Recent Progress for Hydrogen Production from Ammonia and Hydrous Hydrazine

Decomposition: A Review on Heterogeneous Catalysts

Panayiota Adamou1, Silvio Bellomi2, Sanaa Hafeez3, Eleana Harkou1, S.M. Al-Salem4, Alberto Villa2, Nikolaos Dimitratos5, George Manos3 and Achilleas Constantinou1*

1. Department of Chemical Engineering Cyprus University of Technology, 57 Corner of Athinon and Anexartisias, 3036 Limassol, Cyprus
2. Dipartimento di Chimica, Università degli Studi di Milano, via Golgi, 20133 Milan, Italy.
3. Department of Chemical Engineering, University College London, London WCIE 7JE, UK.
4. Environment & Life Sciences Research Centre, Kuwait Institute for Scientific Research, P.O. Box: 24885, Safat 13109, Kuwait.
5. Dipartimento di Chimica Industriale e dei Materiali, ALMA MATER STUDIORUM Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy.

* Author for correspondence: a.konstantinou@cut.ac.cy;

Abstract

In response to the growing trend of greenhouse gas emissions from the production and use of conventional fuels, COx free hydrogen generation is introduced as an alternative and efficient energy carrier. Due to hydrogen’s storage challenges, is more efficient to be produced on-site by other chemical compounds for fuel cell applications. This work outlines the production of hydrogen (H2) from ammonia (NH3) and hydrous hydrazine (N2H4.H2O) catalytic decomposition. Both of these substances are giving nitrogen (N2) as a by-product, which is not toxic. Moreover, heterogeneous catalysts that were studied through the years are presented. Lastly, a reactoristic view of the ammonia decomposition is provided with different reactors such as catalytic membrane reactors (CMRs), fixed-bed reactors (FBRs) and micro-reactors (MRs) for the evaluation of their performance.

Keywords: Ammonia, Hydrous Hydrazine, Hydrogen, Catalysts, Reactors
1 Introduction

Environmental concerns are increasing as the extensive use of fossil fuels in the energy sector is the biggest contributor to climate change. Fossil fuels undergo the process of combustion to release their energy content, polluting the atmosphere with emissions of greenhouse gases (GHGs) and harmful substances. These resources are non-renewable and are not evenly distributed around the world [1]. There is an increasing urge in recent years to find and adopt alternative emission-free energy sources in hope to stabilise the negative impacts conventional fuels have created in the environment. Hydrogen (H$_2$) is preferred as an energy carrier due to its zero emissions during combustion and its generation from various paths such as non-renewable sources, biomass and water electrolysis [2].

Hydrogen can be produced by either from fossil fuels, capturing carbon emissions or renewable resources. Depending on the material, H$_2$ can be classified as grey, blue, and green respectively. Two of the common methods to produce H$_2$ is steam methane reforming and water splitting reactions such as water electrolysis [3–6]. Fuel cells then can be used to convert H$_2$ into power through the electrochemical reaction that follows (Eq. 1):

$$2H_2 + O_2 \rightarrow 2H_2O + \text{Energy}$$  \hspace{1cm} (1)

Eq. 1 shows H$_2$ reaction with oxygen to produce water and energy in the form of electricity or heat as the inverse reaction of electrolysis. Fuel cells are very promising and are already used in various stationary and mobile applications such as back-up power supplies, road vehicles, as well as rockets and space shuttles. The main concept revolves around generating green energy which is considered revolutionary [7]. However, its storage and transportation problems have not yet reached an applicable level for further industrial use.

Ammonia (NH$_3$), among other H$_2$ energy sources, is a promising alternative. It is mainly produced from the decomposition of urea and other nitrogen compounds during wastewater treatment processes or from the microbial decomposition of organic substances containing nitrogen [8]. It possesses high H$_2$ content (17.8 wt%) and a large energy density (3000 Wh/kg). It has greater volumetric hydrogen density than liquid H$_2$ (121 kg H$_2$/m$^3$) and can be liquefied and stored at room temperature facilitating transportation and storage [9–12]. Furthermore, the decomposition of ammonia is CO$_2$-free producing only H$_2$ and nitrogen (N$_2$) (Eq. 2) [13].

$$\text{NH}_3 \rightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2$$  \hspace{1cm} (2)
Ramsay and Young [14] were the first to study the temperature at which ammonia decomposition takes place and the influence of the vessel or tube material that contains the gas in the early 1880s. Then at the beginning of the 20th century Perman and Atkinson [15] studied both the effect of temperature and pressure on the rate of decomposition as well as the catalytic activity of Hg, Fe, and Pt.

