaction times than EDG substituents (methyl, hydroxyl, amino). Adjusting the reaction times, complete conversion and selectivity were achieved in both cases (EWG, EDG). Other reducible functional groups such as carboxylic acid derivatives, double bonds (and in particular 4-nitrostyrene), and nitroheteroarenes were successfully retained, although standard carbonyl compounds (ketones and aldehydes) were not included in the reported reaction scope. L. Kiwi-Minster and co-workers presented a Co-based catalyst supported onto active carbon nanofibers (CoO_x/ACF) obtained by pyrolysis of ACF impregnated with $Co(NO_3)_2$.[126] As in the parental case of Fe and Ni, the catalyst displayed a microporous structure with very high surface area (>2100 m^2g^{-1}) and small NPs composed of CoO (average size of 2 nm). A comparison with the corresponding FeO_x/ACF and NiO_x/ACF interestingly showed how the Co-based one possesses a similar activity to the Fe-based one. Both the Fe and Co catalysts provided a two-fold activity with respect to the Ni-based one. However, only CoO_x/ACF showed both the maximum activity and selectivity in the reduction of 3-nitrostyrene affording the corresponding 3-aminostyrene in quantitative yield under relatively mild conditions. Z. Zhao and co-workers reported on the use of Co-modified molybdenum carbide as catalyst for reduction of nitro compounds.[215] The catalysts were prepared by wet impregnation of $Co(NO_3)_2$ and $(NH_4)_2MoO_4$ onto activated carbon with hydrogen peroxide followed by pyrolysis (Scheme 32).

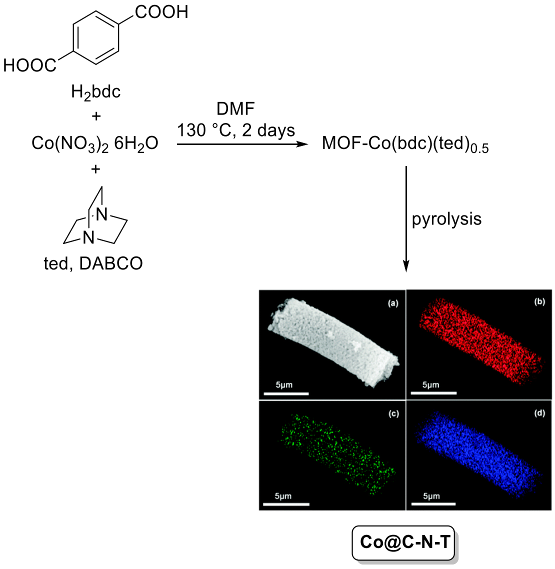
Scheme 32 Preparation of M-Mo_2C/AC and Co-doped MoS_2 developed by the groups of Z. Zhao and M. Rajamathi, respectively. (M = Fe, Ni, Co, Cr; AC = activated carbon)



They found that the addition of a transition-metal (Fe, Ni, Co, Cr) greatly enhanced the catalytic activity through a synergistic interplay between metal and Mo. Compared with the pristine Mo_2C/AC, the Co-modified material turned out to be the most efficient one. The reaction scope included a relatively small number of nitroarenes substituted by various functional groups. Notably, 4-nitrobenzaldehyde was quantitatively transformed into the corresponding amine without hydrazone formation. A work published by M. Rajamathi and co-workers reported on the preparation of a Co-Mo-S material[216] similarly prepared to that proposed by Corma and co-workers within the same year. The catalyst was prepared through a hydrothermal approach starting from cobalt acetate and ammonium tetrathiomolybdate as sources of Co and MoS_2, respectively. The catalyst is composed of MoS_2 layers containing Co(II) species. Using $NaBH_4$ as reducing agent, three benchmark reactions were successfully exploited. In particular, 4-NP, 4-nitroaniline and nitrobenzene were reduced to the corresponding amines within 7 minutes.

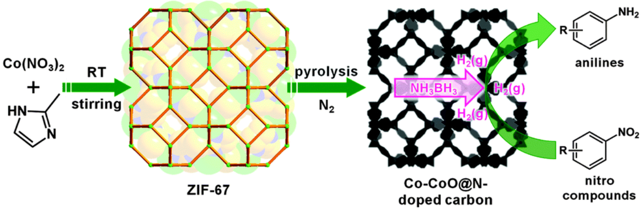
The use of a MOF-derived catalyst in the transfer hydrogenation of nitroarenes was proposed for the first time by Y. Li and co-workers.[217] The Co-MOF was prepared according to a previous report [218] and then pyrolyzed at various temperatures (Scheme 33).

Scheme 33 Preparation of Co@C–N-T developed by Y. Li and co-workers. (Partially reproduced with permission from Ref. 217. Copyright 2015, Royal Society of Chemistry)



As shown for the catalytic hydrogenation of nitroarenes using molecular H_2, the microporous Co-MOF structure was converted thermally to a mesoporous Co-rich (37-41 wt%) carbon-based material. XPRD and XPS confirmed the metallic nature of Co in the catalyst. The authors further demonstrated that both pyrolysis temperature and time have a significant impact on the properties of the materials with respect to the NPs size and the surface area. In particular, long pyrolysis time and high temperatures ensured formation of smaller particles and large surface area. This general trend was later on confirmed by other authors not only in the case of MOF-derived materials (*vide supra*). The most active catalyst turned out to be the one pyrolyzed at 900 °C for 15 h employed in various reductive transformations including the transfer hydrogenation of nitro compounds, where only isopropanol was employed as reductant under base-free conditions. Along with carbonyl compounds (aldehydes and ketones), nitriles and olefins, aromatic nitro compounds were smoothly reduced to the corresponding primary amines. The substrate scope regarding the latter family of compounds was narrow and the only significant example was the reduction of 4-iodonitrobenzene to the corresponding aniline with full selectivity at 98% conversion. However, high catalyst loadings (10 to 20 mol%) and long reaction times (>50 h) were needed. The versatility of such a catalyst might be self-defeating since nitroaromatics carrying carbonyl and/or nitriles groups could be simultaneously reduced. A few years later, H.-L. Jiang and co-workers reported ZIF-67 as precursor for Co-N-C materials (Figure 35).[192]

Figure 35 Preparation and related application ($NH_3{\cdot}BH_3$ dehydrogenation and nitro compounds reduction) of Co-CoO@N-doped carbon. (Reproduced with permission from Ref. 192 Copyright 2016, Royal Society of Chemistry)



The obtained material is composed of Co NPs (mainly Co(0) with an average size of 6-20 nm) bound to nitrogen atoms present in the carbon network. This results are in agreement with the one reported by J. Gascon and co-workers,[162] and Y. Li and co-workers.[161] The catalyst was employed in the tandem dehydrogenation of ammonia borane followed by hydrogenation of nitroarenes. Here again, the best catalyst was the one prepared at lower temperature (500 °C with long reaction time) demonstrating this general feature for Co-N-C materials derived from MOF. The proposed protocol was proved to be general for reducing nitroarenes in the presence of sensitive groups. As rare example, alkyl nitro compounds were reduced to the corresponding anilines with full selectivity. The high Co content (>20 wt%) ensured a magnetic behavior rendering easy the recyclability of the catalyst.

W.-F. Fu and co-workers presented hollow Co_3S_4 as catalyst for the reduction of nitroarenes using Na_2S and Na_2SO_3 as reductants in a sort of catalytic Zinin reaction.[219] The catalyst was produced by treating ZIF-67 with thioacetamide as sulfur-source and subsequently pyrolyzed at 350 °C under inert atmosphere. The mechanism and the role of the two reductants are still unclear and water might be involved in the catalytic cycle as hydrogen donor. The applicability of the proposed system is not general since nitroarenes substituted with different labile groups (ketones, nitriles) and N-heteroaromatic nitro compounds showed low selectivities and activities. Nevertheless, no explanation of this observation was provided.

5. Heterogeneous nickel-based catalysts

5.1. Reduction with molecular H_2

For a long time Raney®-Ni has been employed even in industry as a standard catalyst for the hydrogenation of simple nitroarenes. However, more sensitive and demanding substrates cannot be selectively reduced. In order to overcome these problems, various tailor-made Ni catalysts were developed over the years. For instance, the promoting effect of vanadium additives on the accumulation of the intermediate aryl *N*-

hydroxylamines during the reduction of electron deficient nitro compounds to the corresponding amines with Raney®-Ni was investigated by Studer, Neto and Blaser in 2000.[220] Both supported and unsupported promoters in different oxidation states were tested and compared with respect to unmodified Raney®-Ni. With the use of promoters, it was possible either to increase or decrease both the accumulation of aryl *N*-hydroxylamines and the overall rate. When the accumulation was reduced, however, the catalysts showed a pronounced deactivation at the same time. It was found that for an efficient vanadium-containing modifier, oxidation states of +4 and +5 are optimal, and that a certain solubility of it is necessary. Usually, the most efficient modifier for low accumulation of aryl *N*-hydroxylamines and for reasonable rates is NH_4VO_3. In the case of 2-chloronitrobenzene, only 14% of aryl *N*-hydroxylamine accumulated for this modifier, whereas for unmodified Raney®-Ni it was 71%. It was proposed that the vanadium modifiers catalyze the disproportionation of the intermediate aryl hydroxylamines and in that way affect its accumulation.

X. N. Li and co-workers have shown that the selectivity of Raney®-Ni for the hydrogenation of halonitroarenes towards the corresponding haloanilines can be improved by the addition of dicyandiamide as a ligand.[221] Ni-hydride species were suspected to be responsible for hydrodehalogenation processes in the case of unmodified Raney®-Ni. Those species might be stabilized by dicyandiamide *via* interaction of the N-ligand with Ni-H, which results in a suppression of hydrodehalogenation. However, the tested reaction times for the unmodified Raney®-Ni were about 2-3 times longer, which might also be the reason for unwanted side reactions.

The effect of metal fluorides on the performance of Raney®-Ni was studied by Y. Liu and C. Xia and co-workers in 2015.[222] The addition of a moderate amount of CaF_2, NaF, KF or MgF_2, successfully increased the reactivity. The most effective additive was CaF_2. The effect for this increased activity is not well understood, yet.

As an alternative to Raney®-Ni, Y. W. Chen and co-workers reported a series of nickel borides for nitro reductions. In 2006, the group demonstrated the hydrogenation of 4-chloronitrobenzene in the presence of nano-Ni-B,[223] and a second system consisting of La-promoted Ni-B.[224] In both systems, the catalysts were produced in a very similar way. Either solely $Ni(OAc)_2$, or combined with $LaCl_3$ (Ni/La ratios of 10 and 40 wt%, respectively) in the second system, were dissolved in water and subsequently a 1 M solution of

$NaBH_4$ was added dropwise. The black precipitate was then isolated. For the Ni-B materials, average nanoparticle sizes of 27 nm, 33 nm, and 35 nm were found depending on various parameters related to the catalysts preparation. The lanthanum modified Ni-B materials had average sizes of 14 nm and 25 nm for Ni/La ratios of 10 wt% and 40 wt%, respectively. In both studies, the catalytic activity was investigated for the hydrogenation of 4-chloronitrobenzene in ethanol or methanol. The results indicated that lanthanum is promoting the hydrogenation, giving rise to an accelerated reaction, which could be attributed to electronic modifications of nickel by lanthanum.

In the same year, the same group also used P-modified Ni-P-B nanocatalysts for the reduction of 4-chloronitrobenzene.[225] The materials were prepared by the addition of sodium borohydride to a mixture of nickel acetate and sodium hypophosphite in water/ethanol (1:1). The B:P:Ni ratio was set to 3:3:1 in order to obtain complete reduction of Ni(II) to Ni(0). Overall, six catalysts were prepared and compared. Besides of surface areas/compositions and particle dimensions, the different conditions also affected the catalytic activity of the materials. A lower metal-loading on the catalyst increased its activity. A strong dependence from the solvent was observed as well, as in methanol the reactivity was significantly increased, compared to ethanol as reaction medium. In general, the promoting role of boron and phosphorous were thought to be both owed to electronic effects; whereas boron can donate electrons to nickel within the composite, phosphorous can accept electron density from the metal. This finding was indicated by XPS data.

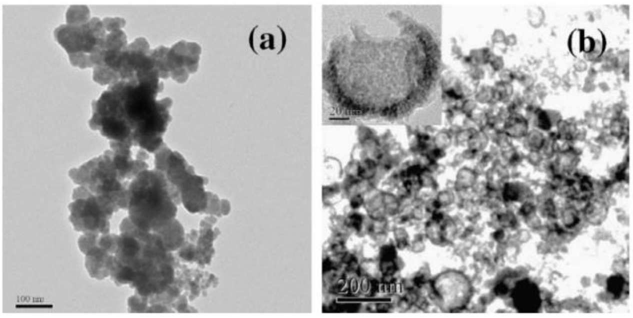
The same group also studied tungsten-modified Ni-Co-B-catalysts for the reduction of 4-chloronitrobenzene (*vide infra*).[226] In 2011, they investigated molybdenum-doped Ni-B cluster catalysts with different Mo/Ni ratios.[227] The synthetic methodology was again comparable to the other systems, starting from a methanolic solution of nickel acetate and ammonium heptamolybdate. The average size of the nanoparticles decreased with an increase amount of molybdenum, resulting in 3-5 nm sized particles. Again, 4-chloronitrobenzene was chosen as model substrate. Mo/Ni ratios of 0.4, 0.6, and 0.8, respectively, resulted in higher active materials compared to Ni-B, among which a ratio of 0.4 showed the highest activity. It was found that Mo did not only act as a spacer and preserved the amorphous state of Ni-B and reduced the particle dimensions, but also donated electron density to Ni, and so modified the electronic structure. In 2013, the authors combined the promotional effects of Mo and La on Ni-B-catalysts, and hence prepared lanthanum-doped Ni-

Mo-B nanocluster catalysts.[228] Applying the same synthetic strategy, a series of materials was prepared with a Ni:Mo:B ratio of 1:0.4:3 and different La:Ni ratios. Particles with a size of 3-4 nm were obtained, which is comparable with the Mo-doped Ni-B materials. The optimum molar ratio of La:Ni was found to be 0.2, resulting in a high content of Ni^0 and higher activities and selectivities.

Ni-B type catalysts were also reported by H. Li and co-workers in 2007.[229] The ultrasound-assisted reduction of $Ni(NH_3)_6^{2+}$ with KBH_4 in 25% $NH_3{\cdot}H_2O$ yielded in a black precipitate, which was then washed with water and ethanol. TEM images of the materials revealed that without ultrasound, almost shapeless particles with a very broad size distribution were obtained. With increasing power during ultrasound treatment, the size of the particles enlarged. Applying 50 W resulted in uniform spherical particles of average 100 nm, which are ascribed to cavitation effects of ultrasound. This generates intense shock waves, which induce a homogeneous and smooth reaction of $Ni(NH_3)_6^{2+}$ and BH_4^-. The formation and destruction of bubbles in solution, induced by ultra-sonication, might create localised supersaturation due to the evaporation of solvent in the bubbles at elevated temperature, which triggers the nucleation. The active surface area of the particles was smaller for 75 W. Using 100 W, this high power induced melting agglomeration of Ni-B particles. The catalytic activity of the as prepared materials was investigated in the hydrogenation of 4-chloronitrobenzene. Due to the greater active surface area and uptake of hydrogen, a power of 50 W resulted in best activity. Noteworthy, all investigated Ni-B type catalysts revealed superior selectivity compared to Raney®-Ni. Responsible for this are both the amorphous alloy structures of the materials, as well as the electronic interactions between B and Ni.

Two years later, the same group reported the synthesis of hollow Ni-B amorphous alloy and its activity in reducing 4-chloronitrobenzene.[230] A mixture of $NiCl_2{\cdot}6H_2O$ and polyethylene glycol (PEG) in water was sonicated and a viscous and slightly opaque solution was obtained. To this mixture, an emulsion of KBH_4, PEG and cyclohexylamine was added during ultrasonication. The obtained black precipitate was washed with water and ethanol, and stored in the latter. The formation of hollow spheres was thought to originate from reversed micelles having hydrophobic groups towards the outside and hydrophilic groups to the inside. In this way water is entrapped inside the micelles. Due to the affinity of Ni(II) towards $–NH_2$ of cyclohexylamine and oxygen of PEG, it accumulates at the interface of oil and water. When BH_4^- is added, NPs are formed in the shape of hollow nano-spheres (Figure 36, (b)). This final reduction is highly exothermic and partially destroyed the spheres. When neither PEG, nor amine were added during preparation, no hollow spheres were observed by TEM (Figure 36, (a)). In the absence of cyclohexylamine solely, monodisperse Ni-B NPs were obtained, and without PEG, hollow spheres and solid NPs coexisted. The simultaneous use of both cyclohexylamine and PEG therefore was crucial for the hollow spheres formation. In addition, these spheres gave a higher activity compared to solid Ni-B NPs, resulting in an improved selectivity and comparable yield after much shorter time. Several chloronitrobenzenes were investigated, and all were converted to the corresponding chloroanilines with high conversions and selectivities.

Figure 36 TEM images of Ni-B (a) without, and (b) with added cyclohexylamine and PEG during preparation. The formation of hollow nano-spheres can be observed. (Reproduced with permission from Ref. 230. Copyright 2009, Elsevier)



In 2008, related Ni-P-B catalysts were disclosed for the reduction of 4-chloronitrobenzene, which demonstrated the synergistic promoting effects of B and P.[231] The materials were prepared by the addition of aqueous KBH_4 to a solution of $NiCl_2$ and NaH_2PO_2 in water at 30 °C. The molar ratio of P/B was varied, and for comparison also materials with either KBH_4 (Ni-B) or NaH_2PO_2 (Ni-P) were prepared. Ni-B showed the highest active surface area, Ni-P the lowest. The hydrogen uptake per gram Ni, however, was by far the greatest for Ni-B-P materials, along with the yield of 4-chloroaniline. The higher gas uptake could be attributed to various reasons, namely alloying degree, B-promoted dispersion of Ni and electronic effects (electron density donation from B to Ni).

F. Li and co-workers studied the catalytic activities of Ni-B particles located either inside or outside of carbon nanotubes for the hydrogenation of chloronitroarenes.[232] By applying slightly different impregnation procedures, Ni(II) was selectively deposited in the tube cavity or outside the tubes, and the subsequent addition of KBH_4 generated Ni(0) NPs. Due to the restricted space, NPs inside the tubes were uniformly sized and smaller (8 nm) than those outside the tubes (12 to 26 nm), and they tend less to agglomeration. As a consequence, more active centres were provided. The promotional effect of Ni-B alloy compared to just Ni was explained by a stronger adsorption of the nitro group. Whereas electron-rich Ni interacts with N atoms, the electron deficient B further activates the nitro group by electronic interaction with the O atoms.

A increased activity of NiO NPs located inside multi-walled carbon nanotubes (MWCNTs) was also observed by R. Li, Z. Li and co-workers in the same year.[233] Whereas inside the channels nitrobenzene was reduced to aniline with a yield of 97%, outside of them only 61% aniline was formed at 15 bar H_2 within 5 h.

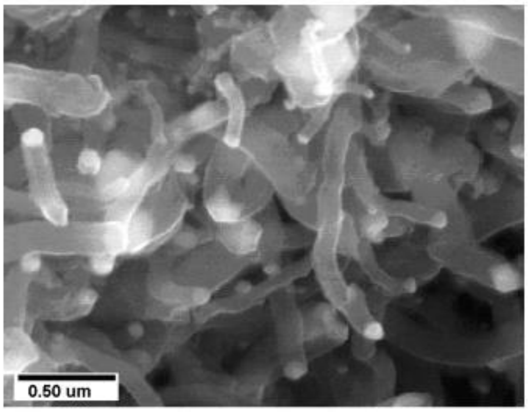
The hydrogenation of 2-chloronitrobenzene using supported catalysts was investigated by J. Chen and co-workers in 2007.[234] Different inorganic supports were tested regarding their influence on the catalytic activity of the material. After aqueous impregnation of ZrO_2, SiO_2 TiO_2, and γ-Al_2O_3, respectively, with $Ni(NO_3)_2$, the mixture was let stand at room temperature for 12 h, dried, and finally calcined at 500 °C for 4 h under air, followed by reduction in a flow of H_2/Ar (1:9) for 2 h. The metal loading was set to 15 wt% for all materials and catalytic reactions were carried out at 90 °C and 15 bars of H_2 in ethanol. A strong dependence of the catalytic performance from the support could be observed. Whereas nickel loaded on TiO_2 (anatase) was found to be the most active catalyst, with a substrate conversion of 99% after 30 min, selectivity towards the amine of 99% and a TOF of 34.9 s^{-1}, γ-Al_2O_3 was the least suitable support. The superior activity of the former catalyst, might be due to a strong polarization of the N=O bond, induced by oxygen vacancies of TiO_x. One year later, the same group investigated the impact of pre-calcination of the support TiO_2 at different temperatures for the catalytic activity in hydrogenation of 2-chloronitrobenzene.[235] The catalysts were prepared as described above,[234] but the support was calcined at 500, 600, 700, 800 and 900 °C before use. The metal content was set to 20% for each material. The properties of the catalysts were strongly affected by the different calcination temperatures. For instance, the specific surface area and the pore volume of the materials decreased with increasing temperature. Optimal activity of the catalyst was observed for a pre-calcination temperature of 700 °C. The authors associated the performances of the catalyst with the active area of metal and the interaction between Ni and TiO_x.

More recently, the promotional effect of surface defects on the catalytic activity of titania supported nickel catalysts was demonstrated by F. Li and co-workers.[236] Materials rich in defects, such as oxygen vacancies or Ti^{3+} species, were prepared *via* dropwise addition of an aqueous mixture of NaOH and Na_2CO_3 to a solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $Ti(SO_4)_2$ in water. The Ni:Ti ratios were set to 1.0, 2.0 and 3.0, respectively. After stirring at pH = 9.5 and subsequent ageing and centrifugation, the dried solid was calcined at 500 °C for 6 h in static air, followed by reduction in an atmosphere of 10% H_2/N_2 at 500 °C for 2 h. The as prepared catalysts were more active in the hydrogenation of 2-chloronitrobenzene compared to materials derived *via* conventional incipient wetness impregnation method. This was mainly attributed to surface defects, including oxygen vacancies and a higher Ti^{3+}:Ti^{4+} ratio on the surface.

In 2008, Keane and co-workers investigated the use of nickel on several supports for the hydrogenation of chloroanilines in the gas phase.[237] In their methodology, a solution of $Ni(NO_3)_2$ in 2-butanol was added dropwise to the support, with constant stirring. The catalytic activity of the resulting materials decreased in the order $Al_2O_3 > SiO_2 >$ AC > graphite for the reduction of 4-chloronitrobenzene. The metal loading of the catalysts was 4-6 wt%. At 120 °C and 1 atm of H_2, the model substrate was hydrogenated to 4-chloroaniline with a selectivity of 100% in a continuous gas phase reaction. Further, 1-chloro-, 2-chloro-, and 4-bromonitrobenzene were successfully tested. Palladium on Al_2O_3 was by far more active than nickel on the same support; however, in this case the main product was not the chloroaniline, but the hydrodehalogenated product.

Also in 2008, J. L. Figueiredo and co-workers showed that the accumulation of the common but hazardous intermediate *N*-phenylhydroxylamine during the reduction of nitrobenzene to aniline can be avoided by using nickel NPs, which are stabilized by filamentous carbon.[238] The only side-product reported was cyclohexylamine, with a yield of <1%. Three catalysts were produced *via* removing aluminium from Raney®-Ni with concentrated NaOH, followed by simultaneous generation of filamentous carbon along with Ni NPs by methane decomposition (see Figure 37). The temperature and the time during the methane decomposition were varied to achieve different materials. All of the catalysts revealed a higher activity than Raney®-Ni towards the reduction of nitrobenzene at 15 bars of H_2 and 120 °C in methanol. Other substrates were not investigated.

Figure 37 SEM image of one of the catalysts. Carbon filaments can be seen, holding Ni-NPs on top. (Reproduced with permission from Ref. 238. Copyright 2008, Elsevier)

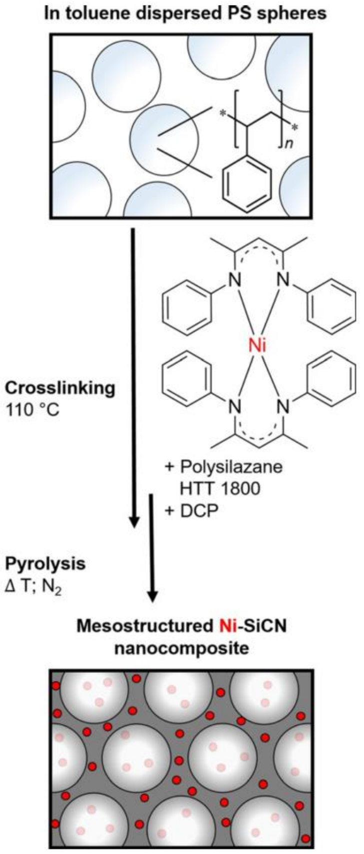


A broad substrate scope was reported for Ni supported on SiO_2 by Y. Zheng R. Li, J. Ma and co-workers in the same year.[239] After passivating the catalyst, it was stable in the air and applied for catalysis without prior activation. At 110 °C and H_2 pressures of 20 to 30 bar, all of the investigated nitroarenes were converted completely, with selectivities of >82% with respect to the primary amine. Alcohols were tolerated, along with halogens, aldehydes, ethers and carboxamides. Due to the high Ni content of the catalyst (about 55 wt%) the material showed magnetic behaviour, which simplified its recycling. While fresh catalyst reduced nitrobenzene to aniline within 7 h, the five times recycled one required prolonged reaction time (10 h) to reach the same activity and selectivity.

In 2015, D. Zhou, Q. H. Xia and co-workers tested Ni catalysts on different supports for the hydrogenation of 1,5-dinitronaphthalene to 1,5-diaminodecahydronaphthalene.[240] The most active catalyst was based on SiO_2 with a Ni loading of 10 wt%, and modified with sesbania powder. It was found that this modifier led to increased BET surface area and pore volume. At H_2 pressure of 52 bar and temperature of 220 °C, the catalyst completely hydrogenated 1,5-dinitronaphthalene to 1,5-diaminodecahydronaphthalene (95%). Both conversion and selectivity dropped slightly during 9 runs in recycling studies.

As previously shown with cobalt,[157] Kempe and co-workers reported a related silicon carbonitride (SiCN) based Ni catalyst with remarkable tolerance towards sensitive functional groups.[241] To a dispersion of polystyrene spheres in toluene, commercial polysilazane was added, together with $Ni(nacnac)_2$ and dicumyl peroxide as cross-linker (see Figure 38). After removal of the solvent and crosslinking at 110 °C, the material was pyrolyzed at 900 °C under N_2. Aldehydes, iodides, C=C bonds and nitriles survived under the reaction conditions of 50 bars of H_2 and 110 °C. The catalyst still had an unchanged activity after five runs despite a metal leaching of 0.1% was observed during catalysis.

Figure 38 Synthesis of the SiCN based Ni catalyst reported by Kempe and co-workers. (Reproduced with permission from Ref. 241. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)



In the same year, Z Qin, Z. Liu and co-workers reported the preparation, characterization and catalytic activity of a supported Ni-B/SiO_2 sol amorphous alloy for nitrobenzene reduction.[242] A sol-gel method was used for the preparation of the silica sol: a mixture of TEOS in ethanol was treated with ammonia in different amounts. Subsequently, an aqueous Ni-solution was added, obtaining a Ni/silica sol after 12 h. The addition of KBH_4 reduced the nickel, finally. A metal loading of 10% and a TEOS:ammonia ratio of 1:1 were found to be optimal, converting nitrobenzene to aniline with full selectivity and the catalyst was successfully recycled four times.

F. Zhao, M. Arai and co-workers demonstrated the beneficial effect of $scCO_2$ as solvent in the hydrogenation of nitrobenzene to aniline with Ni supported on γ-Al_2O_3.[243] Compared to ethanol and *n*-hexane an improved rate was observed for Ni/Al_2O_3 in condensed CO_2 phase. Under a CO_2 pressure of 120 bar, H_2 pressures of 20 to 60 bar and a temperature of 50 °C, the amine was formed with conversions up to 68%. *In situ* FTIR-measurements suggested interactions of $scCO_2$ with nitrobenzene and the potential intermediates nitrosobenzene as well as *N*-phenylhydroxylamine. Based on the observed side-products, the authors postulated the formation of nitrosobenzene from nitrobenzene to be rate-determining. Later, the CO_2-pressures could be reduced to just 8 bar for the hydrogenation of water-insoluble nitrobenzene with Ni/Al_2O_3, by using a H_2O-compressed CO_2 system at 35-50 °C.[244] Both the interactions of H_2O and CO_2 with the reacting species, along with a better dispersion of Ni/Al_2O_3 in H_2O, and the *in situ* formation of acid sites, were determined as crucial factors for this improved system.

In 2010, the same groups documented that a Ni/TiO_2 catalyst can hydrogenate chloronitrobenzenes to chloroanilines selectively in $scCO_2$.[245] Reactions were carried out at 35 °C under pressures of 40 bar H_2 and 100-110 bar CO_2. Compared to ethanol and hexane, again the performance of the catalyst was found to be the best in $scCO_2$. Here, the chemoselectivity was 97-99% in a conversion range of 9-100%. Aniline formation and accumulation of harmful intermediates was sufficiently suppressed. Interestingly, Ni/Al_2O_3 showed similar chemoselectivity, however, the TOF is less than one third. The better performance of Ni/TiO_2 in $scCO_2$ compared to the organic solvents was again explained by interactions of CO_2 with the reacting species, as described above: due to the interaction of the nitroso group with CO_2 its reactivity is increased. Furthermore, the conversion of *N*-chlorophenylhydroxylamine to chloroaniline is likely promoted by CO_2, too. The use of titania-based Ni catalysts in the hydrogenation of nitrobenzene was reported by B. Viswanathan and co-workers two years later.[246]

A nickel sulfide material active for nitro reduction was reported by the group of H. Zhang in 2010. [247] By applying a mild hydrothermal methodology, uniform nanostructured Ni_7S_6-flowers were obtained. They were active in the hydrogenation of chloronitrobenzenes at 40 bars of H_2 and 150 °C. Interestingly, the highest conversion was obtained for 2-chloronitrobenzene (98%), whereas 4-chloronitrobenezene was converted the least (74%). An even lower conversion of 48% was observed for unmodified nitrobenzene. Selectivities were similar for all substrates (96-99%).

Another Ni-based system for the hydrogenation of chloronitrobenzenes was reported by J. Qiu.[248] Here, carbon nanofiber supported Ni catalysts were prepared by a deposition precipitation method in ethylene glycol, which achieved over 98% conversion and 97% selectivity with respect to 2-chloroaniline at 20 bars of H_2 and 140 °C. The size of the Ni particles could be tuned by precipitation temperature, varying from 5 to 15 nm approximately.

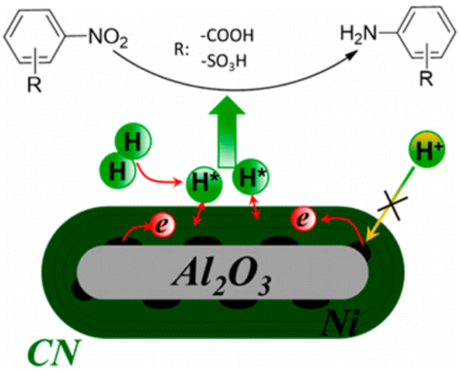
W. Li and co-workers achieved hydrogenation of 4-chloronitrobenezene by Ni-NPs supported on boehmite.[249] The conversion dropped from 88% after 50 min in the first run, to 76% after 120 min in the fourth run. This was accompanied by a selectivity drop from 96% to 89%. In the hydrogenation of 4-NP a decreased conversion was observed as well, although the selectivity stayed constant at 99%.

D. K. Dutta reported a clay supported Ni(0) based catalyst for the hydrogenation of halogenated nitroarenes.[250] *Via* incipient wetness impregnation of Ni into nanopores of activated montmorillonite, and eventual reduction with hydrazine hydrate small Ni(0) NPs with a size of approximately 5 nm were achieved. Six different halogenated nitroarenes were investigated, resulting in conversions between 78 to 100% and selectivities from 96 to 99%. In recycling studies with 4-chloronitrobenzene, a drop of conversion of about 10% during three runs was observed at marginal decrease of selectivity.

A carboxymethyl cellulose (CMC) based Ni catalyst for the hydrogenation of both carbonyl compounds and nitroarenes was reported by M. Ait Ali.[251] At room temperature and under a H_2 pressure of 40 bar, nitrobenzene and derivatives were converted to the respective amines in high yields. In a recycling study with acetophenone as model substrate, the yield of product decreased from 98% in the first run to 81% in the fourth. Furthermore, ICP analysis revealed a loss of Ni of 58% during four runs, and oxidation of Ni to NiO was detected by XPRD. The authors stated that the formation of the latter might not be the cause of the reduced activity during the recycling.

In 2014, W. Ding and co-workers demonstrated a Ni catalyst for the reduction of nitroarenes in strongly acidic medium.[252] Highly dispersed Ni on alumina was encapsulated in CN, which isolated the metal from the reactive environment (see Figure 39).

Figure 39 CN encapsulated, highly dispersed Ni on Al_2O_3 as reported by W. Ding and co-workers. (Reproduced with permission from Ref. 252. Copyright 2014, American Chemical Society)



According to the authors, hydrogen adsorption and activation occurred at surface nitrogen atoms in the CN capsule, by electron donation from nickel. According to the authors the CN shell has two functions: first, adsorption and dissociation of the dihydrogen molecule and protection of Ni from the highly acidic media (H_2SO_4 was added for the conversion of nitrobenzene to 4-AP). In such a particular kind of activation, Ni atoms could be capable to donate electron density to the CN which is the formal responsible for the H_2 dissociation. A similar mode of activation was proposed by Y. Wang and co-workers in the case of Co (Co(0) NPs onto nitrogen-doped carbon nanotubes) supporting it with DFT calculations.[82] Later, K. S. R. Rao and co-workers also reported carbon-covered, Al_2O_3-supported Ni catalysts for the hydrogenation of nitrobenzene.[253] Z. Zhao and co-workers reported a Ni system supported on W_2C and activated carbon (AC), which hydrogenated nitrobenzene to aniline with a yield of 100% in the presence of Lewis acid.[254] In the absence of Lewis acid, only 52% substrate was converted with the same catalyst, demonstrating the synergistic effect between Ni-W_2C and the Lewis acid (in particular, $FeCl_3$ provided the best selectivity). A scope of 16 substrates was reported, with selectivities towards the corresponding amine of >99 %. The recyclability was demonstrated during nine runs with almost no loss of activity and selectivity. Later on, the same group modified this system with mesoporous graphitic CN.[255]

L. C. Yang, Q. S. Gao and co-workers reported Mo_2C nanowires with highly dispersed Ni as novel catalyst for the hydrogenation of nitroarenes.[256] A strong metal-support interaction was supposed to be the responsible for the good dispersion. The nanowires were synthesized by adding aniline to an aqueous solution of ammonium heptamolybdate, followed by acidification to pH = 4-5. $Mo_3O_{10}(C_6H_8N)_2{\cdot}H_2O$ precipitated and subsequently The final catalyst was then obtained through impregnation with $NiCl_2$ and thermal treatment under a stream of 5 vol% H_2/Ar. Using this catalytic material, the nitro reductions was found to be promoted by water, however to the detriment of recyclability (metal leaching was found to be >

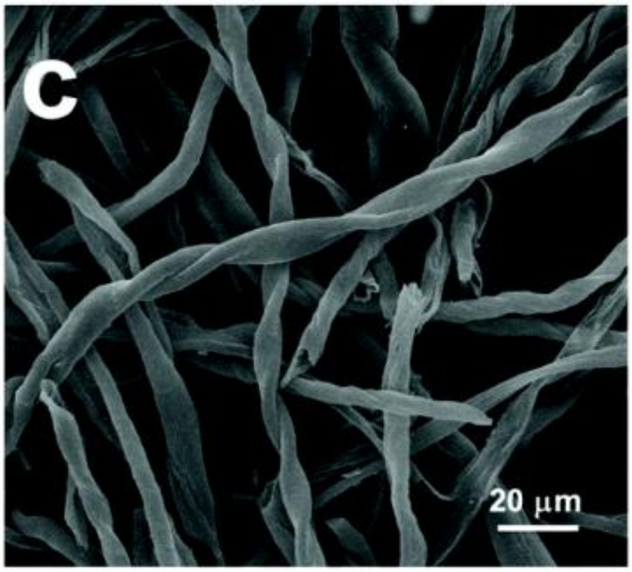
90% in some cases). In order to circumvent this issue, the stability of the catalyst was successfully enhanced by coating it with carbon *via* a hydrothermal approach, which protects Ni from the aqueous acidic medium partially suppressing the Ni leaching and gaining a discreet recyclability.

Besides the nanofiber-based system reported by J. Qiu and co-workers (*vide supra*),[248] also H. Jiang and co-workers used them for the development of their catalyst.[257] By fast pyrolysis (1-2 seconds) of $NiCl_2$ and $FeCl_3$ preloaded lignocellulose at 600 K, Ni-$NiFe_2O_4$/carbon nanofibers were formed. They showed high activity and selectivity in the hydrogenation of various nitroarenes at 10 bars of H_2 and 150 °C, tolerating alcohols, chlorides, and aldehydes. At higher H_2 pressure (40 bar), ketones and aldehydes were reduced to alcohols in high yields, too.

L. Kiwi-Minsker and co-workers published metallic Ni(0) NPs of just about 2.0 nm size, stabilized by microporous network of AC fibers, and their catalytic activity in the hydrogenation of nitroarenes.[125] The catalyst had to be prepared freshly and activated *in situ* by H_2 in order to achieve optimum activity. Furthermore, by pre-treatment of the fibres with nitric acid, the activity of the catalyst was increased, due to a high concentration of oxygen-based functionalities. Compared to Raney®-Ni, the best catalyst was about 20-fold more active in the hydrogenation of 4-chloronitrobenzene. In recycling studies, this catalyst showed a decreased activity during the first six runs, however, it was relatively stable over the following seven consecutive runs.

In addition to the already mentioned materials, a number of carbon supported Ni catalysts were reported in the last decade. Exemplarily, J. Qiu and co-workers reported magnetic, metallic Ni particles on carbon, synthesized by a one-step hydrothermal synthesis, followed by calcination.[258]

Figure 40 Typical SEM image of the Ni-loaded material reported by J. Qiu and co-workers (Reproduced with permission from Ref. 259. Copyright 2015, The Royal Society of Chemistry)



The most active catalyst was obtained at a calcination temperature of 300 °C. It converted nitroarenes to the corresponding amines with high conversions and selectivities, including chloronitroarenes. In recycling experiments with 2-chloronitrobenzene, neither the conversion, nor the selectivity revealed an obvious drop during 10 cycles. One year later, the same group documented the *in-situ* synthesis of cotton-derived, carbon supported Ni catalysts and tested their activity in the same hydrogenation (see Figure 40).[259] This time, 400 °C seemed to be the optimum calcination temperature, which led to very high conversion and good selectivity after 5 h and 5 bar H_2. The size of the well-dispersed nickel particles was about 6-14 nm, and the metal content was 51 wt%, resulting in a magnetic material.

By treating AC with nitric acid, oxygen surface groups are created, as was shown by A. Wang, T. Zhang and co-workers.[260] Those surface groups can stabilize Ni particles by preventing them from sintering, and assist catalysis by interacting with the nitro group of the substrates. In that way, they play a key role in this system and are responsible for high activity and chemoselectivity. Substituted nitroarenes were successfully hydrogenated to the corresponding anilines, whereas α,β-unsaturated nitroarenes were rapidly hydrogenated to oximes.

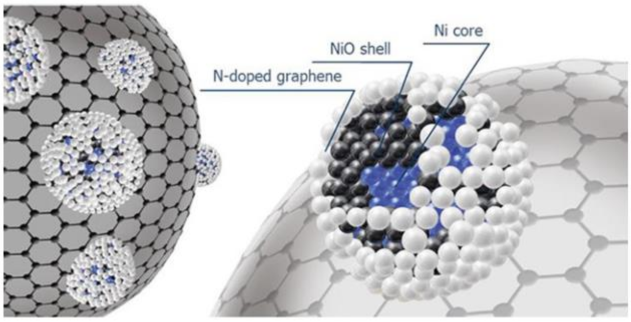
Thermolysis of a nickel containing MOF to achieve graphitic carbon layers, which encapsulate Ni NPs, was reported by E. C. Yang, X. J. Zhao and co-workers in 2017.[261] The MOF structure was build up with terephthalic acid and $NiCl_2·6H_2O$. The prepared MOF was then thermolyzed under nitrogen at 450-750 °C. In that way, a highly active material for the nitro reduction with H_2 was obtained. After 40-80 min at 140 °C and 5 bar H_2, all investigated substrates were successfully hydrogenated with very high conversions and selectivities. The catalyst was recycled five times, without notable loss of activity.

In 2017, T. Chen and co-workers reported a C_{60}-stabilized nickel-catalyst for the hydrogenation of nitrobenzene.[262] It was synthesized by mixing a Ni-precursor with HCl pre-treated C_{60} in ethanol assisted by sonication. The mixture was stirred at 60 °C for 12 h, and after evaporation of the solvent, the material was dried. Prior to use in catalytic experiments, the catalyst was reduced either by $N_2H_4{\cdot}H_2O$ or $NaBH_4$. The material with a Ni-content of 30% reduced nitrobenzene to aniline at 90 °C and 20 bar H_2 within 40 min with almost quantitative conversion and selectivity. $Ni(OAc)_2$ was found to be the best precursor, and the optimal molar ratio of $NaBH_4$ to Ni was 4:1. The catalyst was recycled six times, and both conversion and selectivity showed just small decrease during the runs.

Besides, also N-doped and N-functionalized carbon supported systems were of interest. In this respect, W. Ding and co-workers reported nickel embedded in nitrogen-doped carbon for the direct hydrogenation of nitrobenzene to 4-AP in sulfuric acid.[178] The catalyst was obtained by dipping a nickel nitrate solution into an N-containing polymer, built up with glycoluril and terephthalaldehyde, followed by subsequent pyrolysis at 600 °C for 6 h under argon. The nitrobenzene conversion could be enhanced by increasing the acid concentration, however it remains inly moderate.

A more general hydrogenation catalyst consisting of Ni NPs with N-doped graphene shells, was reported by Beller and co-workers in 2016.[263] With the use of several characterisation techniques it was concluded that the majority of the nickel is present as metallic Ni, however, also NiO is co-existing at its surface (Figure 41).