Hydrous hydrazine (N$_2$H$_4$.H$_2$O) has also been proposed as a promising candidate for H$_2$ generation. It can be produced by the Raschig process that involves the ammonolysis of hypochlorite to hydrazine and ammonia or the oxidation of anhydrous ammonia by chlorine [16]. Hydrous hydrazine has a high hydrogen content (8.0 wt%) and due to its carbon-free content, the generation of H$_2$ has zero emissions [17]–[20]. The products from hydrazine decomposition are H$_2$ and N$_2$; however, an undesirable side reaction of incomplete decomposition may occur producing ammonia, which must be avoided because it reduces the efficiency of the H$_2$ generation process. The two reaction pathways for hydrazine decomposition are depicted in Eqs. (3-4) [21].

$$H_2NNH_2 \rightarrow N_2 + 2H_2 \quad (3)$$
$$3H_2NNH_2 \rightarrow 4NH_3 + N_2 \quad (4)$$

This review will highlight H$_2$ storage challenges and the generation of H$_2$ from ammonia and hydrous hydrazine. Moreover, the heterogeneous catalysts for the decomposition of the substances mentioned above and the structural properties of the catalysts, will be addressed. Furthermore, different types of reactors that have been applied for the ammonia decomposition, will be covered to provide an overview of the most innovative and efficient future systems. Regarding hydrous hydrazine, there are not many studies in reactors and therefore, reactor set-ups will be not discussed.

### 2 Hydrogen Storage Challenges

Although H$_2$ offers an attractive and promising solution as an alternative energy carrier, its storage and transportation are one of the main technical barriers preventing H$_2$ for wider applications. This is due to hydrogen’s very low density of 0.089 kg/m$^3$ at 0°C and 1 bar. At ambient temperatures and 1 atm pressure, 1 kg of H$_2$ occupies 11 m$^3$, which results in a large volume required for storage. Nonetheless, H$_2$ is extremely flammable with a flame speed nearly
an order of magnitude higher than gasoline when mixed with air, therefore, its safety issues must be resolved [22].

Due to the lack of appropriate infrastructure for storage, transportation and distribution of H₂, new methods must be found to store it safely. For large scale and long-term storage, different underground storage sites were proposed such as salt caverns, aquifer formations or depleted oil and gas fields. Salt caverns are currently the most favorable method. No in-situ reactions either with microorganisms or any chemical elements occurred so far and the leakage rates are very low because salt caverns exhibit the required tightness. In contrast with aquifer formations or depleted oil and gas fields that occur naturally, salt caverns need to be developed in an already existing underground salt formations, so not all regions have the necessary geological characteristics [23].

Moreover, it is necessary to increase the volumetric energy (density) of H₂ which can happen either by liquefying it or by compressing it. Pressurised tanks can take the form of cylindrical or spherical vessels or bottles, and while raising the pressure, gaseous H₂ density increases achieving higher storage density. These are currently used in stationary applications mainly to store hydrogen in hydrogen refuelling stations [24]. Their cost may differ from the material used and the pressure applied in the tank. On the other hand, cryogenic tanks store liquefied hydrogen at -253°C (atmospheric pressure) because the liquefaction process increases H₂ volumetric density drastically. These are not designed to withstand high pressures inside, hence they must be isolated to reduce as much as possible heat transfer. However, compressing requires high pressures and liquefying needs extremely low temperatures such as -253°C that can only be achieved with multiple heat exchangers and a combination of multiple cooling cycles [25].