Figure 41 Schematic representation of the N-doped graphene wrapped core-shell structure of the Ni catalyst reported by Beller and co-workers. (Reproduced with permission from Ref. 263. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

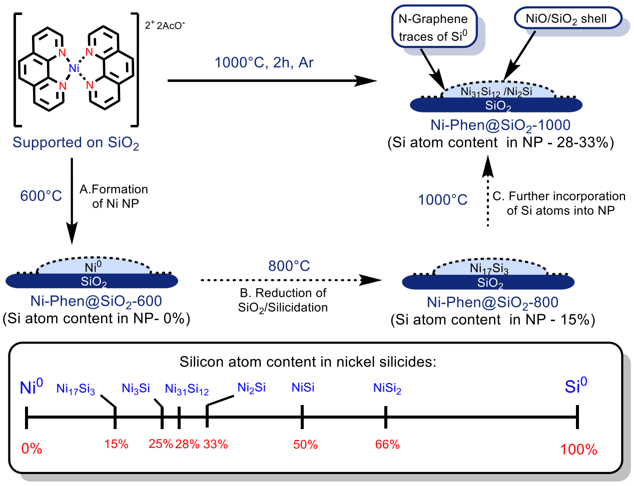


Those particles are highly dispersed and covered with an N-doped graphene-layer matrix. Partially, the Ni particles also occupy pores of the support (Figure 41). The material was synthesized by mixing Ni(OAc)$_2$ and Phen in a 1:2 ratio in ethanol at 70 °C. After 1 h stirring, Vulcan® XC72R as carbon support was added. Finally, the solvent was removed and the dried material pyrolyzed at 600 or 800 °C under argon for 2 h. The obtained catalysts hydrogenated nitrobenzene and other nitroarenes to the corresponding anilines in a THF/H$_2$O mixture at 110 °C, H$_2$ pressure of 50 bar, and 1.0 equivalent of triethylamine. The presence of base improved the activity significantly. Furthermore, reductive amination reaction between phenylacetone and *N*-ethylbenzylamine was successful.

Most recently, also X. Wang, X. Lu and co-workers made use of Phen as nitrogen source for metals activated by N-doped graphene, incorporated in ordered mesoporous carbon for the efficient hydrogenation of a variety of nitroarenes.[264] Typically, a precursor solution consisting of phenol and formaldehyde was added to an ethanolic solution of Pluronic F127 at 40 °C. After 10 min stirring, metal nitrate solubilized in ethanol was added (M = Ni, Co, or Fe). Then, the solution was treated with 2 equivalents of acac and 1 equivalent of Phen, with respect to metal. Finally, the solvent was evaporated and the dried residues were temperature-treated for 3 h under nitrogen. The nickel-containing materials were pyrolyzed between 500 and 900 °C, cobalt and iron loaded ones at 800 °C. XPS analyses revealed that with rising temperature, the nickel content increases on the catalysts surface, and simultaneously the relative amount of nitrogen decreases. This is also true for the actual elemental content of the whole material, determined by elemental analysis. The weight percentage of carbon, however, is constant at the surface with about 80%, whereas overall it increases with rising temperature. Catalytic investigations demonstrated the superior activity of the nickel containing material treated at 800 °C for hydrogenation of nitrobenzene at 100 °C in water and H$_2$ pressure of 50 bars. At lower and higher temperatures, however, the conversions decreased, while the selectivity towards aniline stayed constant. When the addition of Phen was omitted during the catalyst preparation, the activity dropped significantly, too. Exchange of nickel with iron or cobalt, respectively, also yielded catalysts with lower activity. With the most active catalyst, a broad variety of substrates was selectively hydrogenated, and a high functional group tolerance was observed. For instance, esters, halides, olefins and nitriles survived during the reaction. A good recyclability was shown during seven runs. This was compared with a catalyst, which did not contain any nitrogen. A loss of activity was observed for that material, which demonstrated the importance of nitrogen present in the material.

A novel catalytic material for nitro and related reductions was very recently disclosed by Beller and co-workers.[265] In their work they discovered that intermetallic nickel silicide NPs supported on silica showed improved activity and stability compared to the benchmark catalyst Raney®-Ni. Several materials were synthesized *via* the formation of nickel complexes from $Ni(OAc)_2$ and Phen, which were subsequently treated with inorganic supports and pyrolyzed at 600, 800, or 1000 °C, respectively. Among the as prepared catalysts, Ni-Phen@SiO_2-1000 was suitable for the hydrogenation of nitroarenes, nitriles, carbonyl compounds, N-heterocycles and unsaturated carbon-carbon bonds at comparably mild conditions. More specifically, 18 nitroarenes were selectively reduced at 60 °C and 10 bars of H_2 in methanol/water (1:1). A broad variety of functional groups was tolerated, including bromides, (thio)ethers, amides, and a 1,2,5-thiadiazole derivative. During five recycling experiments, neither loss in reactivity, nor leaching of nickel was observed. In contrast to Raney®-Ni, the optimal catalyst is stable and safe to store and handle even in the air, which makes it an interesting alternative. Furthermore, a curious mechanism for the formation of the catalyst was proposed: ppon heating up to 600 °C, metallic Ni NPs are formed. Further increase of temperature to 800 °C leads to the reduction of surface silica and $Ni_{17}Si_3$ is formed. Then, diffusion of Si into the Ni NPs is growing exponentially with the temperature. As a consequence, a mixture of $Ni_{31}Si_{12}/Ni_2Si$ is obtained. The surface of the NPs is oxidized under air, giving rise to NiO/SiO_2 shell. This increased amount of silicon in the nickel NPs was thought to be responsible for the superior activity of this catalyst, compared to lower pyrolysis-temperatures (Figure 42).

Figure 42 Mechanism for the formation of nickel silicide NPs via reductive silicidation, as was proposed by Beller and co-workers.



In 2017, F. Hao, P. Liu and co-workers investigated the hydrogenation of nitro-substituted naphthalenes, catalyzed by Ni NPs supported on N-functionalized active carbon (AC).[266] As in the previous system by Beller,[263] pyrolysis at 800 °C resulted in the most active catalyst. The dispersion of Ni, its particle size and its chemical state distribution were influenced by the nitrogen-containing species on the surface of the carbon, which itself could be partly controlled by the applied temperature during the preparation process. The most active catalyst converted 1-nitronaphthalene, 1,5-, and 1,8-dinitronaphthalene to the corresponding amines with yields >94%.

Recently, a work by A. Corma, M. Boronat and co-workers described a combined experimental (kinetics)/theoretical (DFT) study in order to get some insights into the reaction mechanism of the hydrogenation of nitroarenes, using Ni@C as catalyst.[267] The preparation of the catalyst was earlier reported by the same group in previous work (see Chapter 7.1.1).[180] Using nitrobenzene as model substrate the authors demonstrated that nitrosobenzene is formed as main reaction intermediate and the transformation occurs through the following elementary pathway: $PhNO_2 \rightarrow PhNO \rightarrow PhN \rightarrow PhNH \rightarrow PhNH_2$ in which the rate determining step is located in the H transfer to the PhN species adsorbed onto the Ni surface. This pathway is consistently different from the one possible on Pt surface in which the breaking of the N-O bond is more difficult. Moreover, they also clarified the role of water. Owing to the oxophilic nature of Ni, the oxygen atoms of $PhNO_2$ are transferred onto the Ni surface and then are converted into water by H_2, which represent an energetically demanding step. Further effort was done to understand the preferential selectivity of the Ni@C catalyst towards the hydrogenation of the nitro group in 3-nitrostyrene (a selectivity of 80% in 3-aminostyrene was obtained stopping the reaction at full conversion after which the product is rapidly converted into 3-ethylaniline). This behaviour was rationalized considering the different Ni surface adsorption geometry of 3-nitrostyrene and 3-aminostyrene. 3-Nitrostyrene is adsorbed perpendicularly with the nitro group avoiding the reduction of other moieties present on the arene ring. On the contrary, the latter adopts a parallel geometry in which the C=C bond can be easily attacked by the H atoms present on the surface.

A different approach for stabilizing Ni NPs was reported by Z. Hou and co-workers in 2014.[268] The combination of the ionic liquid (IL) 1-butyl-2,3-dimethylimidazolium acetate [BMMIm]OAc with the symmetric triblock copolymer Pluronic P123, produced Ni NPs stabilized by water-soluble micelles. These materials were active in the hydrogenation of C=C bonds as well as nitrobenzene and derivatives. Very high selectivities of >99% towards amines were reported at H_2 pressures of 15 bar and 60-70 °C. Due to the micelle formation, agglomeration of the usually poorly stable Ni NPs was prevented. The addition of the IL avoided emulsification and simplified product separation. Furthermore, in recycling studies the activity decreased after three cycles in the absence of IL, whereas in the presence of [BMMIm]OAc the conversion did not significantly drop even after five runs. The reduced conversion from the sixth run onwards were mainly be attributed to leaching of Ni, and oxidation and aggregation of NPs. ICP analysis revealed a leaching of 15 ppm of Ni.

5.2. Transfer hydrogenations

5.2.1. Reductions with $NaBH_4$

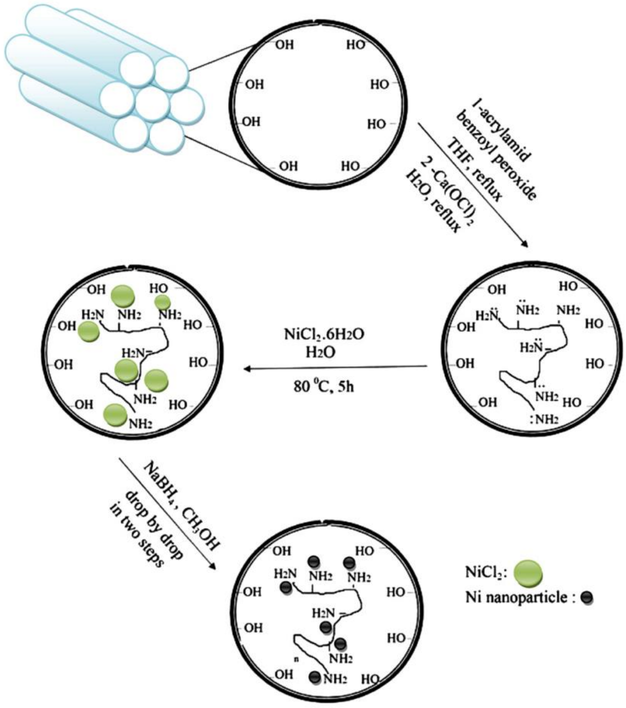
Apart from H_2, also sodium borohydride attracted much attention in nickel catalyzed reductions of nitroarenes. Similar to the previously described metals, numerous academic publications make use of this reductant in the presence of various homogenous and heterogeneous Ni compounds. As an example, in 2007 M. Litvić and co-workers showed that Raney®-Ni successfully reduced nitroarenes in the presence of 2 equivalents of $NaBH_4$.[269] Within 5 to 20 min, all investigated substrates gave the corresponding amines in high yields in MeOH at 30-40 °C. One year later, A. Rahman and S. B. Jonnalagadda investigated the effect of different Ni loadings supported on either silica or titania, respectively.[270] Seven different catalysts were prepared by impregnation method, among which 5% Ni-SiO_2 was found to be most active. In the presence of

>10 equivalents $NaBH_4$, Ni-B was generated *in situ* and various nitroarenes were converted to the corresponding amines during 10-20 min at 5 °C.

In addition, N. Sahinera and co-workers reported Ni NPs of about 100 nm size absorbed within an anionic hydrogel network of poly(2-acrylamido-2-methyl-1-propansulfonic acid).[271] They were generated *in situ* by the reduction of Ni(II) with $NaBH_4$. The material was tested with 2- and 4-NP and reduction rate constants at different temperatures, as well as activation parameters were calculated, revealing activation energies of 22.70 $kJmol^{-1}$ for 4-NP, and 38.69 $kJmol^{-1}$ for 2-NP.

R. J. Kalbasi and co-workers functionalized mesoporous silica SBA-15 with polyvinylamine.[272] Therefore, acryl amide was polymerized by the radical initiator benzoyl peroxide in the presence of SBA-15. Subsequently, the polyacrylamide was converted to a polyvinylamine by treating it with $Ca(OCl)_2$ in water. Afterwards, aqueous $NiCl_2$ was added and in the presence of $NaBH_4$, Ni NPs were formed (see Figure 43). This material was active for eight nitro-group containing substrates. Isolated yields of the corresponding amines of about 98% were achieved at room temperature during 2 to 85 min in the presence of 4.0 equivalents of $NaBH_4$ in water. The catalyst was successfully reused five times, without loss in activity. Later, the system was modified by growing hyperbranched polyamidoamine (PAMAM) dendrimers on its surface.[273] The authors stated that the modified system is advantageous compared to the previous one, by means of higher reactivity and better reusability. Even though the new system was recycled ten times, the yield dropped from the sixth run on. As the recycling of the previous one was stopped after five runs, comparison is difficult.

Figure 43 Synthesis of polyvinylamine-carried nickel NPs, supported on SBA-15. (Reproduced with permission from Ref. 272. Copyright 2011, Elsevier)

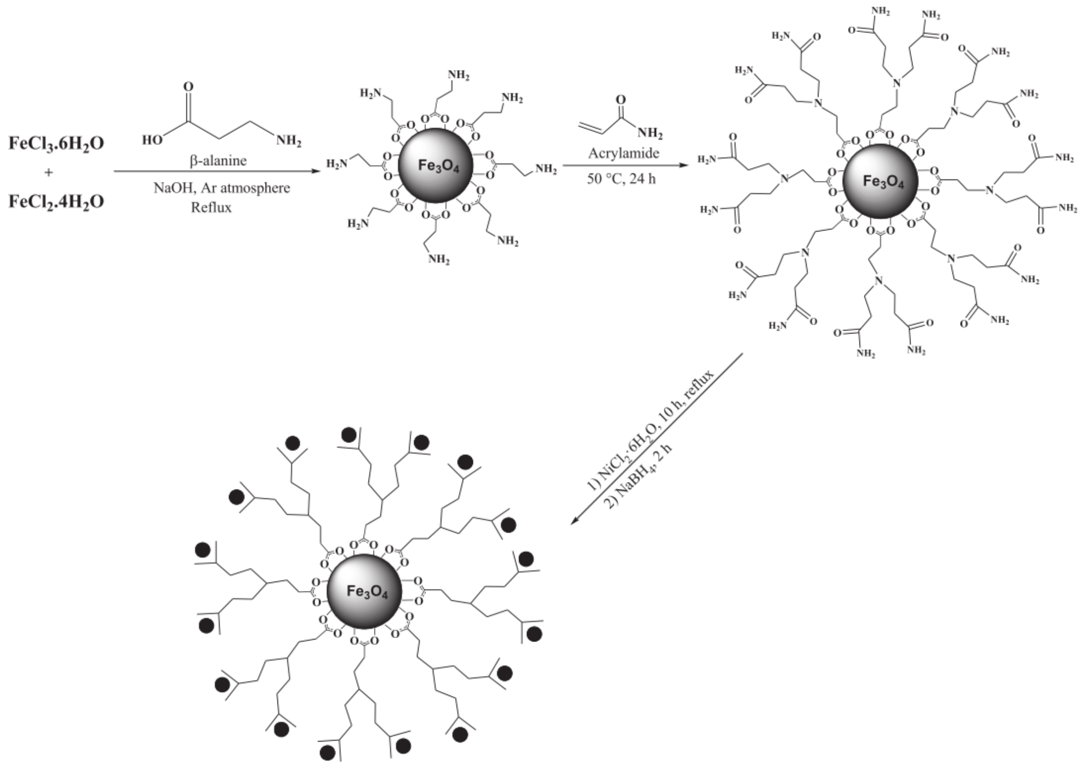


Later, a similar catalyst was prepared by growing Ni NPs-loaded dendrimeric PAMAM on the surface of Fe_3O_4.[274] The material was able to convert nitro compounds and nitriles to amines at 40 °C and 95 °C, respectively, in water. Notably, also aliphatic nitroethane was converted to ethylamine with 89% yield. Functional groups such as carboxylic acid, ketone, aldehyde and halogen were tolerated by this system. A small drop of yield for the hydrogenation of 4-nitroaniline was observed during six runs.

A. Chinnappan and H. Kim made use of transition metal based ILs for the $NaBH_4$ promoted reduction of nitro compounds.[275] As an IL, both 1,1’-hexane-1,6-diylbis (3-methylpyridinium) tetrachloronickelate (II) $[C_6(mpy)_2][NiCl_4]$ and polyvinylidene fluoride (PVDF)-IL nanofiber composites were investigated at ambient temperature in water. The latter material was prepared *via* electrospinning to obtain nanofibers in sub-micrometre sizes. Several functionalized nitroarenes were successfully converted to the corresponding anilines with both materials. The activity of PVDF nanofiber composite outperformed that of $[C_6(mpy)_2][NiCl_4]$. Furthermore, its recyclability was tested during four runs.

Zamani and Kianpour described an easy to prepare Fe_3O_4/β-alanine-acrylamide-Ni nanocomposite, which successfully transformed nine different nitroarenes in short reaction times of maximum 15 min at room temperature in water.[276] Fe(II) and Fe(III) chloride hydrates were heated in basic conditions in presence of β-alanine. Afterwards, acrylamide was added, followed by $NiCl_2{\cdot}6H_2O$. By treatment with $NaBH_4$, Ni NPs were formed (see Figure 44). During eight runs, the yield of aniline in the reduction of nitrobenzene dropped from 98% in the first, to 92% in the last run.

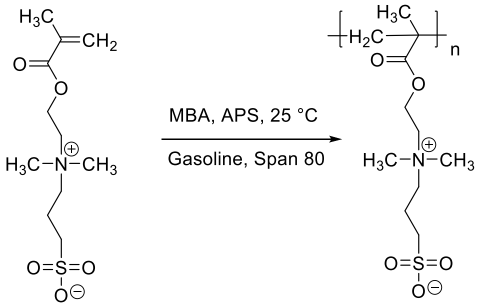
Figure 44 Preparation of a Fe_3O_4/β-alanine-acrylamide-Ni nanocomposite. (Reproduced with permission from Ref. 276. Copyright 2014, Elsevier)



In the same year, X. H. Li, K. X. Wang and co-workers tried to mimic enzymes with NiS_{2+x} NPs on polymeric melon (g-C_3N_4).[277] In comparison with analogous noble metal catalysts (Pd, Au, Pt), the novel NiS_{2+x}/CN showed a better selectivity for the reduction of nitrobenzene at full conversion. For instance, 4-bromo- and 4-iodonitrobenzene produced mainly aniline by dehalogenation-processes using Pd/CN, whereas NiS_{2+x}/CN showed selectivities towards the *p*-halo aniline of >99%. Experiments were conducted in water and in the presence of 1 equivalent of $NaBH_4$, with respect to substrate.

N. Sahiner and co-workers made use of microgel supported Ni NPs for nitro reductions.[278] Poly(sulfobetain methacrylate) hydrogels were prepared by inverse suspension polymerisation of the zwitterionic monomer (Scheme 34). This hydrogel was then loaded with Ni(II) and the addition of $NaBH_4$ generated Ni NPs *in situ*. The resulting material showed to be active in the reduction of 4-NP and, less effective, for 2-NP and 4-nitroaniline. During three cycles of 4-NP reduction, the activity of the catalyst dropped to only 10%.

Scheme 34 Polymerisation of sulfobetain methacrylate.



R. J. Kalbasi and O. Mazaheri reported Ni NPs inside ZSM-5 as another efficient bi-functional catalyst for nitro reduction.[279] Two different catalysts were prepared using specific mesoporous silica (KIT-6) to give Ni/mZSM-5 and its acidic form Ni/H-mZSM-5, which was obtained by ion-exchange with aqueous NH_4Cl solution in reflux. Interestingly, the acidic form was more active in the reduction of nitrobenezene than Ni/mZSM-5, resulting in shorter reaction times and lower amounts of catalyst. 19 Nitro-containing substrates were reduced with Ni/mZSM-5 within 1 to 65 min. For instance, 1-nitronaphthalene was reduced to the corresponding amine with Ni/mZSM-5 after 15 min and with Ni/H-mZSM-5 after just 3 min. Both catalysts revealed a decreased activity in recycling experiments during seven runs. Notably, Ni/H-mZSM-5 was also active in the reductive amination of aldehydes with nitroarenes, resulting in secondary amines.[280]

M. Karthik and P. Suresh synthesized a rGO nickel composite.[281] The material was prepared by the simultaneous reduction of graphene oxide and Ni^{2+} using L-ascorbic acid in water. A relatively high nickel loading of 19.7% was determined, with average particle sizes of 10 nm. In the presence of 13 equivalents of $NaBH_4$ in water, the material was able to reduce a large scope of substrates, including two aliphatic ones. As for most such systems high yields were obtained during short times (10 to 40 min). Noteworthy, a good tolerance towards functional groups was found: even 4-iodonitrobenzene was selectively hydrogenated to 4-iodoaniline with 98% isolated yield. In addition, the magnetic catalyst was used in five consecutive runs with a slight decrease of yield.

A Ni based N-doped mesoporous carbon catalyst was derived by calcination of a MOF by Z. Dong and co-workers in 2016.[282] After the MOF was synthesized from 4,4'-bipyridine, 1,3,5-benzenetricarboxylic acid and $Ni(NO_3)_2 \cdot 6H_2O$, it was calcined at 700 °C under nitrogen for 2 h. The as synthesised material successfully reduced 4-NP, using $NaBH_4$ as reducing agent in large excess.

Another catalyst consisting of Ni NPs anchored on N-doped porous carbon was reported by M. Xue and co-workers recently.[283] An aqueous $NiSO_4 \cdot 6H_2O$ solution was added dropwise to a solution of dimethylglyoxime ($dmgH_2$) in ethanol, resulting in the formation of $Ni(dmgH)_2$ (dmgH: dimethylglyoximate). After purification, it was calcined at different temperatures ranging from 400 to 700 °C under a flow of nitrogen for two hours. The optimum calcination temperature was found to be 700 °C, and that material was able to reduce 4-NP with $NaBH_4$ in water within 3 min.

L. Liu, Z. Xue and co-workers reported amorphous NiB/carbon nanohybrids to be active in the reduction of 4-NP in the presence of $NaBH_4$.[284] It was found that the amorphous NiB layer donates electrons to the carbon template, which makes NiB more electrophilic. Due to this enhanced electrophilicity, adsorption of reactants is favoured, along with the generation of active H species on the surface by cleavage of B-H bond. This facilitates the hydrogenation of 4-NP.

Also X. Su and co-workers reported carbon coated Ni NPs for the reduction of 4-NP.[285] By applying a calcination approach, highly dispersed NPs with a mean diameter of less than 3 nm were obtained. Several calcination temperatures were investigated, revealing 600 °C as the optimum one. With a large $NaBH_4$/substrate ratio of >800, 4-NP was hydrogenated. The catalyst was reused four times without significant decreasing of the conversion.

Ni NPs supported on carbon black were documented by L. Zhang, X. Sun, X. Wang and co-workers in the same year.[286] Their catalyst was prepared from nickel chloride, using hydrazine hydrate as the reducing agent. The magnetic material reduced 4-NP to 4-AP at 30 °C with 105 equivalents of $NaBH_4$. The authors ascribed the activity of this catalyst to the specific characteristics of the nanostructure of the material and the synergistic effect of carbon black and nickel NPs. In recycling studies, the conversion slightly decreased after the 8th run.

A different nickel catalyst for the reduction of 4-NP was reported by Y. Yang and co-workers in 2014.[287] It was prepared by the pyrolysis of surfactant directed CTAB-chitosan-nickel supramolecular aggregates (CTAB: cetyltrimethylammonium bromide). The pyrolysis temperature affected the textural property of the carbonaceous supports, the morphology of the Ni NPs, and the catalytic activity. That catalyst simultaneously possesses uniform spherical Ni NPs of 24 nm, and bottle-neck mesopores. The highest activity of 20.9 $s^{-1}g^{-1}$ was found for the pyrolysis temperature of 750 °C. It was successfully recycled five times, showing almost the same conversion during all runs.

J. Xie and co-workers investigated the reduction of 4-NP, as well.[288] In their studies they used a nano sized nickel core surrounded by a mesoporous silica shell. The size of the metallic core was controlled by addition of chelating EDTA. Dependent from the concentration of the latter, sizes of 40-80 nm were obtained. More specifically, nickel acetate and EDTA were stirred in deionized water, and by adding $NaBH_4$ and heating, Ni NPs were achieved. Afterwards, the particles were coated with TEOS in the presence of CTAB and ammonia using the Stöber method.[289] After calcination at 550 °C for three hours, mesoporous silica was obtained. Increasing amount of catalyst, temperature and pH-value resulted in an increased rate constant. In addition to the good activity, the magnetic behaviour of the catalyst simplified the recycling procedure, resulting in a hardly changing rate constant during five runs.

L. Latterini and co-workers investigated the influence of stabilising agents on the catalytic performance of nickel colloids in the hydrogenation of 4-NP.[290] Both thermolysis and polyol procedures were used for the preparation of NPs, which had mean diameters ranging from 6.7 to 9.9 nm. Tested stabilizers were dioctylamine, trioctylphosphine, and PVP. It was found that alkyl-amine stabilised NPs resulted in a significantly improved reaction rate, TON and TOF. A reduced surface steric hindrance was assumed to be responsible for this. However, along with 4-AP, azobenzene derivatives were observed as side products. The selectivity towards the amine was improved with polyvinyl pyrrolidinone as capping agent.

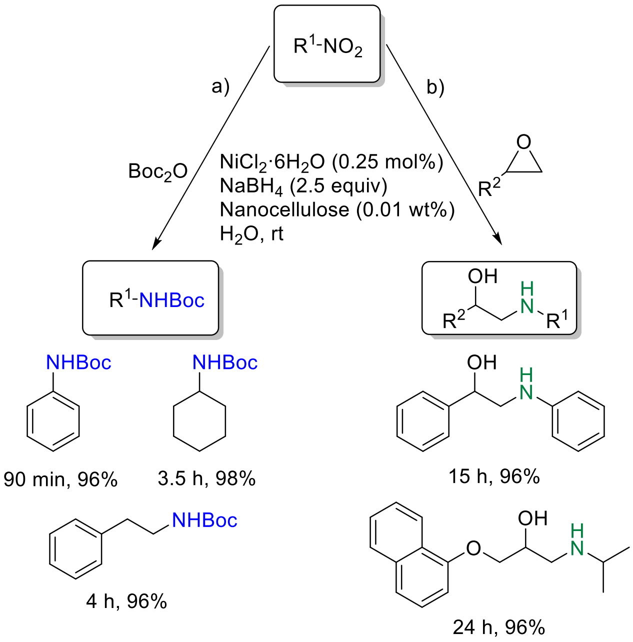
In 2015, S. Thakore and co-workers reported core-shell iron oxide on Ni NPs as a magnetically recyclable catalyst for nitro reductions.[291] Here, a simple procedure for catalyst preparation was applied: addition of nickel acetate and soluble starch as stabilising agent to an aqueous solution of iron oxide was followed by the reduction of Ni^{2+} with $NaBH_4$. The as obtained material reduced a broad scope of substrates to the corresponding anilines in water and in the presence of 4 equivalents of $NaBH_4$. Recyclability was demonstrated during 30 cycles for the reduction of 4-nitroaniline. However, the needed reaction time for full conversion increased from initial 12 min to 140 min in the last run.

One year later, H. Wang, W. Guo and co-workers demonstrated the use of small Ni NPs within ultrathin SiO_2 sheets, covering an iron oxide core in a yolk-shell fashion, for efficient reduction of nitroarenes.[292] The metal

NPs have a mean diameter of 4 nm and the sheets of SiO_2 have a thickness of only 2.6 nm. These latter sheets supresses agglomeration of the NPs which is common for other supported small NPs. Furthermore, the authors claimed that the active Ni sites are better accessible. The materials were synthesized by the addition of urea and nickel(II) nitrate to an aqueous suspension of $Fe_3O_4@SiO_2$. After ultrasonication, the reaction mixture was heated inside an autoclave at 105 °C for 12 h. The as obtained material has mesoporous channels suitable for diffusion of reactants to the active sites. Those channels are provided by the large inner cavities and interlayer spaces between the SiO_2/Ni nanosheets. A comparably high activity for the reduction of nitroanilines and -phenols was observed for the conversion of 4-nitroaniline during 10 runs.

The stabilizing effect of TEMPO-oxidized nanocellulose (TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxyl) on in situ formed nickel boride from $NiCl_2$ and $NaBH_4$ was investigated by P. Dinér and co-workers.[293] With a catalyst loading of 0.25 mol% with respect to Ni, 2.5 equivalents of $NaBH_4$ and 0.01 wt% nanocellulose, several aromatic and three aliphatic nitro compounds were reduced to the corresponding amines in water at room temperature. Several functional groups were tolerated; however, nitro substrates containing aldehyde and ketone groups were reduced to the corresponding amino alcohols. In addition, the authors demonstrated the utility of their protocol in two tandem procedures: in the first one, the *in situ* formed amines were Boc-protected to carbamates, by the addition of Boc_2O (Boc: tert-butyloxycarbonyl) to the crude reaction mixture. Notably, the more difficult substrate trans-β-nitrostyrene was converted to the reduced carbamate in high yield (Scheme 35, path a). In the second one, the generated amines were reacted further with added epoxides, resulting in biological important β-amino alcohols (Scheme 35, path b).

Scheme 35 Tandem reductions of nitro compounds to a) Boc-protected amines (carbamates) and b) *β*-amino alcohols as reported by P. Dinér and co-workers.



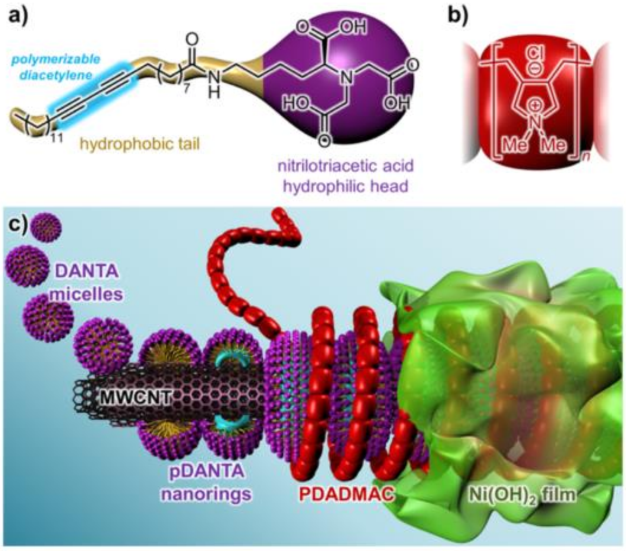
Most recently, M. M. Dell'Anna and co-workers reported another type of Ni NPs to be active in aqueous nitro reduction.[294] Here, the polymerizable complex Ni(AAEMA)$_2$ was synthesized by adding a basic solution of (2-acetoacetoxy)ethyl methacrylate (HAAEMA) in ethanol to a solution of Ni(NO$_3$)$_2$·6H$_2$O in ethanol. After polymerisation of the latter, the material was calcined in a flow of N$_2$ at 300 °C for 30 min. The resulting catalyst converted several nitroarenes to the corresponding amines in the presence of NaBH$_4$ in a H$_2$O/Et$_2$O mixture. Noteworthy, even 4-iodonitrobenzene was reduced to 4-iodoaniline in 82% yield, avoiding hydrodehalogenation. In recycling experiments with 4-bromoaniline, the yields were approximately constant over five runs.

Apart from pure Ni NPs, also nickel-tin bimetallic NPs were reported to be active in the reduction of nitroarenes.[295] In this case, nickel formate, tin(II) chloride and polyvinyl pyrrolidone (PVP) were dissolved in ethylene glycol and heated. As soon as the temperature reached 69 °C, NaBH$_4$ was added and the mixture was refluxed for 2.5 h. By varying the Ni:Sn ratio, the composition of the catalysts could be tuned, yielding in Ni$_{100}$, Ni$_{74}$Sn$_{26}$, Ni$_{59}$Sn$_{41}$ and Ni$_{50}$Sn$_{50}$. With an increasing tin concentration up to 41 mol%, an enhanced activity was achieved with respect to pure nickel, resulting in shorter reaction times. However, further increase of the tin content decreased the activity. The best performance was determined for Ni$_{74}$Sn$_{26}$, which was used for a small scope of substrates at room temperature in water.

One year later, V. Marakatti and S. Peter used related nickel-antimony NPs restricted in SBA-15 for the reduction of nitro compounds.[296] In their work, organosilane-functionalized SBA-15 was treated with Ni and Sb, and upon addition of $NaBH_4$, NPs were formed, which were then calcined in the air and reduced with H_2 at 500 °C. The obtained Ni-Sb NPs had a uniform size of 4-6 nm. In the presence of $NaBH_4$ they were active for four different nitroarenes. Different ratios of Ni:Sb were investigated, revealing 52 wt% of Ni and 48 wt% of Sb to be most active.

A particular catalyst system for the synthesis of *N*-arylhydroxylamines from nitroarenes was published by E. Gravel, E. Doris and co-workers in 2017.[297] Here, Ni(II) hydroxide was supported on carbon-nanotubes by a layer-by-layer strategy. Diacetylene-nitrilotriacetic acid amphiphiles (DANTA, Figure 45 a) were sonicated in water together with MWCNTs, whereby DANTA adsorbed at the surface to form hemi-micellar structures. Afterwards, the addition of poly (diallyldimethylammonium chloride) (PDADMAC, Figure 45 b) created a second layer *via* electrostatic interactions.

Figure 45 a) Structure of DANTA with its hydrophilic head and hydrophobic tail; b) structure of PDADMAC; c) schematic structure of the architecture of the catalyst reported by E. Gravel, E. Doris and co-workers (Reproduced with permission from Ref. 297. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)



Finally, Ni NPs were added to form the active material (Figure 45, c), which showed very high selectivity towards *N*-arylhydroxylamines. Notably, the solvent is crucial for this system: only a THF/H_2O (3:1) mixture with 3 equivalents of $NaBH_4$ was suitable for the desired transformations. Several substrates were successfully investigated, including 4-iodonitrobenzene. The only substrate with a different selectivity was

2-nitrobenzonitrile. In this case, after formation of the desired *N*-arylhydroxylamine a cyclization into a five-membered ring took place, which eventually evolved into aminobenzamide. Recycling experiments were conducted with 4-nitrobenzonitrile, showing a slight decrease of activity during five runs.

5.2.2.Reductions with alcohols/bases, N_2H_4, HCOOH and other reductants

In 2000, T. M. Jyothi and co-workers demonstrated the utility of a NiO catalyst supported on Al_2O_3 for the reduction of nitroarenes and carbonyl compounds using isopropanol as hydrogen-donor in the presence of KOH.[298] The material was prepared from calcination (450 °C, in the air) of a Ni-Al hydrotalcite precursor. The catalyst allowed to isolate anilines from the corresponding nitroarenes in yields of up to 95% within 1-2 h at reflux temperature. In the case of 1,3-dinitrobenzene, a mixture of 3-nitroaniline (65%) and 1,3-phenylenediamine (22%) was obtained. During recycling studies a decrease of activity was observed.

P. Selvam and co-workers reported a mesoporous nickel-containing silicate (MCM-41) to be a transfer hydrogenation catalyst for similar reductions, as well as in the cleavage of azo compounds.[299] Again isopropanol was used as hydrogen donor in the presence of KOH. Several functional groups were tolerated, and both regio- and chemoselective transformations were possible. For instance, in the case of a dinitroarene, only the sterically less hindered nitro group was hydrogenated. Although the catalyst was shown competent catalyst for both nitro and carbonyl groups, in the presence of both, only the nitro group was reduced. Hence, 2-nitrobenzaldehyde gave 2-aminobenzaldehyde in 89% yield. The authors claimed a better adsorption of the nitro group on the catalyst surface to be responsible for this selectivity. For each reported substrate the yield was given after the first and after the sixth run, revealing basically no change. Two years later, the same group reported a catalyst consisting of Ni incorporated in hexagonal mesoporous aluminophosphate molecular sieves, which was able to hydrogenate the same substrates under similar conditions.[300]

Furthermore, Bhaumik and co-workers demonstrated the use of NiO-Al_2O_3 mixed oxides for the transfer hydrogenation of nitroarenes, using isopropanol as both solvent and hydride source.[301] The material was prepared by a hydrothermal strategy in the presence of lauric acid as capping agent. The latter induced a self-assembly of the NPs, leading to voids between the particles. This made the material mesoporous with a BET surface of 337 m^2g^{-1}. The catalytic activity of the as obtained material was rather moderate. At reflux and in the presence of 1 equivalent of NaOH as promoter, nitrobenzene (50%), 4-chloronitrobenzene (58%) and 1,3-dinitrobenzene (36%) were investigated.

Apart from isopropanol, also ethanol was used as hydrogen donor in transfer hydrogenation reactions. As an example, S. Farhadi and co-workers reported NiO NPs for the microwave-assisted transfer hydrogenation of nitroarenes.[302] This catalyst was prepared by thermal decomposition of $Ni(dmgH)_2$ at 400 °C for 30 min under air. Several alcohols were tested as hydrogen donors, exposing ethanol as the optimal one. 50 mg of catalyst were used to hydrogenate 5 mmol of substrate with 1 equivalent of KOH in 20 mL ethanol both under microwave or conventional heating. Nitrobenzene was reduced to aniline in 60 min with a yield of 96% by using conventional heating, whereas microwave heating yielded in 98% of the product after just 13 min. Furthermore, the catalytic system tolerated several functional groups, including aldehydes, and showed chemoselectivity in the case of dinitroarenes, which led to nitroanilines. In recycling studies the conversion of nitrobenzene slightly dropped from 98% in the first, to 95% in the fourth run.

In addition to alcohols, also hydrazine hydrate was investigated as hydrogen donor. Specifically, H. Wen and co-workers reported the hydrogenation of nine nitroarenes in the presence of N_2H_4 in methanol under reflux using a nano-amorphous Ni-B catalyst supported on a polymer.[303] The material was produced by ion-exchange chemical reduction, and the polymer was an anionic exchange resin, which was incorporated inside a megaporous glass. All substrates were hydrogenated with yields ranging from 72% for 2,6-dinitrotoluene to >99% for nitrobenzene. In the presence of two nitro-groups, only one was hydrogenated.

Another protocol, which made use of hydrazine hydrate as hydrogen donor, was published by X. Liang and co-workers in 2015.[304] In this case, nickel NPs were highly dispersed on SiO_2 *via* atomic layer deposition, starting from $NiCp_2$. As silica source both 20-30 nm dense silica NPs and porous silica gel particles were used. The Ni/silica gel catalyst was able to activate N_2H_2 and hydrogenate nitroarenes to the corresponding anilines. This constitutes the first report of Ni NPs for the transfer hydrogenation of nitroarenes, synthesized by atomic layer deposition. The system converted eight different nitroarenes in the presence of 8 equivalents of hydrazine hydrate in ethanol at 100 °C with high selectivities and yields, including chloro- and fluoro-substituted nitroarenes, as well as ester- and acid-containing substrates. The catalyst was recycled four times, with constant activity.

Recently, Muralidharan and co-workers reported a Ni_3S_4 nanocatalyst for the nitro reduction in the presence of 8 equivalents of hydrazine.[305] It was synthesized by simply reacting $NiCl_2$ with thiourea and $HN(SiMe_3)_2$ at 130 °C. The purified material was able to hydrogenate nitrobenzene and derivatives in ethanol at 125 °C with N_2H_4 at 1 mol% loading. Halogens were tolerated (including 4-iodonitrobenzene), along with alcohols, nitriles, acids and amines. Also 1,2-dinitrobenzene was hydrogenated to the diamine. The catalyst was recycled ten times, revealing just a small decrease of yield.

In 2010, also Maksod and Saleh used hydrazine hydrate for the reduction of 4-NP, by applying Ni catalysts supported on Al_2O_3 and SiO_2, respectively, with different metal loadings of 20, 5, and 2.5 wt%.[306] The supports were impregnated with nickel, which was subsequently reduced with hydrazine hydrate. The catalytic tests were performed at 80 °C in methanol. In general, the Al_2O_3-supported catalysts were more efficient. Recycling studies revealed that a threefold reaction time in the fifth run was necessary for a complete conversion of 4-NP.

Complementary to these works, Singh and co-workers studied Ni-, Co-, and Cu-based NPs for the chemoselective nitro reduction in the presence of hydrazine hydrate.[307] Typically, an aqueous solution of $NaBH_4$ was added to the respective metal chloride and PVP in water, and after sonication, the materials were obtained as black precipitates. The NPs had sizes of about 10 nm in average. Both Ni and Co catalysts exhibited high activity for aromatic and aliphatic substrates in water, including several functionalized derivatives, such as bromides and iodides. In most cases Ni-based catalysts outperformed the other metals. A subsequent work by the same group studied the mechanism of this transformation using DFT calculations. They found that the direct reduction pathway is preferred over the indirect one (see Scheme 3) both from a thermodynamic and kinetic point of view.[308]

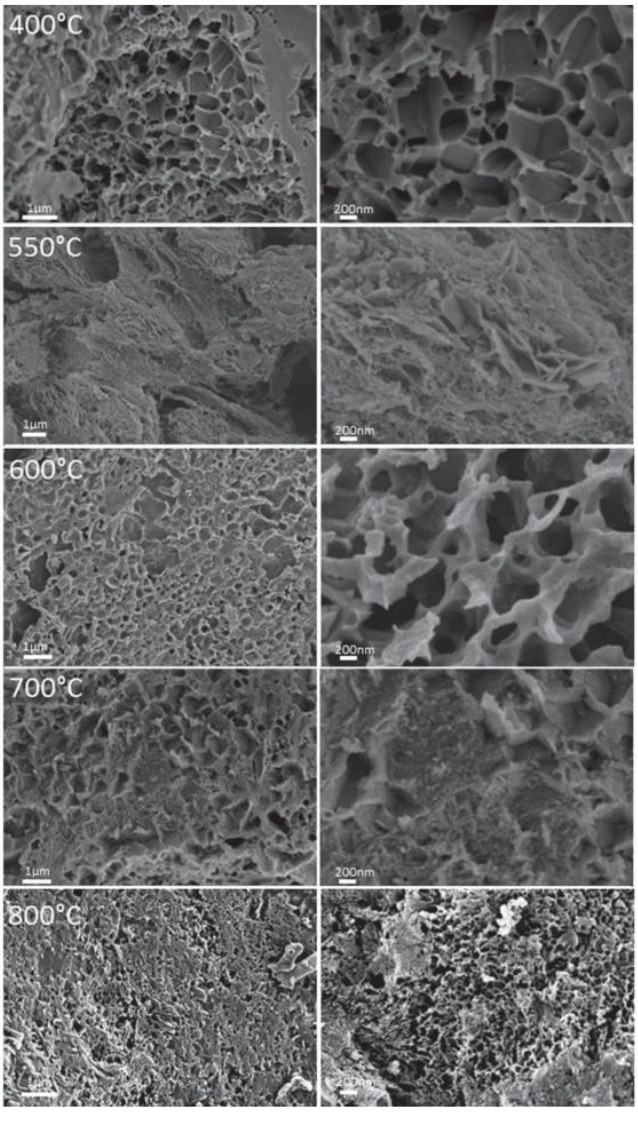
More recently, X. Wang, X. Lu and co-workers demonstrated that Ni-Mo oxide on SBA-15 exhibits high chemoselectivity in the catalytic reduction of nitroarenes.[309] To prepare active catalysts, SBA-15 was added to a solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in water/ethanol (1:1). After evaporation of the solvents, the remaining solids were calcined at 400 °C for 2 h in the air. The content of Ni was fixed to 6 %, but the amount of Mo was varied from 0 to 7.5% in steps of 1.5%. After calcination, the materials were added to a solution of Phen in water/ethanol (1:3) and sonicated for 30 min. Finally, they were again dried and pyrolyzed under a flow of N_2 for 2 h at 700 °C. Catalytic test reactions revealed a Ni:Mo ratio of 1:1 (both 6%) to be optimal for the reduction of nitroarenes with hydrazine hydrate in ethanol at 40 °C. A broad substrate scope demonstrated the activity, selectivity and functional group tolerance. All substrates were converted almost quantitatively with a selectivity of >99% in maximum 60 min. In addition, the catalyst was successfully recovered by magnetic separation and recycled nine times in the reduction of 2,4-dichloronitrobenzene, without decrease in conversion (74%) and selectivity (>99%). The activity of this catalyst was attributed to synergistic effects of metal Ni and MoO_3. The latter mainly activates hydrazine and therefore accelerates the rate determining step.