New technologies such as metal hydrides and carbon nanotubes are gaining attention for their H₂ storage properties. Metal hydrides can store H₂ due to their large storage capacity at ambient pressure and temperature. Hydrogen reacts with metals which have the ability to absorb and desorb it by breaking or bonding the chemical bonds making them an efficient form of hydrogen storage [26]. Adsorption of H₂ in carbon nanostructures is an attractive solution for hydrogen storage due to the high surface area of carbon. There are a variety of carbon materials, such as single walled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs) and carbon nanofibers (CNFs). However due to some controversial results that were obtained from some studies regarding the H₂ adsorption measurements, much research is still needed for
their efficient usage [27]. For example, in the late 1990s, Dillon et al. [28] suggested that SWCNTs have a very high H\textsubscript{2} uptake up to 5-10\%. Moreover, Chambers et al. [29] published an even more extraordinary result. It was claimed that the hydrogen storage capacity of graphite nanofibers (GNFs) materials was up to 67.55\%. Both of these results were questionable thus research groups [30]–[32] tried to reproduce and validate the results without success since the capacity of the materials was very much lower.

3 Hydrogen Production Routes

Various raw materials can be utilised to produce H\textsubscript{2} following different production routes. Given the raw material, H\textsubscript{2} can be colour coded as black, grey, blue or green.

In spite of the growing number of studies focusing on renewable hydrogen production, fossil fuel-based hydrogen generation is still being examined. Black or brown H\textsubscript{2} is produced from coal through the process of gasification. It is considered a very environmentally damaging method as carbon dioxide and carbon monoxide are also generated and emitted in the atmosphere. Liu et al. [33] investigated the gasification mechanism and developed a coal supercritical water gasification reaction kinetic model taking into consideration the migration mechanism of nitrogen and sulfur. The model could not only predict the generation of hydrogen, carbon monoxide and carbon dioxide but ammonia and hydrogen sulfide as well, proving the interaction between hydrocarbon gas and the gasification products of nitrogen and sulfur.

H\textsubscript{2} is labelled grey when extracted from natural gas via steam-methane reforming. It is the most common form nowadays with over 95\% of the global hydrogen production coming from reforming of conventional fuels and around 50\% of that is generated from steam reforming of natural gas [4]. SMR is an endothermic reaction (600-700\,°C) and the catalysts mostly used for this reaction are nickel-based. Ngo et al. [34] utilised a SMR unit with a furnace and a reactor, where the furnace produces heat via the natural gas reaction with oxygen and the reactor consumes heat and generates H\textsubscript{2}. Another study conducted by Cho et al. [35] used facility-level data to examine the pollutant emissions which may differ from the theoretical estimates due to various process conditions and types of pollution controlled equipment. Direct emissions from the 33 facilities used were 9.35 kg CO\textsubscript{2}/kg H\textsubscript{2} and increased up to 11.2 kg CO\textsubscript{2}/kg H\textsubscript{2} when the
full cycle of H₂ production was included. Increasing 10% in hydrogen production efficiency
the global warming impact can be reduced up to 11.1%.

Blue H₂ is produced from fossil fuels like black and grey H₂ but the carbon generated from the
process is captured. It can be described with the term carbon neutral but low-carbon H₂ would
be a more appropriate term since not all carbon emissions are captured. Even though CO₂ can
be captured by absorbents or amine solvents, it must be stored after, which is costly. Therefore
Khan et al. [36] explored the possibility to use the carbon captured by converting into formic
acid by the electrodereduction. An amine-based CO₂ capture unit was utilised with 90% capture
efficiency. The carbon could either be stored or utilised. It was concluded that by utilising it
instead of storing it, is more cost-effective and is a promising approach for further future work.

Lastly, green H₂ uses renewable sources such as biomass, geothermal, wind and solar energy
[37]. One of the most common methods used to obtain green H₂ is water splitting reactions
such as electrolysis of water. Water reacts at the cell’s anode and under the influence of current
it decomposes and produces O₂ at the anode of the cell and finally H₂ at the cathode [38].
Another common method is the dehydrogenation of hydrogen carrier compounds with zero
CO₂ emissions that will be discussed later.