D. C. Gowda and co-workers made use of hydrazinium monoformate as hydrogen donor for Raney® Ni-catalyzed nitro- and nitrile-reductions.[310] At room temperature, both aliphatic and aromatic nitro compounds including several functional groups, such as ethers, alcohols, amides, esters, acids, halides, and others were reduced. It was found that also nitriles were converted to the corresponding amines. Furthermore, the authors stated that hydrazinium monoformate is a more efficient hydrogen donor than hydrazine or formic acid, for which they published a nickel-system two years earlier.[311] Back then it was shown that activated nickel can reduce both aliphatic and aromatic nitro compounds to the corresponding primary amines at room temperature using formic acid or ammonium formate as reductants.[311] High yields were achieved for nitroarenes after short reaction times of 10-30 min with Raney®-Ni in methanol. Aliphatic nitro compounds gave lower yields, because of their higher volatility.

In 2003, Bhaumik and co-workers showed that, apart from H_2,[220-222] $NaBH_4$,[269] and hydrazinium monoformate,[310,311] also NH_4Cl can be used as hydrogen donor for the Raney®-Ni-catalyzed nitro reduction.[312] However, even for 2-chloronitrobenzene, 20% hydrodehalogenated product was observed.

Finally, Shalom and co-workers demonstrated the use of formic acid as hydrogen donor for the reduction of nitrobenzene in 2014.[313] Sponge-like, nanoporous Ni- and Ni_3N-based materials, partly embedded in an amorphous carbon-nitrogen matrix, were synthesized by calcination of dicyandiamide together with a 1:1 mixture of $NiCl_2$ and LiCl at temperatures between 400 and 800 °C. $NiCl_2$ and LiCl have a eutectic melting point at 600 °C, which means that at lower temperatures, reactions can be considered as solid state synthesis, whereas above 600 °C it is a salt flux process. It was found that the materials syntheses started as solid-state condensation of dicyandiamide. Then, nickel carbodiimide is formed at temperatures below 600 °C. By further increasing the temperature to the eutectic melting point of the salt mixture, sponge-like Ni_3N was formed, embedded in an amorphous, nitrogen-rich carbon, possessing a high surface area. At even higher temperatures, Ni_3N is converted completely towards sponge-like Ni and the surface area increased further. SEM images for each calcination-temperature can be seen in Figure 46. Regarding catalytic activity it was found that a calcination temperature of 800 °C is the optimal among the investigated ones, for the reduction of nitrobenzene. The catalyst was also recycled; however only once.

Figure 46 SEM images for the dicyandiamide-$NiCl_2$/LiCl-materials at different calcination temperatures reported by Shalom and co-workers. (Reproduced with permission from Ref. 313. Copyright 2014, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)



6. Heterogeneous copper-based catalysts

6.1. Reduction with molecular H_2

Copper-based NPs have gained tremendous interest in recent years, particularly in catalysis.[314] Hence, also for the reduction of nitroarenes a series of Cu-catalysts were reported; however, only few of them working with molecular hydrogen as reductant. In 2015, as a special case, M. A. Keane and co-workers demonstrated a system that made use of H_2, which was generated *in situ* by dehydrogenation of 2-butanol to 2-butanone.[315] Two systems of copper supported on silica with different loadings of 15.9 wt% and 1.8 wt%, respectively, were prepared by dispersing silica in a $Cu(NO_3)_2$ solution. After the mixture was basified to pH > 10 with NaOH and heated, the solid was isolated, neutralized with water, dried, and finally calcined at 450 °C for 2 h and passivated with 1 vol% O_2/He. The catalytic investigation was carried out in continuous flow fixed bed vertical glass reactor at 150-250 °C. The hydrogen produced from 2-butanol was directly utilized in the reduction of nitrobenzene to aniline. The dehydrogenation was more efficient with the catalyst consisting of 15.9 wt% of copper particles with a mean diameter of 7.8 nm. The 1.8 wt% material with mean diameter of 3.1 nm, however, was more active in the nitro reduction. When using the material with a higher loading, exclusive production of aniline and 2-butanone at full conversion was obtained. The utilization efficiency of H_2 was by a factor of 50 greater than in the conventional procedure with pressurized H_2.

One year later, M. Gupta and co-workers made use of copper on N-CNTs for the reduction of nitro compounds with H_2.[316] The catalyst synthesis started by treating sugar with concentrated H_2SO_4. After neutralisation, it was oxidized with hydrogen peroxide and dried. A 1:1 mixture of the as prepared CNTs and nitrogen containing guanidine carbonate was calcined under air flow at 300 °C. Finally, Cu NPs were prepared by reduction of $Cu(acac)_2$ with hydrazine hydrate, followed by its addition to the N-doped CNTs. With a loading of 0.11 mol% based on copper, several nitroarenes were reduced to the corresponding amines in few hours under a H_2 atmosphere and in the presence of acetic acid in ethanol at room temperature. The material was recycled five times, during which a slight decrease of yield was observed.

Recently, Nuzhdin and co-workers demonstrated both the reduction of nitroarenes to anilines, and their reductive coupling with aldehydes to secondary amines, applying a flow reactor.[317] Therefore, copper was loaded on different supports, applying a simple impregnation procedure followed by calcination in the air at 300 °C. Al_2O_3 was found to be superior support compared to SiO_2, giving higher conversions of nitroarenes and very high selectivities, with respect to anilines. The coupling of nitroarenes with aldehydes was also found to be efficient giving secondary amines with yields up to 97%.

In the same year, Hosono and co-workers reported a copper-based intermetallic electride for the hydrogenation of both nitroarenes to anilines, and ketones and aldehydes to alcohols.[318] The material with the formula $LaCu_{0.67}Si_{1.33}$ was prepared by arc-melting lanthanum, copper and silicon ingots under argon. The obtained material selectively hydrogenated nitroarenes with TOFs up to 5084 h^{-1}. The transfer of electrons from La to Cu increases the electron density of the latter, and therefore the energy barrier for H_2 dissociation decreases, as was determined by mechanistic investigations. In the hydrogenation of nitrobenzene, a kinetic isotope effect with $r_H/r_D = 3.8$ was determined, which implied that the H-H cleavage was rate-determining. A broad scope of substrates was successfully investigated including nitroarenes bearing olefins, nitriles, ketones, amides and esters that were retained by the system at 30-50 bar H_2 and 120 °C. The selective hydrogenation of nitro groups next to carbonyl groups was explained with a more stable adsorption of the substrate *via* two oxygen atoms of the nitro, compared to just one oxygen atom of the carbonyl group. In methanol, however, a variety of ketones and aldehydes were hydrogenated to the corresponding alcohol. The catalyst was successfully recycled several times.

6.2. Transfer hydrogenations

6.2.1. Reductions with $NaBH_4$

Most of copper-based heterogeneous systems for nitro reductions published since 2000 make use of $NaBH_4$ as reductant. T. Pal and co-workers investigated the activity of copper, silver and gold NPs for this kind of reaction.[319] NPs were obtained either prior to hydrogenation by treating metal salts with $NaBH_4$, or *in situ* by adding an aqueous solution of metal salt to a solution of substrate and $NaBH_4$. Time-dependent conversions were detected by UV/Vis spectroscopy. It was found that NPs of all three coinage metals were active in the nitro reduction with the order Au > Ag > Cu.

In 2012, H. K. Kadam and S. G. Tilve used $CuBr_2$ as pre-catalyst, which was *in situ* reduced to copper NPs.[320] Typically, substrate and copper or iron salts were mixed in ethanol, and $NaBH_4$ was added in portions. In a first screening, iron showed only small conversion of nitrobenzene, however, copper was more active. $CuBr_2$ showed full conversion and high yield of aniline at room temperature after 5 h. It was successfully applied for a variety of substrates, showing a good functional group tolerance, including halides. However, nitriles and olefins were also hydrogenated to the corresponding amine and alkane, respectively. The catalytic loading of this system was quite high with 10 mol% of $CuBr_2$, at the presence of up to 5 equivalents of $NaBH_4$ at room temperature.

Two years later, another *in situ* approach was reported by P. Bharali and co-workers.[321] Here, the pre-catalyst was prepared following a hydrothermal approach by heating urea and $CuCl_2·2H_2O$ at 120 °C for 6 h inside a stainless-steel autoclave. Finally, the catalyst was recovered by filtration. Its catalytic activity was investigated by addition to an aqueous mixture of 4-NP and $NaBH_4$, which resulted in the formation of Cu NPs. Dependent from the added amount of pre-catalyst, the reduction of 4-NP was completed within 45 to >100 min.

J. Santhanalakshmi and L. Parimala studied the effect of stabilizers in the Cu NPs catalyzed reduction of nitroarenes in 2012.[322] The NPs were produced by reducing copper(II) chloride with hydrazine hydrate in the presence of the stabilizer, which were PEG, CMC, and PVP, respectively. From the reported results it can be stated that the PVP capped NPs have the lowest activity, while PEG and CMC capped ones show a similar one.

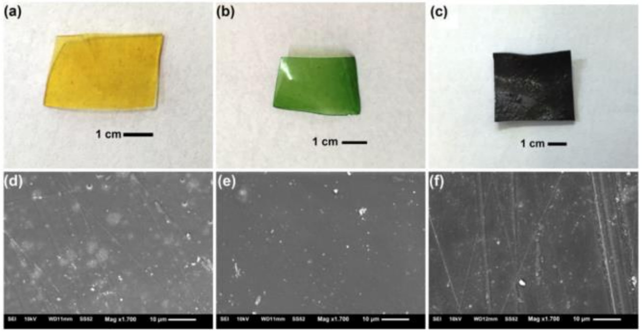
R. Srivastava and M. Tumma investigated the catalytic activity of transition metal NPs supported on mesoporous polyaniline for the reduction of nitroarenes.[323] A variety of materials with different metal loadings was synthesized by adding a metal salt (M = Mn, Fe, Co, Ni, and Cu) to an aqueous solution of polyaniline, followed by the addition of $NaBH_4$, in order to form NPs. The authors stated that the Cu catalyst with initial 10% metal loading was the most active one, giving full conversion of 4-nitroaniline to the amine within 45 min in a 1:1 mixture of water and ethanol. A small scope of substrates was shown to be successfully converted to the corresponding amine.

L. G. Qiu and co-workers have reported a MIL-101 (Cr) MOF-based copper catalyst for the nitroreduction in 2013.[324] The composite was synthesized by microwave-assisted hydrazine reduction of MIL-101 (Cr) loaded with copper nitrate. Here, three substrates were investigated, which were hydrogenated to the corresponding amine with high yields and selectivities.

One year later, C. Tamuly and co-workers prepared a CuO-catalyst, by making use of biomass.[325] The peel of the wild-type banana plant *Musa balbisiana* was burned and an aqueous suspension of it was filtered. To the filtrate, copper sulphate was added and the dry precipitate was heated at 300 °C for 2 h. SEM images revealed a flowerlike architecture of the material. It showed to be catalytically active in the reduction of nitroarenes in the presence of 5 equivalents $NaBH_4$ in water at 30 °C. In the first run, a yield of 96% of 4-AP was obtained in water, in the fifth run 91%. Five more substrates were investigated, with fluorine-, chlorine-, bromine-, and ether-functionalities, giving yields of 74% to 88%.

Another biomass-derived catalyst for nitroreduction was reported by A. R. Fajardo and co-workers in 2017.[326] They produced Cu NPs supported on chitosan-based films by blending a solution of chitosan in acetic acid and an aqueous solution of polyvinyl alcohol (chitosan/polyvinyl alcohol mass ratio of 1:2). Afterwards, a glutaraldehyde solution was added dropwise and after transferring the solution into petri dishes the volatiles were evaporated (Figure 47). Finally, the films were immersed in a $CuCl_2 \cdot 2H_2O$ solution, and by the addition of $NaBH_4$, the Cu^{2+} ions were reduced forming Cu NPs. The latter material was able to catalyze the hydrogenation of nitrobenzene to aniline in the presence of $NaBH_4$ showing high mechanical stability and chemical resistance. The activity was more or less constant during six runs.

Figure 47 Photographs and corresponding SEM images of chitosan/polyvinylalcohol-films (a, d,), loaded with Cu^{2+} (b, e) and with reduced Cu(0) (c, f), as reported by A. R. Fajardo and co-workers. (Reproduced with permission from Ref. 326. Copyright 2017, Elsevier)



A. Veerappan and co-workers reported the synthesis of Cu NPs with pectin as a capping agent.[327] $CuCl_2$ was added to an aqueous solution of pectin, followed by concentrated ammonia solution, in order to get basic conditions. Finally, the addition of hydrazine hydrated in the air led to the formation of Cu NPs within 3 hours. The as synthesized material was tested in the hydrogenation of 4-NP to 4-AP in the presence of

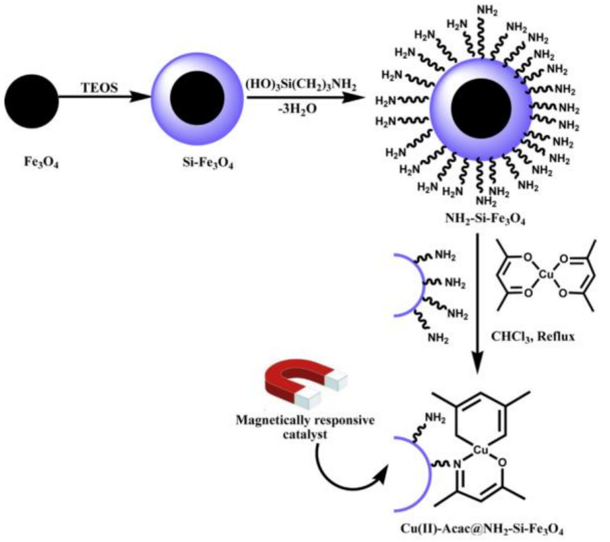
$NaBH_4$. An induction period of about 120 s was observed, and the reaction was complete after 250 s, with a *pseudo* first-order kinetic, due to a large excess of $NaBH_4$, and a rate constant $k = 1.08 \cdot 10^{-2}\ s^{-1}$. Four further substrates were investigated, with induction periods of about 80 to 170 s. It was observed that nitro groups in *para* position are hydrogenated more rapid than *ortho* or *meta*, along with a shortened induction period. Interestingly, besides of nitro reductions also C-N couplings of amines with bromobenzene were successfully catalyzed by the NPs. Two years later, the same group used the same synthetic approach, replacing pectin with guar gum as capping agent, in order to get a material, which was catalytically active in nitroreduction although with a slightly lower activity.[328]

In the same year, V. Singh and co-workers investigated gum acacia-silica hybrid anchored Cu NPs for the reduction of 4-NP in the presence of $NaBH_4$.[329] To an aqueous solution of acacia gum and $CuSO_4$, hydrazine was added as reducing agent. A solution of the formed NPs was mixed with TMOS and methanol, and after polymerisation and drying, the final material was obtained. The average size of the NPs was about 18 nm. The material was active in the hydrogenation of aromatic nitro compounds. It was recycled six times, revealing a reaction time of 2.5 min in the first run and 28.3 min in the seventh run, in order to obtain complete conversion of 4-NP.

In 2014, N. Sahiner and co-workers investigated metal loaded poly(methacrylic acid) microgels for degradation of organic dyes and reduction of nitroarenes.[330] Copper, cobalt and nickel were investigated, among which copper showed superior catalytic activities in both kinds of reactions. The microgels were prepared by inverse suspension polymerisation, and subsequently loaded with metal chlorides in aqueous medium. After their isolation by centrifugation, they were washed and treated with $NaBH_4$. Finally, they were washed again and used in catalytic tests. Therefore, 2-NP, 4-NP and 4-nitroaniline were hydrogenated by the metal loaded microgels in the presence of $NaBH_4$. Furthermore, the degradation of the organic dyes Eosin Y and methyl orange was successfully catalyzed. Additionally, copper loaded microgel was able to hydrogenate 4-NP and Eosin Y. Eventually, recycling was studied revealing an almost constant activity of the loaded copper; however, a greatly decreased one for the cobalt loaded microgel during four runs.

A number of composites were reported, in which iron was used as magnetic core, in order to obtain an easily separable material. R. K. Sharma and co-workers demonstrated Cu(II) on silica-coated Fe_3O_4 as magnetically separable core-shell composite for the reduction of nitroarenes in water.[331] Freshly prepared iron NPs were activated with 0.1 M HCl in ethanol and water, followed by the addition of 25% NH_4OH and TEOS (Figure 48).

Figure 48 Synthesis of a magnetically separable copper-based catalyst for nitroreduction, as reported by R. K. Sharma and co-workers. (Reproduced with permission from Ref. 331. Copyright 2014, Elsevier)



After heating for 6 h at 60 °C, the material was magnetically separated, washed and dried. Then, an ethanolic mixture of it was treated with 3-aminopropyltriethoxysilane, to functionalize it with amino groups. Once the material was isolated, it was grafted covalently with $Cu(acac)_2$ in chloroform. In the presence of $NaBH_4$, the material was catalytically active for the reduction of nitroarenes within up to one hour. Several substrates were tested, giving high conversions and selectivities. Recyclability was shown during nine consecutive runs, maintaining the conversion constant. In addition, test reactions of solely Fe_3O_4 or $Cu(acac)_2$, respectively, showed a reduced conversion, indicating the importance of the combination of all components for the catalytic activity. Despite the authors did not mention the possible formation of Cu NPs on Fe_3O_4 during the reaction, this usually happens for this kind of systems.

H. Eshghi and co-workers modified the silica shell around Fe_3O_4 differently.[332] The free OH-groups of silica were functionalized with epibromohydrin (3-bromopropylene oxide), which itself was further reacted with ethylenediamine. An additional equivalent of the epoxide was added to the free NH_2-moiety, and then converted to the diol, *via* reaction with NaOH. Finally, $Cu(OAc)_2$ was added and the copper cation could be complexated by the lone pairs of the NH- and OH-groups. The treatment with $NaBH_4$ yielded in the formation of NPs of about 20 nm. Several substrates were rapidly hydrogenated to the corresponding anilines.

Another approach for a magnetically separable Cu-catalyst was shown by U. Kurtan and co-workers one year later.[333] Instead of silica, they used isonipecotic acid (4-piperidinecarboxylic acid) for coating of freshly prepared Fe_3O_4. The surface amine-groups were then loaded with $CuSO_4$ and subsequently reduced with $NaBH_4$, giving NPs of 21 nm size. The material was catalytically active for the reduction of 4-nitroaniline and 4-NP, as well as for the degradation of the dyes methylene blue and methyl orange. It was recycled three times, yielding in slightly decreased conversion during the cycles.

In addition, E. Ghonchepour and co-workers treated Fe_3O_4 NPs with citric acid in basic medium, and loaded that material with $CuCl_2$ in the presence of Na_2CO_3.[334] The copper NPs had a mean diameter of 25-35 nm. By using $NaBH_4$ as hydrogen source, several nitro compounds were reduced to the corresponding anilines within 5 to 120 min. The material was recycled seven times, revealing a small drop in activity.

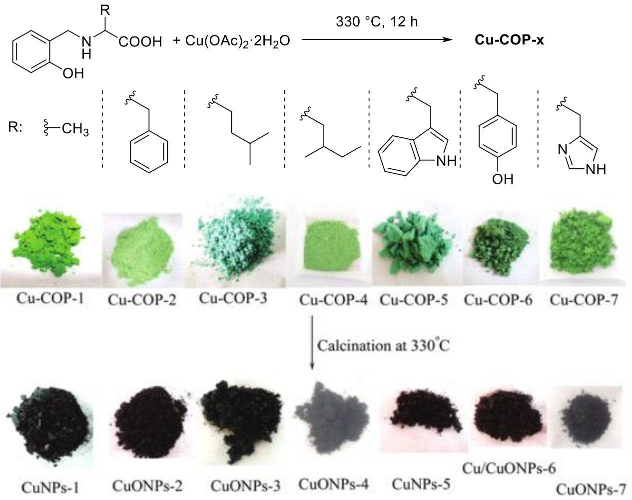
In 2017, the use of an Fe_3O_4 supported Cu-MOF was demonstrated by Z. H. Zhang, L. Wang and co-workers.[335] Here, 1,3,5-benzenetricarboxylate was used as linker for the preparation of the MOF. The material was active for the reduction of different aromatic and aliphatic nitro compounds within 2-3 h in an ethanol/water (1:3) mixture. The heterogeneity of the catalyst was demonstrated by a hot-filtration test: after 15 min of reaction, the catalyst was removed and the filtrate was kept stirring. This resulted in termination of the reaction and no further product was formed. Additionally, six consecutive runs were conducted for the reduction of nitrobenzene giving 99% of aniline in the first and 92% in the last run.

A. Goyal and S. Singhal coated magnetic $CoFe_2O_4$ with Ag and Cu nanoparticles in 2016.[336] The core was treated with dopamine hydrochloride and eventually loaded with the metal, which were reduced to NPs with hydrazine hydrate. Silver and copper in different loadings were investigated, revealing that the copper-based materials were in general more efficient. For the substrate scope, the catalyst with 10% Cu was used, in the presence of 50 equivalents of $NaBH_4$ in methanol. 15 Substrates were successfully hydrogenated within few minutes. Also for this system a hot filtration test and recycling were conducted, indicating its heterogeneity.

M. V. Parmekar and A. V. Salker treated a $NiFe_2O_4$ core with silica *via* the so-called Stöber method. Then, $Cu(NO_3)_2$ was deposited on it, which produced NPs by treatment with $NaBH_4$.[337] Average particle sizes of 25-28 nm were detected by TEM. As a model substrate for reduction 4-NP was chosen. Recycling studies indicated a decrease of activity during five runs. Additionally, ICP-AES analysis revealed a loss of copper of 0.03% after the first, and 0.5% after the fifth run. Ten substrates were investigated using this catalyst system demonstrating a reasonable substrate scope. Notably, for 4-iodonitrobenzene, a conversion of 60% and a yield of 59% were observed, indicating that hydrodehalogenation processes can be neglected.

S. P. Anthony and co-workers recently demonstrated copper on coordination polymers (COPs) as reusable catalysts for the reduction of nitroarenes.[338] Seven different materials were synthesized by complexation of Cu^{2+} with an amino acid-based reduced Schiff base ligand, followed by calcination at 330 °C for 12 h. The structure of the ligands only differed in one moiety from each other (Figure 49).

Figure 49 Synthesis of Cu NPs and CuO NPs from Cu-COPs, as was demonstrated by Anthony and co-workers. (Reproduced with permission from Ref. 338. Copyright 2017, The Royal Society of Chemistry)



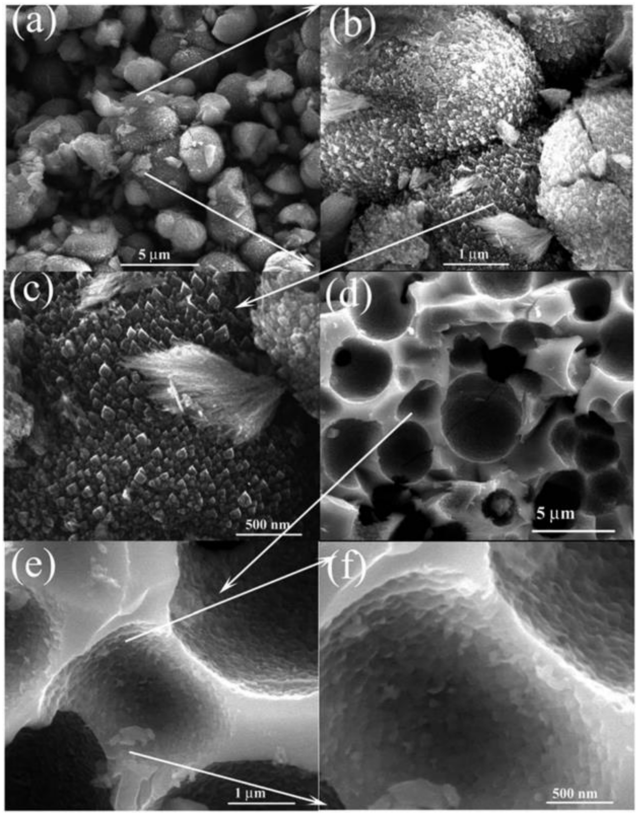
Depending from the used ligand, either pure Cu NPs (Cu-COP-1 and Cu-COP-5), or CuO NPs (Cu-COP-2, Cu-COP-3, Cu-COP-4 and Cu-COP-7) encapsulated by carbon matrix were formed. In one example, a mixture of both was obtained (Cu-COP-6). CuNPs-1 was tested in the solvent-free A^3-coupling of a terminal alkyne with an amine and an aldehyde in order to obtain propargylamines, whereas CuONPs-4 was tested in nitroreductions in the presence of $NaBH_4$. A scope of 15 substrates was investigated, with yields between

66% and 96%. Recyclability of CuONPs-4 was demonstrated within five runs, revealing a yield from 88% to 84%.

T. Pal and co-workers demonstrated Cu_2O and Cu(0) NPs without any support or surfactant to be active in nitro reductions.[339] $Cu(OAc)_2\cdot H_2O$ was reduced with altering amounts of hydrazine hydrate, yielding either Cu_2O or Cu(0). In the presence of $NaBH_4$, both catalysts hydrogenated 4-NP to 4-AP at room temperature in water. The Cu_2O as pre-catalyst was found to be much more active in this reaction than Cu(0). Its rate constant was even higher than for some noble metal catalysts. According to the authors, this high activity is owed to *in situ* formation of a ternary Cu_2O-Cu-CuO nanocomposite, which can transfer electrons fast and acts as a better catalyst. The Cu(0) phase in this composite is responsible for the transfer of hydrides. For comparison, the authors produced a Cu_2O-Cu-CuO composite by the reduction of Cu_2O with $NaBH_4$, however, the rate constant was lower. For the most active system, a small scope of substrates was investigated, revealing fast (3-5 min) and complete conversions.

In the same year, also S. P. Anthony and co-workers investigated Cu_2O and CuO for the reduction of nitroarenes.[340] By hydrothermal heating of $Cu(OAc)_2$, CuO was produced at 125 °C, Cu_2O at 175 °C, and a mixture of both at 150 °C. Contrary, $Cu(acac)_2$ only gave Cu_2O at all three temperatures. The decomposition of acetate and acetylacetonate played a key role in the formation of the nano- and micro-sized oxide particles, as indicated by mechanistic investigations. The shape of the obtained materials was affected by the temperature: CuO with microsphere morphology was formed at 125 °C, whereas heating to 175 °C led to micro-cups of Cu_2O (see Figure 50) demonstrated by field emission scanning electron microscopy (FE-SEM).

Figure 50 FE-SEM images of CuO (a-c) and Cu_2O (d-f), produced by hydrothermal heating of $Cu(OAc)_2$ at 125 °C and 175 °C, respectively. (Reproduced with permission from Ref. 340. Copyright 2016, The Royal Society of Chemistry)

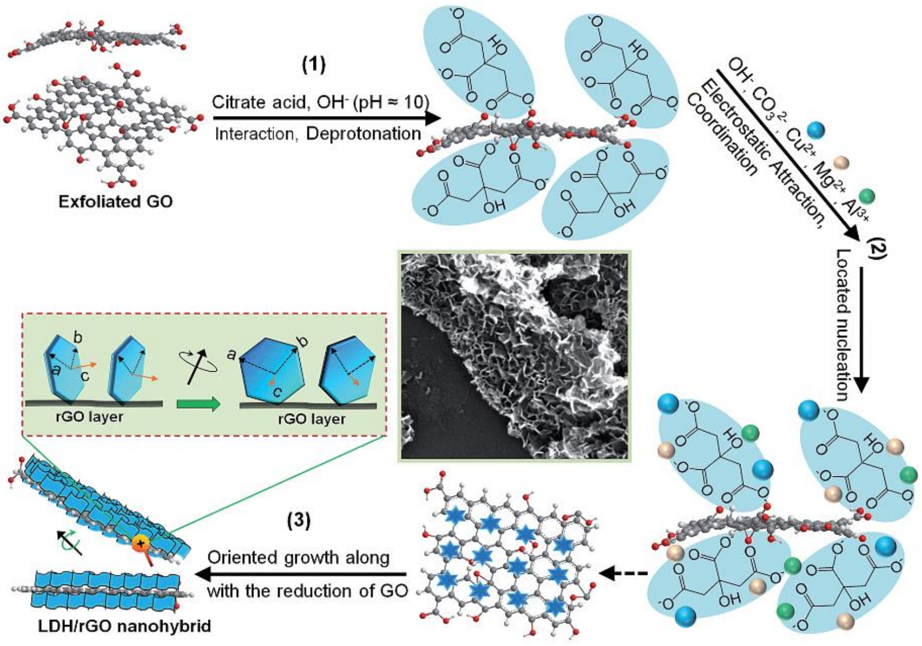


When Cu_2O was synthesized from $Cu(acac)_2$, nanowires and elliptical cylinders were observed. Calcination at 500 °C yielded in crystalline CuO nano/microparticles, independently of the precursor. The latter were investigated for the reduction of nitro compounds, revealing that those obtained from $Cu(acac)_2$ exhibited the highest activity.

Bhattacharjee and Ahmaruzzaman reported two dimensional CuO nanoleafs as catalyst for the reduction of 4-NP, 4-nitroaniline, and 2,4,6-trinitrophenol, most recently.[341] After preparing an aqueous solution of L-glutamic acid as capping agent and $CuSO_4 \cdot 5H_2O$ as metal precursor, and basifying it with a NaOH solution, the mixture was placed in a microwave oven. Irradiation resulted in the formation of a black precipitate, which was characterized as 2D CuO nanoleafs with a length of 720-800 nm and a width of 136-160 nm. Besides of the photocatalytic degradation of dyes, the reduction of the above mentioned nitroaromatic compounds was investigated. All three substrates were reduced to the corresponding amine within few minutes in the presence of $NaBH_4$.

Finally, L. Dou and H. Zhang prepared hierarchical nano-hybride materials $Cu_xMg_{3-x}Al$ (x = 0.5, 1.0, 1.5) layered double hydroxide (LDH)/reduced graphene oxide (rGO) with sheets-like structure, that efficiently catalyzed nitro reductions.[342] After graphite oxide (GO) was exfoliated in water by sonication, a negatively charged surface (-21.7 to -48.2 mV) formed as suggested by zeta potential analysis. This was due to ionisation of phenolic hydroxyl and carboxylic acid groups. Then, citric acid was added, followed by a solution of NaOH and Na_2CO_3 to adjust a pH of about 10 (Figure 51).

Figure 51 Synthesis of nanoarray-like nanohybrids as reported by Dou and Zhang. (Reproduced with permission from Ref. 342. Copyright 2016, The Royal Society of Chemistry)



This lead to deprotonation of citric acid, and to a lowering of the negative potential of GO to about -65 mV, indicating a higher charge density on its surface. Citric acid ions might be attached onto the nanosheets *via* hydrogen bonding. In the next step, a solution containing $Cu(NO_3)_2{\cdot}3H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, and $Al(NO_3)_3{\cdot}9H_2O$ in a 1:2:1 ratio was added simultaneously with an alkaline solution. This resulted in coordination of the metal ions to citric acid anions adsorbed on the surface of GO. Finally, the precipitate was allowed to age for 4 h at 65 °C. The LDH nanoplates had dimensions of about 70 nm x 4.5 nm. The catalytic activity was investigated for the reduction of the model substrate 4-NP, using $NaBH_4$ as reductant and water as solvent. It was found that all tested hybrids obtained a higher activity than pure Cu/LDH, commercial Pt/C, and other reported Cu catalysts. An explanation was the *in situ* reduction of Cu^{2+} to ultrafine, well-dispersed Cu_2O with about 7 nm sizes. This leads to a strong interaction between LDH on rGO and Cu_2O, which enhances the activity for the reduction. A possible synergistic effect between Cu_2O NPs, *x*Cu-LDH nanoplates and reduced graphite oxide layers was hypothesized to play a crucial role, along with enhanced adsorption capacity *via* π-π-interaction and the ultrathin nanosheet array-like morphology. Finally, recyclability of the catalyst was demonstrated. Even after 20 cycles, the catalytic activity persisted high. Additionally, TEM of the recycled catalyst still showed the nanoarray-like morphology, however, with partially damaged LDH plates.

6.2.2.Reductions with alcohols/bases, N_2H_4, HCOOH and other reductants

In 2008, A. Saha and B. Ranu reported a highly chemoselective heterogeneous system for the reduction of nitroarenes, using a hydrogen transfer methodology.[343] More specifically, Cu NPs of 4-6 nm size were reacted with 15 different nitro compounds and ammonium formate as hydrogen donor (ethylene glycol, 120 °C, 8-12 h). Regarding functional group tolerance, it is interesting to note that even 4-iodonitrobenzene was hydrogenated selectively to 4-iodoaniline (85% yield). However, olefinic moieties were partially hydrogenated under these conditions. Mechanistic investigations were carried out by reducing nitrosobenzene (77% converted to aniline) and hydroxylamine (74% converted to aniline) in separate experiments. These findings suggested that in the reduction of nitrobenzene first nitrosobenzene is formed, which is then further reduced to hydroxylamine and finally to aniline (Scheme 3). A pathway *via* azobenzene and hydrazobenzene is unlikely, as both compounds were only poorly hydrogenated to aniline (13% and 15%, respectively).

In 2012, T. Subramanian and K. Pitchumani demonstrated Cu NPs supported on zeolite for the transfer hydrogenation of nitroarenes with isopropanol as hydrogen donor.[344] The catalyst was prepared from copper exchanged Y-zeolite. At 80 °C inside an autoclave, it was able to reduce a variety of nitroarenes to the corresponding amines within 1-3 h. In addition, this system showed a remarkable functional group tolerance, including 4-iodonitrobenzene (yield for 4-iodoaniline: 96%). In analogy to the report of A. Saha and B. Ranu (*vide supra*), possible intermediates were tested for the hydrogenation, in order to get a mechanistic insight (Scheme 3). Again, a pathway *via* hydroxylamine was determined as likely, as it was reduced in high yields to aniline (85%), whereas the other investigated intermediates were hardly converted at much longer reaction times. Eventually, the system was recycled six times, revealing a drop of product yield from 98% to 79%.

Two years later, G. Song and co-workers combined microwave and ultrasound irradiation for the reduction of nitroarenes with copper NPs and hydrazine hydrate as hydrogen donor.[345] Copper acetate was *in situ* reduced to NPs by 2 equivalents of hydrazine hydrate in ethylene glycol under microwave irradiation. Afterwards, the NPs were used for the reduction of nitrobenzene with the same agent under combined microwave and ultrasound irradiation. Aniline was obtained from nitrobenzene within 3.5 min in 89% yield. In addition, $Cu(OAc)_2$ was used directly, and NPs were formed *in situ*, giving a yield of aniline of 97%. However, when the separated NPs were reused in a second run, the yield dropped significantly to 72%, due to agglomeration of the NPs. As was reported before by A. Saha and B. Ranu (*vide supra*), only the solvent ethylene glycol gave satisfying yields. In the investigated substrate scope, high yields were obtained in short time (maximum 6.5 min) for all eleven substrates.

Also in 2014, van der Waals and co-workers coupled the dehydrogenation of amino boranes with the transfer hydrogenation of nitro groups in aqueous medium.[346] First, the authors intended the ruthenium catalyzed coupling of nitroarenes with a nitrile to the secondary amine, in the presence of a co-catalyst for an increased electrophilicity of the nitrile group. However, instead of the secondary amine, the addition of $Cu(OAc)_2$ afforded full conversion of the nitro group, with the primary amine as major product. In following control experiments without ruthenium, almost all investigated copper salts converted the nitroarene to the primary amine in the presence of 3.3 equivalents of $Me_2NH \cdot BH_3$ in moderate to good yields. Further optimisation showed that 5 mol% $Cu(OTf)_2$ and 3 equivalents $Me_2NH \cdot BH_3$ in water at 30 °C gave the best results. A small scope of nitro compounds was investigated, along with ketone-reduction to alcohols, hydrogenation of internal alkynes and terminal alkenes to internal alkenes and alkanes, respectively, as well as the reduction of imines to amines at somewhat harsher conditions. During the reactions, a black precipitate was formed, which is an indication for a heterogeneous character of this system. In order to proof this hypothesis, a mercury test for the imine hydrogenation was conducted first, showing a decrease of yield from 88% with just $Cu(OAc)_2$ and 22% with added Hg. When neither catalyst nor Hg was used, the yield was also 22%. Kinetic investigations also revealed an induction period of the reaction, which is in agreement with the formation of metal particles.

Finally, N. Singh and co-workers reported stabilised Cu NPs to be active reduction catalysts in aqueous medium.[347] The reaction of copper perchlorate and 1-methyl-3-ethanoicacid-3-imidazolium bromide, followed by the addition of hydrazine hydrate and subsequent sonication resulted in the catalytically active material. Ten different nitro compounds gave the corresponding amines using five equivalents of ammonium formate as hydrogen donor in water under reflux. Notably, olefins and alkynes were tolerated by the system. The catalyst was recycled four times.

7. Multimetallic heterogeneous catalysts

Several of the heterogeneous systems discussed above contain more than one metal. In some cases the metals are alloyed in the catalyst and in some others one metal is present as doping (or poisoning) agent or simply acts as the support. In this section, we will solely deal with systems containing at least two *3d* metals, of which both might have an activity, independent from the other (i.e.: Mn, Fe, Co, Ni, Cu, Zn). On the contrary, systems in which one of the two metals is not involved in the catalytic reaction (e.g. core-shell or protected ferrite nanoparticles in which the iron oxide is used for magnetic recovery of the catalyst) have not been included, but discussed in the previous chapters. Multimetallic systems containing both noble metals and *3d* metals are excluded.

In general, non-noble metals have a lower catalytic activity compared to noble ones; however, the combination of two or more of them in an alloy can give rise to a synergistic effect that increases the performance of the resulting catalyst. The addition of a second metal obviously has an effect on the morphology of the material, on its stability and on its electronic properties. In the following part, the structural and electronic effects as well as the influence on the catalytic performance derived from the combination of two 3*d* metals will be discussed.

7.1. Reduction with molecular H_2

7.1.1. Nickel and cobalt based catalysts

As described (see chapter 5), amorphous Ni alloys, Ni-B and Ni-P, exhibited higher activities than Raney®-nickel in selected hydrogenation reactions.[348] Generally, bimetallic amorphous Ni alloy particles were synthesized by the reduction of an aqueous solution of nickel and another metal salt with borohydride or hypophosphite as reductant. The structure and the catalytic activity of the resulting materials are strongly dependent on the preparation and the parameters of the reduction reaction such as pH, temperature, metal precursors ratio and metal precursor/reductant ratio. This kind of materials has been in particular studied for the reduction of chloronitrobenzenes for which Raney®-Ni is known to give dehalogenation as a side reaction and accumulation of hydroxylamine intermediates.[220]

Yan and co-workers studied the effect of the addition of iron to Ni-P alloys.[349] More specifically, the reduction of $NiCl_2$ and $FeCl_3$ in different ratios with NaH_2PO_2 at 70 °C in aqueous solution at pH = 11 afforded amorphous Ni-Fe-P alloys. XPS analysis of a sample prepared with a molar ratio Fe/(Fe+Ni) of 0.25 showed that Ni was present only in the metallic state, while iron was present both as metallic and as oxide (Fe_2O_3). XPS studies suggested an electron donation from metallic Fe to Ni, thus affording electron-enriched nickel and electron-deficient iron species. From a physical point of view, Fe_2O_3 has a dispersing effect, stabilizing the particles against crystallization and aggregation at high temperatures. Catalytic hydrogenation tests of 4- and 3-chloronitrobenzene, showed that increasing amount of Fe in the Ni-P alloy increased the activity of the catalyst until an optimum molar ratio of 0.25, after which the active Ni sites were covered by less active/inactive iron. A comparison between this catalyst and Raney®-Ni showed a similar activity but a higher selectivity of the Fe-Ni-P alloy. The effect of additional Fe species was also studied in Ni-B alloys;[350] however, the results are not directly comparable due to a different preparation method. Reduction of Ni and Fe salts by $NaBH_4$ in 50 vol% methanol/water solution at 25 °C in the absence of base, afforded a series of alloys in which Ni was present both as Ni(0) and Ni(II). In contrast to the Ni-Fe-P alloy, the metalloid in the elemental state donates partial electron density to Ni(0), while iron has a negligible electronic effect. The addition of iron had an effect on the boron content affecting both the total amount and the ratio between oxidized and elemental B. The authors demonstrated that addition of a small amount of iron to the Ni-B alloy led to an increased catalytic activity in the hydrogenation of 4-chloronitrobenzene.

When the alloy was prepared using Co instead of Fe, the resulting Ni-Co-B alloy showed similar catalytic behavior to that of Ni-Fe-B.[351] The authors reported that Co-B in the absence of nickel did not catalyze the hydrogenation of 4-chloronitrobenzene, thus concluding that in the Ni-Co-B alloy, cobalt mainly effects the morphology and composition. Different modifiers were employed to tune the activity of Ni-Co-B alloys prepared in methanol solution. Similar to Co, the addition of Mo up to a Mo/Ni ratio of 0.6 had a beneficial effect both on the selectivity and on the activity of the resulting alloys.[352] The main effect of the molybdenum is an increase of the electron density on nickel by partial electron donation. Moreover, a positive effect on the catalysis was noticed when W was used as dopant.[226] In this case, the activity increased with W/Ni fraction up to a 1:1 ratio, however also a larger extent of C-Cl hydrogenolysis occurred. The authors attributed this behavior to the lower content of B^{3+} in the doped catalyst.

Besides the electronic effect, the main role of the second metal in such amorphous alloys is the stabilization of the Ni NPs against aggregation. This is also true for multi-metallic systems. Indeed, for a series of M-Ni-Co-B catalysts with a metal ratio 0.1 : 1 : 0.1 a decreasing activity for the hydrogenation of 4-chloronitrobenzene was observed in the following order: Mo-Ni-Co-B > W-Ni-Co-B > Ni-Co-B ~ La-Ni-Co-B > Fe-Ni-Co-B.[353] However, it should be mentioned that the optimal ratio between the three metals strongly varied with the nature of the dopant. Thus, a direct comparison is difficult.

As mentioned above, the preparation of the alloy has also a significant effect on the catalytic performance of the material. For example, a different catalytic behavior was reported for catalysts obtained from the reduction of nickel and cobalt nitrates with KBH_4 in aqueous basic solution at 0 °C.[354] Here, a comparable catalytic activity of monometallic Co-B,Ni-B and Ni-Co-B (Co:Ni = 1:1) was observed, while materials obtained with different Co:Ni ratios were less effective. The Ni-Co-B (1:1) bimetallic alloy was successfully employed in the hydrogenation of 2-chlorobenzene and 3,4-dichloronitrobenzene showing a lower amount of dehalogenated side-products compared to the two monometallic alloys.

In addition to bulk alloys, Ni-B[232] and Co-B[355] alloys deposited on CNTs have been prepared by Li and co-workers for the hydrogenation of nitrochlorobenzenes as described before. The same group studied the effect of metallic modifiers in Co-B/CNTs catalysts. The materials were prepared by impregnation of CNTs with an ethanolic solution of $CoCl_2$ and a second metal (Fe, Sn, Cr, Cu or Zn) followed by reduction with KBH_4. Morphological studies were done only for the Fe modified catalyst that, similar to the unsupported alloys, showed improved thermal stability. The binding energies of the components indicated an electron donation from Fe atoms to Co. The Fe dopant had also a secondary effect on the composition, increasing the amount of elemental Co and B in the material. Thus, the authors concluded that the addition of Fe increased the number of active sites and weakened the hydrogen absorption at the surface, allowing for an easier surface-flow of the H-species. As a result, Fe–Co–B/CNTs had a higher catalytic activity and selectivity for the hydrogenation of 3-chloronitrobenzene. The order of activity of the modified Co-B catalysts was Fe-Co-B/CNTs > Sn-Co-B/CNTs > Co-B/CNTs > Cr-Co-B/CNTs > Zn-Co-B/CNTs > Cu-Co-B/CNTs.

Besides the amorphous metal-metalloid alloys, other more structured catalysts have been reported. Recently, Corma and co-workers studied the catalytic properties of mono- and bimetallic nanoparticles coated by thin carbon layers.[180] Metal oxide NPs were treated with glucose under hydrothermal conditions and the obtained metal hydroxide/carbon composites were thermally annealed affording the M@C catalysts. The role of the carbon coating is to protect catalytically active metal species. Anyway, in Co@C catalyst, CoO_x was present on the particles due to re-oxidation after exposure to air. In comparison with the fully alloyed structure of a Co-Ni@C catalyst (Co/Ni = 77/23), the amount of metal oxides patches was lower due to a stabilization of metallic cobalt by nickel. The latter was found to promote the reducibility of CoO_x by dihydrogen. The activity of mono- and bimetallic Co and Ni catalysts was studied in the H_2-D_2 exchange reaction and in the hydrogenation of 3-nitrostyrene. Here, an activity order of Co@C < Co-Ni@C < Ni@C was found. However, the higher activity of Ni@C catalyst was accompanied by a lower selectivity (~80%) to 3-aminostyrene at high 3-nitrostyrene conversions, while Co-Ni@C retained the high selectivity exhibited by the Co@C catalyst (>97%). The results clearly indicate a synergistic effect between Ni and Co that was maintained even after several recyclings of the catalyst. The Co-Ni@C system had a broad scope at mild conditions (7-10 bar H_2 at 120 °C), tolerating keto, ester and amido groups, as well as 4-chloro-, 4-bromo-, and 3-iodonitrobenzenes. Notably, triple bonds in the respective substrates were also not reduced. Interestingly, the Co-Ni@C catalyst outperformed the noble metal catalyst Au/TiO_2 developed by the same authors,[356] thus showing that non-noble bimetallic nanoparticles have a potential to replace precious metal catalysts.

In contrast to previous reports, Corma and co-workers argued that the presence of nitrogen as dopant in the carbon coating for Co and Co-Ni NPs is not necessarily beneficial to the activity of the system. This study highlights the question of the actual role of nitrogen in metal-based N-doped carbonaceous catalytic materials. Since the effect of nitrogen on the activity of a catalyst was demonstrated to be also dependent on the used precursors and the synthetic procedures, general conclusions on this aspect cannot be drawn at the moment and more comparative studies are needed. In the same year, a study on the use of Ni_xCo_{1-x} alloys encapsulated in nitrogen doped carbon in different hydrogenation reactions was published by Zhang, Ma and co-workers.[357] The catalysts were prepared by thermal decomposition of Ni_xCo_{1-x}-EDTA complexes and the authors noticed a synergistic effect between Co and Ni analogous to that reported by Corma. Ni@NC showed lower catalytic activity in the hydrogenation of 4-chlorostyrene than Co@NC, while all the Ni_xCo_{1-x}@NC were more active. $Ni_{0.5}Co_{0.5}$@NC was employed for the reduction of substituted nitroarenes exhibiting an activity comparable to the catalyst reported by Corma and co-workers under similar conditions (20 bar H_2 at 80 °C). Although the hydrogenation of nitroarenes containing double and triple bonds were not reported it can be argued that this catalyst may not be selective towards NO_2 reduction in this case since it was initially developed for olefin hydrogenation. Interestingly, selectivities around 90% were reported for the challenging substrates 4-iodonitrobenzene and 4-nitrobenzaldehyde.

In addition to the more disordered heterobimetallic systems described above, Co-Ni nanocrystals with a defined topology were used as catalysts for the hydrogenation of nitrobenzene, too.[358] Zhu and co-workers synthesized different nanostructures by solvothermal growth with stearic acid as capping agent and ethylene glycol as reductant. The shape of the crystals was strongly dependent from the reaction conditions and for Ni loading <10% singular needle-like nanostructures with a hexagonal cap were obtained. The catalytic activity of the nanocrystals was higher compared to unprotected Co-Ni NPs, presumably due to both a stronger influence of Ni on the electronic properties in the Co-Ni nanowire, as suggested by Co and Ni binding energies, and a lower tendency to aggregation.

7.1.2.Copper-nickel based catalysts

Few copper-based catalysts have been developed for the reduction of nitroarenes with molecular hydrogen. In general, the activity is lower compared to Co- or Ni-based catalysts. However, some interesting chemoselectivities have been observed in hydrogenation reactions. As an example, in 2009 Reddy and co-workers reported a study on the use of bimetallic nanocomposite oxides deposited on CeO_2–SiO_2 in the gas-phase hydrogenation of 3-chloronitrobenzene.[359] CuO/CeO_2–SiO_2 (10 wt.% CuO), CuO–CoO/CeO_2–SiO_2 and CuO–NiO/CeO_2–SiO_2 (5 wt% each) catalysts were prepared by aqueous-impregnation of CeO_2–SiO_2 with the Cu, Co and Ni nitrate salts followed by calcination at 500 °C. The XPRD diffraction pattern indicated a high dispersion of the CoO particles on the support even in the monometallic catalyst. However, the addition of Co and Ni to the CuO/CeO_2–SiO_2 increased the dispersion degree, preventing aggregation. Furthermore, the presence of the second metal was noticed to favor the reduction of copper oxide to the metallic state. Comparing the catalysts in the hydrogenation of 3-chloronitrobenzene in a flow reactor under 1 bar of H_2 at 310 °C, the monometallic system showed an higher initial activity than the bimetallic ones, but also a fast deactivation due to sintering. The bimetallic samples exhibited stability up to 10 h with the following order of activity: $CuO–NiO/CeO_2–SiO_2$ > $CuO–CoO/CeO_2–SiO_2$.

Furthermore, the selective hydrogenation of 4-chloronitrobenzene was reported using Cu-containing hydrotalcites prepared by co-precipitation of metal nitrates with NaOH and Na_2CO_3 followed by calcination.[360] The resulting Cu, Cu-Al and Cu-Fe catalysts showed a complete selectivity towards 4-chloroaniline with an order of activity Cu-Al > Cu-Fe > Cu attributed to an increasing copper dispersion. The addition of Ni as dopant (Ni:Cu = 1:11) in the Cu-Al catalyst further increased the activity of the catalyst maintaining the intrinsically high selectivity of the Cu system. The better performances were attributed to a facilitated copper oxide reduction and to increased surface hydrogen availability. The stability of the material was lower than the above described $CuO–NiO/CeO_2–SiO_2$, since it showed deactivation over the time on stream. More recently the use of copper-based catalysts was also reported for the liquid phase hydrogenation of 1,4-dinitrobenzene to 1,4-phenylenediamine.[361,362] For this transformation, a series of silica supported multimetallic Cu-Zn-Mn, Cu-Zn, and monometallic Cu catalysts were compared.[362] A negative effect of the Mn on the selectivity was noticed, however comparable results were obtained for some of the monometallic and bimetallic Cu-Zn materials. Later on, studies on bimetallic $Fe-Cu/SiO_2$ catalysts showed poorer performances of this class of catalysts with respect to the Cu-Zn and Cu based ones.[361]

7.2. Transfer hydrogenations

7.2.1. Reductions with alcohols, N_2H_4 and ammonia-boranes

Only few studies have been reported on the use of multimetallic 3*d* catalysts for the transfer hydrogenation of nitroarenes. In this respect, Chaubal and Sawant compared the catalytic performances of co-precipitated NiO, CoO, and $NiCo_2O_4$ for the reduction of 4-chloronitrobenzene using different alcohols as H-donor.[363] The bimetallic catalyst exhibited a higher activity compared to monometallic ones using 2-propanol in combination with NaOH as promoter. The effect was partially attributed to a higher surface area of the bimetallic material. A tentative mechanism was proposed in which electron-deficient sites in the catalyst are responsible for the initial absorption of the NO_2 group, while 2-propanol interacts with electron-rich sites. Although characterization of the electronic features of the surface was lacking, presumably the nickel sites are more electron-rich while the cobalt ones electron-poor, thus explaining the better performance of the bimetallic catalysts. The reaction was insensitive to the presence of EDG or EWG on the nitroarene. Notably, Cl- and -CHO groups were tolerated, but hydrogenolysis of C-X bond was detected for Br- and I- substituted nitroarenes.

Two other Ni-based systems were later reported using glycerol as the hydrogen source. In the first case, Gawande and co-workers selectively hydrogenated various substituted nitroarenes with Ni-Fe_3O_4 NPs.[364] The catalyst was prepared by deposition of Ni on the ferrite NPs surface by wet impregnation followed by chemical reduction. Although a positive effect of the ferrite on the activity cannot be excluded, it is more probable that it acts only as a magnetic support allowing an easy recovery of the catalyst, which indeed was effectively recycled several times. Unfortunately, a comparison with unsupported Ni NPs was lacking. The system was tolerant to various functional groups including halogens (Cl and Br) and nitriles. Interestingly, the selective reduction of the nitro group in 4-nitroacetophenone was attained although the catalyst is also able to reduce some acetophenones under similar reaction conditions. A series of $CuNiAlO_x$ was later prepared by Shi and co-workers by co-precipitation method and employed in the reduction of different nitro compounds with a stoichiometric amount of glycerol.[365] The catalysts were prepared with variable amounts of the three components, calcined at temperatures ranging from 350 to 650 °C and then reduced under H_2 flow. The resulting materials contained Ni in a crystalline form, while Cu and Al were present in amorphous state. The best catalytic performances were obtained with $Cu_1Ni_4Al_{0.5}O_x$ calcined at 450 °C. The ratios of the three metals had a strong effect on the reaction outcome. Higher nickel contents decreased the activity but improved the selectivity, while an increase of the copper or aluminum content resulted in a drop of the activity and selectivity of the system (azo- and azoxybenzene were given as major side products). A similar effect was observed in the absence of Al.

Apart from alcohols, hydrazine was used as H-donor for nitro reductions using bi- or multimetallic catalysts. In this context, an iron-nickel catalyst obtained by thermal decomposition of a hydrotalcite-like precursor was described in 2007.[366] The system was active in the reduction of differently substituted nitroarenes, although no challenging substrates bearing easily reducible groups were employed. Interestingly, several thioether-containing nitro compounds were reduced affording high yields of the corresponding products. In comparison, related nickel-aluminum and nickel-magnesium-aluminum materials did not show any activity.

Almost ten years later Cai and co-workers screened a series of nickel-based bimetallic NPs, containing Fe, Co, Zn or Cu in 1:1 ratio with respect to Ni, in the reduction of 4-nitrotoluene with hydrazine.[367] The NPs were prepared by reduction of metal salts with $NaBH_4$ using PVP as stabilizer. $Ni_{0.5}Co_{0.5}$ NPs showed better selectivity towards 4-methylaniline than the two monometallic catalysts and gave improved yields compared to the Fe, Cu and Zn containing Ni-NPs. Remarkably, when the catalyst loading was low azo- and azoxyarenes accumulated, thus suggesting their formation as intermediates (Scheme 3, condensation route). The bimetallic NPs had a smaller size than the monometallic ones and a higher content of Ni than Co on the surface influencing the catalytic activity. In addition, the authors proposed that electron transfer from Co to active Ni sites facilitates the reduction of the absorbed nitroarenes on the surface. The catalyst showed tolerance for chloro- and bromo-substituted nitroarenes and good activity for substrates bearing either electron-donating or -withdrawing groups. Noteworthy, double and triple bonds as well as nitriles were tolerated, while aldehydes were reduced, too. Upon recycling, the catalyst showed poor activity due to aggregation and oxidation.

Also a magnetically recoverable catalyst with the composition $Co_{0.2}Fe_{2.8}O_4$ has been studied in the reduction of chloronitrobenzenes with hydrazine.[368] The mixed oxides NPs had higher activity than Fe_3O_4. In these nanocrystals the addition of Co transforms the inverse spinel-type structure of Fe_3O_4 to the normal spinel structure of $CoFe_2O_4$. Thus, adding a small amount of Co to Fe_3O_4 increased the number of defects in the spinel structure modifying the absorption of the reactants on the surface during the reaction. Contrary to the above-mentioned Ni-Co system, the latter catalyst is air stable.

In recent years, ammonia borane attracted interest as a convenient hydrogen source in addition to the more commonly used transfer reagents. Two Ni-Cu bimetallic catalysts have been reported for NH_3BH_3 dehydrogenation-nitroarene hydrogenation reaction sequence: $Cu_{0.36}Ni_{0.64}$ NPs of an average diameter of 16 nm assembled over graphene[369] and CuNi NPs of *ca.* 3 nm obtained by co-precipitation of Ni and Cu salts inside the pore of MOF MIL-101 with the chemical formula $Cr_3F(H_2O)_2O(BDC)_3{\cdot}nH_2O$ (BDC = benzene-1,4-dicarboxylate).[370] In the first case, an improved catalytic activity of the bimetallic NPs with respect to the monometallic Ni and Cu NPs in the hydrogen release by NH_3BH_3 methanolysis was demonstrated. However, in both cases a lack of direct comparison with monometallic catalysts in the hydrogenation of nitroarenes does not allow to make any speculation on a possible synergistic effect of the two metals. Both the catalysts showed good activity and recyclability in the reduction of some nitroarenes, although the catalytic performances were in general lower than those obtained by catalysts containing Pd under similar reaction conditions.[371-374]

7.2.2. Reductions with $NaBH_4$

As for the monometallic heterogeneous catalysts, the reduction of nitrophenols has been used as a general probe to test the catalytic behavior of different materials.[375] As said before (see chapter 2) due to the high catalyst loading - commonly the total weight of the catalyst exceeded that of the substrate by 10 to >100 times - it is difficult to evaluate the real catalytic potential of a material.

7.2.2.1. Bimetallic alloy nanoparticles

From 2011 on, several reports concerned the use of Ni-Co nanocatalysts. The materials were generally prepared by reduction of Ni and Co salts with hydrazine in basic conditions in the presence of a capping reagent or a support. Chain-like nanostructures could be obtained using polymers as additives[376,377] and dendritic and flower-like microstructures using surfactants.[378,379] When the reduction was performed in the presence of GO, nanoparticles uniformly grown on rGO sheets were obtained.[380] Ni-Co NPs supported on CeO_2 nanorods have been reported recently, too.[381] The mixed metals nanostructures contained mainly Co and Ni in the elemental state and in most cases could be magnetically separated from the reaction mixture thus facilitating the recovery procedure. Varying the relative content of the two metals, the magnetic and the catalytic properties of the catalyst changed. In general, the overall magnetization was higher for extended nanostructures and increased with the cobalt loading. On the other hand, the best Co/Ni ratio strongly depended on the synthetic procedure and on the morphology of the catalyst. However, monometallic Co systems, when studied, usually showed a higher activity than Ni measured in the same conditions. For the alloys in some cases higher nickel content was beneficial,[376,377] in other cases cobalt.[380,381] In addition, the dependence of the catalytic activity from the composition is often not clear, even within a series of catalysts prepared in the same way. Instead, a better activity-composition relation is observed for Fe-Co alloyed nanoparticles supported on rGO obtained by reduction with hydrazine.[382] All the bimetallic Fe-Co catalysts showed higher activity compared to the monometallic rGO/Co and rGO/Fe due to a synergistic effect. Generally, the activity increased with the content of cobalt.

Ni-Fe NPs obtained by solvothermal reduction of the metal salts with hydrazine have been also studied.[383] The dimension and the shape of the particles were strongly dependent from the employed capping agent, the concentration of base, the solvent, the temperature and the ratio between metals. A series of these Ni-Fe NPs of different sizes with a Fe:Ni ratio of 1:2 were used as catalyst for the reduction of 4-NP. A Decrease of the particle size led to an increase of activity. In general, the iron containing systems showed a lower activity compared to the Ni-Co catalysts in the reduction of 4-NP.

A more synthetically focused study on the application of Fe-Ni NPs was reported by Chikate and co-workers.[384] Their catalyst was obtained by treatment of a 1:1 molar mixture of the salts of the two metals in water with $NaBH_4$. Using nitrobenzene as model substrate with a metal loading of 10 mol%, the Fe-Ni NPs catalyzed the complete reduction of the nitro group in 35 min, while monometallic Fe(0) and Ni(0) NPs afforded 50% and no conversion, respectively. This surprising result indicates that the most catalytically active metal in this specific alloy was Fe rather than Ni, opposite to what was noticed for Fe-Ni-P[349] and Fe-Ni-B[350] alloys used for catalytic reduction of nitroarenes with H_2. The authors proposed that the Ni in the alloy acted as an electron-shuttle between Fe and the nitro group. The reduction of selected substituted nitroarenes was accomplished with high selectivities, although substrates bearing easily reducible groups were lacking in the reaction scope.

Wen and co-workers introduced a further improvement in the Fe-Ni alloy system by preparing a nanostructure in which an oxidic Fe_3O_4 phase was embedded in an active Fe-Ni amorphous phase.[385] Compared to Fe_3O_4, Fe-Ni, Fe and Ni NPs, the Fe_3O_4/Fe-Ni nanostructure showed higher activity in the reduction of nitrophenol. In contrast to what reported by Chikate and co-workers[384] Ni NPs had higher activity than both Fe and Fe_3O_4 NPs, indicating Ni as the most catalytically active site. Despite its low activity, the Fe_3O_4 phase had the important double role of helping the absorption of the reactant on the surface of the catalyst and separating the active sites of the amorphous alloy.

Recently, copper-based alloys have been reported to efficiently catalyze the reduction of nitro compounds with $NaBH_4$. Hence, in 2014 Christensen and co-workers systematically examined the effect of small amounts of other transition metals on copper catalysts.[386] They identified copper-cobalt in a 10:1 ratio as the best combination for the *in situ* generation of active Cu-Co-B particles. The reduction of substituted nitroarenes at room temperature was complete in less than 30 min for most of the substrates using only

3.3 mol% of metal loading. The limited number of nitroarenes reduced does not allow to appreciate the chemoselectivity of the catalyst. In this respect, halogens were tolerated, although the formation of small amounts of dehalogenated products was noticed for 4-bromo- and 4-iodo-substituted nitroarenes. Unfortunately, due to the synthetic focus of the paper, structural information on the obtained heterogeneous catalyst and comparison of the bimetallic with the monometallic systems were not presented.

Several studies have been performed on the synthesis of Ni-Cu alloys and their use in the reduction of 4-nitrophenol. Although those reports are interesting for a better understanding of the synergy between Ni and Cu in alloys/nanocomposites, the very small scale on which the catalytic reactions were performed, and the low catalytic ratios employed make it difficult to evaluate the real potential of the materials. As an example, Borah and Bharali synthesized Cu-Ni nanocrystals of ~10 nm with different Ni/Cu ratios by treatment of aqueous solution of the precursors with hydrazine.[387] The lowest catalytic activity was obtained with monometallic Ni and Cu NPs while Cu_3Ni_2 NPs the highest one. A physical mixing of 3:2 mixture of Cu and Ni NPs afforded worse results, thus the increased catalytic activity of the bimetallic catalyst was attributed both to a synergistic effect between Cu and Ni and to the increased surface area of the mixed metals alloys. A following study by the same group showed that supporting the Cu-Ni alloy nanoparticle on Co_3O_4 led to a dramatic enhancement of the catalytic performance both in the reduction of 4-NP and other 4-substituted nitroarenes.[388] Based on the very low activity of Co_3O_4 alone, the authors suggested that cobalt oxide had the main role of stabilizing the active components (Cu and Ni) by preventing NPs agglomeration and increasing the catalyst surface area. A stabilization effect of the support was detected also in Cu-Ni/GO nanocomposites prepared with different protocols.[389,390] The material was synthesized by Shen and co-workers by reduction of the metals salts with hydrazine in ethylene glycol in the presence of GO.[389] Hollow Cu-Ni NPs of ~35 nm supported on GO nanosheets were obtained. The catalyst was more active than bare Ni-Cu NPs and monometallic Ni/GO in the reduction of 4-nitrophenol. In addition to the stabilization features, GO was found to increase the catalytic activity of the NPs by facilitating the absorption of the nitroarene and the transfer of electrons. An improved activity and stability of the system was achieved by Wen and co-workers by modifying the synthetic method.[390] Very small Cu-Ni NPs (~2 nm) were prepared by electrostatic-adsorption of the metal precursors on GO followed by simultaneous reduction at 180 °C *in-situ* with ethylene glycol acting both as solvent and reductant. A screening of different Cu/Ni ratios showed that the 4-NP reduction rate increased from a minimum using the NPs of the pure metals up to a maximum with a Cu/Ni ratio of 61:39. High selectivities were obtained in the reduction of 4-substituted nitroarenes containing amino, keto, aldehydic and ether groups.

In addition to the above described alloy system, recently, also Co-Cu[391] and Zn-Co[392] NPs embedded in nitrogen doped porous carbon, derived by pyrolysis of nitrogen containing MOF, and quaternary CuZnFeS nanocrystals[393] have been used as catalysts in the reduction of 4-nitrophenol.

7.2.2.2. Ferrite-based nanoparticles

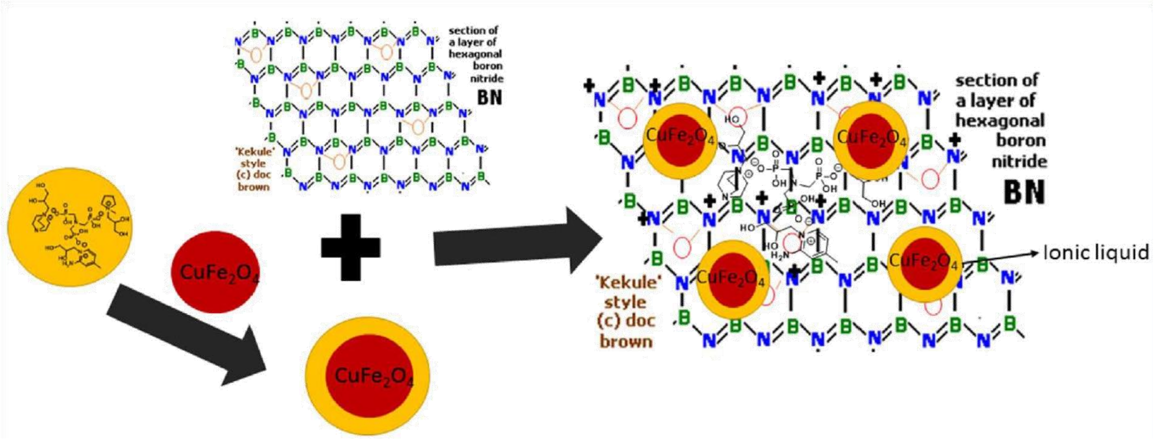
Ferrite nanoparticles have been extensively used as support for the synthesis of magnetically recoverable catalysts.[394] In previous sections (see chapter 3 and 6), systems were described in which ferrite was the active species itself in the absence of a second 3*d* metal or it was used only as a support, not participating in the catalytic event. In this latter cases Fe species were separated from the active 3*d* metal nanoparticle by an organic or inorganic layer. In the following, ferrite-based catalysts in which another metal is either embedded in the lattice of the spinel ferrite or attached to the surface of the magnetic nanoparticle are summarized.

Ferrites MFe_2O_4 (M = Mn, Co, Ni, Cu, or Zn) have spinel structure based on a close packed oxygen lattice, in which tetrahedral and octahedral sites are occupied by metal cations. The divalent M^{2+} ions occupy either the tetrahedral or the octahedral sites of the spinel lattice. However, since the octahedral sites are mainly those exposed on the surface of the spinel, the catalytic activity is mostly related to the metal present at those sites.[395]

Specifically using cobalt-ferrites, the group of Singhal thoroughly studied the effect of different dopants. The parent $CoFe_2O_4$ itself was found to be inactive for the reduction of 4-nitrophenol with $NaBH_4$.[396] Interestingly, the addition of Ni as dopant, in a series of $Ni_xCo_{1-x}Fe_2O_4$ (x = 0.2, 0.4, 0.6, 0.8) catalysts prepared by reverse micellar method, resulted in catalytic activity of the NPs. The authors attribute the catalytic performance as a result of the presence of active Ni^{2+} on the cobalt-ferrite surface (octahedral sites) and its effect on the NPs size and surface area. $Ni_{0.6}Co_{0.4}Fe_2O_4$ and $NiFe_2O_4$ showed the best activity. The same group studied also a series of related catalysts, prepared by sol-gel method, with the composition $CoM_{0.2}Fe_{1.8}O_4$ (M = Mn, Ni, Cu or Zn).[397] Here, the Cu-doped material revealed good catalytic activity, although lower than that of $Ni_{0.6}Co_{0.4}Fe_2O_4$ and $NiFe_2O_4$. Notably, the best activity was obtained with the Mn-doped catalyst. The study of a series of catalysts with the composition $CoMn_xFe_{2-x}O_4$,[398] showed that cobalt-ferrite (x = 0) is activated by the addition of a small amount of manganese ions (x = 0.2). Owing to the low catalytic activity of Mn itself, the increased reactivity was attributed to a synergistic effect between Co-Mn and Fe-Mn. In the reduction of nitroanilines and halogen-substituted nitroarenes, $CoMn_{0.2}Fe_{0.8}O_4$ [399] was two to three times more active than $CoCu_{0.20.8}O_4$[397] and also showed improved chemoselectivity. Singhal and co-workers also reported a comparison between $CuFe_2O_4$, $NiFeO_4$ and $ZnFe_2O_4$, synthesized by sol-gel method, for the reduction of nitrophenols. The study made clear that copper-ferrite has the highest activity while zinc-ferrite is completely inactive.[400] Indeed, the first copper-ferrite catalyst for the reduction of nitrophenols with $NaBH_4$ was reported in 2013 by C. Wang and co-workers.[401] This catalyst, synthesized by a hydrothermal method, was composed by spherical clusters (~160 nm) of smaller $CuFe_2O_4$ NPs (~5 nm). In contrast, monometallic Fe_2O_3 and Fe_3O_4 NPs were ineffective for the same reaction. Although the active catalyst could be separated magnetically, the structure of $CuFe_2O_4$ NP was partially destroyed by $NaBH_4$, mainly due to reduction of Cu^{2+} to metallic copper. The addition of a carbon-based support stabilized the copper-ferrite NPs.[402-404] More specifically, bubbling O_2 in an acetone/cetylamine suspension of the copper-ferrite NPs followed by thermal treatment at 400 °C under N_2, afforded $CuFe_2O_4$ NPs embedded in a three-dimensional porous carbon cage.[404] The stability of the catalytic system for the reduction of 4-NP was higher than that of bare NPs, although a low catalyst/substrate ratio was employed. A good recyclability and a broader substrate scope was realized using a $CuFe_2O_4$ catalyst containing 25 wt% of graphene.[402] The graphene in the nanocomposites enhanced the catalytic activity with respect to the bare NP and avoided fast deterioration of $CuFe_2O_4$. Faster reaction rates for the reduction of EWG- and EDG-substituted nitroarenes were achieved upon addition of a small amount of Co (Cu/Co = 6:1) to the copper-ferrite graphene catalyst.[403] The Cu-Co synergistic effect was ascribed to the overlapping of the 3*d* bands of the transition metal ions.

Recently, Gengan and co-workers capped $CuFe_2O_4$ NPs with a tri-cationic phosphonate ionic liquid (TCPIL) and supported them on partially oxidized modified boron nitride nanosheets (BNONS) (Figure 52).[405] The TCPIL/$CuFe_2O_4$/BNONS catalyst was used in the reduction of different nitroanilines and could be recycled several times. The authors proposed that the TCPIL phase enhances the electron transitions between $CuFe_2O_4$ NPs, on which $NaBH_4$ is activated, and BNONS, on which nitroanilines are absorbed. The formation of p-n junctions between $CuFe_2O_4$ NPs and BNO layers facilitated the reduction. This, in addition to the good dispersion of the NPs on the BNONS, was suggested to be the reason for the good activity of the system. TCPIL/$CuFe_2O_4$/BNONS and $CuFe_2O_4$-graphene composites[402,403] were able to catalyze the reduction of 4-nitroaniline in comparable reaction times, although the metal loading for the former was lower. Despite the good catalytic activity, the complex synthetic procedure for the preparation of the BNONS supported catalyst constitutes a drawback with respect to the graphene-based system.

Figure 52 Preparation of TCPIL/$CuFe_2O_4$/BNONS nanocomposite. (Reproduced with permission from Ref. 405. Copyright 2018, Elsevier)

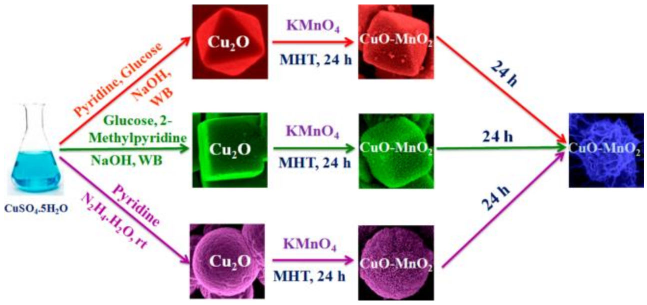


In addition to the Cu-containing catalysts with the metal ions included in the spinel structure of the ferrite, two other systems have been reported in which metallic Cu was supported on Fe_3O_4[406] and $NiFe_2O_4$.[407] In these cases, the ferrite mainly acts as dispersing agent and as magnetic support allowing the recovery and recycling of the catalyst. As for most of the metal-based systems the reduction of substituted nitroarenes with $NaBH_4$ was accomplished in short reaction time, however carbonyl groups including ketones and aldehydes were also reduced.

7.2.2.3. Manganese-containing composites

So far no Mn-based heterogenous catalysts without the addition of other metals have been reported for the reduction of nitroarenes. However, owing to the low cost and absorptive abilities, manganese oxides have been used as versatile supports and as modifiers of a number of nano-scaled catalysts with unique structural features. The first report of such systems by Pal and co-workers described the use of CuO-MnO_2 composites, which were prepared by treating cubic, octahedral and spherical-shaped Cu_2O nanoparticles with $KMnO_4$ under modified hydrothermal conditions (MHT).[408] Depending on the reaction time, porous structures with retained size and shape of the parental NPs or smaller spherical porous particles could be attained (Figure 53).

Figure 53 Synthesis of CuO-MnO_2 nanocomposites. (Reproduced with permission from Ref. 408. Copyright 2014, American Chemical Society)



Interestingly, the catalytic performances of these materials in the reduction of 4-NP is directly related to their surface area. An improved catalytic activity was observed applying Cu@MnO_2 core–shell nanowires prepared by reduction of Cu^{2+} with hydrazine in a NaOH/EDTA aqueous solution followed by hydrothermal treatment with $KMnO_4$ solution.[409] Here, the obtained material was composed by an internal Cu core whose surface area, and thus the capability of absorbing the reagents, was increased by a porous MnO_2 shell. In spite of the apparently delicate structures, both the CuO-MnO_2 NPs[408] and Cu@MnO_2 nanowires[409] retained their morphological and catalytic features even after several recycling experiments. Due to the negligible catalytic activity of MnO_2 alone,[408] the role of manganese in such copper-MnO_2 catalysts is limited to morphological modifications (*i.e.* increased porosity) during the synthesis and to structural stabilization effects. Nevertheless, as in several other bimetallic systems it is not possible to exclude a synergistic effect between copper and MnO_2.

In addition to Cu, two different catalysts have been reported on the use of manganese oxides in combination with Ni, again for the reduction of nitro compounds with $NaBH_4$. In the first case, Lee and co-workers studied single Ni(0) particles confined in the hollow cavities of a manganese-silicate nanoshell.[410] The material exhibits a high surface area and a pore size of the external shell sufficient to allow the reagents to reach the interior cavity. Interestingly the hollow NPs catalyzed the reduction of nitroarenes substituted with amino-, methoxy- and aldehyde-groups but not nitrophenols. This peculiar selectivity was attributed to the repulsion of the phenolate anion by the negatively charged manganese-silicate shell. Later, Bharali and co-workers reported the use of zero-valent Ni NPs (~2-3 nm) supported on □-Mn_2O_3 for the reduction of 4-

NP.[411] This composite had a lower catalytic activity than the bare Ni NPs, although the manganese oxide support had a stabilization effect allowing a slightly improved recyclability of the bimetallic catalyst with respect to the monometallic one. Finally, Co-Mn oxide catalysts should be mentioned here, which have been prepared by treatment of *in situ* synthesized cobalt nanoparticles with aqueous $KMnO_4$ at 120 °C. They catalyzed the reduction of nitroarenes with $NaBH_4$ or hydrazine.[412] Co and Mn in the catalytic material were mainly present in the oxidation states +2 and +4, thus affording the composition $Co_2Mn_3O_8$. The authors compared the activity of the catalyst in the reduction of 4-NP with that of MnO_2 and Co_3O_4 NPs, prepared with the same procedure, noticing a higher activity. Although a cooperativity of the two metals was claimed on the base of these results, no other evidences were provided. In fact, the higher reduction rate of the heterobimetallic material could also be due to morphological features. Using $Co_2Mn_3O_8$ as catalyst, a comparison between $NaBH_4$ and hydrazine for the reduction of substituted nitrobenzenes was done. Faster reaction rate and higher selectivities were reported for the sodium borohydride system. Interestingly, it was shown that when $NaBH_4$ was employed as the H-source, 4-nitrostyrene could be effectively reduced to the unsaturated aniline, while using hydrazine the double bond was also hydrogenated. $Co_2Mn_3O_8$ had also a good stability allowing recycling it up to ten times without any activity drops and structural changes (detected by XPRD and XPS), however a progressive depletion of the content of the two metals was noticed.

8. Homogeneous catalysts

To the best of our knowledge, all industrially applied catalytic nitro reductions to amines make use of heterogeneous catalysts. Hence, it is not surprising that the vast majority of recent studies in this area deal with the use of new solid catalysts. However, parallel to their development, several homogeneous catalytic systems have been also studied especially for structurally more diverse substrates. In general, the structure, properties and catalytic performance of a molecular complex, in particular regarding selectivity, can be more easily tuned by changing the structure of the ligand and, of course, modifying the nature of the metal. Although a number of successful homogenous catalysts have been reported, it is clear that none of these complexes can compete so far with the heterogeneous ones for existing large scale continuous processes. Nevertheless, such systems might find applications in the synthesis of specialty chemicals and/or pharmaceuticals. For these products, the cost of the catalyst itself might not be the most relevant point considering the value of the final product. Here, excellent selectivity and low toxicity of the catalyst system itself are important, too. In this respect, homogenous or heterogenized homogenous catalysts for nitro reduction employing first row transition metals are gaining increasing interest.

8.1. Iron-based catalysts

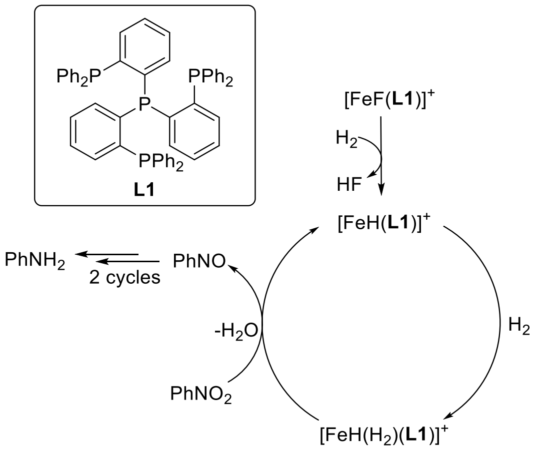
8.1.1. Reduction with gaseous reductants

Before 2000, very few catalytic systems employing soluble iron complexes have been reported for the reduction of nitroarenes. Among those, the most studied systems were based on the use of iron carbonyls as catalytic precursors, carbon monoxide as the reductant and water or alcohol as hydrogen sources. The advantages of these methods are the selectivity and the low cost of carbon monoxide, in addition to the low cost of iron. In most cases however, considering the number of electrons that can be provided by carbon monoxide ligands coordinated to iron, the reduction was stoichiometric and, when a real catalytic reaction was involved, the turnover numbers were low.[413] In spite of the potential industrial interest of the reaction, it was less studied in recent years.

An alternative to CO/H_2O mixtures is the use of molecular hydrogen. Pioneering studies by Knifton in 1976, reported the use of $Fe(CO)_3(PPh_3)_2$ and $Fe(CO)_3(AsPh_3)_2$ as catalysts for the reduction of nitrobenzene.[414] Knifton reported a higher activity and selectivity of bis(triphenylarsine)tricarbonyliron(0) compared to the PPh_3 containing one, but also a lower stability. Although the reaction required relatively harsh conditions, 80 bar H_2 at 125 °C, and was performed with a low catalytic ratio, the results were encouraging. However, the studies on other iron-based catalysts were abandoned in favor of the more active noble metals-based ones. Almost 30 years later, Chaudhari and co-workers tested different iron salts and complexes in the catalytic hydrogenation of nitrobenzene.[415] As the reduction of the nitro group with hydrogen is accompanied by the formation of two equivalents of water, a water-tolerant catalyst is required for achieving high TON. Working in this direction the group of Chaudhari found good activity (TOF up to 1300) and high selectivity towards aniline (>98%) using either iron nitrate, iron sulfate or iron acetylacetonate at relatively low hydrogen pressure (about 28 bar) at 150 °C. The highest activities were obtained using iron sulfate either in toluene, alcohol or water. Based on these results they developed an organic phase/water biphasic system that allowed an easy separation of the product from the catalyst. Either toluene or the neat nitroarene could be used as the organic solvent, but in both cases ethylenediaminetetraacetic acid disodium salt ($EDTANa_2$) had to be added as ligand to avoid massive leaching of the metal to the organic phase. The biphasic nature of the system and the addition of the ligand resulted in a reduced catalytic activity, however, the system showed robustness. The aqueous phase containing the catalyst was recycled 5 times without significant loss of activity and a cumulative TON above 6000 was obtained. Although the reaction temperature was rather high, nitriles, carboxylic acids and keto groups were not reduced. Also, dehalogenation did not occur when a chloride substituent was present on the substrate. More sensitive groups such as bromide, iodide and double bonds were not tested. In the case of the reduction of 4-nitrobenzoic acid, 4-nitrobenzyl nitrile and 2-nitroanisole the formation of azo- and diazo-derivatives lowered the selectivity to the corresponding aniline. These side-products resulted from the reaction of nitrosobenzene thus indicating its accumulation during the reaction (Scheme 3, direct pathway).

A rare example of iron-catalyzed hydrogenations of nitroarenes, that makes use of defined iron/tetraphosphines complexes, was reported by the group of Beller almost 10 years later.[416] Both the pre-formed and *in-situ* generated iron complex (using $Fe(BF_4)_2\cdot 6H_2O$) of tris[(2-diphenylphosphino)phenyl]phosphine (**L1**, Scheme 36) showed higher catalytic activity towards reduction of nitrobenzene than complexes of the commercially available tris[2-(diphenylphosphino)ethyl]phosphine (**L2**, Scheme 39). Under optimized conditions (120 °C at 20 bar H_2 in *tert*-amylalcohol) the catalyst required one equivalent of trifluoroacetic acid with respect to the substrate to get significant hydrogenation activity. Based on NMR studies of the complex $[FeF(\mathbf{L1})][BF_4]$ under the reaction conditions, the authors presented a mechanistic proposal. Already at room temperature and under 20 bar of H_2, the preformed complex was partially converted to the diamagnetic iron hydride complex $[FeH(H_2)(\mathbf{L1})][BF_4]$ in the absence of nitroarenes. Thus, it was proposed that the coordinated fluoride in the initial precursor readily forms an $[FeH(\mathbf{L1})]^+$ species. This activates H_2 to give $[FeH(H_2)(\mathbf{L1})]^+$, which is responsible for the hydrogenation of the nitro group (Scheme 36). No accumulation of intermediates such as hydroxylamine, azo- and azoxy-compound was detected during the reaction. Nevertheless, no reduction pathway was suggested because the system is able to reduce *N*-phenylhydroxylamine and diazobenzene with a similar rate (Scheme 3). From a synthetic point of view the system is very selective towards the nitro reduction and even double bonds were tolerated. Dehalogenation was not detected for 3- and 4-halide-substituted nitroarenes.