Apart from these, H₂ can be classified to turquoise, pink, yellow and white which are not
commonly used. Turquoise refers to H₂ produced from methane pyrolysis with solid carbon as
a by-product. Even though methane pyrolysis is not a sustainable process since natural gas
reserves are depleting, it can provide a temporary solution until renewable technologies are
fully developed. The process begins with the cracking of methane to H₂ and solid carbon, then
the removal of the carbon from the stream and lastly, the purification of the gas stream. High
temperatures are needed for methane pyrolysis, up to 1000°C for non-catalytic systems.
Suitable catalysts such as nickel, iron, and carbon have been extensively studied and the
decomposition of methane can be triggered at lower temperatures (500-800°C) [39].

Pink (or purple) and yellow H₂ are both produced through electrolysis using nuclear power and
solar power respectively [40]. Water electrolysis technology consists of an anode, a cathode,
an electrolyte, and power supply. Then, electrons flow from the direct current source’s to
cathode where hydrogen is formed along with oxygen. The difference from conventional
electrolysis to nuclear high temperature electrolysis (HTE), is that the later uses heat from
nuclear power plants to moderate electricity consumed for electrolysis. In general, nuclear HTE
occurs at 800-1000°C and an yttria-stabilised zirconia is used as an electrolyte [41]. A solar-
based electrolysis consists of a concentrating collector, a heat engine, an electrical generator, and electrolyser. A part of the absorbed solar radiation is converted to mechanical work and then the electrical generator transforms it to electrical power. Then, the generated electricity is used to electrolyse water and produce H$_2$ and O$_2$ [42].

White H$_2$ refers to the by-product obtained from industrial processes such as catalytic thermochemical splitting of water, or it may be referred to as its natural occurring form. The thermochemical splitting occurs without intermediate step and is based on the use of concentrated solar energy. This pathway may further reduce economic and environmental costs [43].

Potential applications of H$_2$ after its production are its use as an industrial feedstock, power generation, stationary and transportation [44]. Fig. 1 summarises the H$_2$ colour spectrum according to the feedstock and production used.

![Hydrogen colour spectrum](image)

Fig.1. Hydrogen colour spectrum.

4 Ammonia Decomposition as a sustainable hydrogen production method

4.1 Heterogeneous Catalysis of Ammonia

Heterogeneous catalysis can be described as the catalysis whereas the phase of the catalyst is different from the phase of the reactants/products. Thus, heterogeneous catalysts are, mostly, in the solid state while the reactant mixture is either liquid or gas, in contrast with homogeneous
catalysts that exist in the same phase with the mixture. Heterogeneous catalysts have the ability
to regenerate, separate easily from the products, shaped into different geometries and give high
rates [45]. Table 1 summarises the most effective heterogeneous catalysts utilized for the
decomposition of ammonia.

Since the 19th century, ammonia decomposition has been investigated mostly to understand the
ammonia synthesis with the presence or absence of catalysts. Over the last decade, the catalytic
decomposition of ammonia has gained a lot of attention and catalysts such as platinum (Pt)
[46], palladium (Pd) [47], ruthenium (Ru) [48] and, rhodium (Rh) [49] that were known to
catalyse ammonia synthesis have been used in different experiments [50]. Ru was found to be
the most active and studied catalyst as there is a plethora of studies according to Ru-based
catalysts [51]–[55]. Unfortunately, the large scale of application of Ru catalysts is not cost
effective and their limited availability leads to the necessary development of cheaper catalytic
systems with the same efficacy. The production steps of H₂ by ammonia are depicted in Fig.2.

Fig.2. Production steps of hydrogen by ammonia [12].

Ni metal particles were used as catalysts with MgAl₂O₄ as supports by Qiu et al. [56] for
investigation of the support effect on the catalytic decomposition of ammonia. From the
catalysts tested Ni/MgAl₂O₄ – LDH, developed by hydrothermal synthesis, had the best
catalytic activity with 88.7% NH₃ conversion and a H₂ production rate of 1782.6 mmol g₉cat⁻¹ h⁻¹
at 600 °C with a stable performance for a period of 30 h. Ni/MgAl₂O₄ – LDH catalyst had the
highest surface area (148.3 m²/g) and therefore it resulted in high Ni dispersion (29.6 %)
enhancing the NH$_3$ conversion and weakening the H$_2$ poisoning. Ni/MgAl$_2$O$_4$ – LDH catalyst was further examined for its stability at a temperature range of 550-650°C for 24 h and the results showed that the catalyst was highly stable due to the strong metal-support interactions. It was concluded that this catalyst with high stability, activity, and low cost is essential to be developed more and used in upscale application for H$_2$ generation.