Scheme 36 Proposed mechanism for the reduction of nitroarenes with H_2 catalyzed by Fe-**L1** complexes.

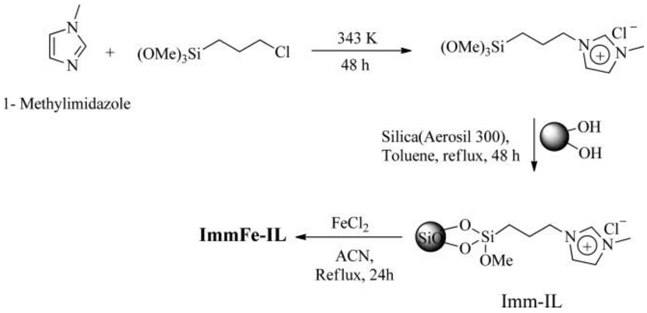


8.1.2. Transfer hydrogenations

Iron complexes have been also reported to catalyze transfer hydrogenations of nitroarenes. The first example of such reactions employed 1,1-dimethyl-hydrazine as the hydrogen source and $FeCl_3{\cdot}6H_2O$ as catalyst in the presence of charcoal.[417] Although the metallic precursor is completely soluble, it is not possible to exclude the formation of a heterogeneous catalytic system during the reaction. Later on, the simple $FeSO_4{\cdot}7H_2O$ salt was reported to quantitatively catalyze the reduction of 4-nitrobenzonitrile to 4-aminobenzonitrile in a H_2O/EtOH 1:1 mixture using hydrazine hydrate as the hydrogen source. However, the catalyst was not effective when formic acid, formates, $NaBH_4$ and NH_4Cl were used.[418] Other simple iron salts have been tested in combination with $NaBH_4$. A conversion was noticed with most of them, but selectivity was not always good. $FeCl_3$[419,420] and $Fe(OTf)_3$[420] afforded good selectivities towards the amine. Comparing the two salts under the same conditions Thomas and co-workers noticed a better performance of the latter.[420] Using 10 mol% of $Fe(OTf)_3$, the reduction of nitrobenzene took place at room temperature in 4 h, although 20 equivalents of reductant were needed. The catalyst well tolerated *ortho*-substitutents, electron-donating and electron-withdrawing groups including esters and amides; however, ketones were reduced to the corresponding alcohols and a partial dehalogenation was noticed for 4-bromonitrobenzene.

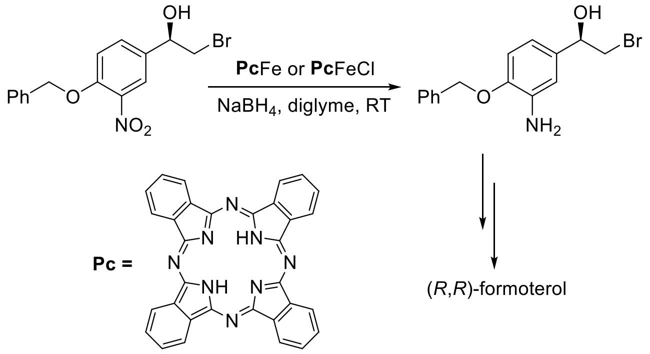
A catalytic system for the hydrogenation of nitroaromatics with hydrazine showing a good tolerance towards sensitive groups and selectivity in the mono-reduction of dinitroarenes was obtained by Bhanage and co-workers using a 1-alkyl-3-methylimidazolium-iron complex immobilized over silica, ImmFe-IL, (Scheme 37).[421] From EXAFS analysis of the freshly prepared heterogeneous material, in the ImmFe-IL iron was uniformly distributed in the form of one $[FeCl_3]^-$ for each imidazolium cation, thus resembling the homogeneous complex $[Bmim]_2FeCl_4$ (Bmim = 1-butyl-3-methylimidazolium). Although the catalyst could be recycled, loss of activity was detected already after the third cycle.

Scheme 37 Synthesis of immobilized iron complex ImmFe-IL. (Reproduced with permission from Ref. 421. Copyright 2015, American Chemical Society)



In all the above mentioned systems the formation of nanoparticles cannot be excluded, however, at least for $Fe(OTf)_3$ the absence of an induction period suggested against it.[420] In addition, FePc is a versatile catalyst, which was used successfully in combination of $N_2H_4 \cdot H_2O$,[418,419] $NaBH_4$[419,422] and silanes.[419] For example, N. Kumar, B. Singh and co-workers compared $FeSO_4 \cdot 7H_2O$, FePc or a 1:1 combination of them using hydrazine hydrate as the reductant.[418] A wide range of nitroaromatics were reduced showing that the method tolerates a large number of functional groups. However, it is difficult to state the superiority of one of the three systems owing to the different conditions used. In most cases selectivities were 99% with the best pre-catalyst and the optimal solvent depending on the substrate. Worth noting the FePc is able to selectively reduce only one nitro group in *meta*-, *ortho*-, and *para*-dinitrobenzene, while $FeSO_4 \cdot 7H_2O$ yielded the corresponding phenylenediamine. In 2001, phthalocyanine-iron complexes PcFe(II) and PcFe(III)Cl were used for the first time for the reduction of a nitro group in combination with $NaBH_4$. More specifically, an intermediate in the total synthesis of (*R*,*R*)-formoterol was prepared (Scheme 38).[422]

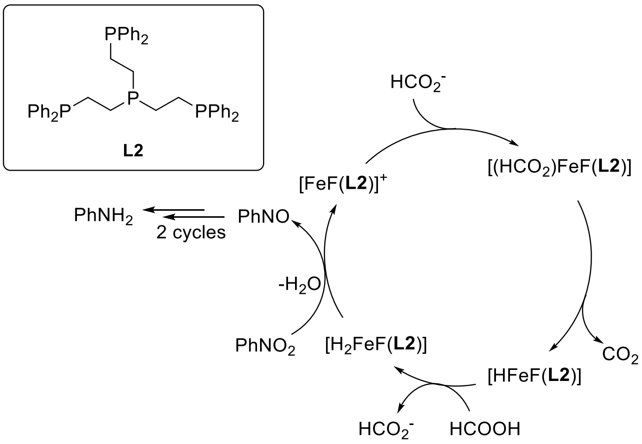
Scheme 38 Selective reduction of a pharmaceutical relevant intermediate with iron-phthalocyanine catalyst.



In comparison with the more expensive and less-stable tetraphenylporphyrinatoiron(III) chloride ((TPP)FeCl), both Pc complexes showed a higher activity, while $CoCl_2$ or $Fe(acac)_3$ were ineffective, yielding mainly debrominated side products. PcFe(II) and PcFe(III)Cl pre-catalysts gave similar results since the same active Fe(II) species were formed prior to the addition of the nitroarene. The authors noticed that addition of one equivalent of HBr with respect to the substrate substantially accelerated the reduction and decreased dehalogenation side reactions. This effect was explained by a faster *in-situ* generation of hydrogen. Using 2-bromoethanol to generate HBr in a more controlled way in the presence of PcFe(II) in diglyme at room temperature allowed the authors to extend the substrate scope. Hence, in this protocol benzyl ether, benzyl carbamate as well as halogen groups were well tolerated and also for the sensitive 4-iodobenzene a good yield was obtained. Although the authors demonstrated the superiority of FePc compared to (TPP)FeCl in the reduction of the specific intermediate of formoterol, it should be noted that reduction of simpler substrates (*i.e.* nitrobenzene and 4-chloronitrobenzene) with (TPP)FeCl were previously reported to occur with higher TON and TOF.[423]

Based on their iron-catalyzed hydrogenations of nitroarenes,[416] a related molecular-defined iron complex employing a tetradentate phosphine as the ligand was reported by Beller and co-workers for the reduction of nitroarenes using formic acid.[424] Here, the commercial so-called tetraphos ligand **L2** gave good results, while it was not effective in the former case. The active catalyst prepared *in-situ* from $Fe(BF_4)_2 \cdot 6H_2O$ was able to reduce nitro aromatics with formic acid already at 40 °C in the absence of any base. This feature is quite rare since most of the hydrogen transfer reactions require the presence of at least stoichiometric amounts of a base. By testing a series of defined iron-**L2** complexes the authors noticed that a fluoride coordinated to the metal is necessary to ensure good catalytic performance. This is opposite to what was found for the catalytic hydrogenation of nitroarenes, in which the initially coordinated fluoride, in the precursor $[FeF(\mathbf{L1})]^+$, was readily displaced under H_2 pressure. Thus, the active species in the two systems seems to be different. Indeed the authors found that [FeX(**L2**)][BPh_4] complexes (X= H or Cl) were inactive for the reduction of the nitro group using formic acid as H-donor in the absence of added fluoride salts. The proposed reaction mechanism is shown in Scheme 39. It is worth mentioning, that this system was not able to effectively hydrogenate azobenzene to aniline. Owing to the mild conditions and the nature of the H-source, the procedure tolerates a large number of functional groups, including ketones, double bonds and halide substituents.

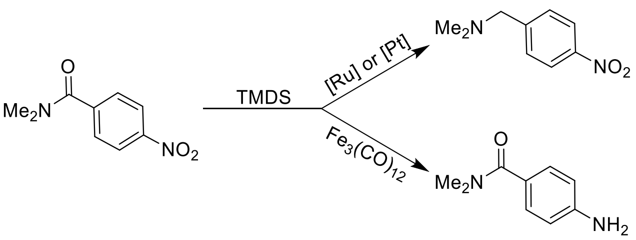
Scheme 39 Proposed mechanism for the reduction of nitroarenes with HCOOH catalyzed by Fe-**L2** complexes.



8.1.3.Reductions with hydrosilanes

The first example of iron assisted reductions of nitroarenes using hydrosilanes as H-donors is rather recent. In 2009, Nagashima and co-workers observed an unexpected selective reduction of the nitro group while investigating the carbonyl reduction of *N*,*N*-dimethyl-4-nitrobenzamide with 1,1,3,3-tetramethyldisiloxane in the presence of 10 mol% [$Fe_3(CO)_{12}$].[425] Remarkably, the catalytic behavior of the simple triiron dodecacarbonyl cluster was orthogonal to that shown by ruthenium and platinum[426] complexes, which selectively reduced the carbonyl group (Scheme 40). Hence, the same system was employed for the reduction of 4-halo nitrobenzenes affording the corresponding anilines in very good to excellent yields.

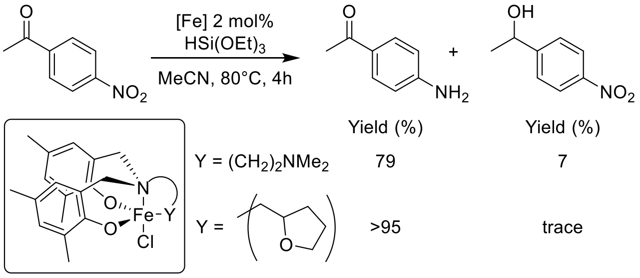
Scheme 40 Orthogonal selectivity of noble metals and $Fe_3(CO)_{12}$ in the reduction of *N*,*N*-dimethyl-4-nitrobenzamide.



An extensive study on nitro reductions with silanes was done by Beller and co-workers.[427] A large number of iron precursors formed active catalysts in the presence of tricyclohexyl phosphine (PCy_3) for the reduction of 4-bromonitrobenzene with phenylsilane in toluene at 110 °C. Best results were obtained with simple $FeBr_2$ and PPh_3 as the ligand. In the absence of ligands only poor yields were achieved. The protocol could be applied to nitroarenes containing halogen in *ortho*-, *meta*-, or *para*- position, affording only small amounts of dehalogenated by-products. Nitro compounds bearing double bonds, hydroxo, cyano, carbonyl and carboxylic groups as well as aromatic ethers and thioethers were reduced to the corresponding anilines in good to high yields. In addition, the hydrogenation of 1,4-dinitrobenzene to 4-nitroaniline was attained chemoselectively. Around the same time, the group of Lemaire optimized a catalytic system based on $Fe(acac)_2$ or $Fe(acac)_3$ and TMDS as hydrogen source affording product yields comparable to those reported by Beller.[428,429] The reductions were performed at slightly lower temperature (60 °C), although longer reaction times were needed.

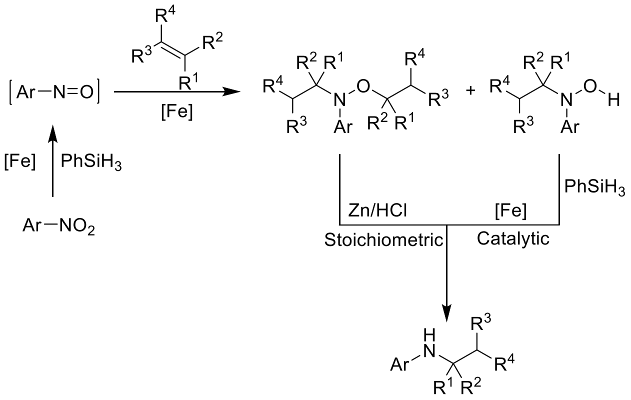
More recently, also Fe(II)Pc has been employed as catalyst for similar transformations using diphenylsilane (DPH) as the reductant. Using this complex, high yields of the corresponding anilines were achieved for most of the employed nitroarenes using only 1 mol% catalyst loading. Mono- and diaminobenzenes could be selectively obtained from di-nitroarenes upon variation of the silane amount. In agreement with the work of Lemaire and co-workers,[429] the authors noticed a faster reduction of aldehydes and double bonds compared to the nitro groups.

Scheme 41 Fe(III) amine-bis(phenolate) catalyzed reduction of 4-nitrobenzamide with silanes: ligand effect.



A fast and active catalyst based on iron(III)-amine-bis(phenolate) complexes was reported by Shaver and Thomas.[430] Performing the reduction of 4-nitroacetophenone the authors noticed a marked effect of the donor group Y bound to the amino moiety (Scheme 41). When a weakly coordinating tetrahydro-2-furanyl group was present instead of a strongly coordinating dimethylamino group, the reaction was faster and reduction of the carbonyl group was suppressed. Optimization of the reaction conditions allowed the selective reduction of a considerable number of nitroarenes bearing esters, thioesters, thioethers, nitriles, bromo and chloro substituents. Despite the relatively low temperature (80 °C) and catalyst loading (2 mol%), aniline yields >80% were generally attained in less than 8 hours while most of the other reported iron-based systems required longer reaction times for the reduction of nitroarenes with hydrosilanes. Interestingly, exploiting the feature of the complex to catalyze radical and reduction reactions, the authors envisaged the possibility of coupling the reductive transformation of nitroarenes with radical hydrogen-atom transfer to an alkene.[430,431] The formal hydroamination took place at room temperature in less than two hours with only 2 mol% of catalyst. *N*-Alkylated hydroxylamine and *N*,*O*-alkylated adducts were formed as intermediates. While the former intermediate could be reduced by Fe catalyst/hydrosilane, the latter required reduction by Zn/HCl to afford the hydroamination products in good yields (Scheme 42). It should be mentioned that this general synthetic strategy was previously reported by the group of Baran using 30 mol% of $Fe(acac)_3$ as catalyst.[432]

Scheme 42 Iron catalyzed hydroamination of olefins with nitroarenes.

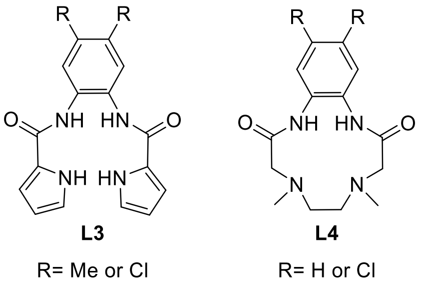


8.2. Cobalt-based catalysts: Transfer hydrogenations

In contrast to ligand-free iron systems, simple $CoCl_2$ was ineffective as catalyst for nitroarene reduction both using hydrazine[433] and $NaBH_4$[419]. However, cobalt(II) phthalocyanine was shown to be effective for the reduction of a wide range of nitroaromatics in combination with 2 equivalents of hydrazine hydrate in ethylene glycol.[433] In these reactions CoPc showed a comparable chemoselectivity to the FePc catalyst.[418] In general, this catalyst tolerated the presence of halide substituents, keto, nitrile, ester groups and heterocyclic rings. In addition, polycyclic nitroarenes afforded the corresponding anilines in high yields, while for such substrates FePc gave only poor conversions. Interestingly, also 4-iodonitrobenzene was selectively reduced without dehalogenation. Mechanistic insights of the reaction evidenced a direct reduction of the nitro as the main pathway under the used conditions (Scheme 3). The authors observed a fast reduction of the Co(II) to Co(I) upon addition of hydrazine to the Co(II)Pc solution. They proposed that a partial electron transfer from the ligand to the metal promotes the coordination of the nitroarene, which is then reduced to the amine by H_2 generated *in-situ* from the CoPc catalyzed decomposition of hydrazine. Due to the robustness of the catalyst, it was possible to recycle it four times by simple extraction from the ethylene glycol phase. A more efficient recycling system was later reported by Chao and Bergbreiter using a polyisobutylene-bound phthalocyanine cobalt complex.[434] Running the reaction in a partially thermomorphic heptane/ethylene glycol solvent system allowed to recycle the catalyst up to ten times, although longer reaction time were required to get full conversions.

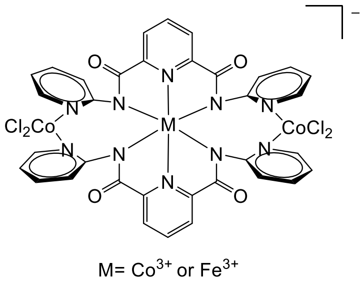
Very recently, Gupta and co-workers synthesized two sets of cobalt complexes using tetradentate pyrrolecarboxamido ligands (**L3**)[435] and amino-amido based macrocycles (**L4**, Scheme 43).[436] Best results for nitro reductions were obtained when the cobalt in the catalytic pre-cursor was in oxidation state +3 and when electron-withdrawing –Cl groups were present on the aromatic scaffold of the ligands. Cobalt complexes of both **L3** and **L4** were able to reduce a wide range of nitroaromatics in 6 h using 2 equivalents of hydrazine at 60 °C. Only little conversion was attained using Co-**L3** complexes when *ortho*-disubstituted nitroarenes were employed. Other dinitroaromatics were fully reduced to dianilines with both systems.

Scheme 43 Tetradentate nitrogen ligands employed in the Co catalyzed reduction of nitroarenes with hydrazine.



These complexes were not able to reduce styrene or stilbene; however, when 3-nitrostyrene or 1-nitro-4-(2-nitrovinyl)benzene were employed as substrates, the double bond was partially reduced. The authors ascribed this behavior to an activation of the olefin group towards hydrogenation as a result of the initial reduction of the nitro group to the aniline. In addition, both systems were able to catalyze the reduction of secondary and tertiary nitroalkanes. The same group also described the use of trinuclear [Co^{2+}–Co^{3+}–Co^{2+}] and [Co^{2+}–Fe^{3+}–Co^{2+}] complexes (Scheme 44) as active catalysts for the reduction of nitro compounds with hydrazine.[437]

Scheme 44 Anionic part of trinuclear [Co^{2+}–Co^{3+}–Co^{2+}] and [Co^{2+}–Fe^{3+}–Co^{2+}] complexes used as catalysts in the reduction of nitroarenes with hydrazine.



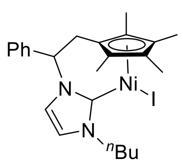
However, using the trinuclear complexes a large excess (6 equivalents) of reductant is required to reach complete conversion. Noteworthy, 4-iodonitrobenzene was reduced to the amine in 99% yield. From a mechanistic point of view, the authors suggested that the peripheral Co(II) are reduced to Co(I) upon addition of hydrazine, thus involving different oxidation states of the cobalt respect to the above described tetradentate ligands.[435,436] On the other hand, the central metal atom is not reduced by hydrazine thus indicating a marginal role in the redox process. This is in line with the very similar results obtained using $[Co^{2+}–Co^{3+}–Co^{2+}]$ and $[Co^{2+}–Fe^{3+}–Co^{2+}]$. Poor catalytic results were obtained when a $[(Neoc)Co(II)Cl_2]$ complex was employed as the catalyst to mimic the peripheral active sites.

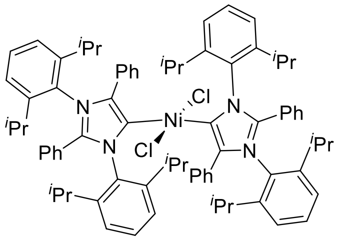
8.3. Nickel-based catalysts: Reductions with hydrosilanes

Despite the importance of Ni-based heterogeneous materials for hydrogenation reactions, the number of homogeneous Ni complexes for the reduction of nitro compounds reported so far is very limited. In particular, only hydrosilane-based reductions are known. However, simple nickel halides did not show any activity to reduce nitrobenzene even in the presence of PPh_3 using PMHS. Instead, $Ni(acac)_2$ was found to be active in the absence of any additional ligand.[438] Compared to the to the $FeBr_2/PR_3$[427] or the ligand-free iron[428,429] catalysts described above, $Ni(acac)_2$ required shorter reaction time (3-5 h instead of 16-48 h) at comparable reaction temperatures and catalyst loading (10 mol%). Although the reported product yields were mainly between 60% and 85%, the authors stated that only reduction of the nitro group was noticed for carbonyl-, Cl- and Br-containing substrates. Main differences with the iron-based hydrosilylation catalysts were the high selectivity towards the nitro group reduction in 4-nitrobenzaldehyde and in olefin-containing substrates. In addition, no detrimental steric *ortho*-effect was noticed as it was reported for $Fe(acac)_2$.[429]

A faster reduction of a number of nitroarenes was obtained using either an abnormal N-heterocyclic carbene based nickel complex, $NiCl_2(aNHC)_2$, (*a*NHC = 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-2,3-dihydro-1*H*-imidazole) [439] or a half-sandwich Ni–NHC complexes (Scheme 45).[440]

Scheme 45 Half-sandwich Ni-NHC (left)[440] and abnormal NHC-Ni complex (right)[439] for the reduction of nitroarenes with silanes.





The catalysts were able to reduce a number of nitroarenes substituted with electron-withdrawing and electron-donating groups in less than 3 h using $PhSiH_3$ as the hydrogen source. For example, nitrile and iodine containing nitroarenes were reduced to the corresponding anilines in high yields. Between the two catalysts a different behavior towards substrates bearing double bonds was noticed: $NiCl_2(a\mathrm{NHC})_2$ did not reduce olefin groups, while the half-sandwich Ni–NHC complex yielded a mixture of products. From a mechanistic point of view both complexes did not directly react with the nitroarene in the absence of silanes. In an attempt to identify the active species by reacting the complexes with $PhSiH_3$, the authors were unable to detect any Ni-H species by ^1H NMR. However, at least for complex $NiCl_2(a\mathrm{NHC})_2$, signals related to Si-H in ^1H NMR and ^{29}Si NMR suggested the formation of a Ni-silyl intermediate.

8.4. Other metals

The importance of phthalocyanines as ligands in the catalytic reduction of nitroarenes was furthermore demonstrated using CuPc[433] and ZnPc complexes.[441] For both metals, the sulfate, chloride and bromide salts in the absence of any ligands afforded far lower yields when hydrazine was used as the reductant. It is interesting to note that $ZnCl_2$ alone catalyzed the reduction of nitro groups in up to 89% yield. This fairly good result is surprising, since only in two other catalytic systems Zn was used as the (heterogeneous) active metal in which the reduction of nitrophenol was accomplished with high catalyst loadings.[442,443]

The CuPc catalyst showed very similar catalytic performances to the CoPc described above.[433] Indeed in both cases hydrazine was identified as the best reductant in ethylene glycol, although some reduction occurred using formate salts. For most substrates, the reaction rates and yields were comparable in the presence of CuPc and CoPc. In line with these results the ZnPc[441] showed also a comparable activity and selective reduction of substituted nitroarenes with hydrazine was accomplished in PEG-400 at 100 °C. Dinitroarenes were converted to the corresponding nitroaniline, although for 1,2-dinitrobenzene phenyl hydrazine had to be used since 1*H*-benzotriazole was obtained as the main product using N_2H_4. Furthermore, the authors reported that changing the hydride source from hydrazine to $NaBH_4$ selective reduction of ketones at room temperature was accomplished on substrates containing nitro groups.

9. Conclusions and outlook

In the last two decades an enormous interest aroused using non-noble metal catalysts for the synthesis of amines from nitroarenes. Although this classic reduction is a well-established process – first reported in 1842 – it continues to attract scientific and economic interest. On the one hand, both substrates and products constitute highly important intermediates in academic organic synthesis, but also represent valuable industrial intermediates. In fact, aniline and the majority of substituted anilines are produced on large scale by this transformation, which experienced a renaissance period recently. Hence, the majority of the catalytic systems reviewed in this paper were published after 2010.

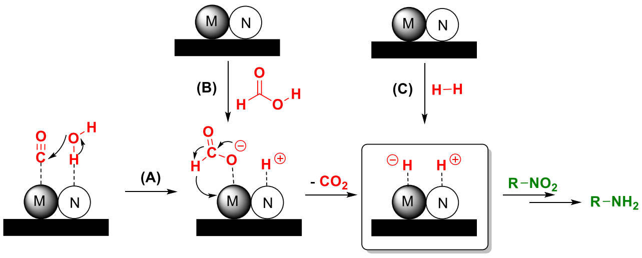
In general, apart from dihydrogen, most of the (more reactive) reducing agents described above are able to convert nitroarenes to amines in the presence of even very simple metal precursors or oxides as catalysts. The synthesis of tailor-made catalytic materials, however, offers the possibility of gaining higher activities and selectivities. Instead, for the activation of dihydrogen, usually more specific systems have to be used. In this regard, for long time the use of non-noble metals for nitroarenes hydrogenation was mainly limited to nickel-based catalysts, especially Raney®-Ni. In recent years, a plethora of catalysts based on Fe, Co, Ni and Cu have been investigated. Concerning the identity of the metal, the lower cost and toxicity of iron compared to other *3d*-metals (i.e. Co, Ni, Cu) makes it the “perfect” candidate for sustainable applications, although reaching a industrially sufficient activity continues to be highly challenging. In addition, due to its comparably low price and toxicity, manganese is a promising candidate for new catalysts design. However, the application of Mn in catalytic systems for nitro reduction is still underdeveloped.

Even though the price of the metal is an important parameter, the most relevant factors for a suitable catalyst for practical applications are activity and stability under operative conditions. However, owing to the conservative attitude of industry towards innovation, the ideal catalyst for an actual application should exhibit its best performance in an already existing plant.

A promising broad class of active catalysts makes use of metal/metal oxide NPs supported onto carbonaceous materials. Worth of note is the high selectivity that can be achieved in particular for transformations involving functional groups. Especially, nitrogen-doping in carbon matrixes became a crucial aspect to exert the activity and tuning the selectivity of many catalysts. However, the role of nitrogen in these materials is rarely well understood and it remains unclear if the doping is important for a specific catalytic event (e.g. dihydrogen activation) or just be a crucial component in the growing process of the NPs. Notably, nitrogen-free carbonaceous materials have been reported to act as catalysts in nitro reductions, too and the carbon layer is claimed to act as protective shell with respect to the NPs.

Both the amount and the type of nitrogen atoms present in the carbon network seem to have an impact on the activity.[68] In more detail, the metal-nitrogen specific configuration suggested in some cases a heterolytic activation of dihydrogen. The hypothesis was also suggested when CO/H_2O[191] or formic acid[187,189] were used as reductants indicating a common activation pathway as described in Figure 54.

Figure 54. Proposed common intermediate for the activation of CO/H_2O (A), formic acid (B) and dihydrogen (C) using metal-containing nitrogen-doped carbon materials.

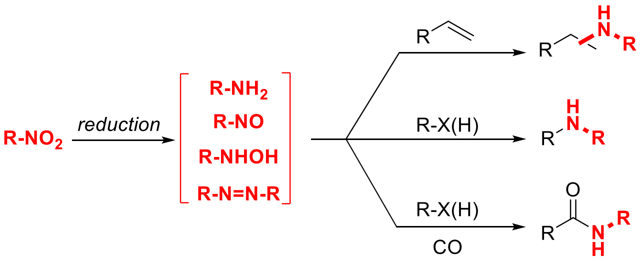


On the other hand, active catalysts based onto undoped carbon supports have been also reported. In this case, the activation of dihydrogen was proposed to occur on the surface of the metal nanoparticle.[174,179,180] Anyhow, despite the high selectivities gained with tailor-made monometallic *3d* systems, the activities often remain lower than those obtained with noble-metal based catalysts. Another strategy towards high efficiency makes use of bimetallic catalytic systems. Through the careful preparation of the catalyst, metal-metal synergies and specific morphologies can be achieved with a remarkable impact on the activity.

Compared to the heterogeneous systems, few homogeneous catalysts were proposed. Most of them display lower activity and only few examples were reported using dihydrogen as the reductant. In addition, in some of the reports the homogeneous nature of the system was not fully examined, especially for ligand-free ones. Owing to the excellent activity and selectivity as well as the recyclability shown by many heterogeneous catalysts described above, the use of a *3d*-metal based homogeneous system for an industrial application to date seems unlikely. Nevertheless, homogeneous catalysts might offer the possibility for coupling the nitro reduction with other transformations. In addition, the properties of molecular complexes can be often tuned and studied more easily and thus continue to be interesting for academic research.

Besides the strong interest in conversion of nitro compounds to primary amines, also selective reductions of nitroarenes to the corresponding *N*-arylhydroxylamines, azo- or azoxyarenes are valuable for industry. In this regard, most of the known catalysts rely on noble metals, especially Pd and Pt (hydrogen) or Ru (CO/H_2O). Therefore, this topic offers multiple opportunities for the development of novel 3*d*-metal catalyst systems. Additionally, other valuable products could be obtained by effecting the reduction of the nitro moiety to other reactive intermediates (such as amino-, nitroso-, hydroxylamino- or azo compounds) in the presence of another molecule that could react in a domino type process. Selected examples are shown in Scheme 46.

Scheme 46. Examples of possible direct use of nitro compounds in domino processes.



In recent years, many groups are gaining interest in these types of reactions. For example, as mentioned in chapter 8.1.3, the groups of Baran[432] and Thomas[430,431] already reported on the selective homogeneous Fe-catalyzed hydroamination of olefins with nitroarenes. In addition, the groups of Hu,[444,445] Wu,[446] Driver[447] and Beller[448] contributed to the field. However, the reduction of the nitro moiety is either stoichiometric or catalyzed by Pd-based systems. Although these transformations would be of high interest regardless to the nature of the employed metal, the use of non-noble based catalysts would be preferable.

To finally conclude, there are some questions that the chemical community should consider: Do specific reductants (borohydrides, silanes, etc.), which are more costly and generate wastes, have an actual chance to be applied? How relevant are investigations of the reductions under batch liquid-phase conditions for addressing the need of industry for new base-metal catalysts? What are the economically feasible conditions for an industrial application? How many of the synthetic procedures described for the catalysts could be scaled up (complexity, reproducibility, availability of starting materials, etc.)? Besides these questions, the field of nitroreductions offers still interesting possibilities for innovation with respect to catalysts and methodologies. We invite you to contribute.

10. Acknowledgments

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11. Abbreviations

AC activated carbon

Acac acetylacetonate

BET Brunauer-Emmett-Teller theory for surface area determination

Boc tert-butyloxycarbonyl

CMC carboxy methylcellulose

CNTs carbon nanotubes

Co-N-C general abbreviation indicating materials composed by Co onto N-doped carbons

CTAB Cetyltrimethylammonium bromide

DABCO 1,4-Diazabicyclo[2.2.2]octane

DANTA Diacetylene-nitrilotriacetic acid amphiphiles

DFT Density functional therory

dmgH dimethylglyoximate monoanion

dmgH_2 dimethylglyoxime

EDG electron donating group/s

EDTA ethylendiaminotetraacetic acid

EDX energy-dispersive X-ray analysis

EWG electron-withdrawing group/s

GO graphene oxide

HAAEMA (2-acetoacetoxy)ethyl methacrylate

(HR)TEM (high resolution) transmission electron microscopy

IL Ionic liquid

LDH layered double hydroxide

MEK mitogen-activated protein kinase kinase

MIm 1-methylimidazole

MOF metal-organic frameworks

MW microwave irradiation

MWCNTs multi-walled carbon nanotubes

N-CNTs nitrogen-doped carbon nanotubes

nacnac anion of *N*,*N*´-diphenylpentane-2,4-diimine

NC nitrogen-doped carbon

Neoc neocuproine (2,9-dimethyl-1,10-phenanthroline)

NP Nitrophenol

NPs nanoparticles

NT nanotube

NW nanowire

Pc phthalocyanine

PDADMAC poly(diallyldimethylammonium chloride)

PEG polyethylene glycol

Phen 1,10-phenanthroline

PNP poly N-vinyl pyrrolidone

PVDF polyvinylidene fluoride

PVP polyvinyl pyrrolidone

r-GO reduced graphene oxide

R-Ni = Raney®-Nickel

SiCN silicon carbonitride

TEMPO 2,2,6,6-tetramethylpiperidin-1-yl)oxyl

TEOS tetraethyl orthosilicate

TMOS tetramethyl orthosilicate

TMDS 1,1,3,3-tetramethyldisiloxane

TPR temperature-programmed reduction

US ultrasound

XAS X-ray adsorption spectroscopy

XPRD X-ray powder diffraction

XPS X-ray photoelectron spectroscopy

ZIF zeolitic imidazolate frameworks

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12.3. Biography

Dario Formenti was born in Milano, Italy in December 1989. After obtaining his Bachelor's Degree (2011) and his Master's Degree (2013) in Industrial Chemistry from Università degli Studi di Milano, in 2014 he started his PhD under the supervision Prof. Fabio Ragaini. His main research topic were reductive carbonylation reactions under CO-free conditions for fine chemicals synthesis and hydrogenation reactions of nitro compounds using both homogeneous and heterogeneous catalysts. After obtaining his PhD in 2017, he moved to Leibniz-Institut für Katalyse (LIKAT, Rostock) working under the supervision of Prof. Matthias Beller and Dr. Kathrin Junge. His currently research topics include the preparation and characterization of noble and non-noble heterogeneous catalysts for reduction and oxidation reactions.

Francesco Ferretti was born in Milano, Italy in 1983. After conducting his undergraduate studies in Chemistry, he started his PhD under the supervision of Prof. Fabio Ragaini at Università degli Studi di Milano. From 2013 to 2017 he was post-doctoral fellow in the same group. The work during this time was mostly devoted to the development of Pd-based catalysts in the reductive and oxidative carbonylation reactions for the production of fine and bulk chemicals. In 2016, he moved to the Leibniz-Institut für Katalyse (LIKAT, Rostock) working under the supervision of Prof. Matthias Beller and Dr. Ralf Jackstell. Currently, his research areas include CO_2 valorization and other transformations through homogeneous and heterogeneous catalysts based on noble and non-noble metals.

Florian Scharnagl was born in 1991 in Munich. He obtained his Bachelor's Degree in 2014 from the University of Würzburg, Germany, under the supervision of Prof. Ingo Fischer. After an ERASMUS-supported stay in the group of Prof. Kosmas Prassides at the Durham University, UK, he joined the group of Prof. Todd B. Marder at the University of Würzburg. There he investigated metal catalyzed borylation reactions, and gained his Master's Degree in 2016. Currently he is conducting his PhD in the group of Prof. Matthias Beller at the Leibniz-Institut für Katalyse (LIKAT, Rostock). His research is comprises both homogeneously and heterogeneously catalyzed hydrogenation and carbonylation reactions.

Matthias Beller, born 1962 in Gudensberg, studied chemistry at the University of Göttingen, Germany, where he completed his PhD thesis in 1989 in the group of L.-F. Tietze. As recipient of a Liebig scholarship, he then spent one-year with K. B. Sharpless at MIT (Massachusetts Institute of Technology), USA. From 1991 to 1995, Beller worked in the industry. Then he moved to the Technical University of Munich as Professor for Inorganic Chemistry. In 1998, he relocated to Rostock to head the Institute for Organic Catalysis, which became the Leibniz-Institut für Katalyse in 2006. The work of his group has been published in nearly 700 original publications and reviews, and >90 patent applications have been filed in the last decade. He has received several awards including the Otto-Roelen Medal and the Leibniz-Prize of the DFG. In 2006, he was also awarded "Entrepreneur of the Year" of Rostock and he received the German Federal Cross of Merit. He received the first "European Prize for Sustainable Chemistry", the "Paul-Rylander Award" of the Organic Reaction Catalysis Society of the USA and the Gay-Lussac-Alexander-von-Humboldt-Prize of the French Academy of Sciences. Matthias Beller is head of the German Chemical Society working group "Sustainable Chemistry" and a member of three German Academies of Sciences including the German National Academia "Leopoldina". He is married to Dr. Anja Fischer-Beller and they have two sons.

13. References

(1) Vogt, P. F.; Gerulis, J. J. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000; p 699.

(2) Roose, P.; Eller, K.; Henkes, E.; Rossbacher, R.; Höke, H. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000; p 1.

(3) Porter, H. K. In *Organic Reactions*; John Wiley & Sons, Inc.: Hoboken, NJ, 2011; p 455.

(4) Wang, Z. In *Comprehensive Organic Name Reactions and Reagents*; Wang, Z., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2010; p 2244.

(5) Wang, Z. In *Comprehensive Organic Name Reactions and Reagents*; Wang, Z., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2010; p 284.

(6) Arpe, H.-J. *Industrial Organic Chemistry*; Wiley-VCH, 2010.

(7) Amini, B.; Lowenkron, S. In *Kirk‐Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc.: Hoboken, NJ, 2003; p 783.

(8) Baumeister, P.; Blaser, H. U.; Scherrer, W. In *Stud. Surf. Sci. Catal.*; Elsevier, 1991; p 321.

(9) Xu, D.-Q.; Hu, Z.-Y.; Li, W.-W.; Luo, S.-P.; Xu, Z.-Y. Hydrogenation in Ionic Liquids: An Alternative Methodology toward Highly Selective Catalysis of Halonitrobenzenes to Corresponding Haloanilines. *J. Mol. Catal. A: Chem.* **2005,** *235*, 137-142.

(10) Wu, G.; Huang, M.; Richards, M.; Poirier, M.; Wen, X.; Draper, R. W. Novel ZnX_2-Modulated Pd/C and Pt/C Catalysts for Chemoselective Hydrogenation and Hydrogenolysis of Halogen-Substituted Nitroarenes, Alkenes, Benzyl Ethers, and Aromatic Ketones. *Synthesis* **2003,** *2003*, 1657-1660.

(11) Rao, P. N.; Peterson, D. M.; Acosta, C. K.; Bahr, M. L.; Kim, H. K. Synthesis of cis and trans-4-Aminocyclohexyl-D-Alanine Derivatives and Determination of their Stereochemistry. *Org. Prep. Proced. Int.* **1991,** *23*, 103-110.

(12) Blaser, H.-U.; Steiner, H.; Studer, M. Selective Catalytic Hydrogenation of Functionalized Nitroarenes: An Update. *ChemCatChem* **2009,** *1*, 210-221.

(13) Blaser, H.-U.; Schnyder, A.; Steiner, H.; Rössler, F.; Baumeister, P. In *Handbook of Heterogeneous Catalysis*; Wiley-VCH Verlag GmbH & Co. KGaA, 2008; p 3284.

(14) Pietrowski, M. Recent developments in Heterogeneous Selective Hydrogenation of Halogenated Nitroaromatic Compounds to Halogenated Anilines. *Curr. Org. Synth.* **2012,** *9*, 470-487.

(15) Blaser, H.-U.; Schnyder, A.; Steiner, H.; Rössler, F.; Baumeister, P. In *Handbook of Heterogeneous Catalysis*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2008; p 3284.

(16) Corma, A.; Serna, P. Chemoselective Hydrogenation of Nitro Compounds with Supported Gold Catalysts. *Science* **2006,** *313*, 332-334.

(17) Corma, A.; Concepción, P.; Serna, P. A Different Reaction Pathway for the Reduction of Aromatic Nitro Compounds on Gold Catalysts. *Angew. Chem. Int. Ed.* **2007,** *46*, 7266-7269.

(18) Boronat, M.; Concepción, P.; Corma, A.; González, S.; Illas, F.; Serna, P. A Molecular Mechanism for the Chemoselective Hydrogenation of Substituted Nitroaromatics with Nanoparticles of Gold on TiO2 Catalysts: A Cooperative Effect between Gold and the Support. *J. Am. Chem. Soc.* **2007,** *129*, 16230-16237.

(19) Chen, Y.; Wang, C.; Liu, H.; Qiu, J.; Bao, X. Ag/SiO_2: A Novel Catalyst with high Activity and Selectivity for Hydrogenation of Chloronitrobenzenes. *Chem. Commun.* **2005**, 5298-5300.

(20) Egorova, K. S.; Ananikov, V. P. Which Metals are Green for Catalysis? Comparison of the Toxicities of Ni, Cu, Fe, Pd, Pt, Rh, and Au Salts. *Angew. Chem. Int. Ed.* **2016,** *55*, 12150-12162.

(21) Wang, D.; Astruc, D. The Recent Development of Efficient Earth-Abundant Transition-Metal Nanocatalysts. *Chem. Soc. Rev.* **2017,** *46*, 816-854.

(22) Pototschnig, G.; Maulide, N.; Schnürch, M. Direct Functionalization of C−H Bonds by Iron, Nickel, and Cobalt Catalysis. *Chem. Eur. J.* **2017,** *23*, 9206-9232.

(23) Kaushik, M.; Moores, A. New Trends in Sustainable Nanocatalysis: Emerging Use of Earth Abundant Metals. *Curr. Opin. Green Sustain. Chem.* **2017,** *7*, 39-45.

(24) Holzwarth, M. S.; Plietker, B. Biorelevant Metals in Sustainable Metal Catalysis—A Survey. *ChemCatChem* **2013,** *5*, 1650-1679.

(25) Shang, R.; Ilies, L.; Nakamura, E. Iron-Catalyzed C–H Bond Activation. *Chem. Rev.* **2017,** *117*, 9086–9139.

(26) Fürstner, A. Iron Catalysis in Organic Synthesis: A Critical Assessment of What It Takes To Make This Base Metal a Multitasking Champion. *ACS Cent. Sci.* **2016,** *2*, 778-789.

(27) Greenhalgh, M. D.; Jones, A. S.; Thomas, S. P. Iron-Catalysed Hydrofunctionalisation of Alkenes and Alkynes. *ChemCatChem* **2015,** *7*, 190-222.

(28) Bauer, I.; Knölker, H.-J. Iron Catalysis in Organic Synthesis. *Chem. Rev.* **2015,** *115*, 3170-3387.

(29) Garbe, M.; Junge, K.; Beller, M. Homogeneous Catalysis by Manganese-Based Pincer Complexes. *Eur. J. Org. Chem.* **2017,** *2017*, 4344-4362.

(30) Carney, J. R.; Dillon, B. R.; Thomas, S. P. Recent Advances of Manganese Catalysis for Organic Synthesis. *Eur. J. Org. Chem.* **2016,** *2016*, 3912-3929.

(31) Kallmeier, F.; Kempe, R. Manganese Complexes for (De)Hydrogenation Catalysis: A Comparison to Cobalt and Iron Catalysts. *Angew. Chem. Int. Ed.* **2018,** *57*, 46-60.

(32) Valyaev, D. A.; Lavigne, G.; Lugan, N. Manganese Organometallic Compounds in Homogeneous Catalysis: Past, Present, and Prospects. *Coord. Chem. Rev.* **2016,** *308*, 191-235.

(33) Moselage, M.; Li, J.; Ackermann, L. Cobalt-Catalyzed C–H Activation. *ACS Catal.* **2016,** *6*, 498-525.

(34) Cahiez, G.; Moyeux, A. Cobalt-Catalyzed Cross-Coupling Reactions. *Chem. Rev.* **2010,** *110*, 1435-1462.

(35) Baumeister, P.; Blaser, H.-U.; Studer, M. Strong Reduction of Hydroxylamine Accumulation in the Catalytic Hydrogenation of Nitroarenes by Vanadium Promoters. *Catal. Lett.* **1997,** *49*, 219-222.

(36) Boymans, E.; Boland, S.; Witte, P. T.; Müller, C.; Vogt, D. Chemoselective Hydrogenation of Functionalized Nitroarenes using Supported Mo Promoted Pt Nanoparticles. *ChemCatChem* **2013,** *5*, 431-434.

(37) Formenti, D.; Topf, C.; Junge, K.; Ragaini, F.; Beller, M. Fe_2O_3/NGr@C- and Co-Co_3O_4/NGr@C-Catalysed Hydrogenation of Nitroarenes under Mild Conditions. *Catal. Sci. Technol.* **2016,** *6*, 4473-4477.

(38) Liu, X.; Ye, S.; Li, H.-Q.; Liu, Y.-M.; Cao, Y.; Fan, K.-N. Mild, Selective and Switchable Transfer Reduction of Nitroarenes Catalyzed by Supported Gold Nanoparticles. *Catal. Sci. Technol.* **2013,** *3*, 3200-3206.

(39) Bolje, A.; Hohloch, S.; Košmrlj, J.; Sarkar, B. RuII, IrIII and OsII Mesoionic Carbene Complexes: Efficient Catalysts for Transfer Hydrogenation of Selected Functionalities. *Dalton Trans.* **2016,** *45*, 15983-15993.

(40) Liu, W.; Zhang, L.; Yan, W.; Liu, X.; Yang, X.; Miao, S.; Wang, W.; Wang, A.; Zhang, T. Single-Atom Dispersed Co-N-C Catalyst: Structure Identification and Performance for Hydrogenative Coupling of Nitroarenes. *Chem. Sci.* **2016,** *7*, 5758-5764.

(41) Srilakshmi, C.; Vijay Kumar, H.; Praveena, K.; Shivakumara, C.; Muralidhar Nayak, M. A Highly Efficient Iron Doped $BaTiO_3$ Nanocatalyst for the Catalytic Reduction of Nitrobenzene to Azoxybenzene. *RSC Adv.* **2014,** *4*, 18881-18884.

(42) Gelder, E. A.; Jackson, S. D.; Lok, C. M. The Hydrogenation of Nitrobenzene to Aniline: A New Mechanism. *Chem. Commun.* **2005**, 522-524.

(43) Furukawa, S.; Takahashi, K.; Komatsu, T. Well-Structured Bimetallic Surface Capable of Molecular Recognition for Chemoselective Nitroarene Hydrogenation. *Chem. Sci.* **2016,** *7*, 4476-4484.

(44) Zhang, L.; Shao, Z.-J.; Cao, X.-M.; Hu, P. Insights into Different Products of Nitrosobenzene and Nitrobenzene Hydrogenation on Pd(111) under Realistic Reaction Conditions. *J. Phys. Chem. C* **2018,** *122*, 20337-20350.

(45) Song, J.; Huang, Z.-F.; Pan, L.; Li, K.; Zhang, X.; Wang, L.; Zou, J.-J. Review on Selective Hydrogenation of Nitroarene by Catalytic, Photocatalytic and Electrocatalytic Reactions. *Appl. Catal., B* **2018,** *227*, 386-408.

(46) Kadam, H. K.; Tilve, S. G. Advancement in Methodologies for Reduction of Nitroarenes. *RSC Adv.* **2015,** *5*, 83391-83407.

(47) Serna, P.; Corma, A. Transforming Nano Metal Nonselective Particulates into Chemoselective Catalysts for Hydrogenation of Substituted Nitrobenzenes. *ACS Catal.* **2015**, *5*, 7114-7121.

(48) Goksu, H.; Sert, H.; Kilbas, B.; Sen, F. Recent Advances in the Reduction of Nitro Compounds by Heterogenous Catalysts. *Curr. Org. Chem.* **2017,** *21*, 794-820.

(49) Sedghi, R.; Heravi, M. M.; Asadi, S.; Nazari, N.; Nabid, M. R. Recently Used Nanocatalysts in Reduction of Nitroarenes. *Curr. Org. Chem.* **2016,** *20*, 696-734.

(50) Orlandi, M.; Brenna, D.; Harms, R.; Jost, S.; Benaglia, M. Recent Developments in the Reduction of Aromatic and Aliphatic Nitro Compounds to Amines. *Org. Process Res. Dev.* **2018,** *22*, 430-445.

(51) Zhao, P.; Feng, X.; Huang, D.; Yang, G.; Astruc, D. Basic Concepts and Recent Advances in Nitrophenol Reduction by Gold- and other Transition Metal Nanoparticles. *Coord. Chem. Rev.* **2015,** *287*, 114-136.

(52) Lara, P.; Philippot, K. The Hydrogenation of Nitroarenes Mediated by Platinum Nanoparticles: an Overview. *Catal. Sci. Technol.* **2014,** *4*, 2445-2465.

(53) Naseem, K.; Begum, R.; Farooqi, Z. H. Catalytic Reduction of 2-Nitroaniline: a Review. *Environ. Sci. Pollut. Res.* **2017,** *24*, 6446-6460.

(54) Li, B.; Sortais, J.-B.; Darcel, C. Amine Synthesis via Transition Metal Homogeneous Catalysed Hydrosilylation. *RSC Adv.* **2016,** *6*, 57603-57625.
(55) Puylaert, P.; Savini, A.; Hinze, S. In *Catalytic Reduction in Organic Synthesis 2*; Georg Thieme Verlag: Stuttgart, Germany, 2018; p 331.
(56) Peng, J.-B.; Qi, X.; Wu, X.-F. Recent Achievements in Carbonylation Reactions: A Personal Account. *Synlett* **2017,** *28*, 175-194.
(57) Wu, L.; Liu, Q.; Jackstell, R.; Beller, M. Carbonylations of Alkenes with CO Surrogates. *Angew. Chem. Int. Ed.* **2014,** *53*, 6310-6320.
(58) Morimoto, T.; Kakiuchi, K. Evolution of Carbonylation Catalysis: No Need for Carbon Monoxide. *Angew. Chem. Int. Ed.* **2004,** *43*, 5580-5588.
(59) Taleb, A. B.; Jenner, G. Catalytic Reduction of Nitrobenzene to Aniline with Aqueous Methyl Formate. *J. Organomet. Chem.* **1993,** *456*, 263-269.
(60) Ragaini, F. Away from Phosgene: Reductive Carbonylation of Nitroarenes and Oxidative Carbonylation of Amines, Understanding the Mechanism to Improve Performance. *Dalton Trans.* **2009**, 6251-6266.
(61) Tafesh, A. M.; Weiguny, J. A Review of the Selective Catalytic Reduction of Aromatic Nitro Compounds into Aromatic Amines, Isocyanates, Carbamates, and Ureas Using CO. *Chem. Rev.* **1996,** *96*, 2035-2052.
(62) Ragaini, F.; Cenini, S.; Gallo, E.; Caselli, A.; Fantauzzi, S. Fine Chemicals by Reductive Carbonylation of Nitroarenes, Catalyzed by Transition Metal Complexes. *Curr. Org. Chem.* **2006,** *10*, 1479-1510.
(63) Ferretti, F.; Formenti, D.; Ragaini, F. The Reduction of Organic Nitro Compounds by Carbon Monoxide as an Effective Strategy for the Synthesis of N-Heterocyclic Compounds: a Personal Account. *Rend. Fis. Acc. Lincei* **2017,** *28*, 97-115.
(64) Tsygankov, A. A.; Makarova, M.; Chusov, D. Carbon Monoxide as a Selective Reducing Agent in Organic Chemistry. *Mendeleev Commun.* **2018,** *28*, 113-122.
(65) S. Srivastava, R.; M. Nicholas, K. Iron-Catalyzed Allylic Amination by Nitroorganics. *Chem. Commun.* **1998**, 2705-2706.
(66) Pasto, D. J.; Taylor, R. T. In *Organic Reactions*; John Wiley & Sons, Inc.: Hoboken, NJ, 2004; p 91.
(67) Wang, D.; Deraedt, C.; Ruiz, J.; Astruc, D. Sodium Hydroxide-Catalyzed Transfer Hydrogenation of Carbonyl Compounds and Nitroarenes using Ethanol or Isopropanol as both Solvent and Hydrogen Donor. *J. Mol. Catal. A: Chem.* **2015,** *400*, 14-21.
(68) Formenti, D.; Ferretti, F.; Topf, C.; Surkus, A.-E.; Pohl, M.-M.; Radnik, J.; Schneider, M.; Junge, K.; Beller, M.; Ragaini, F. Co-Based Heterogeneous Catalysts from Well-Fefined α-Diimine Complexes: Discussing the Role of Nitrogen. *J. Catal.* **2017,** *351*, 79-89.
(69) Aditya, T.; Pal, A.; Pal, T. Nitroarene Reduction: A Trusted Model Reaction to Test Nanoparticle Catalysts. *Chem. Commun.* **2015,** *51*, 9410-9431.
(70) Mitchell, S. C.; Waring, R. H. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000; p 59.
(71) Sordakis, K.; Tang, C.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M.; Laurenczy, G. Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols. *Chem. Rev.* **2018,** *118*, 372-433.
(72) Nagai, Y. Hydrosilanes as Reducing Agents. A Review. *Org. Prep. Proced. Int.* **1980,** *12*, 13-48.
(73) Liu, Y.; Lu, Y.; Prashad, M.; Repič, O.; Blacklock, T. J. A Practical and Chemoselective Reduction of Nitroarenes to Anilines Using Activated Iron. *Adv. Synth. Catal.* **2005,** *347*, 217-219.
(74) Chandrappa, S.; Vinaya, K.; Ramakrishnappa, T.; Rangappa, K. S. An Efficient Method for Aryl Nitro Reduction and Cleavage of Azo Compounds Using Iron Powder/Calcium Chloride. *Synlett* **2010,** *2010*, 3019-3022.
(75) Korich, A. L.; Hughes, T. S. A Facile, One-Pot Procedure for Forming Diarylimines from Nitroarenes and Benzaldehydes. *Synlett* **2007**, 2602-2604.
(76) Agrawal, A.; Tratnyek, P. G. Reduction of Nitro Aromatic Compounds by Zero-Valent Iron Metal. *Environ. Sci. Technol.* **1995,** *30*, 153-160.
(77) Jagadeesh, R. V.; Surkus, A.-E.; Junge, H.; Pohl, M.-M.; Radnik, J.; Rabeah, J.; Huan, H.; Schünemann, V.; Brückner, A.; Beller, M. Nanoscale Fe_2O_3-Based Catalysts for Selective Hydrogenation of Nitroarenes to Anilines. *Science* **2013,** *342*, 1073-1076.

(78) Jagadeesh, R. V.; Stemmler, T.; Surkus, A.-E.; Junge, H.; Junge, K.; Beller, M. Hydrogenation Using Iron Oxide–Based Nanocatalysts for the Synthesis of Amines. *Nat. Protocols* **2015,** *10*, 548-557.

(79) Stemmler, T.; Surkus, A.-E.; Pohl, M.-M.; Junge, K.; Beller, M. Iron-Catalyzed Synthesis of Secondary Amines: On the Way to Green Reductive Aminations. *ChemSusChem* **2014,** *7,* 3012-3016.

(80) Chen, J.; Yao, Y.; Zhao, J.; Zhao, Y. P.; Zheng, Y. Y.; Li, M. R.; Yang, Q. H. A Highly Active Non-Precious Metal Catalyst Based on Fe-N-C@CNTs for Nitroarene Reduction. *RSC Adv.* **2016,** *6*, 96203-96209.

(81) Shi, J.; Wang, Y.; Du, W.; Hou, Z. Synthesis of Graphene Encapsulated Fe_3C in Carbon Nanotubes from Biomass and its Catalysis Application. *Carbon* **2016,** *99*, 330-337.

(82) Wei, Z.; Wang, J.; Mao, S.; Su, D.; Jin, H.; Wang, Y.; Xu, F.; Li, H.; Wang, Y. In Situ-Generated Co^0-Co_3O_4/N-Doped Carbon Nanotubes Hybrids as Efficient and Chemoselective Catalysts for Hydrogenation of Nitroarenes. *ACS Catal.* **2015,** *5*, 4783-4789.

(83) Xu, S.; Yu, D.; Liao, S.; Ye, T.; Sheng, H. Nitrogen-Doped Carbon Supported Iron Oxide as Efficient Catalysts for Chemoselective Hydrogenation of Nitroarenes. *RSC Adv.* **2016,** *6*, 96431-96435.

(84) Sahoo, B.; Formenti, D.; Topf, C.; Bachmann, S.; Scalone, M.; Junge, K.; Beller, M. Biomass-Derived Catalysts for Selective Hydrogenation of Nitroarenes. *ChemSusChem* **2017,** *10*, 3035-3039.

(85) Wang, Y.; Shi, J.; Zhang, Z.; Fu, J.; Lü, X.; Hou, Z. Carbon Film Encapsulated Fe_2O_3: An Efficient Catalyst for Hydrogenation of Nitroarenes. *Chinese J. Catal.* **2017,** *38*, 1909-1917.

(86) Ma, B.; Tong, X.; Guo, C.; Guo, X.; Guo, X.; Keil, F. J. Pyrite Nanoparticles: an Earth-Abundant Mineral Catalyst for Activation of Molecular Hydrogen and Hydrogenation of Nitroaromatics. *RSC Adv.* **2016,** *6*, 55220-55224.

(87) Morse, J. R.; Callejas, J. F.; Darling, A. J.; Schaak, R. E. Bulk Iron Pyrite as a Catalyst for the Selective Hydrogenation of Nitroarenes. *Chem. Commun.* **2017,** *53*, 4807-4810.

(88) Niu, H.; Lu, J.; Song, J.; Pan, L.; Zhang, X.; Wang, L.; Zou, J.-J. Iron Oxide as a Catalyst for Nitroarene Hydrogenation: Important Role of Oxygen Vacancies. *Ind. Eng. Chem. Res.* **2016,** *55*, 8527-8533.

(89) Hirashima, T.; Manabe, O. Catalytic Reduction of Aromatic Nitro Compounds with Hydrazine in the Presence of Iron(III) Chloride and Active Carbon. *Chem. Lett.* **1975,** *4*, 259-260.

(90) Miyata, T.; Ishino, Y.; Hirashima, T. Catalytic Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate in the Presence of Iron(III) Oxide Hydroxide. *Synthesis* **1978,** *1978*, 834-835.

(91) Ayyangar, N. R.; Lugade, A. G.; Nikrad, P. V.; Sharma, V. K. Catalytic Reduction of Nitroarenes with Hydrazine Hydrate in Suitable Solvents. *Synthesis* **1981,** *1981*, 640-643.

(92) Benz, M.; van der Kraan, A. M.; Prins, R. Reduction of Aromatic Nitrocompounds with Hydrazine Hydrate in the Presence of an Iron Oxide Hydroxide Catalyst: II. Activity, X-ray Diffraction and Mössbauer Study of the Iron Oxide Hydroxide Catalyst. *Appl. Catal., A* **1998,** *172*, 149-157.

(93) Benz, M.; Prins, R. Kinetics of the Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate in the Presence of an Iron Oxide Hydroxide Catalyst. *Appl. Catal., A* **1999,** *183*, 325-333.

(94) Jambor, J. L.; Dutrizac, J. E. Occurrence and Constitution of Natural and Synthetic Ferrihydrite, a Widespread Iron Oxyhydroxide. *Chem. Rev.* **1998,** *98*, 2549-2586.

(95) Lauwiner, M.; Rys, P.; Wissmann, J. Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate in the Presence of an Iron Oxide Hydroxide Catalyst. I. The Reduction of Monosubstituted Nitrobenzenes with Hydrazine Hydrate in the Presence of Ferrihydrite. *Appl. Catal., A* **1998,** *172*, 141-148.

(96) Lauwiner, M.; Roth, R.; Rys, P. Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate in the Presence of an Iron Oxide/Hydroxide Catalyst. III. The Selective Reduction of Nitro Groups in Aromatic Azo Compounds. *Appl. Catal., A* **1999,** *177*, 9-14.

(97) Merino, E. Synthesis of Azobenzenes: the Coloured Pieces of Molecular Materials. *Chem. Soc. Rev.* **2011,** *40*, 3835-3853.

(98) Shi, Q.; Lu, R.; Jin, K.; Zhang, Z.; Zhao, D. Simple and Eco-Friendly Reduction of Nitroarenes to the Corresponding Aromatic Amines using Polymer-Supported Hydrazine Hydrate over Iron Oxide Hydroxide Catalyst. *Green Chem.* **2006,** *8*, 868-870.

(99) Vass, A.; Dudas, J.; Toth, J.; Varma, R. S. Solvent-Free Reduction of Aromatic Nitro Compounds with Alumina-Supported Hydrazine Under Microwave Irradiation. *Tetrahedron Lett.* **2001,** *42,* 5347-5349.

(100) Kumbhar, P. S.; Sanchez-Valente, J.; Figueras, F. Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate in the Presence of the Iron(III) Oxide-MgO Catalyst Prepared from a Mg-Fe Hydrotalcite Precursor. *Tetrahedron Lett.* **1998,** *39*, 2573-2574.

(101) Kumbhar, P. S.; Sanchez-Valente, J.; Millet, J. M. M.; Figueras, F. Mg-Fe Hydrotalcite as a Catalyst for the Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate. *J. Catal.* **2000,** *191*, 467-473.

(102) Kim, S.; Kim, E.; Kim, B. M. Fe_3O_4 Nanoparticles: A Conveniently Reusable Catalyst for the Reduction of Nitroarenes Using Hydrazine Hydrate. *Chem. Asian J.* **2011,** *6*, 1921-1925.

(103) Datta, K. J.; Rathi, A. K.; Kumar, P.; Kaslik, J.; Medrik, I.; Ranc, V.; Varma, R. S.; Zboril, R.; Gawande, M. B. Synthesis of Flower-Like Magnetite Nanoassembly: Application in the Efficient Reduction of Nitroarenes. *Sci. Rep.* **2017,** *7*, 11585.

(104) He, G.; Liu, W.; Sun, X.; Chen, Q.; Wang, X.; Chen, H. Fe_3O_4@Graphene Oxide Composite: A Magnetically Separable and Efficient Catalyst for the Reduction of Nitroarenes. *Mater. Res. Bull.* **2013,** *48*, 1885-1890.

(105) Feng, C.; Zhang, H.-Y.; Shang, N.-Z.; Gao, S.-T.; Wang, C. Magnetic Graphene Nanocomposite as an Efficient Catalyst for Hydrogenation of Nitroarenes. *Chin. Chem. Lett.* **2013,** *24,* 539-541.

(106) Gao, Y.; Ma, D.; Wang, C.; Guan, J.; Bao, X. Reduced Graphene Oxide as a Catalyst for Hydrogenation of Nitrobenzene at Room Temperature. *Chem. Commun.* **2011,** *47,* 2432-2434.

(107) Larsen, J. W.; Freund, M.; Kim, K. Y.; Sidovar, M.; Stuart, J. L. Mechanism of the Carbon Catalyzed Reduction of Nitrobenzene by Hydrazine. *Carbon* **2000,** *38,* 655-661.

(108) Byung, H. H.; Dae, H. S.; Sung, Y. C. Graphite Catalyzed Reduction of Aromatic and Aliphatic Nitro Compounds with Hydrazine Hydrate. *Tetrahedron Lett.* **1985,** *26*, 6233-6234.

(109) Cantillo, D.; Baghbanzadeh, M.; Kappe, C. O. In Situ Generated Iron Oxide Nanocrystals as Efficient and Selective Catalysts for the Reduction of Nitroarenes using a Continuous Flow Method. *Angew. Chem. Int. Ed.* **2012,** *51*, 10190-10193.

(110) Cantillo, D.; Moghaddam, M. M.; Kappe, C. O. Hydrazine-mediated Reduction of Nitro and Azide Functionalities Catalyzed by Highly Active and Reusable Magnetic Iron Oxide Nanocrystals. *J. Org. Chem.* **2013,** *78*, 4530-4542.

(111) Moghaddam, M. M.; Pieber, B.; Glasnov, T.; Kappe, C. O. Immobilized Iron Oxide Nanoparticles as Stable and Reusable Catalysts for Hydrazine-Mediated Nitro Reductions in Continuous Flow. *ChemSusChem* **2014,** *7*, 3122-3131.

(112) Gu, X.; Sun, Z.; Wu, S.; Qi, W.; Wang, H.; Xu, X.; Su, D. Surfactant-Free Hydrothermal Synthesis of sub-10 nm γ-Fe_2O_3-Polymer Porous Composites with High Catalytic Activity for Reduction of Nitroarenes. *Chem. Commun.* **2013,** *49*, 10088-10090.

(113) Ai, Y.; He, M.; Lv, Q.; Liu, L.; Sun, H.-b.; Ding, M.; Liang, Q. 3D Porous Carbon Framework Stabilized Ultra-Uniform Nano γ-Fe2O3: A Useful Catalyst System. *Chem. Asian J.* **2018,** *13*, 89-98.

(114) Li, Y.; Zhou, Y.-X.; Ma, X.; Jiang, H.-L. A Metal-Organic Framework-Ttemplated Synthesis of g-Fe_2O_3 Nanoparticles Encapsulated in Porous Carbon for Efficient and Chemoselective Hydrogenation of Nitro Compounds. *Chem. Commun.* **2016,** *52,* 4199-4202.

(115) Tian, M.; Cui, X.; Yuan, M.; Yang, J.; Ma, J.; Dong, Z. Efficient Chemoselective Hydrogenation of Halogenated Nitrobenzenes over an Easily Prepared γ-Fe2O3-Modified Mesoporous Carbon Catalyst. *Green Chem.* **2017,** *19*, 1548-1554.

(116) Tian, M.; Cui, X.; Liang, K.; Ma, J.; Dong, Z. Efficient and Chemoselective Hydrogenation of Nitroarenes by γ-Fe_2O_3 Modified Hollow Mesoporous Carbon Microspheres. *Inorg. Chem. Front.* **2016,** *3*, 1332-1340.

(117) Jagadeesh, R. V.; Wienhofer, G.; Westerhaus, F. A.; Surkus, A.-E.; Pohl, M.-M.; Junge, H.; Junge, K.; Beller, M. Efficient and Highly Selective Iron-Catalyzed Reduction of Nitroarenes. *Chem. Commun.* **2011,** *47,* 10972-10974.

(118) Cui, X.; Zhang, Q.; Tian, M.; Dong, Z. Facile fabrication of γ-Fe_2O_3-Nanoparticle Modified N-Doped Porous Carbon Materials for the Efficient Hydrogenation of Nitroaromatic Compounds. *New J. Chem.* **2017,** *41*, 10165-10173.

(119) Papadas, I. T.; Fountoulaki, S.; Lykakis, I. N.; Armatas, G. S. Controllable Synthesis of Mesoporous Iron Oxide Nanoparticle Assemblies for Chemoselective Catalytic Reduction of Nitroarenes. *Chem. - Eur. J.* **2016,** *22*, 4600-4607.

(120) Dementyev, P.; Dostert, K.-H.; Ivars-Barceló, F.; O'Brien, C. P.; Mirabella, F.; Schauermann, S.; Li, X.; Paier, J.; Sauer, J.; Freund, H.-J. Water Interaction with Iron Oxides. *Angew. Chem. Int. Ed.* **2015,** *54*, 13942-13946.

(121) Rim, K. T.; Eom, D.; Chan, S.-W.; Flytzani-Stephanopoulos, M.; Flynn, G. W.; Wen, X.-D.; Batista, E. R. Scanning Tunneling Microscopy and Theoretical Study of Water Adsorption on Fe_3O_4: Implications for Catalysis. *J. Am. Chem. Soc.* **2012,** *134*, 18979-18985.

(122) Yamamoto, S.; Kendelewicz, T.; Newberg, J. T.; Ketteler, G.; Starr, D. E.; Mysak, E. R.; Andersson, K. J.; Ogasawara, H.; Bluhm, H.; Salmeron, M.et al. Water Adsorption on α-Fe_2O_3(0001) at near Ambient Conditions. *J. Phys. Chem. C* **2010,** *114*, 2256-2266.

(123) Cui, X.; Zhou, X.; Dong, Z. Ultrathin γ-Fe_2O_3 Nanosheets as a Highly Efficient Catalyst for the Chemoselective Hydrogenation of Nitroaromatic Compounds. *Catal. Commun.* **2018,** *107*, 57-61.

(124) Beswick, O.; Yuranov, I.; Alexander, D. T. L.; Kiwi-Minsker, L. Iron Oxide Nanoparticles Supported on Activated Carbon Fibers Catalyze Chemoselective Reduction of Nitroarenes under Mild Conditions. *Catal. Today* **2015,** *249*, 45-51.

(125) Beswick, O.; Lamey, D.; Muriset, F.; LaGrange, T.; Oberson, L.; Yoon, S.; Sulman, E.; Dyson, P. J.; Kiwi-Minsker, L. Ni-based Structured Catalyst for Selective 3-Phase Hydrogenation of Nitroaromatics. *Catal. Today* **2016,** *273*, 244-251.

(126) Beswick, O.; Parastaev, A.; Yuranov, I.; LaGrange, T.; Dyson, P. J.; Kiwi-Minsker, L. Highly Dispersed Cobalt Oxides Nanoparticles on Activated Carbon Fibres as Efficient Structured Catalysts for the Transfer Hydrogenation of *m*-Nitrostyrene. *Catal. Today* **2017,** *279*, 29-35.

(127) Sun, H.-b.; Ai, Y.; Li, D.; Tang, Z.; Shao, Z.; Liang, Q. Bismuth Iron Oxide Nanocomposite Supported on Graphene Oxides as the High Efficient, Stable and Reusable Catalysts for the Reduction of Nitroarenes under Continuous Flow Conditions. *Chem. Eng. J.* **2017,** *314*, 328-335.

(128) Ai, Y.; Liu, L.; Jing, K.; Qi, L.; Fan, Z.; Zhou, J.; Sun, H.-b.; Shao, Z.; Liang, Q. Noncovalently Functionalized Carbon Nanotubes Immobilized Fe-Bi Bimetallic Oxides as a Heterogeneous Nanocatalyst for Reduction of Nitroaromatics. *Nano-Struct. Nano-Objects* **2017,** *10*, 116-124.

(129) Bhoi, Y. P.; Mishra, B. G. Single Step Combustion Synthesis, Characterization and Photocatalytic Application of α-Fe_2O_3-Bi_2S_3 Heterojunctions for Efficient and Selective Reduction of Structurally Diverse Nitroarenes. *Chem. Eng. J.* **2017,** *316*, 70-81.

(130) Qi, L.; Li, Y.; Liu, L.; Zhou, J.; Ai, Y.; Tang, Z.; Wang, J.; Bao, H.; Zhang, C.; Liang, Q.et al. Immobilizing Multifunctional Fe_2O_3-SnO_2 Nanoparticles to Carbon Nanospheres: An Extremely Active and Selective Catalyst for Hydrogen Transfer Reaction. *ChemistrySelect* **2017,** *2*, 8288-8295.

(131) Sonavane, S. U.; Mohapatra, S. K.; Jayaram, R. V.; Selvam, P. Catalytic Transfer Hydrogenation of Nitro and Carbonyl Compounds over Novel Fe(III) Substituted Hexagonal Mesoporous Aluminophosphates. *Chem. Lett.* **2003,** *32*, 142-143.

(132) Mohapatra, S. K.; Sonavane, S. U.; Jayaram, R. V.; Selvam, P. Reductive Cleavage of Azo Dyes and Reduction of Nitroarenes over Trivalent Iron Incorporated Hexagonal Mesoporous Aluminophosphate Molecular sieves. *Appl. Catal., B* **2003,** *46*, 155-163.

(133) Ouali, A.; Majoral, J. P.; Caminade, A. M.; Taillefer, M. NaOH-Promoted Hydrogen Transfer: Does NaOH or Traces of Transition Metals Catalyze the Reaction? *ChemCatChem* **2009,** *1*, 504-509.

(134) Polshettiwar, V.; Varma, R. S. Revisiting the Meerwein-Ponndorf-Verley Reduction: a Sustainable Protocol for Transfer Hydrogenation of Aldehydes and Ketones. *Green Chem.* **2009,** *11*, 1313-1316.

(135) Veerakumar, P.; Muthuselvam, I. P.; Hung, C. T.; Lin, K. C.; Chou, F. C.; Liu, S. B. Biomass-Derived Activated Carbon Supported Fe_3O_4 Nanoparticles as Recyclable Catalysts for Reduction of Nitroarenes. *ACS Sustain. Chem. Eng.* **2016,** *4*, 6772-6782.

(136) Sanjini, N. S.; Velmathi, S. Iron impregnated SBA-15, a Mild and Efficient Catalyst for the Catalytic Hydride Transfer Reduction of Aromatic Nitro Compounds. *RSC Adv.* **2014,** *4*, 15381-15388.

(137) Kulkarni, A. S.; Jayaram, R. V. Liquid Phase Catalytic Transfer Hydrogenation of Aromatic Nitro Compounds on Perovskites Prepared by Microwave Irradiation. *Appl. Catal., A* **2003,** *252*, 225-230.

(138) Farhadi, S.; Siadatnasab, F. Perovskite-type $LaFeO_3$ Nanoparticles Prepared by Thermal Decomposition of the $La[Fe(CN)_6]\cdot 5H_2O$ Complex: A New Reusable Catalyst for Rapid and Efficient Reduction of Aromatic Nitro Compounds to Arylamines with Propan-2-ol under Microwave Irradiation. *J. Mol. Catal. A: Chem.* **2011,** *339*, 108-116.

(139) Bae, S.; Gim, S.; Kim, H.; Hanna, K. Effect of $NaBH_4$ on Properties of Nanoscale Zero-Valent Oron and its Catalytic Activity for Reduction of *p*-Nitrophenol. *Appl. Catal., B* **2016,** *182*, 541-549.

(140) He, S.; Niu, H.; Zeng, T.; Wang, S.; Cai, Y. A Facile and Efficient Method for Continuous Reduction of Nitroaromatic Compounds Through the Cyclic Transformation Between Fe(II)-complexes and Nano Zero-valent Iron. *ChemistrySelect* **2016,** *1*, 2821-2825.

(141) Zhang, X.; Chen, L.; Yun, J.; Wang, X.; Kong, J. Constructing Magnetic Si-C-Fe Hybrid Microspheres for Room Temperature Nitroarenes Reduction. *J. Mater. Chem., A* **2017,** *5*, 10986-10997.

(142) Zeng, T.; Hu, X.; Feng, H.; Zhang, H.; Chen, J.; Song, S. Rational Design of Double-Shelled Fe-, N-, and S-Tridoped Hollow Mesoporous Carbon Spheres as High-Performance Catalyst for Organic Reaction. *Chem. Commun.* **2018,** *54*, 2974-2977.

(143) Wang, C. L.; Salmon, L.; Ciganda, R.; Yate, L.; Moya, S.; Ruiz, J.; Astruc, D. An Efficient Parts-per-Million α-Fe_2O_3 Nanocluster/Graphene Oxide Catalyst for Suzuki-Miyaura Coupling Reactions and 4-Nitrophenol Reduction in Aqueous Solution. *Chem. Commun.* **2017,** *53*, 644-646.

(144) Datta, K. J.; Rathi, A. K.; Gawande, M. B.; Ranc, V.; Zoppellaro, G.; Varma, R. S.; Zboril, R. Base-Free Transfer Hydrogenation of Nitroarenes Catalyzed by Micro-Mesoporous Iron Oxide. *ChemCatChem* **2016,** *8*, 2351-2355.

(145) Wienhofer, G.; Sorribes, I.; Boddien, A.; Westerhaus, F.; Junge, K.; Junge, H.; Llusar, R.; Beller, M. General and Selective Iron-Catalyzed Transfer Hydrogenation of Nitroarenes without Base. *J. Am. Chem. Soc.* **2011,** *133*, 12875-12879.

(146) Choudary, B. M.; Kantam, M. L.; Ranganath, K. V. S.; Rao, K. K. Hydrogen Processing by FeIII-Exchanged Montmorillonite: A Unique Geochemical Protocol. *Angew. Chem. Int. Ed.* **2005,** *44*, 322-325.

(147) Natte, K.; Neumann, H.; Jagadeesh, R. V.; Beller, M. Convenient Iron-Catalyzed Reductive Aminations Without Hydrogen for Selective Synthesis of N-Nethylamines. *Nat. Commun.* **2017,** *8*, 1344.

(148) Brown, O. W.; Henke, C. O. Catalytic Preparation of Aniline. II. *J. Phys. Chem.* **1921,** *26*, 272-287.

(149) Griffitts, F. A.; Brown, O. W. The Catalytic Activity of Cobalt Sulfide for the Gas-phase Reduction of Nitro benzene to Aniline. *J. Phys. Chem.* **1937,** *41*, 477-484.

(150) Braden, R.; Knupfer, H.; Ziemann, H.; Bayer A.-G. 1975. German Patent DE2362780, 1975.

(151) Raja, R.; Golovko, V. B.; Thomas, J. M.; Berenguer-Murcia, A.; Zhou, W.; Xie, S.; Johnson, B. F. G. Highly Efficient Catalysts for the Hydrogenation of Nitro-Substituted Aromatics. *Chem. Commun.* **2005**, 2026-2028.

(152) Westerhaus, F. A.; Jagadeesh, R. V.; Wienhöfer, G.; Pohl, M.-M.; Radnik, J.; Surkus, A.-E.; Rabeah, J.; Junge, K.; Junge, H.; Nielsen, M.et al. Heterogenized Cobalt Oxide Catalysts for Nitroarene Reduction by Pyrolysis of Molecularly Defined Complexes. *Nat. Chem.* **2013,** *5*, 537-543.

(153) Jagadeesh, R. V.; Stemmler, T.; Surkus, A.-E.; Bauer, M.; Pohl, M.-M.; Radnik, J.; Junge, K.; Junge, H.; Bruckner, A.; Beller, M. Cobalt-Based Nanocatalysts for Green Oxidation and Hydrogenation Processes. *Nat. Protocols* **2015,** *10*, 916-926.

(154) Formenti, D.; Topf, C.; Junge, K.; Ragaini, F.; Beller, M. Fe_2O_3/NGr@C- and Co-Co_3O_4/NGr@C-Catalysed Hydrogenation of Nitroarenes under Mild Conditions. *Catal. Sci. Technol.* **2016,** *6*, 4473-4477.

(155) Stemmler, T.; Westerhaus, F. A.; Surkus, A.-E.; Pohl, M.-M.; Junge, K.; Beller, M. General and Selective Reductive Amination of Carbonyl Compounds Using a Core-sShell Structured Co_3O_4/NGr@C catalyst. *Green Chem.* **2014,** *16*, 4535-4540.

(156) Chen, P.; Yang, F.; Kostka, A.; Xia, W. Interaction of Cobalt Nanoparticles with Oxygen- and Nitrogen-Functionalized Carbon Nanotubes and Impact on Nitrobenzene Hydrogenation Catalysis. *ACS Catal.* **2014,** *4*, 1478-1486.

(157) Schwob, T.; Kempe, R. A Reusable Co Catalyst for the Selective Hydrogenation of Functionalized Nitroarenes and the Direct Synthesis of Imines and Benzimidazoles from Nitroarenes and Aldehydes. *Angew. Chem. Int. Ed.* **2016,** *55*, 15175-15179.

(158) Eckardt, M.; Zaheer, M.; Kempe, R. Nitrogen-Doped Mesoporous SiC Materials with Catalytically Active Cobalt Nanoparticles for the Efficient and Selective Hydrogenation of Nitroarenes. *Sci. Rep.* **2018,** *8*, 2567.

(159) Cui, X.; Liang, K.; Tian, M.; Zhu, Y.; Ma, J.; Dong, Z. Cobalt Nanoparticles Supported on N-Doped Mesoporous Carbon as Highly Efficient Catalyst for Synthesis of Aromatic Amines. *J. Colloid Interface Sci.* **2017,** *501*, 231-240.

(160) Sahoo, B.; Surkus, A.-E.; Pohl, M.-M.; Radnik, J.; Schneider, M.; Bachmann, S.; Scalone, M.; Junge, K.; Beller, M. A Biomass-Derived Non-Noble Cobalt Catalyst for Selective Hydrodehalogenation of Alkyl and (Hetero)Aryl Halides. *Angew. Chem. Int. Ed.* **2017,** *56*, 11242-11247.

(161) Wang, X.; Li, Y. Chemoselective Hydrogenation of Functionalized Nitroarenes Using MOF-Derived Co-Based Catalysts. *J. Mol. Catal. A: Chem.* **2016,** *420*, 56-65.

(162) Sun, X.; Olivos-Suarez, A. I.; Oar-Arteta, L.; Rozhko, E.; Osadchii, D.; Bavykina, A.; Kapteijn, F.; Gascon, J. Metal-Organic Framework Mediated Cobalt/Nitrogen-Doped Carbon Hybrids as Efficient and Chemoselective Catalysts for the Hydrogenation of Nitroarenes. *ChemCatChem* **2017,** *9*, 1854-1862.

(163) Cheng, T.; Yu, H.; Peng, F.; Wang, H.; Zhang, B.; Su, D. Identifying Active Sites of CoNC/CNT From Pyrolysis of Molecularly Defined Complexes for Oxidative Esterification and Hydrogenation Reactions. *Catal. Sci. Technol.* **2016,** *6*, 1007-1015.

(164) Sun, X.; Olivos-Suarez, A. I.; Osadchii, D.; Romero, M. J. V.; Kapteijn, F.; Gascon, J. Single Cobalt Sites in Mesoporous N-Doped Carbon Matrix for Selective Catalytic Hydrogenation of Nitroarenes. *J. Catal.* **2017,** *357*, 20-28.

(165) Zhang, F.; Zhao, C.; Chen, S.; Li, H.; Yang, H.; Zhang, X.-M. In Situ Mosaic Strategy Generated Co-Based N-Doped Mesoporous Carbon for Highly Selective Hydrogenation of Nitroaromatics. *J. Catal.* **2017,** *348*, 212-222.

(166) Zhou, P.; Jiang, L.; Wang, F.; Deng, K.; Lv, K.; Zhang, Z. High Performance of a Cobalt–Nitrogen Complex for the Reduction and Reductive Coupling of Nitro Compounds into Amines and -their Derivatives. *Sci. Adv.* **2017,** *3*, e1601945.

(167) Jiang, L.; Zhou, P.; Zhang, Z.; Chi, Q.; Jin, S. Environmentally Friendly Synthesis of Secondary Amines via One-Pot Reductive Amination over a Heterogeneous Co-N_x Catalyst. *New J. Chem.* **2017,** *41*, 11991-11997.

(168) Jagadeesh, R. V.; Murugesan, K.; Alshammari, A. S.; Neumann, H.; Pohl, M.-M.; Radnik, J.; Beller, M. MOF-Derived Cobalt Nanoparticles Catalyze a General Synthesis of Amines. *Science* **2017,** *358*, 326-332.

(169) Liu, W.; Zhang, L.; Yan, W.; Liu, X.; Yang, X.; Miao, S.; Wang, W.; Wang, A.; Zhang, T. Single-Atom Dispersed Co-N-C Catalyst: Structure Identification and Performance for Hydrogenative Coupling of Nitroarenes. *Chem. Sci.* **2016,** *7*, 5758-5764.

(170) Dixon, D. J.; Pando Morejón, O. In *Comprehensive Organic Synthesis II (Second Edition)*; Elsevier: Amsterdam, 2014; p 479.

(171) Yang, S.; Peng, L.; Oveisi, E.; Bulut, S.; Sun, D. T.; Asgari, M.; Trukhina, O.; Queen, W. L. MOF-Derived Cobalt Phosphide/Carbon Nanocubes for Selective Hydrogenation of Nitroarenes to Anilines. *Chem. Eur. J.* **2018**, *24*, 4234-4238.

(172) Ma, B.; Wang, Y.; Tong, X.; Guo, X.; Zheng, Z.; Guo, X. Graphene-Supported CoS_2 Particles: an Efficient Photocatalyst for Selective Hydrogenation of Nitroaromatics in Visible Light. *Catal. Sci. Technol.* **2017,** *7*, 2805-2812.

(173) Wei, Z.; Mao, S.; Sun, F.; Wang, J.; Mei, B.; Chen, Y.; Li, H.; Wang, Y. The Synergic Effects at the Molecular Level in CoS_2 for Selective Hydrogenation of Nitroarenes. *Green Chem.* **2018**, *20*, 671-679.

(174) Liu, L.; Concepcion, P.; Corma, A. Non-Noble Metal Catalysts for Hydrogenation: A Facile Method for Preparing Co Nanoparticles Covered with Thin Layered Carbon. *J. Catal.* **2016,** *340*, 1-9.