Cobalt particles supported on carbon doped with nitrogen were prepared via pyrolys of ZIF-67 at a range of temperatures (Co/NC-X, X = 500, 600, 700 and 800°C) by Li et al. [57]. The synthesis process of the catalysts resulted in an evenly dispersion of the Co particles hindering their aggregation. At temperatures below 300°C the catalysts were inactive. While increasing the temperature the conversion of ammonia increased and the best catalytic activity was obtained by Co/NC-600 with an NH$_3$ conversion of 80% and H$_2$ production rate of 26.78 mmol H$_2$ g$_{cat}^{-1}$ min$^{-1}$ at 500°C and hardly decreased even after 72 h. The bond strength between the metal and nitrogen, according to previous studies, plays a key role in the decomposition of ammonia. If the bond is either too weak or too strong it affects the adsorption of NH$_3$ and the desorption of the intermediate products resulting in a low catalytic activity. Thus, medium metal-nitrogen bond strength is required for this reaction and from further investigation it was found that the Co-N bond energy of Co/NC-600 catalyst is in the middle range and thus acting beneficial for the reaction.

Ru particles supported on SmCeO$_x$ were investigated by Tang et al. [58] for evaluation of the effect of the Sm doping to the catalysts. At 400°C, the Ru/SmCeO$_x$ catalyst, with 1.4 nm average particle size, obtained a conversion rate of 74.9% corresponding to a H$_2$ production rate of 161.1 mmol g$_{Ru}^{-1}$ min$^{-1}$, much higher than other supports with Ru particles tested for this catalytic reaction. Characterization techniques were used to study the properties and structure of the Ru/SmCeO$_x$ catalyst. The high activity was attributed to the doping of Sm that formed in plenty of oxygen vacancies which have strong interaction with Ru resulting in a high Ru dispersion.

A series of Co$_3$O$_4$ catalysts supported on barium hexaaluminate (BHA) with various mass loadings of Co (XCo/BHA, X = 10%, 20%, 30%, 35% and 40%) and 0.5 g BHA were prepared by Li et al. [59]. BHA alone was inactive and with an increase of Co loading the activity also increased. The 35Co/BHA catalyst demonstrated the highest catalytic activity among the others with a conversion rate of 87.2% at 500°C and a H$_2$ production rate of 29.2 mmol H$_2$ g$_{cat}^{-1}$ min$^{-1}$. After 200 h the conversion rate was at 85% indicating the catalysts great stability.
Ru-based catalysts supported on reduced graphene oxide were developed by Pinzón et al. [60] for hydrogen generation by ammonia decomposition. The effect of the Ru loading as well as the effect of the amount of the support material were examined. With a content of Ru up to 2.5 wt% , an increase in the catalytic activity was noticed (92%), while Ru loading higher than 2.5 wt% resulted in agglomeration decreasing the number of active sites and therefore the ammonia conversion. With the addition of the pre-reducing agent the catalytic activity increased. The optimal catalytic activity was observed from 2.5Ru/10C-rGO catalyst with a conversion of 96% and H₂ production rate of 349.7 mmol H₂ g₆₆₁ min⁻¹. After 60 h of reaction the catalyst did not show any significant change in its performance.

In an attempt to imitate the activity of the Ru catalysts, Kirste et al. [61] developed alloys of different unsupported bimetallic catalysts (CoRe₁.₆, Ni₂Mo₂N and Co₃Mo₃N) for the on-demand production of H₂ via ammonia decomposition. In parallel, 7 wt% Ru/CNTs catalytic particles were also synthesized to compare the catalytic activities. CoRe₁.₆ obtained a similar activity with Ru/CNTs due to the alloy synergistic effect. The catalyst was pre-reduced at a temperature range of 400-600°C, which had a major impact on the catalytic performance with an increase of the temperature. At 500 °C reaction temperature and 600°C reduction temperature, NH₃ conversion was above 90 % and after 6 consecutive runs CoRe₁.₆ presented excellent stability with no significant changes in the structure except the partial oxidation and re-reduction of the Co particles that acts in favour on the restart of the NH₃ decomposition.