(175) Sorribes, I.; Liu, L.; Corma, A. Nanolayered Co–Mo–S Catalysts for the Chemoselective Hydrogenation of Nitroarenes. *ACS Catal.* **2017**, *7*, 2698–2708.

(176) Ji, P.; Manna, K.; Lin, Z.; Feng, X.; Urban, A.; Song, Y.; Lin, W. Single-Site Cobalt Catalysts at New $Zr_{12}(\mu^3\text{-}O)_8(\mu^3\text{-}OH)_8(\mu^2\text{-}OH)_6$ Metal-Organic Framework Nodes for Highly Active Hydrogenation of Nitroarenes, Nitriles, and Isocyanides. *J. Am. Chem. Soc.* **2017,** *139*, 7004-7011.

(177) Nandi, S.; Patel, P.; Khan, N.-u. H.; Biradar, A. V.; Kureshy, R. I. Nitrogen-Rich Graphitic-Carbon Stabilized Cobalt Nanoparticles for Chemoselective Hydrogenation of Nitroarenes at Milder Conditions. *Inorg. Chem. Front.* **2018,** *5*, 806-813.

(178) Wang, T.; Dong, Z.; Fu, T.; Zhao, Y.; Wang, T.; Wang, Y.; Chen, Y.; Han, B.; Ding, W. Nickel Embedded in N-Doped Porous Carbon for the Hydrogenation of Nitrobenzene to *p*-Aminophenol in Sulphuric Acid. *Chem. Commun.* **2015,** *51*, 17712-17715.

(179) Chen, B.; Li, F.; Huang, Z.; Yuan, G. Recyclable and Selective Nitroarene Hydrogenation Catalysts Based on Carbon-Coated Cobalt Oxide Nanoparticles. *ChemCatChem* **2016,** *8*, 1132-1138.

(180) Liu, L.; Gao, F.; Concepción, P.; Corma, A. A New Strategy to Transform Mono and Bimetallic Non-Noble Metal Nanoparticles Into Highly Active and Chemoselective Hydrogenation Catalysts. *J. Catal.* **2017,** *350*, 218-225.

(181) Baramov, T.; Loos, P.; Hassfeld, J.; Alex, H.; Beller, M.; Stemmler, T.; Meier, G.; Gottfried, M.; Roggan, S. Encapsulated Cobalt Oxide on Carbon Nanotube Support as Catalyst for Selective Continuous Hydrogenation of the Showcase Substrate 1-Iodo-4-nitrobenzene. *Adv. Synth. Catal.* **2016,** *358*, 2903-2911.

(182) Loos, P.; Alex, H.; Hassfeld, J.; Lovis, K.; Platzek, J.; Steinfeldt, N.; Huebner, S. Selective Hydrogenation of Halogenated Nitroaromatics to Haloanilines in Batch and Flow. *Org. Process Res. Dev.* **2016,** *20*, 452-464.

(183) Said, M. B.; Baramov, T.; Herrmann, T.; Gottfried, M.; Hassfeld, J.; Roggan, S. Continuous Selective Hydrogenation of Refametinib Iodo-nitroaniline Key Intermediate DIM-NA over Raney Cobalt Catalyst at kg/Day Scale with Online UV–Visible Conversion Control. *Org. Process Res. Dev.* **2017,** *21*, 705-714.

(184) Jagadeesh, R. V.; Banerjee, D.; Arockiam, P. B.; Junge, H.; Junge, K.; Pohl, M.-M.; Radnik, J.; Bruckner, A.; Beller, M. Highly Selective Transfer Hydrogenation of Functionalised Nitroarenes Using Cobalt-Based Nanocatalysts. *Green Chem.* **2015,** *17*, 898-902.

(185) Westerhaus, F. A.; Sorribes, I.; Wienhöfer, G.; Junge, K.; Beller, M. Reduction of Nitroarenes Using CO and H_2O in the Presence of a Nanostructured Cobalt Oxide/Nitrogen-Doped Graphene (NGr) Catalyst. *Synlett* **2015,** *26*, 313-317.

(186) Jagadeesh, R. V.; Senthamarai, T.; Murugesan, K.; Natte, K.; Kalevaru, N.; Neumann, H.; Kamer, P. Expedient Synthesis of N-Methyl and -Alkylamines via Reductive Amination using Reusable Cobalt Oxide Nanoparticles. *ChemCatChem* **2018,** *10*, 1235-1240.

(187) Zhou, P.; Zhang, Z. One-pot Reductive Amination of Carbonyl Compounds with Nitro Compounds by Transfer Hydrogenation over Co-N_x as Catalyst. *ChemSusChem* **2017,** *10*, 1892-1897.

(188) Gong, Z.; Lei, Y.; Zhou, P.; Zhang, Z. One-Pot Synthesis of N-Substituted Pyrroles from Nitro Compounds and 2,5-Hexadione over a Heterogeneous Cobalt Catalyst. *New J. Chem.* **2017,** *41*, 10613-10618.

(189) Zhou, P.; Zhang, Z.; Jiang, L.; Yu, C.; Lv, K.; Sun, J.; Wang, S. A Versatile Cobalt Catalyst for the Reductive Amination of Carbonyl Compounds with Nitro Compounds by Transfer Hydrogenation. *Appl. Catal., B* **2017,** *210*, 522-532.

(190) Jiang, L.; Zhou, P.; Zhang, Z.; Jin, S.; Chi, Q. Synthesis of Secondary Amines from One-Pot Reductive Amination with Formic Acid as the Hydrogen Donor over an Acid-Resistant Cobalt Catalyst. *Ind. Eng. Chem. Res.* **2017,** *56*, 12556-12565.

(191) Zhou, P.; Yu, C.; Jiang, L.; Lv, K.; Zhang, Z. One-Pot Reductive Amination of Carbonyl Compounds with Nitro Compounds with CO/H_2O as the Hydrogen Donor over Non-Noble Cobalt Catalyst. *J. Catal.* **2017,** *352*, 264-273.

(192) Ma, X.; Zhou, Y.-X.; Liu, H.; Li, Y.; Jiang, H.-L. A MOF-Derived Co-CoO@N-Doped Porous Carbon for Efficient Tandem Catalysis: Dehydrogenation of Ammonia Borane and Hydrogenation of Nitro Compounds. *Chem. Commun.* **2016,** *52*, 7719-7722.

(193) Mandlimath, T. R.; Gopal, B. Catalytic Activity of First Row Transition Metal Oxides in the Conversion of *p*-Nitrophenol to *p*-Aminophenol. *J. Mol. Catal. A: Chem.* **2011,** *350*, 9-15.

(194) Mogudi, B. M.; Ncube, P.; Meijboom, R. Catalytic Activity of Mesoporous Cobalt Oxides with Controlled Porosity and Crystallite Sizes: Evaluation Using the Reduction of 4-Nitrophenol. *Appl. Catal., B* **2016,** *198*, 74-82.

(195) Mogudi, B. M.; Ncube, P.; Bingwa, N.; Mawila, N.; Mathebula, S.; Meijboom, R. Promotion Effects of Alkali- and Alkaline Earth Metals on Catalytic Activity of Mesoporous Co_3O_4 for 4-Nitrophenol Reduction. *Appl. Catal., B* **2017,** *218*, 240-248.

(196) Chen, H.; Yang, M.; Tao, S.; Chen, G. Oxygen Vacancy Enhanced Catalytic Activity of Reduced Co_3O_4 towards *p*-Nitrophenol Reduction. *Appl. Catal., B* **2017,** *209*, 648-656.

(197) Al Nafiey, A.; Addad, A.; Sieber, B.; Chastanet, G.; Barras, A.; Szunerits, S.; Boukherroub, R. Reduced Graphene Oxide Decorated with Co_3O_4 Nanoparticles (rGO-Co_3O_4) Nanocomposite: A Reusable Catalyst for Highly Efficient Reduction of 4-Nitrophenol, and Cr(VI) and Dye Removal from Aqueous Solutions. *Chem. Eng. J.* **2017,** *322*, 375-384.

(198) Meziane, D.; Benadda-Kordjani, A.; Nezzal, G.; Benammar, S.; Djadoun, A. *Para*-Nitrophenol Reduction on Solvothermally Prepared Cobalt@Silica Core–Shell catalysts. *React. Kinet. Mech. Cat.* **2017,** *122*, 1145-1158.

(199) Hasan, Z.; Ok, Y. S.; Rinklebe, J.; Tsang, Y. F.; Cho, D.-W.; Song, H. N Doped Cobalt-Carbon Composite for Reduction of *p*-Nitrophenol and Pendimethaline. *J. Alloys Compd.* **2017,** *703*, 118-124.

(200) Liu, X.; Li, X.; Qin, L.; Mu, J.; Kang, S.-Z. Co_3O_4/CoP Composite Hollow Polyhedron: A Superior Catalyst with Dramatic Efficiency and Stability for the Room Temperature Reduction of 4-Nitrophenol. *Appl. Surf. Sci.* **2018,** *434*, 967-974.

(201) Yuan, F.; Ni, Y.; Zhang, L.; Ma, X.; Hong, J. Rod-Like Co_2P Nanostructures: Improved Synthesis, Catalytic Property and Application in the Removal of Heavy Metal. *J. Cluster Sci.* **2013,** *24*, 1067-1080.

(202) Wu, H.; Ni, Y.; Hong, F.; Lu, D.; Xiao, Y. Grass-like Co_2P Superstructures: Direct Synthesis Between Elements, Forming Mechanism and Catalytic Properties. *RSC Adv.* **2016,** *6*, 5154-5160.

(203) Piña, S.; Cedillo, D. M.; Tamez, C.; Izquierdo, N.; Parsons, J. G.; Gutierrez, J. J. Reduction of Mitrobenzene Derivatives Using Sodium Borohydride and Transition Metal Sulfides. *Tetrahedron Lett.* **2014,** *55*, 5468-5470.

(204) Yan, N.; Zhao, Z.; Li, Y.; Wang, F.; Zhong, H.; Chen, Q. Synthesis of Novel Two-Phase Co@SiO_2 Nanorattles with High Catalytic Activity. *Inorg. Chem.* **2014,** *53*, 9073-9079.

(205) Sahiner, N.; Ozay, H.; Ozay, O.; Aktas, N. A Soft Hydrogel Reactor for Cobalt Nanoparticle Preparation and Use in the Reduction of Nitrophenols. *Appl. Catal., B* **2010,** *101*, 137-143.

(206) Li, H.; Chi, L.; Yang, C.; Zhang, L. G.; Yue, F.; Wang, J. D. MOF Derived Porous Co@C Hexagonal-Shaped Prisms with High Catalytic Performance. *J. Mater. Res.* **2016,** *31*, 3069-3077.

(207) Zhang, Z. J.; Wei, X. R.; Yao, Y.; Chen, Z.; Zhang, A. J.; Li, W.; Wu, W. D.; Wu, Z. X.; Chen, X. D.; Zhao, D. Y. Conformal Coating of Co/N-Doped Carbon Layers into Mesoporous Silica for Highly Efficient Catalytic Dehydrogenation-Hydrogenation Tandem Reactions. *Small* **2017,** *13*.

(208) Hasan, Z.; Cho, D.-W.; Chon, C.-M.; Yoon, K.; Song, H. Reduction of *p*-Nitrophenol by Magnetic Co-Carbon Composites Derived from Metal Organic Frameworks. *Chem. Eng. J.* **2016,** *298*, 183-190.

(209) Li, X.; Zeng, C.; Jiang, J.; Ai, L. Magnetic Cobalt Nanoparticles Embedded in Hierarchically Porous Nitrogen-Doped Carbon Frameworks for Highly Efficient and Well-Recyclable Catalysis. *J. Mater. Chem., A* **2016,** *4*, 7476-7482.

(210) Zhao, H.; Zhao, L. Magnetic N-Doped Co-Carbon Composites Derived from Metal Organic Frameworks as Highly Efficient Catalysts for *p*-Nitrophenol Reduction Reaction. *Dalton Trans.* **2018,** *47*, 3321-3328.

(211) Pariyar, A.; Gopalakrishnan, S.; Stansbery, J.; Patel, R. L.; Liang, X.; Gerasimchuk, N.; Choudhury, A. A 1-D Coordination Polymer Route to Catalytically Active Co@C Nanoparticles. *RSC Adv.* **2016,** *6*, 38533-38540.

(212) Sheng, J.; Wang, L.; Deng, L.; Zhang, M.; He, H.; Zeng, K.; Tang, F.; Liu, Y.-N. A MOF-Templated Fabrication of Hollow Co_4N@N-Doped Carbon Porous Nanocages with Superior Catalytic Activity. *ACS Appl. Mater. Interfaces* **2018,** *10*, 7191–7200.

(213) Reddy, P. L.; Tripathi, M.; Arundhathi, R.; Rawat, D. S. Chemoselective Hydrazine-mediated Transfer Hydrogenation of Nitroarenes by Co_3O_4 Nanoparticles Immobilized on an Al/Si-mixed Oxide Support. *Chem. Asian J.* **2017,** *12*, 785-791.

(214) Huang, H.; Tan, M.; Wang, X.; Zhang, M.; Guo, S.; Zou, X.; Lu, X. Synthesis of Mesoporous γ-Alumina-Supported Co-Based Catalysts and Their Catalytic Performance for Chemoselective Reduction of Nitroarenes. *ACS Appl. Mater. Interfaces* **2018,** *10*, 5413–5428.

(215) Zhao, Z.; Yang, H.; Li, Y.; Guo, X. Cobalt-Modified Molybdenum Carbide as an Efficient Catalyst for Chemoselective Reduction of Aromatic Nitro Compounds. *Green Chem.* **2014,** *16*, 1274-1281.

(216) Nethravathi, C.; Prabhu, J.; Lakshmipriya, S.; Rajamathi, M. Magnetic Co-Doped MoS_2 Nanosheets for Efficient Catalysis of Nitroarene Reduction. *ACS Omega* **2017,** *2*, 5891-5897.

(217) Long, J.; Zhou, Y.; Li, Y. Transfer Hydrogenation of Unsaturated Bonds in the Absence of Base Additives Catalyzed by a Cobalt-Based Heterogeneous Catalyst. *Chem. Commun.* **2015,** *51*, 2331-2334.

(218) Tan, K.; Nijem, N.; Canepa, P.; Gong, Q.; Li, J.; Thonhauser, T.; Chabal, Y. J. Stability and Hydrolyzation of Metal Organic Frameworks with Paddle-Wheel SBUs upon Hydration. *Chem. Mater.* **2012,** *24*, 3153-3167.

(219) Xu, Y.; Lv, X.-J.; Chen, Y.; Fu, W.-F. Highly Selective Reduction of Nitroarenes to Anilines Catalyzed using MOF-Derived Hollow Co_3S_4 in Water Under Ambient Conditions. *Catal. Commun.* **2017,** *101*, 31-35.

(220) Studer, M.; Neto, S.; Blaser, H.-U. Modulating the Hydroxylamine Accumulation in the Hydrogenation of Substituted Nitroarenes using Vanadium-Promoted RNi Catalysts. *Top. Catal.* **2000,** *13*, 205-212.

(221) Lu, C. S.; Lv, J. H.; Ma, L.; Zhang, Q. F.; Feng, F.; Li, X. N. Highly Selective Hydrogenation of Halonitroaromatics to Aromatic Haloamines by Ligand Modified Ni-Based Catalysts. *Chin. Chem. Lett.* **2012,** *23*, 545-548.

(222) Liu, X.; Ma, X.; Liu, S.; Liu, Y.; Xia, C. Metal Fluoride Promoted Catalytic Hydrogenation of Aromatic Nitro Compounds Over RANEY® Ni. *RSC Adv.* **2015,** *5*, 36423-36427.

(223) Liu, Y.-C.; Huang, C.-Y.; Chen, Y.-W. Hydrogenation of *p*-Chloronitrobenzene on Ni–B Nanometal Catalysts. *J. Nanopart. Res.* **2006,** *8*, 223-234.

(224) Liu, Y.-C.; Chen, Y.-W. Hydrogenation of *p*-Chloronitrobenzene on Lanthanum-Promoted NiB Nanometal Catalysts. *Ind. Eng. Chem. Res.* **2006,** *45*, 2973-2980.

(225) Liu, Y.-C.; Huang, C.-Y.; Chen, Y.-W. Liquid-Phase Selective Hydrogenation of *p*-Chloronitrobenzene on Ni−P−B Nanocatalysts. *Ind. Eng. Chem. Res.* **2006,** *45*, 62-69.

(226) Zhao, B.; Chou, C.-J.; Chen, Y.-W. Hydrogenation of *p*-Chloronitrobenzene on Tungsten-Modified NiCoB Catalyst. *Ind. Eng. Chem. Res.* **2010,** *49*, 1669-1676.

(227) Su, J.-F.; Zhao, B.; Chen, Y.-W. Hydrogenation of *p*-Chloronitrobenzene on Mo-Doped NiB Cluster Catalysts. *Ind. Eng. Chem. Res.* **2011,** *50*, 1580-1587.

(228) Lee, D.-S.; Chen, Y.-W. Hydrogenation of *p*-Chloronitrobenzene on La-Doped NiMoB Nanocluster Catalysts. *Chinese J. Catal.* **2013,** *34*, 2018-2028.

(229) Li, H.; Zhang, J.; Li, H. Ultrasound-Assisted Preparation of a Novel Ni–B Amorphous Catalyst in Uniform Nanoparticles for *p*-Chloronitrobenzene Hydrogenation. *Catal. Commun.* **2007,** *8*, 2212-2216.

(230) Li, H.; Xu, Y.; Liu, J.; Zhao, Q.; Li, H. Hollow Ni–B Amorphous Alloy with Enhanced Catalytic Efficiency Prepared in Emulsion System. *J. Colloid Interface Sci.* **2009,** *334*, 176-182.

(231) Li, H.; Zhao, Q.; Li, H. Selective Hydrogenation of *p*-Chloronitrobenzene over Ni–P–B Amorphous Catalyst and Synergistic Promoting Effects of B and P. *J. Mol. Catal. A: Chem.* **2008,** *285*, 29-35.

(232) Li, F.; Ma, R.; Cao, B.; Liang, J.; Song, H.; Song, H. Effect of Loading Method on Selective Hydrogenation of Chloronitrobenzenes over Amorphous Ni–B/CNTs Catalysts. *Catal. Commun.* **2016,** *80*, 1-4.

(233) Chen, G.; Gao, W.; Wang, X.; Huo, H.; Li, W.; Zhang, L.; Li, R.; Li, Z. Magnetic NiO Nanoparticles Confined Within Open Ends MWCNTs: A Novel and Highly Active Catalyst for Hydrogenation and Synthesis of Imines. *RSC Adv.* **2016,** *6*, 58805-58812.

(234) Xiong, J.; Chen, J.; Zhang, J. Liquid-Phase Hydrogenation of *o*-Chloronitrobenzene over Supported Nickel Catalysts. *Catal. Commun.* **2007,** *8*, 345-350.

(235) Yao, N.; Chen, J.; Zhang, J.; Zhang, J. Influence of Support Calcination Temperature on Properties of Ni/TiO_2 for Catalytic Hydrogenation of *o*-Chloronitrobenzene to *o*-Chloroaniline. *Catal. Commun.* **2008,** *9*, 1510-1516.

(236) Li, Y. Z.; Yu, J. Y.; Li, W.; Fan, G. L.; Yang, L.; Li, F. The Promotional Effect of Surface Defects on the Catalytic Performance of Supported Nickel-Based Catalysts. *PCCP* **2016,** *18*, 6548-6558.

(237) Cárdenas-Lizana, F.; Gómez-Quero, S.; Keane, M. A. Clean Production of Chloroanilines by Selective Gas Phase Hydrogenation over Supported Ni Catalysts. *Appl. Catal., A* **2008,** *334*, 199-206.

(238) Mahata, N.; Cunha, A. F.; Órfão, J. J. M.; Figueiredo, J. L. Hydrogenation of Nitrobenzene over Nickel Nanoparticles Stabilized by Filamentous Carbon. *Appl. Catal., A* **2008,** *351*, 204-209.

(239) Zheng, Y.; Ma, K.; Wang, H.; Sun, X.; Jiang, J.; Wang, C.; Li, R.; Ma, J. A Green Reduction of Aromatic Nitro Compounds to Aromatic Amines Over a Novel Ni/SiO_2 Catalyst Passivated with a Gas Mixture. *Catal. Lett.* **2008,** *124*, 268-276.

(240) Lu, X. H.; Wei, X. L.; Zhou, D.; Jiang, H. Z.; Sun, Y. W.; Xia, Q. H. Synthesis, Structure and Catalytic Activity of the Supported Ni Catalysts for Highly Efficient One-Step Hydrogenation of 1,5-Dinitronaphthalene to 1,5-Diaminodecahydronaphthalene. *J. Mol. Catal. A: Chem.* **2015,** *396*, 196-206.

(241) Hahn, G.; Ewert, J.-K.; Denner, C.; Tilgner, D.; Kempe, R. A Reusable Mesoporous Nickel Nanocomposite Catalyst for the Selective Hydrogenation of Nitroarenes in the Presence of Sensitive Functional Groups. *ChemCatChem* **2016,** *8*, 2461-2465.

(242) Liu, Z.; Li, Y.; Huang, X.; Zuo, J.; Qin, Z.; Xu, C. Preparation and Characterization of Ni-B/SiO_2sol Amorphous Catalyst and its Catalytic Activity for Hydrogenation of Nitrobenzene. *Catal. Commun.* **2016,** *85*, 17-21.

(243) Meng, X.; Cheng, H.; Akiyama, Y.; Hao, Y.; Qiao, W.; Yu, Y.; Zhao, F.; Fujita, S.-i.; Arai, M. Selective Hydrogenation of Nitrobenzene to Aniline in Dense Phase Carbon Dioxide over Ni/γ-Al_2O_3: Significance of Molecular Interactions. *J. Catal.* **2009,** *264*, 1-10.

(244) Meng, X.; Cheng, H.; Fujita, S.-i.; Yu, Y.; Zhao, F.; Arai, M. An Effective Medium of H_2O and Low-Pressure CO_2 for the Selective Hydrogenation of Aromatic Nitro Compounds to Anilines. *Green Chem.* **2011,** *13*, 570-572.

(245) Meng, X.; Cheng, H.; Fujita, S.-i.; Hao, Y.; Shang, Y.; Yu, Y.; Cai, S.; Zhao, F.; Arai, M. Selective Hydrogenation of Chloronitrobenzene to Chloroaniline in Supercritical Carbon Dioxide over Ni/TiO_2: Significance of Molecular Interactions. *J. Catal.* **2010,** *269*, 131-139.

(246) Raj, K. J. A.; Prakash, M. G.; Mahalakshmy, R.; Elangovan, T.; Viswanathan, B. Liquid Phase Hydrogenation of Nitrobenzene over Nickel Supported on Titania. *Chinese Journal of Catalysis* **2012,** *33*, 1299-1305.

(247) Cao, F.; Liu, R.; Zhou, L.; Song, S.; Lei, Y.; Shi, W.; Zhao, F.; Zhang, H. One-pot Synthesis of Flowerlike Ni_7S_6 and its Application in Selective Hydrogenation of Chloronitrobenzene. *J. Mater. Chem.* **2010,** *20*, 1078-1085.

(248) Wang, C.; Qiu, J.; Liang, C.; Xing, L.; Yang, X. Carbon Nanofiber Supported Ni Catalysts for the Hydrogenation of Chloronitrobenzenes. *Catal. Commun.* **2008,** *9*, 1749-1753.

(249) Liu, H.; Deng, J.; Li, W. Synthesis of Nickel Nanoparticles Supported on Boehmite for Selective Hydrogenation of *p*-Nitrophenol and *p*-Chloronitrobenzene. *Catal. Lett.* **2010,** *137*, 261-266.

(250) Dutta, D.; Dutta, D. K. Selective and Efficient Hydrogenation of Halonitrobenzene Catalyzed by Clay Supported NiO-Nanoparticles. *Appl. Catal., A* **2014,** *487*, 158-164.

(251) Harrad, M. A.; Boualy, B.; El Firdoussi, L.; Mehdi, A.; Santi, C.; Giovagnoli, S.; Nocchetti, M.; Ait Ali, M. Colloidal Nickel(0)-Carboxymethyl Cellulose Particles: A Biopolymer-Inorganic Catalyst for Hydrogenation of Nitro-Aromatics and Carbonyl Compounds. *Catal. Commun.* **2013,** *32*, 92-100.

(252) Fu, T.; Wang, M.; Cai, W.; Cui, Y.; Gao, F.; Peng, L.; Chen, W.; Ding, W. Acid-Resistant Catalysis without Use of Noble Metals: Carbon Nitride with Underlying Nickel. *ACS Catal.* **2014,** *4*, 2536-2543.

(253) Venkateshwarlu, V.; Mohan, V.; Rao, M. V.; Nagaiah, P.; Raju, B. D.; Rao, K. S. R. Advantage of Carbon Coverage over Al_2O_3 as Support for Ni/C-Al_2O_3 Catalyst in Vapour Phase Hydrogenation of Nitrobenzene to Aniline. *Catal. Commun.* **2016,** *86*, 1-4.

(254) Zhao, Z.; Yang, H.; Li, Y. Synergistic Effect From Lewis Acid and the Ni-W_2C/AC Catalyst for Highly Active and Selective Hydrogenation of Aryl Nitro to Aryl Amine. *RSC Adv.* **2014,** *4*, 22669-22677.

(255) Zhao, Z.; Yang, H. Ni–W_2C/mpg–C_3N_4 as a Promising Catalyst for Selective Hydrogenation of Nitroarenes to Corresponding Aryl aAmines in the Presence of Lewis Acid. *J. Mol. Catal. A: Chem.* **2015,** *398*, 268-274.

(256) Shu, Y. J.; He, S. N.; Xie, L. F.; Chan, H. C.; Yu, X.; Yang, L. C.; Gao, Q. S. Ni/Mo_2C Nanowires and their Carbon-Coated Composites as Efficient Catalysts for Nitroarenes Hydrogenation. *Appl. Surf. Sci.* **2017,** *396*, 339-346.

(257) Liu, W. J.; Tian, K.; Jiang, H. One-Pot Synthesis of Ni-$NiFe_2O_4$/Carbon Nanofiber Composites from Biomass for Selective Hydrogenation of Aromatic Nitro Compounds. *Green Chem.* **2015,** *17*, 821-826.

(258) Zhang, P.; Yu, C.; Fan, X. M.; Wang, X. N.; Ling, Z.; Wang, Z. H.; Qiu, J. S. Magnetically Recoverable Ni/C Catalysts with Hierarchical Structure and High-Stability for Selective Hydrogenation of Nitroarenes. *PCCP* **2015,** *17*, 145-150.

(259) Zhang, P.; Zhao, Z.; Dyatkin, B.; Liu, C.; Qiu, J. In Situ Synthesis of Cotton-Derived Ni/C Catalysts with Controllable Structures and Enhanced Catalytic Performance. *Green Chem.* **2016,** *18*, 3594-3599.

(260) Ren, Y.; Wei, H.; Yin, G.; Zhang, L.; Wang, A.; Zhang, T. Oxygen Surface Groups of Activated Carbon Steer the Chemoselective Hydrogenation of Substituted Nitroarenes over Nickel Nanoparticles. *Chem. Commun.* **2017,** *53*, 1969-1972.

(261) Tang, B.; Song, W.-C.; Yang, E.-C.; Zhao, X.-J. MOF-Derived Ni-Based Nanocomposites as Robust Catalysts for Chemoselective Hydrogenation of Functionalized Nitro Compounds. *RSC Adv.* **2017,** *7*, 1531-1539.

(262) Qu, Y.; Yang, H.; Wang, S.; Chen, T.; Wang, G. Hydrogenation of Nitrobenzene to Aniline Catalyzed by C_{60}-Stabilized Ni. *Catal. Commun.* **2017,** *97*, 83-87.

(263) Pisiewicz, S.; Formenti , D.; Surkus, A.-E.; Pohl, M.-M.; Radnik, J.; Junge, K.; Topf, C.; Bachmann, S.; Scalone, M.; Beller, M. Synthesis of Nickel Nanoparticles with N-Doped Graphene Shells for Catalytic Reduction Reactions. *ChemCatChem* **2016,** *8*, 129-134.

(264) Huang, H.; Wang, X.; Sheng, Y.; Chen, C.; Zou, X.; Shang, X.; Lu, X. Nitrogen-Doped Graphene-Activated Metallic Nanoparticle-Incorporated Ordered Mesoporous Carbon Nanocomposites for the Hydrogenation of Nitroarenes. *RSC Adv.* **2018,** *8*, 8898-8909.

(265) Ryabchuk, P.; Agostini, G.; Pohl, M.-M.; Lund, H.; Agapova, A.; Junge, H.; Junge, K.; Beller, M. Intermetallic Nickel Silicide Nanocatalyst—A Non-Noble Metal–Based general Hydrogenation Catalyst. *Sci. Adv.* **2018,** *4*, eaat0761.

(266) Xiong, W.; Wang, L.; Cai, G.; Yang, Y.; Hao, F.; Liu, P.; Luo, H. Nitrogen-Functionalized Active Carbon-Supported Non-Noble Nickel Nanoparticles with High Dispersity and Enhanced Catalytic Performance in Nitro Naphthalene Hydrogenation. *ChemistrySelect* **2017,** *2*, 11244-11249.

(267) Millán, R.; Liu, L.; Boronat, M.; Corma, A. A New Molecular Pathway Allows the Chemoselective Reduction of Nitroaromatics on Non-Noble Metal Catalysts. *J. Catal.* **2018,** *364*, 19-30.

(268) Yu, Y.; Zhu, W.; Hua, L.; Yang, H.; Qiao, Y.; Zhang, R.; Guo, L.; Zhao, X.; Hou, Z. Ionic Liquid-Pluronic P123 Mixed Micelle Stabilized Water-Soluble Ni Nanoparticles for Catalytic Hydrogenation. *J. Colloid Interface Sci.* **2014,** *415*, 117-126.

(269) Pogorelić, I.; Filipan-Litvić, M.; Merkaš, S.; Ljubić, G.; Cepanec, I.; Litvić, M. Rapid, Efficient and Selective Reduction of Aromatic Nitro Compounds with Sodium Borohydride and Raney Nickel. *J. Mol. Catal. A: Chem.* **2007,** *274*, 202-207.

(270) Rahman, A.; Jonnalagadda, S. B. Swift and Selective Reduction of Nitroaromatics to Aromatic Amines with Ni–Boride–Silica Catalysts System at Low Temperature. *Catal. Lett.* **2008,** *123*, 264-268.

(271) Sahiner, N.; Ozay, H.; Ozay, O.; Aktas, N. New Catalytic Route: Hydrogels as Templates and Reactors for *in situ* Ni Nanoparticle Synthesis and Usage in the Reduction of 2- and 4-Nitrophenols. *Appl. Catal., A* **2010,** *385*, 201-207.

(272) Kalbasi, R. J.; Nourbakhsh, A. A.; Babaknezhad, F. Synthesis and characterization of Ni nanoparticles-polyvinylamine/SBA-15 catalyst for simple reduction of aromatic nitro compounds. *Catal. Commun.* **2011,** *12*, 955-960.

(273) Kalbasi, R. J.; Zamani, F. Synthesis and Characterization of Ni Nanoparticles Incorporated into Hyperbranched Polyamidoamine-Polyvinylamine/SBA-15 Catalyst for Simple Reduction of Nitro Aromatic Compounds. *RSC Adv.* **2014,** *4*, 7444-7453.

(274) Tabatabaei Rezaei, S. J.; Mashhadi Malekzadeh, A.; Poulaei, S.; Ramazani, A.; Khorramabadi, H. Chemo-Selective Reduction of Nitro and Nitrile Compounds Using Ni Nanoparticles Immobilized on Hyperbranched Polymer-Functionalized Magnetic Nanoparticles. *Appl. Organomet. Chem.* **2018,** *32*, e3975.

(275) Chinnappan, A.; Kim, H. Transition Metal Based Ionic Liquid (Bulk and Nanofiber Composites) Used as Catalyst for Reduction of Aromatic Nitro Compounds Under Mild Conditions. *RSC Adv.* **2013,** *3*, 3399-3406.

(276) Zamani, F.; Kianpour, S. Fast and Efficient Reduction of Nitro Aromatic Compounds over Fe_3O_4/β-Alanine-Acrylamide-Ni Nanocomposite as a New Magnetic Catalyst. *Catal. Commun.* **2014,** *45*, 1-6.

(277) Zhang, Y.-N.; Li, X.-H.; Cai, Y.-Y.; Gong, L.-H.; Wang, K.-X.; Chen, J.-S. Bio-Inspired Noble Metal-Free Reduction of Nitroarenes Using NiS_2+x/g-C_3N_4. *RSC Adv.* **2014,** *4*, 60873-60877.

(278) Ajmal, M.; Demirci, S.; Siddiq, M.; Aktas, N.; Sahiner, N. Betaine Microgel Preparation From 2-(Methacryloyloxy)Ethyl] Dimethyl (3-Sulfopropyl) Ammonium Hydroxide and its Use as a Catalyst System. *Colloids Surf., A* **2015,** *486*, 29-37.

(279) Mazaheri, O.; Kalbasi, R. J. Preparation and Characterization of Ni/mZSM-5 Zeolite With a Hierarchical Pore Structure by Using KIT-6 as Silica Template: an Efficient Bi-Functional Catalyst for the Reduction of Nitro Aromatic Compounds. *RSC Adv.* **2015,** *5*, 34398-34414.

(280) Kalbasi, R. J.; Mazaheri, O. Synthesis and Characterization of Hierarchical ZSM-5 Zeolite Containing Ni Nanoparticles for One-Pot Reductive Amination of Aldehydes with Nitroarenes. *Catal. Commun.* **2015,** *69*, 86-91.

(281) Karthik, M.; Suresh, P. Greener Synthesis of Reduced Graphene Oxide-Nickel Nanocomposite: Rapid and Sustainable Catalyst for the Reduction of Nitroaromatics. *ChemistrySelect* **2017,** *2*, 6916-6928.

(282) Zuo, W.; Yu, G.; Dong, Z. A MOF-Derived Nickel Based N-Doped Mesoporous Carbon Catalyst With High Catalytic Activity for the Reduction of Nitroarenes. *RSC Adv.* **2016,** *6*, 11749-11753.

(283) Xu, D.; Pan, Y.; Zhu, L.; Yusran, Y.; Zhang, D.; Fang, Q.; Xue, M.; Qiu, S. Simple Coordination Complex-Derived Ni NP Anchored N-Doped Porous Carbons With High Performance for Reduction of Nitroarenes. *CrystEngComm* **2017,** *19*, 6612-6619.

(284) Liu, W.; Chen, R.; Liu, L.; Li, S.; Xue, Z.; He, C. Amorphous NiB/Carbon Nanohybrids: Synthesis and Catalytic Enhancement Induced by Electron Transfer. *RSC Adv.* **2016,** *6*, 94451-94458.

(285) Wu, G.; Liang, X.; Zhang, H.; Zhang, L.; Yue, F.; Wang, J.; Su, X. Highly Stable and sub-3nm Ni Nanoparticles Coated with Carbon Nanosheets as a Highly Active Heterogeneous Hydrogenation Catalyst. *Catal. Commun.* **2016,** *79*, 63-67.

(286) Xia, J.; He, G.; Zhang, L.; Sun, X.; Wang, X. Hydrogenation of Nitrophenols Catalyzed by Carbon Black-Supported Nickel Nanoparticles Under Mild Conditions. *Appl. Catal., B* **2016,** *180*, 408-415.

(287) Yang, Y.; Ren, Y.; Sun, C.; Hao, S. Facile Route Fabrication of Nickel Based Mesoporous Carbons With High Catalytic Performance Towards 4-Nitrophenol Reduction. *Green Chem.* **2014,** *16*, 2273-2280.

(288) Jiang, Z.; Xie, J.; Jiang, D.; Jing, J.; Qin, H. Facile Route Fabrication of Nano-Ni Core Mesoporous-Silica Shell Particles With High Catalytic Activity Towards 4-Nitrophenol Reduction. *CrystEngComm* **2012,** *14*, 4601-4611.

(289) Stöber, W.; Fink, A.; Bohn, E. Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range. *J. Colloid Interface Sci.* **1968,** *26*, 62-69.

(290) Tarpani, L.; Mencarelli, E.; Nocchetti, M.; Fanò, L.; Taglieri, L.; Latterini, L. Spectrophotometric Analysis of Nickel Colloid Performances as Catalysts for Hydrogenation of Nitrophenol: Influence of the Stabilizing Agents. *Catal. Commun.* **2016,** *74*, 28-32.

(291) Rathore, P. S.; Patidar, R.; Shripathi, T.; Thakore, S. Magnetically Separable Core-Shell Iron Oxide@Nickel Nanoparticles as High-Performance Recyclable Catalysts for Chemoselective Reduction of Nitroaromatics. *Catal. Sci. Technol.* **2015,** *5*, 286-295.

(292) Jiao, J.; Wang, H. Y.; Guo, W. C.; Li, R. F.; Tian, K. S.; Xu, Z. P.; Jia, Y.; Wu, Y. H.; Cao, L. In Situ Confined Growth Based on a Self-Templating Reduction Strategy of Highly Dispersed Ni Nanoparticles in Hierarchical Yolk-Shell Fe@SiO_2 Structures as Efficient Catalysts. *Chem. Asian J.* **2016,** *11*, 3534-3540.

(293) Prathap, K. J.; Diner, P.; Wu, Q.; Olsson, R. T. Catalytic Reductions and Tandem Reactions of Nitro Compounds Using in Situ Prepared Nickel Boride Catalyst in Nanocellulose Solution. *Org. Lett.* **2017,** *19*, 4746-4749.

(294) Romanazzi, G.; Fiore, A. M.; Mali, M.; Rizzuti, A.; Leonelli, C.; Nacci, A.; Mastrorilli, P.; Dell'Anna, M. M. Polymer Supported Nickel Nanoparticles as Recyclable Catalyst for the Reduction of Nitroarenes to Anilines in Aqueous Medium. *Molecular Catalysis* **2018,** *446*, 31-38.

(295) Shah, M.; Guo, Q.-X.; Fu, Y. The Colloidal Synthesis of Unsupported Nickel-Tin Bimetallic Nanoparticles with Tunable Composition that Have High Activity for the Reduction of Nitroarenes. *Catal. Commun.* **2015,** *65*, 85-90.

(296) Marakatti, V. S.; Peter, S. C. Nickel-Antimony Nanoparticles Confined in SBA-15 as Highly Efficient Catalysts for the Hydrogenation of Nitroarenes. *New J. Chem.* **2016,** *40*, 5448-5457.

(297) Prakash, P.; De Masi, D.; Geertsen, V.; Miserque, F.; Li, H.; Namboothiri, I. N. N.; Gravel, E.; Doris, E. Selective Conversion of Nitroarenes to N-Aryl Hydroxylamines Catalysed by Carbon-Nanotube-Supported Nickel(II) Hydroxide. *ChemistrySelect* **2017,** *2*, 5891-5894.

(298) Jyothi, T. M.; Raja, T.; Talawar, M. B.; Sreekumar, K.; Sugunan, S.; Rao, B. S. NiO-Al_2O_3 Prepared from a Ni-Al Hydrotalcite Precursor as an Efficient Catalyst for Transfer Hydrogenation Reactions. *Synth. Commun.* **2000,** *30*, 1573-1579.

(299) Mohapatra, S. K.; Sonavane, S. U.; Jayaram, R. V.; Selvam, P. Regio- and Chemoselective Catalytic Transfer Hydrogenation of Aromatic Nitro and Carbonyl as Well as Reductive Cleavage of Azo Compounds over Novel Mesoporous NiMCM-41 Molecular Sieves. *Org. Lett.* **2002,** *4*, 4297-4300.

(300) Selvam, P.; Mohapatra, S. K.; Sonavane, S. U.; Jayaram, R. V. Chemo- and Regioselective Reduction of Nitroarenes, Carbonyls and Azo Dyes over Nickel-Incorporated Hexagonal Mesoporous Aluminophosphate Molecular sieves. *Tetrahedron Lett.* **2004,** *45*, 2003-2007.

(301) Paul, M.; Pal, N.; Bhaumik, A. Mesoporous Nickel–Aluminum Mixed Oxide: A Promising Catalyst in Hydride-Transfer Reactions. *Eur. J. Inorg. Chem.* **2010,** *2010*, 5129-5134.

(302) Farhadi, S.; Kazem, M.; Siadatnasab, F. NiO Nanoparticles Prepared via Thermal Decomposition of the Bis(Dimethylglyoximato)Nickel(II) Complex: A Novel Reusable Heterogeneous Catalyst for Fast and Efficient Microwave-Assisted Reduction of Nitroarenes with Ethanol. *Polyhedron* **2011,** *30*, 606-613.

(303) Wen, H.; Yao, K.; Zhang, Y.; Zhou, Z.; Kirschning, A. Catalytic Transfer Hydrogenation of Aromatic Nitro Compounds in Presence of Polymer-Supported Nano-Amorphous Ni-B Catalyst. *Catal. Commun.* **2009,** *10*, 1207-1211.

(304) Jiang, C.; Shang, Z.; Liang, X. Chemoselective Transfer Hydrogenation of Nitroarenes Catalyzed by Highly Dispersed, Supported Nickel Nanoparticles. *ACS Catal.* **2015,** *5*, 4814-4818.

(305) Billakanti, S.; Baskaran, G. K.; Muralidharan, K. Recyclable Ni_3S_4 Nanocatalyst for Hydrogenation of Nitroarenes. *ChemistrySelect* **2017,** *2*, 4753-4758.

(306) Abd El Maksod, I. H.; Saleh, T. S. The Use of Nano Supported Nickel Catalyst in Reduction of *p*-Nitrophenol Using Hydrazine as Hydrogen Donor. *Green Chem. Lett. Rev.* **2010,** *3*, 127-134.

(307) Rai, R. K.; Mahata, A.; Mukhopadhyay, S.; Gupta, S.; Li, P.-Z.; Nguyen, K. T.; Zhao, Y.; Pathak, B.; Singh, S. K. Room-Temperature Chemoselective Reduction of Nitro Groups Using Non-Noble Metal Nanocatalysts in Water. *Inorg. Chem.* **2014,** *53*, 2904-2909.

(308) Mahata, A.; Rai, R. K.; Choudhuri, I.; Singh, S. K.; Pathak, B. Direct vs. Indirect Pathway for Nitrobenzene Reduction Reaction on a Ni Catalyst Surface: a Density Functional Study. *PCCP* **2014,** *16*, 26365-26374.

(309) Huang, H.; Wang, X.; Li, X.; Chen, C.; Zou, X.; Ding, W.; Lu, X. Highly Chemoselective Reduction of Nitroarenes over Non-Noble Metal Nickel-Molybdenum Oxide Catalysts. *Green Chem.* **2017,** *19*, 809-815.