Potassium promoted iron catalysts supported on carbon (K⁺-Fe/C) were studied by Jedynak et al. [62] to show the influence of the iron particle sizes on the rate of ammonia decomposition. Results showed that smaller particles gave higher TOFs in contrast with larger particles. K⁺-Fe5.7/C (12.5 nm) gave a TOF value of 0.5 s⁻¹ in contrast with the K⁺-Fe24/C (24 nm) that displayed a TOF value of 0.25 s⁻¹ concluding, that the smaller the surface of iron crystallites is, the more advantageous are the catalytic properties.

Ganley et al. [63] examined 13 metallic catalysts (Ru, Ni, Rh, Co, Ir, Fe, Pt, Cr, Pd, Cu, Te, Se, Pb) supported on pellets of activated alumina in order to suggest potential alternatives of Ru catalysts due to their high cost. Ru was the most active catalyst and besides Ni that had 40% lower activity than Ru, all the others were not efficient for the ammonia decomposition reaction. Also, depending on the catalyst that is used, the rate limiting step differs regarding nitrogen desorption or N-H bond scission. This suggests that is unlikely to predict catalytic
behaviour using only one parameter by assuming that a range of metallic catalysts have the
same rate determining step for a given reaction. Carbon nanotubes (CNTs) with residual Co or Fe nanoparticles were used as catalysts by Zhang et al. [64] for ammonia decomposition. With an increase in the temperature, ammonia conversion also increased and even at higher temperatures such as 700 °C the chemical composition and microstructure of CNTs remained the same as it was before the reaction took place. Fe containing CNTs had an activation period of 1200 min with a conversion up to 76 % but Co containing CNTs showed the highest activity overall with a conversion almost up to 100 %. The higher activity of Co-containing CNTs might be due to their smaller particle size (4-20 nm) when compared with Fe-containing particles that were 10-50 nm, and the capacity of CNTs as electron reservoirs.

El-Shafie et al. [65] developed zeolite (SA-600A)-based catalysts with Ru and Li as supporting materials at different mixing ratios for H₂ generation from ammonia decomposition. For all the developed catalysts it was observed that increasing the temperature the conversion rate increased as well. It was observed that the catalyst was enhanced when the Li mixing ratio was increased, and the highest NH₃ conversion rate (99.9%) was obtained from the catalyst with a Li mixing ratio of 4 %. The increase of Ru ratio enhanced the conversion rate even more at lower temperatures. The catalyst with mixing ratio of 40 g (SA-600A)/5 g RuCl₃.nH₂O/3 g LiOH.H₂O obtained the highest catalytic activity and NH₃ conversion of 99.87 % at 490 °C.

Core-shell iron-based catalysts (α-Fe₂O₃-x@pSiO₂) were synthesized for ammonia decomposition by Feyen et al. [66]. The catalysts were found to be highly stable up to temperatures of 800 °C with higher reaction rates and full conversion for all the tested catalysts. Moreover, particle sizes between 35 and 75 mm showed a limited influence on the catalytic activity. Lastly, there were no diffusion limitations up to flow rates of 120000 cm³ g⁻¹ h⁻¹ that could have been observed from the porous silica shells.

Cobalt catalysts supported on different carbon materials were developed for H₂ production from ammonia decomposition by Zhang et al. [67]. The carbon materials that were utilized for the research were multi-walled carbon nanotubes (MWCNTs), single wall carbon nanotube (SWCNTs), three types of activated carbons (AC) and reduced graphene oxides (RGO). The highest NH₃ conversion was conducted by the Co/MWCNTs catalyst. The conversion of Co/RGO and Co/SWCNTs catalysts was very low and therefore they weren’t used for further studies. Moreover, the influence of post-treatment temperature on the catalytic performance of
10Co/MWCNTs (10% wt Co) was evaluated in this study at a temperature range of 230-700 °C. Highest TOF value was obtained at 600 °C and it reached up to 8.15 s⁻¹. Even after 20 h of catalytic test there was no significant change in the Co particle size. The fresh catalyst had a mean size of 4.8 nm while the used catalyst had 5.6 nm. Due to its higher catalytic stability and the excellent catalytic activity for the decomposition of ammonia, Co/MWCNTs catalyst could be promising for future applications.

Catalysts with 2 % Ru content supported on lanthania-ceria materials with different molar ratios were synthesized by Le et al. [68] to evaluate the H₂ production by ammonia decomposition. The catalytic activity was tested at temperature range of 300-500 °C and the Ru/La₀.₃₃Ce₀.₆₇ exhibited the best catalytic performance with an ammonia conversion of 91.9 % and H₂ formation rate of 6.2 mmol g⁻¹ cat⁻¹ min⁻¹. The acid-base properties of the LaₓCe₁-xOᵧ supports combined with the high dispersion of Ru particles resulted in the enhanced catalytic activity. After 100 h the catalyst maintained its high catalytic activity due to its excellent stability, since fresh and used catalyst had a mean particle size of 3.3 nm and 3.6 nm respectively, showing no significant difference in the size and structural morphology of the particle.

Monometallic Ni, Co and bimetallic Ni-Co alloy catalysts supported on SiO₂ were prepared by a co-impregnation method by Wu et al [69]. Bimetallic catalysts had better catalytic performance obtaining higher ammonia conversion due to the alloy synergistic effect between Ni and Co. Among the tested catalysts, the Ni₅Co₅/SiO₂ exhibited the highest catalytic activity achieving 76.8 % NH₃ conversion and H₂ formation rate of 25.71 mmol g⁻¹ cat⁻¹ min⁻¹ under GHSV of 30,000 mL h⁻¹ g⁻¹ cat at 550 °C. The effect of GHSV was also examined showing that the increase of GHSV resulted the conversion decrease. With lower GHSV of 6000 mL h⁻¹ g⁻¹ cat the catalyst achieved 94.7 % NH₃ conversion. Further enhancement on the conversion (78.1 %) was observed when K was added during the Ni₅Co₅/SiO₂ synthesis (K/(Ni + Co) molar ratio of 1:10) indicating that alkali act in favour of the catalytic decomposition of ammonia. The Ni₅Co₅/SiO₂-K was evaluated for its stability for 30 h where it showed negligible decrease in conversion and thus excellent stability.

Studies have reported that the stronger basicity of the support the more efficient is the catalyst and thus promoting the catalytic decomposition of ammonia. Therefore, Podila et al. [70] utilized different Mg oxide systems (MgAl, MgCe and MgLa) as supports for cobalt catalysts (5 wt% Co) with Mg to X (X = Al, Ce, La) ratio of 2. Among these three, 5CMLa-2 presented
the highest activity. The 5CMAl-2 and the 5CMCe-2 catalysts had lower activities. La-containing catalysts were further studied with different Mg/La molar ratios (Mg/La = 1, 2, 3, 5, 9 and 14). All the catalysts were active even at lower temperatures with 5CMLa-5 being the most active. The higher activity of the 5CMLa-5 catalyst might be due to the increased surface area, higher metal dispersion and the presence of basic sites that favour the ammonia decomposition. It was concluded that Mg-La is a promising support for the reaction of ammonia decomposition.

Pinzón et al. [71] developed Co catalysts supported on β-SiC for the H₂ production by ammonia decomposition at reaction temperatures below 500 °C. The catalysts were modified with different metals (K, Cs, Ca, Mg, La and Ce) to study the effect of promoters. The catalysts with the addition of 1 % of Cs, Mg, Ca or Ce showed poorer performance while the catalysts loaded with K or La enhanced the catalytic activity due their electron-donor properties that modified the electronic structure of cobalt active sites. A conversion of 97.3 % and H₂ production rate of 69.3 mmol H₂ g⁻¹ min⁻¹ was obtained by the 1K-Co/SiC catalyst (4.1 wt % Co) at 450 °C. Different K loadings were also studied, and results showed that the increase of metal loading above 1% decreased the conversion of ammonia because the excess amount of metal blocked the active sites of the cobalt catalysts. Lastly, the stability of the catalyst was tested for over 24 h at 400 °C and 83 % conversion of ammonia was reached providing excellent stability.