(310) Gowda, S.; Gowda, D. C. Application of Hydrazinium Monoformate as New Hydrogen Donor with Raney Nickel: a Facile Reduction of Nitro and Nitrile Moieties. *Tetrahedron* **2002,** *58*, 2211-2213.

(311) Gowda, D. C.; Prakasha Gowda, A. S.; Baba, A. R.; Gowda, S. Nickel-Catalyzed Formic Acid Reductions. A Selective Method for the Reduction of Nitro Compounds. *Synth. Commun.* **2000,** *30*, 2889-2895.

(312) Bhaumik, K.; Akamanchi, K. G. Nitroarene Reduction Using Raney Nickel Alloy with Ammonium Chloride in Water. *Can. J. Chem.* **2003,** *81*, 197-198.

(313) Shalom, M.; Molinari, V.; Esposito, D.; Clavel, G.; Ressnig, D.; Giordano, C.; Antonietti, M. Sponge-like Nickel and Nickel Nitride Structures for Catalytic Applications. *Adv. Mater.* **2014,** *26*, 1272-1276.

(314) Gawande, M. B.; Goswami, A.; Felpin, F.-X.; Asefa, T.; Huang, X.; Silva, R.; Zou, X.; Zboril, R.; Varma, R. S. Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis. *Chem. Rev.* **2016,** *116*, 3722-3811.

(315) Li, M. S.; Hao, Y. F.; Cardenas-Lizana, F.; Yiu, H. H. P.; Keane, M. A. "Hydrogen-Free" Hydrogenation of Nitrobenzene Over Cu/SiO_2 Via Coupling with 2-Butanol Dehydrogenation. *Top. Catal.* **2015,** *58*, 149-158.

(316) Kour, G.; Gupta, M.; Vishwanathan, B.; Thirunavukkarasu, K. (Cu/NCNTs): a New High Temperature Technique to Prepare a Recyclable Nanocatalyst for Four Component Pyridine Derivative Synthesis and Nitroarenes Reduction. *New J. Chem.* **2016,** *40*, 8535-8542.

(317) Nuzhdin, A. L.; Artiukha, E. A.; Bukhtiyarova, G. A.; Derevyannikova, E. A.; Bukhtiyarov, V. I. Synthesis of Secondary Amines by Reductive Amination of Aldehydes with Nitroarenes Over Supported Copper Catalysts in a Flow Reactor. *Catal. Commun.* **2017,** *102*, 108-113.

(318) Ye, T.-N.; Lu, Y.; Li, J.; Nakao, T.; Yang, H.; Tada, T.; Kitano, M.; Hosono, H. Copper-Based Intermetallic Electride Catalyst for Chemoselective Hydrogenation Reactions. *J. Am. Chem. Soc.* **2017,** *139*, 17089-17097.

(319) Pradhan, N.; Pal, A.; Pal, T. Catalytic Reduction of Aromatic Nitro Compounds by Coinage Metal Nanoparticles. *Langmuir* **2001,** *17*, 1800-1802.

(320) Kadam, H. K.; Tilve, S. G. Copper(II) Bromide as a Procatalyst for *in situ* Preparation of Active Cu Nanoparticles for Reduction of Nitroarenes. *RSC Adv.* **2012,** *2*, 6057-6060.

(321) Deka, P.; Deka, R. C.; Bharali, P. In Situ Generated Copper Nanoparticle Catalyzed Reduction of 4-Nitrophenol. *New J. Chem.* **2014,** *38*, 1789-1793.

(322) Santhanalakshmi, J.; Parimala, L. The Copper Nanoparticles Catalyzed Reduction of Substituted Nitrobenzenes: Effect of Nanoparticle Stabilizers. *J. Nanopart. Res.* **2012,** *14*, 1090, 1014 pp.

(323) Tumma, M.; Srivastava, R. Transition Metal Nanoparticles Supported on Mesoporous Polyaniline Catalyzed Reduction of Nitroaromatics. *Catal. Commun.* **2013,** *37*, 64-68.

(324) Wu, F.; Qiu, L.-G.; Ke, F.; Jiang, X. Copper Nanoparticles Embedded in Metal-Organic Framework MIL-101(Cr) as a High Performance Catalyst for Reduction of Aromatic Nitro Compounds. *Inorg. Chem. Commun.* **2013,** *32*, 5-8.

(325) Tamuly, C.; Saikia, I.; Hazarika, M.; Das, M. R. Reduction of Aromatic Nitro Compounds Catalyzed by Biogenic CuO Nanoparticles. *RSC Adv.* **2014,** *4*, 53229-53236.

(326) de Souza, J. F.; da Silva , G. T.; Fajardo, A. R. Chitosan-Based Film Supported Copper Nanoparticles: A Potential and Reusable Catalyst for the Reduction of Aromatic Nitro Compounds. *Carbohydr. Polym.* **2017,** *161*, 187-196.

(327) Venkatakrishnan, S.; Veerappan, G.; Elamparuthi, E.; Veerappan, A. Aerobic Synthesis of Biocompatible Copper Nanoparticles: Promising Antibacterial Agent and Catalyst for Nitroaromatic Reduction and C-N Cross Coupling Reaction. *RSC Adv.* **2014,** *4*, 15003-15006.

(328) Megarajan, S.; Ayaz Ahmed, K. B.; Rajmohan, R.; Vairaprakash, P.; Anbazhagan, V. An Easily Accessible and Recyclable Copper Nanoparticle Catalyst for the Solvent-Free Synthesis of Dipyrromethanes and Aromatic Amines. *RSC Adv.* **2016,** *6*, 103065-103071.

(329) Singh, V.; Pandey, A. K.; Preeti; Singh, J.; Malviya, T. Gum Acacia-CuNp-Silica Hybrid: an Effective, Stable and Recyclable Catalyst for Reduction of Nitroarenes. *RSC Adv.* **2016,** *6*, 31074-31082.

(330) Ajmal, M.; Siddiq, M.; Al-Lohedan, H.; Sahiner, N. Highly Versatile p(MAc)-M (M: Cu, Co, Ni) Microgel Composite Catalyst for Individual and Simultaneous Catalytic Reduction of Nitro Compounds and Dyes. *RSC Adv.* **2014,** *4*, 59562-59570.

(331) Sharma, R. K.; Monga, Y.; Puri, A. Magnetically Separable Silica@Fe_3O_4 Core-Shell Supported Nano-Structured Copper(II) Composites as a Versatile Catalyst for the Reduction of Nitroarenes in Aqueous Medium at Room Temperature. *J. Mol. Catal. A: Chem.* **2014,** *393*, 84-95.

(332) Rajabzadeh, M.; Eshghi, H.; Khalifeh, R.; Bakavoli, M. Generation of Cu Nanoparticles on Novel Designed Fe_3O_4@SiO_2/EP.EN.EG as Reusable Nanocatalyst for the Reduction of Nitro Compounds. *RSC Adv.* **2016,** *6*, 19331-19340.

(333) Kurtan, U.; Onus, E.; Amir, M.; Baykal, A. Fe_3O_4@Hpipe-4@Cu Nanocatalyst for Hydrogenation of Nitro-Aromatics and Azo Dyes. *J. Inorg. Organomet. Polym. Mater.* **2015,** *25*, 1120-1128.

(334) Ghonchepour, E.; Yazdani, E.; Saberi, D.; Arefi, M.; Heydari, A. Preparation and Characterization of Copper Chloride Supported on Citric Acid-Modified Magnetite Nanoparticles (Cu^{2+}-CA@Fe_3O_4) and Evaluation of its Catalytic Activity in the Reduction of Nitroarene Compounds. *Appl. Organomet. Chem.* **2017,** *31*, e3822.

(335) Yang, S.; Zhang, Z.-H.; Chen, Q.; He, M.-Y.; Wang, L. Magnetically Recyclable Metal-Organic Framework@Fe_3O_4 Composite-Catalyzed Facile Reduction of Nitroarene Compounds in Aqueous Medium. *Appl. Organomet. Chem.* **2018**, DOI:10.1002/aoc.4132 10.1002/aoc.4132, e4132.

(336) Goyal, A.; Singhal, S. Robust and Economic Reduction Protocol Employing Immensely Stable and Leach-Proof Magnetically Separable Nanocomposites. *RSC Adv.* **2016,** *6*, 91275-91294.

(337) Parmekar, M. V.; Salker, A. V. Room Temperature Complete Reduction of Nitroarenes Over a Novel Cu/SiO_2@$NiFe_2O_4$ Nano-Catalyst in an Aqueous Medium - a Kinetic and Mechanistic Study. *RSC Adv.* **2016,** *6*, 108458-108467.

(338) Vinod Kumar, V.; Rajmohan, R.; Vairaprakash, P.; Mariappan, M.; Anthony, S. P. Copper-Coordination Polymer-Controlled Cu@N-rGO and CuO@C Nanoparticle Formation: Reusable Green Catalyst for A^3-Coupling and Nitroarene-Reduction Reactions. *Dalton Trans.* **2017,** *46*, 11704-11714.

(339) Sasmal, A. K.; Dutta, S.; Pal, T. A Ternary Cu_2O-Cu-CuO Nanocomposite: a Catalyst with Intriguing Activity. *Dalton Trans.* **2016,** *45*, 3139-3150.

(340) Vinod Kumar, V.; Dharani, A.; Mariappan, M.; Anthony, S. P. Synthesis of CuO and Cu_2O Nano/Microparticles From a Single Precursor: Effect of Temperature on CuO/Cu_2O Formation and Morphology Dependent Nitroarene Reduction. *RSC Adv.* **2016,** *6*, 85083-85090.

(341) Bhattacharjee, A.; Ahmaruzzaman, M. Microwave Assisted Facile and Green Route for Synthesis of CuO Nanoleaves and Their Efficacy as a Catalyst for Reduction and Degradation of Hazardous Organic Compounds. *J. Photochem. Photobiol., A* **2018,** *353*, 215-228.

(342) Dou, L.; Zhang, H. Facile Assembly of Nanosheet Array-Like CuMgAl-Layered Double Hydroxide/rGO Nanohybrids for Nighly Efficient Reduction of 4-Nitrophenol. *J. Mater. Chem. A* **2016,** *4*, 18990-19002.

(343) Saha, A.; Ranu, B. Highly Chemoselective Reduction of Aromatic Nitro Compounds by Copper Nanoparticles/Ammonium Formate. *J. Org. Chem.* **2008,** *73*, 6867-6870.

(344) Subramanian, T.; Pitchumani, K. Selective Reduction of Nitroarenes by using Zeolite-Supported Copper Nanoparticles with 2-Propanol as a Sustainable Reducing Agent. *ChemCatChem* **2012,** *4*, 1917-1921.

(345) Feng, H.; Li, Y.; Lin, S.; Van der Eycken, E. V.; Song, G. Nano Cu-Catalyzed Efficient and Selective Reduction of Nitroarenes Under Combined Microwave and Ultrasound Irradiation. *Sustain. Chem. Process.* **2014,** *2*, 14.

(346) van der Waals, D.; Pettman, A.; Williams, J. M. J. Copper-Catalysed Reductive Amination of Nitriles and Organic-Group Reductions Using Dimethylamine Borane. *RSC Adv.* **2014,** *4*, 51845-51849.

(347) Singh, A.; Raj, T.; Singh, N. Highly Selective and Efficient Reduction of Nitroarenes by Imidazolium Salt Stabilized Copper Nanoparticles in Aqueous Medium. *Catal. Lett.* **2015,** *145*, 1606-1611.

(348) Alexander, A.-M.; Hargreaves, J. S. J. Alternative Catalytic Materials: Carbides, Nitrides, Phosphides and Amorphous Boron Alloys. *Chem. Soc. Rev.* **2010,** *39*, 4388-4401.

(349) Yan, X.; Sun, J.; Wang, Y.; Yang, J. A Fe-Promoted Ni–P Amorphous Alloy Catalyst (Ni–Fe–P) for Liquid Phase Hydrogenation of *m*- and *p*-Chloronitrobenzene. *J. Mol. Catal. A: Chem.* **2006,** *252*, 17-22.

(350) Chen, Y.-W.; Sasirekha, N. Preparation of NiFeB Nanoalloy Catalysts and Their Applications in Liquid-Phase Hydrogenation of *p*-Chloronitrobenzene. *Ind. Eng. Chem. Res.* **2009,** *48*, 6248-6255.

(351) Shen, J.-H.; Chen, Y.-W. Catalytic Properties of Bimetallic NiCoB Nanoalloy Catalysts for Hydrogenation of *p*-Chloronitrobenzene. *J. Mol. Catal. A: Chem.* **2007,** *273*, 265-276.

(352) Lin, M.-H.; Zhao, B.; Chen, Y.-W. Hydrogenation of *p*-Chloronitrobenzene over Mo-Modified NiCoB Nanoalloy Catalysts: Effect of Mo Content. *Ind. Eng. Chem. Res.* **2009,** *48*, 7037-7043.

(353) Zhao, B.; Chen, Y.-W. Hydrogenation of *p*-Chloronitrobenzene on Mo, La, Fe, and W-Modified NiCoB Nanoalloy Catalysts. *J. Non-Cryst. Solids* **2010,** *356*, 839-847.

(354) Yan, X.; Sun, J.; Xu, Y.; Yang, J. Liquid-Phase Hydrogenation of Chloronitrobenzene to Chloroaniline over Ni-Co-B Amorphous Alloy Catalyst. *Chinese Journal of Catalysis* **2006,** *27*, 119-123.

(355) Li, F.; Ma, R.; Cao, B.; Liang, J.; Ren, Q.; Song, H. Effect of Co-B Supporting Methods on the Hydrogenation of *m*-Chloronitrobenzene over Co-B/CNTs Amorphous Alloy Catalysts. *Appl. Catal., A* **2016,** *514*, 248-252.

(356) Serna, P.; Corma, A. Transforming Nano Metal Nonselective Particulates into Chemoselective Catalysts for Hydrogenation of Substituted Nitrobenzenes. *ACS Catal.* **2015,** *5*, 7114-7121.

(357) Ni, T.; Zhang, S.; Cao, F.; Ma, Y. NiCo Bimetallic Nanoparticles Encapsulated in Graphite-Like Carbon Layers as Efficient and Robust Hydrogenation Catalysts. *Inorg. Chem. Front.* **2017,** *4*, 2005-2011.

(358) Wang, J.; Liu, J.; Yang, N.; Huang, S.; Sun, Y.; Zhu, Y. Designing Axial Growth of Co-Ni Bimetallic Nanowires with Hexagon-Like Caps and their Catalytic Hydrogenation for Nitrobenzene. *Nanoscale* **2016,** *8*, 3949-3953.

(359) Rao, K. N.; Reddy, B. M.; Park, S.-E. Superior Copper Promoted Bimetallic Catalysts for Chemoselective Hydrogenation of *ortho*-Chloro-Nitrobenzene. *Catal. Commun.* **2009,** *11*, 142-145.

(360) Cardenas-Lizana, F.; Bridier, B.; Shin, C. C. K.; Perez-Ramirez, J.; Kiwi-Minsker, L. Promotional Effect of Ni in the Selective Gas-Phase Hydrogenation of Chloronitrobenzene over Cu-based Catalysts. *ChemCatChem* **2012,** *4*, 668-673.

(361) Shesterkina, A. A.; Shuvalova, E. V.; Kirichenko, O. A.; Strelkova, A. A.; Nissenbaum, V. D.; Kapustin, G. I.; Kustov, L. M. Application of Silica-Supported Fe–Cu Nanoparticles in the Selective Hydrogenation of *p*-Dinitrobenzene to *p*-Phenylenediamine. *Russ. J. Phys. Chem. A* **2017,** *91*, 201-204.

(362) Shuvalova, E. V.; Kirichenko, O. A.; Kapustin, G. I.; Kustov, L. M. Silica-Supported Copper Nanoparticles as Efficient Catalysts for the Liquid-Phase Selective Hydrogenation of *p*-Dinitrobenzene by Molecular Hydrogen. *Russ. Chem. Bull.* **2016,** *65*, 2850-2854.

(363) Chaubal, N. S.; Sawant, M. R. Nitro Compounds Reduction via Hydride Transfer Using Mesoporous Mixed Oxide Catalyst. *J. Mol. Catal. A: Chem.* **2007,** *261*, 232-241.

(364) Gawande, M. B.; Rathi, A. K.; Branco, P. S.; Nogueira, I. D.; Velhinho, A.; Shrikhande, J. J.; Indulkar, U. U.; Jayaram, R. V.; Ghumman, C. A. A.; Bundaleski, N.et al. Regio- and Chemoselective Reduction of Nitroarenes and Carbonyl Compounds over Recyclable Magnetic Ferrite-Nickel Nanoparticles by Using Glycerol as a Hydrogen Source. *Chem. Eur. J.* **2012,** *18*, 12628-12632.

(365) Dai, X.; Cui, X.; Yuan, H.; Deng, Y.; Shi, F. Cooperative Transformation of Nitroarenes and Biomass-Based Alcohols Catalyzed by $CuNiAlO_x$. *RSC Adv.* **2015,** *5*, 7970-7975.

(366) Shi, Q.; Lu, R.; Lu, L.; Fu, X.; Zhao, D. Efficient Reduction of Nitroarenes over Nickel-Iron Mixed Oxide Catalyst Prepared from a Nickel-Iron Hydrotalcite Precursor. *Adv. Synth. Catal.* **2007,** *349*, 1877-1881.

(367) Zhang, J.-w.; Lu, G.-p.; Cai, C. Chemoselective Transfer Hydrogenation of Nitroarenes by Highly Dispersed Ni-Co BMNPs. *Catal. Commun.* **2016,** *84*, 25-29.

(368) Yang, B.; Zhang, Q.; Ma, X.; Kang, J.; Shi, J.; Tang, B. Preparation of a Magnetically Recoverable Nanocatalyst via Cobalt-Doped Fe_3O_4 Nanoparticles and its Application in the Hydrogenation of Nitroarenes. *Nano Res.* **2016,** *9*, 1879-1890.

(369) Yu, C.; Fu, J.; Muzzio, M.; Shen, T.; Su, D.; Zhu, J.; Sun, S. CuNi Nanoparticles Assembled on Graphene for Catalytic Methanolysis of Ammonia Borane and Hydrogenation of Nitro/Nitrile Compounds. *Chem. Mater.* **2017,** *29*, 1413-1418.

(370) Zhou, Y.-H.; Yang, Q.; Chen, Y.-Z.; Jiang, H.-L. Low-cost CuNi@MIL-101 as an Excellent Catalyst Toward Cascade Reaction: Integration of Ammonia Borane Dehydrogenation with Nitroarene Hydrogenation. *Chem. Commun.* **2017,** *53*, 12361-12364.

(371) Göksu, H.; Can, H.; Şendil, K.; Gültekin, M. S.; Metin, Ö. CoPd Alloy Nanoparticles Catalyzed Tandem Ammonia Borane Dehydrogenation and Reduction of Aromatic Nitro, Nitrile and Carbonyl Compounds. *Appl. Catal., A* **2014,** *488*, 176-182.

(372) Göksu, H.; Ho, S. F.; Metin, Ö.; Korkmaz, K.; Mendoza Garcia, A.; Gültekin, M. S.; Sun, S. Tandem Dehydrogenation of Ammonia Borane and Hydrogenation of Nitro/Nitrile Compounds Catalyzed by Graphene-Supported NiPd Alloy Nanoparticles. *ACS Catal.* **2014,** *4*, 1777-1782.

(373) Metin, O.; Mendoza-Garcia, A.; Dalmzrak, D.; Gultekin, M. S.; Sun, S. FePd Alloy Nanoparticles Assembled on Reduced Graphene Oxide as a Catalyst for Selective Transfer Hydrogenation of Nitroarenes to Anilines Using Ammonia Borane as a Hydrogen Source. *Catal. Sci. Technol.* **2016,** *6*, 6137-6143.

(374) Metin, Ö.; Can, H.; Şendil, K.; Gültekin, M. S. Monodisperse Ag/Pd Core/Shell Nanoparticles Assembled on Reduced Graphene Oxide as Highly Efficient Catalysts for the Transfer Hydrogenation of Nitroarenes. *J. Colloid Interface Sci.* **2017,** *498*, 378-386.

(375) Herves, P.; Perez-Lorenzo, M.; Liz-Marzan, L. M.; Dzubiella, J.; Lu, Y.; Ballauff, M. Catalysis by Metallic Nanoparticles in Aqueous Solution: Model Reactions. *Chem. Soc. Rev.* **2012,** *41*, 5577-5587.

(376) Rashid, M. H.; Raula, M.; Mandal, T. K. Polymer Assisted Synthesis of Chain-Like Cobalt-Nickel Alloy Nanostructures: Magnetically Recoverable and Reusable Catalysts with high Activities. *J. Mater. Chem.* **2011,** *21*, 4904-4917.

(377) Raula, M.; Rashid, M. H.; Lai, S.; Roy, M.; Mandal, T. K. Solvent-Adoptable Polymer Ni/NiCo Alloy Nanochains: Highly Active and Versatile Catalysts for Various Organic Reactions in both Aqueous and Nonaqueous Media. *ACS Appl. Mater. Interfaces* **2012,** *4*, 878-889.

(378) Wu, K.-L.; Wei, X.-W.; Zhou, X.-M.; Wu, D.-H.; Liu, X.-W.; Ye, Y.; Wang, Q. $NiCo_2$ Alloys: Controllable Synthesis, Magnetic Properties, and Catalytic Applications in Reduction of 4-Nitrophenol. *J. Phys. Chem. C* **2011,** *115*, 16268-16274.

(379) Wu, K.-L.; Yu, R.; Li, X.-Z.; Wei, X.-W. Dendritic and Flowerlike Ni-Co Alloy Microstructures: A Comparison Study of their Catalytic Activities. *Micro Nano Lett.* **2012,** *7*, 1041-1045, 1045 pp.

(380) Bai, S.; Shen, X.; Zhu, G.; Li, M.; Xi, H.; Chen, K. In situ Growth of Ni_xCo_{100-x} Nanoparticles on Reduced Graphene Oxide Nanosheets and Their Magnetic and Catalytic Properties. *ACS Appl. Mater. Interfaces* **2012,** *4*, 2378-2386.

(381) Kohantorabi, M.; Gholami, M. R. M_xNi_{100-x} (M = Ag, and Co) Nanoparticles Supported on CeO_2 Nanorods Derived from Ce-Metal Organic Frameworks as an Effective Catalyst for Reduction of Organic Pollutants: Langmuir-Hinshelwood Kinetics and Mechanism. *New J. Chem.* **2017,** *41*, 10948-10958.

(382) Chen, F.; Xi, P.; Ma, C.; Shao, C.; Wang, J.; Wang, S.; Liu, G.; Zeng, Z. In Situ Preparation, Characterization, Magnetic and Catalytic Studies of Surfactant Free RGO/Fe_xCo_{100-x} Nanocomposites. *Dalton Trans.* **2013,** *42*, 7936-7942.

(383) Wu, K.-L.; Yu, R.; Wei, X.-W. Monodispersed $FeNi_2$ Alloy Nanostructures: Solvothermal Synthesis, Magnetic Properties and Size-Dependent Catalytic Activity. *CrystEngComm* **2012,** *14*, 7626-7632.

(384) Petkar, D. R.; Kadu, B. S.; Chikate, R. C. Highly Efficient and Chemoselective Transfer Hydrogenation of Nitroarenes at Room Temperature over Magnetically Separable Fe-Ni Bimetallic Nanoparticles. *RSC Adv.* **2014,** *4*, 8004-8010.

(385) Wu, D.; Zhang, Y.; Wen, M.; Fang, H.; Wu, Q. Fe_3O_4/FeNi Embedded Nanostructure and Its Kinetic Law for Selective Catalytic Reduction of *p*-Nitrophenyl Compounds. *Inorg. Chem.* **2017,** *56*, 5152-5157.

(386) Ficker, M.; Petersen, J. F.; Hansen, J. S.; Christensen, J. B. Hydrogenation of Aromatic Nitro Compounds with an Inexpensive and Efficient $CuSO_4$/$CoCl_2$ Catalyst Prepared in situ using $NaBH_4$ as the Hydrogen Source. *Org. Prep. Proced. Int.* **2014,** *46*, 176-182.

(387) Borah, B. J.; Bharali, P. Surfactant-Free Synthesis of CuNi Nanocrystals and their Application for Catalytic Reduction of 4-Nitrophenol. *J. Mol. Catal. A: Chem.* **2014,** *390*, 29-36.

(388) Deka, P.; Choudhury, R.; Deka, R. C.; Bharali, P. Influence of Ni on Enhanced Catalytic Activity of Cu/Co_3O_4 Towards Reduction of Nitroaromatic Compounds: Studies on the Reduction Kinetics. *RSC Adv.* **2016,** *6*, 71517-71528.

(389) Yang, J.; Shen, X.; Ji, Z.; Zhou, H.; Zhu, G.; Chen, K. In Situ Growth of Hollow CuNi Alloy Nanoparticles on Reduced Graphene Oxide Nanosheets and their Magnetic and Catalytic Properties. *Appl. Surf. Sci.* **2014,** *316*, 575-581.

(390) Fang, H.; Wen, M.; Chen, H.; Wu, Q.; Li, W. Graphene Stabilized Ultra-Small CuNi Nanocomposite with High Activity and Recyclability Toward Catalysing the Reduction of Aromatic Nitro-Compounds. *Nanoscale* **2016,** *8*, 536-542.

(391) Li, H.; Yue, F.; Yang, C.; Xue, P.; Li, N.; Zhang, Y.; Wang, J. Structural Evolution of a Metal-Organic Framework and Derived Hybrids Composed of Metallic Cobalt and Copper Encapsulated in Nitrogen-Doped Porous Carbon Cubes with High Catalytic Performance. *CrystEngComm* **2017,** *19*, 64-71.

(392) Xu, X.; Li, H.; Xie, H.; Ma, Y.; Chen, T.; Wang, J. Zinc Cobalt Bimetallic Nanoparticles Embedded in Porous Nitrogen-Doped Carbon Frameworks for the Reduction of Nitro Compounds. *J. Mater. Res.* **2017,** *32*, 1777-1786.

(393) Dalui, A.; Thupakula, U.; Khan, A. H.; Ghosh, T.; Satpati, B.; Acharya, S. Mechanism of Versatile Catalytic Activities of Quaternary CuZnFeS Nanocrystals Designed by a Rapid Synthesis Route. *Small* **2015,** *11*, 1829-1839.

(394) Gawande, M. B.; Branco, P. S.; Varma, R. S. Nano-Magnetite (Fe_3O_4) as a Aupport for Recyclable Catalysts in the Development of Sustainable Methodologies. *Chem. Soc. Rev.* **2013,** *42*, 3371-3393.

(395) Jacobs, J. P.; Maltha, A.; Reintjes, J. G. H.; Drimal, J.; Ponec, V.; Brongersma, H. H. The Surface of Catalytically Active Spinels. *J. Catal.* **1994,** *147*, 294-300.

(396) Singh, C.; Goyal, A.; Singhal, S. Nickel-Doped Cobalt Ferrite Nanoparticles: Efficient Catalysts for the Reduction of Nitroaromatic Compounds and Photo-Oxidative Degradation of Toxic Dyes. *Nanoscale* **2014,** *6*, 7959-7970.

(397) Goyal, A.; Kapoor, S.; Samuel, P.; Kumar, V.; Singhal, S. Facile Protocol for Reduction of Nitroarenes using Magnetically Recoverable $CoM_{0.2}Fe_{1.8}O_4$ (M = Co, Ni, Cu and Zn) Ferrite Nanocatalysts. *RSC Adv.* **2015,** *5*, 51347-51363.

(398) Goyal, A.; Bansal, S.; Kumar, V.; Singh, J.; Singhal, S. Mn Substituted Cobalt Ferrites ($CoMn_xFe_{2-x}O_4$ (x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0)): As Magnetically Separable Heterogeneous Nanocatalyst for the Reduction of Nitrophenols. *Appl. Surf. Sci.* **2015,** *324*, 877-889.

(399) Goyal, A.; Bansal, S.; Samuel, P.; Kumar, V.; Singhal, S. $CoMn_{0.2}Fe_{1.8}O_4$ Ferrite Nanoparticles Engineered by Sol-Gel Technology: An Expert and Versatile Catalyst for the Reduction of Nitroaromatic Compounds. *J. Mater. Chem. A* **2014,** *2*, 18848-18860.

(400) Goyal, A.; Bansal, S.; Singhal, S. Facile Reduction of Nitrophenols: Comparative Catalytic Efficiency of MFe_2O_4 (M = Ni, Cu, Zn) Nano Ferrites. *Int. J. Hydrogen Energy* **2014,** *39*, 4895-4908.

(401) Feng, J.; Su, L.; Ma, Y.; Ren, C.; Guo, Q.; Chen, X. $CuFe_2O_4$ Magnetic Nanoparticles: A Simple and Efficient Catalyst for the Reduction of Nitrophenol. *Chem. Eng. J.* **2013,** *221*, 16-24.

(402) Zhang, H.; Gao, S.; Shang, N.; Wang, C.; Wang, Z. Copper Ferrite-Graphene Hybrid: a Highly Efficient Magnetic Catalyst for Chemoselective Reduction of Nitroarenes. *RSC Adv.* **2014,** *4*, 31328-31332.

(403) Zhang, H. Y.; Zhao, Y.; Liu, W. H.; Gao, S. T.; Shang, N. Z.; Wang, C.; Wang, Z. Preparation of Magnetically Separable $Cu_{6/7}Co_{1/7}Fe_2O_4$-Graphene Catalyst and its Application in Selective Reduction of Nitroarenes. *Catal. Commun.* **2015,** *59*, 161-165.

(404) Zhuang, Y. T.; Gao, W.; Yu, Y. L.; Wang, J. H. Facile Fabrication of Three-Dimensional Porous $CuFe_2O_4$ Cages as Highly Efficient and Recyclable Heterogeneous Catalyst. *Mater. Des.* **2017,** *130*, 294-301.

(405) Arumugam, V.; Sriram, P.; Yen, T.-J.; Redhi, G. G.; Gengan, R. M. Nano-Material as an Excellent Catalyst for Reducing a Series of Nitroanilines and Dyes: Triphosphonated Ionic Liquid- $CuFe_2O_4$-Modified Boron Nitride. *Appl. Catal., B* **2018,** *222*, 99-114.

(406) Sajadi, S. M.; Nasrollahzadeh, M.; Maham, M. Aqueous Extract from sSeeds of Silybum Marianum L. as a Green Material for Preparation of the Cu/Fe_3O_4 Nanoparticles: A Magnetically Recoverable and Reusable Catalyst for the Reduction of Nitroarenes. *J. Colloid Interface Sci.* **2016,** *469*, 93-98.

(407) Zeynizadeh, B.; Mohammadzadeh, I.; Shokri, Z.; Hosseini, S. A. Synthesis and Characterization of $NiFe_2O_4$@Cu Nanoparticles as a Magnetically Recoverable Catalyst for Reduction of Nitroarenes to Arylamines with $NaBH_4$. *J. Colloid Interface Sci.* **2017,** *500*, 285-293.

(408) Pal, J.; Mondal, C.; Sasmal, A. K.; Ganguly, M.; Negishi, Y.; Pal, T. Account of Nitroarene Reduction with Size- and Facet-Controlled CuO-MnO_2 Nanocomposites. *ACS Appl. Mater. Interfaces* **2014,** *6*, 9173-9184.

(409) Du, C.; He, S.; Gao, X.; Chen, W. Hierarchical Cu@MnO_2 Core–Shell Nanowires: A Nonprecious-Metal Catalyst with an Excellent Catalytic Activity Toward the Reduction of 4-Nitrophenol. *ChemCatChem* **2016,** *8*, 2885-2889.

(410) Kim, J. G.; Kim, S. M.; Lee, I. S. Mechanistic Insight into the Yolk@Shell Transformation of MnO@Silica Nanospheres Incorporating Ni^{2+} Ions toward a Colloidal Hollow Nanoreactor. *Small* **2015,** *11*, 1930-1938.

(411) Deka, P.; Sarmah, P.; Deka, R. C.; Bharali, P. Hetero–Nanostructured Ni/α-Mn_2O_3 as Highly Active Catalyst for Aqueous Phase Reduction Reactions. *ChemistrySelect* **2016,** *1*, 4726-4735.

(412) Sarmah, K.; Pal, J.; Maji, T. K.; Pratihar, S. Magnetically Recoverable Heterobimetallic $Co_2Mn_3O_8$: Selective and Sustainable Oxidation and Reduction Reactions. *ACS Sustainable Chem. Eng.* **2017,** *5*, 11504-11515.

(413) Cenini, S.; Ragaini, F. *Catalytic Reductive Carbonylation of Organic Nitro Compounds*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996.

(414) Knifton, J. F. Homogeneous catalyzed reduction of nitro compounds. IV. Selective and Sequential Hydrogenation of Nitroaromatics. *J. Org. Chem.* **1976,** *41*, 1200-1206.

(415) Deshpande, R. M.; Mahajan, A. N.; Diwakar, M. M.; Ozarde, P. S.; Chaudhari, R. V. Chemoselective Hydrogenation of Substituted Nitroaromatics Using Novel Water-Soluble Iron Complex Catalysts. *J. Org. Chem.* **2004,** *69*, 4835-4838.

(416) Wienhofer, G.; Baseda-Kruger, M.; Ziebart, C.; Westerhaus, F. A.; Baumann, W.; Jackstell, R.; Junge, K.; Beller, M. Hydrogenation of Nitroarenes using Defined Iron-Phosphine Catalysts. *Chem. Commun.* **2013,** *49*, 9089-9091.

(417) Boothroyd, S. R.; Kerr, M. A. A Mild and Efficient Method for the Preparation of Anilines from Nitroarenes. *Tetrahedron Lett.* **1995,** *36*, 2411-2414.

(418) Sharma, U.; Verma, P. K.; Kumar, N.; Kumar, V.; Bala, M.; Singh, B. Phosphane-Free Green Protocol for Selective Nitro Reduction with an Iron-Based Catalyst. *Chem. Eur. J.* **2011,** *17*, 5903-5907.

(419) Verma, P. K.; Bala, M.; Thakur, K.; Sharma, U.; Kumar, N.; Singh, B. Iron and Palladium(II) Phthalocyanines as Recyclable Catalysts for Reduction of Nitroarenes. *Catal. Lett.* **2014,** *144*, 1258-1267.

(420) MacNair, A. J.; Tran, M.-M.; Nelson, J. E.; Sloan, G. U.; Ironmonger, A.; Thomas, S. P. Iron-Catalysed, General and Operationally Simple Formal Hydrogenation Using Fe(OTf)$_3$ and NaBH$_4$. *Org. Biomol. Chem.* **2014,** *12*, 5082-5088.

(421) Patil, N. M.; Sasaki, T.; Bhanage, B. M. Immobilized Iron Metal-Containing Ionic Liquid-Catalyzed Chemoselective Transfer Hydrogenation of Nitroarenes into Anilines. *ACS Sustainable Chem. Eng.* **2016,** *4*, 429-436.

(422) Wilkinson, H. S.; Tanoury, G. J.; Wald, S. A.; Senanayake, C. H. Chemoselective Reductions of Nitroarenes: Bromoethanol-Assisted Phthalocyanatoiron/NaBH$_4$ Reductions. *Tetrahedron Lett.* **2001,** *42*, 167-170.

(423) Shigeyoshi, S.; Shinji, M.; Katsutoshi, O. New Reduction Catalysis of Metalloporphyrins. Catalytic Reduction of Nitrobenzene to Aniline with Tetraphenylporphyrinato-iron(III) Chloride–NaBH$_4$ System. *Chem. Lett.* **1991,** *20*, 195-198.

(424) Wienhöfer, G.; Sorribes, I.; Boddien, A.; Westerhaus, F.; Junge, K.; Junge, H.; Llusar, R.; Beller, M. General and Selective Iron-Catalyzed Transfer Hydrogenation of Nitroarenes without Base. *J. Am. Chem. Soc.* **2011,** *133*, 12875-12879.

(425) Sunada, Y.; Kawakami, H.; Imaoka, T.; Motoyama, Y.; Nagashima, H. Hydrosilane Reduction of Tertiary Carboxamides by Iron Carbonyl Catalysts. *Angew. Chem., Int. Ed.* **2009,** *48*, 9511-9514, S9511/9511-S9511/9519.

(426) Hanada, S.; Tsutsumi, E.; Motoyama, Y.; Nagashima, H. Practical Access to Amines by Platinum-Catalyzed Reduction of Carboxamides with Hydrosilanes: Synergy of Dual Si-H Groups Leads to High Efficiency and Selectivity. *J. Am. Chem. Soc.* **2009,** *131*, 15032-15040.

(427) Junge, K.; Wendt, B.; Shaikh, N.; Beller, M. Iron-Catalyzed Selective Reduction of Nitroarenes to Anilines Using Organosilanes. *Chem. Commun.* **2010,** *46*, 1769-1771.

(428) Pehlivan, L.; Metay, E.; Laval, S.; Dayoub, W.; Demonchaux, P.; Mignani, G.; Lemaire, M. Iron-Catalyzed Selective Reduction of Nitro Compounds to Amines. *Tetrahedron Lett.* **2010,** *51*, 1939-1941.

(429) Pehlivan, L.; Métay, E.; Laval, S.; Dayoub, W.; Demonchaux, P.; Mignani, G.; Lemaire, M. Alternative Method for the Reduction of Aromatic Nitro to Amine Using TMDS-Iron Catalyst System. *Tetrahedron* **2011,** *67*, 1971-1976.

(430) Zhu, K.; Shaver, M. P.; Thomas, S. P. Chemoselective Nitro Reduction and Hydroamination Using a Single Iron Catalyst. *Chem. Sci.* **2016,** *7*, 3031-3035.

(431) Zhu, K.; Shaver, M. P.; Thomas, S. P. Amine-Bis(Phenolate) Iron(III)-Catalyzed Formal Hydroamination of Olefins. *Chem. Asian J.* **2016,** *11*, 977-980.

(432) Gui, J.; Pan, C.-M.; Jin, Y.; Qin, T.; Lo, J. C.; Lee, B. J.; Spergel, S. H.; Mertzman, M. E.; Pitts, W. J.; La Cruz, T. E. *et al.* Practical Olefin Hydroamination with Nitroarenes. *Science* **2015,** *348*, 886-891.

(433) Sharma, U.; Kumar, P.; Kumar, N.; Kumar, V.; Singh, B. Highly Chemo- and Regioselective Reduction of Aromatic Nitro Compounds Catalyzed by Recyclable Copper(II) as well as Cobalt(II) Phthalocyanines. *Adv. Synth. Catal.* **2010,** *352*, 1834-1840.

(434) Chao, C.-G.; Bergbreiter, D. E. Highly Organic Phase Soluble Polyisobutylene-Bound Cobalt Phthalocyanines as Recyclable Catalysts for Nitroarene Reduction. *Catal. Commun.* **2016,** *77*, 89-93.

(435) Yadav, S.; Kumar, S.; Gupta, R. Cobalt Complexes of Pyrrolecarboxamide Ligands as Catalysts in Nitro Reduction Reactions: Influence of Electronic Substituents on Catalysis and Mechanistic Insights. *Inorg. Chem. Front.* **2017,** *4*, 324-335.

(436) Kumar, S.; Gupta, R. Cobalt Complexes Catalyze Reduction of Nitro Compounds: Mechanistic Studies. *ChemistrySelect* **2017,** *2,* 8197-8206.

(437) Srivastava, S.; Dagur, M. S.; Ali, A.; Gupta, R. Trinuclear {Co^{2+}-M^{3+}-Co^{2+}} Complexes Catalyze Reduction of Nitro Compounds. *Dalton Trans.* **2015,** *44*, 17453-17461.

(438) Sun, S.; Quan, Z.; Wang, X. Selective Reduction of Nitro-Compounds to Primary Amines by Nickel-Catalyzed Hydrosilylative Reduction. *RSC Adv.* **2015,** *5*, 84574-84577.

(439) Vijaykumar, G.; Mandal, S. K. An Abnormal N-Heterocyclic Carbene Based Nickel Complex for Catalytic Reduction of Nitroarenes. *Dalton Trans.* **2016,** *45*, 7421-7426.

(440) Lopes, R.; Pereira, M. M.; Royo, B. Selective Reduction of Nitroarenes with Silanes Catalyzed by Nickel N-Heterocyclic Carbene Complexes. *ChemCatChem* **2017,** *9*, 3073-3077.

(441) Sharma, U.; Kumar, N.; Verma, P. K.; Kumar, V.; Singh, B. Zinc Phthalocyanine with PEG-400 as a Recyclable Catalytic System for Selective Reduction of Aromatic Nitro Compounds. *Green Chem.* **2012,** *14*, 2289-2293.

(442) Bhattacharjee, A.; Ahmaruzzaman, M. A Facile and Green Strategy for the Synthesis of 1-Dimensional Luminescent ZnO Nanorods and their Reduction Behavior for Aromatic Nitro-Compounds. *RSC Adv.* **2016,** *6*, 527-533.

(443) Saba, J.; Muhammad Ramzan Saeed Ashraf, J.; Shanza Rauf, K.; Nazish, J. Synthesis, Characterization and Catalytic Application of Polyhedron Zinc Oxide Microparticles. *Mater. Res. Express* **2017,** *4*, 015902.

(444) Cheung, C. W.; Leendert Ploeger, M.; Hu, X. Amide Synthesis via Nickel-Catalysed Reductive Aminocarbonylation of Aryl Halides with Nitroarenes. *Chem. Sci.* **2018,** *9*, 655-659.

(445) Cheung, C. W.; Hu, X. Amine Synthesis via Iron-Catalysed Reductive Coupling of Nitroarenes with Alkyl Halides. *Nat. Commun.* **2016,** *7*, 12494pp.

(446) Peng, J.-B.; Geng, H.-Q.; Li, D.; Qi, X.; Ying, J.; Wu, X.-F. Palladium-Catalyzed Carbonylative Synthesis of α,β-Unsaturated Amides from Styrenes and Nitroarenes. *Org. Lett.* **2018,** *20*, 4988-4993.

(447) Zhou, F.; Wang, D.-S.; Guan, X.; Driver, T. G. Nitroarenes as the Nitrogen Source in Intermolecular Palladium-Catalyzed Aryl C–H Bond Aminocarbonylation Reactions. *Angew. Chem. Int. Ed.* **2017,** *56*, 4530-4534.

(448) Fang, X.; Jackstell, R.; Beller, M. Selective Palladium-Catalyzed Aminocarbonylation of Olefins with Aromatic Amines and Nitroarenes. *Angew. Chem. Int. Ed.* **2013,** *52*, 14089-14093.

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