Table 1. Heterogeneous catalysts used for the ammonia decomposition.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
<th>TOF (1/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/MgAl₂O₄ – LDH</td>
<td>600</td>
<td>88.7</td>
<td>2.18</td>
<td>[56]</td>
</tr>
<tr>
<td>Co/NC-600</td>
<td>500</td>
<td>80</td>
<td></td>
<td>[57]</td>
</tr>
<tr>
<td>Ru/SmCeOₓ</td>
<td>400</td>
<td>74.9</td>
<td>25.81</td>
<td>[58]</td>
</tr>
<tr>
<td>35Co/BHA</td>
<td>500</td>
<td>87.2</td>
<td></td>
<td>[59]</td>
</tr>
<tr>
<td>2.5Ru/10C-rGO</td>
<td>400</td>
<td>96</td>
<td>75.4</td>
<td>[60]</td>
</tr>
<tr>
<td>CoRe₁.₆</td>
<td>500</td>
<td>~90</td>
<td></td>
<td>[61]</td>
</tr>
<tr>
<td>K⁺-Fe/C</td>
<td>470</td>
<td>20</td>
<td>~0.5</td>
<td>[62]</td>
</tr>
<tr>
<td>Ru/Al₂O₃</td>
<td>580</td>
<td>~100</td>
<td>6.85</td>
<td>[63]</td>
</tr>
<tr>
<td>Ni/Al₂O₃</td>
<td>580</td>
<td>4.21</td>
<td></td>
<td>[63]</td>
</tr>
<tr>
<td>Co-containing CNTs</td>
<td>700</td>
<td>~76</td>
<td></td>
<td>[64]</td>
</tr>
<tr>
<td>Fe-containing CNTs</td>
<td>700</td>
<td>76</td>
<td></td>
<td>[64]</td>
</tr>
<tr>
<td>(SA-600A)/RuCl₃.nH₂O/LiOH·H₂O (40:5:3)</td>
<td>490</td>
<td>99.87</td>
<td></td>
<td>[65]</td>
</tr>
<tr>
<td>α-FeO₂O₃·50@pSiO₂</td>
<td>800</td>
<td>100</td>
<td></td>
<td>[66]</td>
</tr>
<tr>
<td>10%Co/MWCNTs</td>
<td>600</td>
<td></td>
<td>8.15</td>
<td>[67]</td>
</tr>
<tr>
<td>Ru/La₀.₃3Ce₀.₆₇</td>
<td>450</td>
<td>91.9</td>
<td>11.4</td>
<td>[68]</td>
</tr>
<tr>
<td>Ni₅Co₅/SiO₂</td>
<td>550</td>
<td>76.8</td>
<td></td>
<td>[69]</td>
</tr>
<tr>
<td>5CMLa-5</td>
<td>550</td>
<td>82.7</td>
<td></td>
<td>[70]</td>
</tr>
</tbody>
</table>
As observed from Table 1, the temperature ranges from 400 to 800 °C because ammonia requires higher temperatures for its decomposition. At higher temperatures the conversion is higher and in some cases the catalysts achieve almost complete conversion. Even though Ru is a precious and expensive metal, many studies have focused on Ru catalysts due to their excellent catalytic properties [58], [60], [63], [65], [68]. However, other novel catalysts are investigated with promising results for future experiments [56], [59], [61], [64], [71]. Supporting materials are also studied because of their properties for enhanced catalytic operation as they can offer higher surface area, chemical stability and mechanical strength [72]. Generally, the most common ones are alumina and silica [63], [69], but other materials are used as well [57]–[60], [67], [71].

4.1.1 Structural and physicochemical properties of heterogeneous catalysts

It’s necessary to consider any chemical and physical transformation that will occur during the development process of efficient catalysts. The structure and properties of the catalysts play a significant role for the decomposition of any reaction. It is well known that the catalytic decomposition of ammonia is structure sensitive and strongly depends on the size, shape and properties of the catalyst. Mazzone et al. [73] synthesized unpromoted and sodium promoted Ru particles supported on carbon xerogels. The purpose of this study was to investigate the behaviour of the catalysts with support and with or without the promoter. During the second reaction run the un-promoted catalysts exhibited higher reaction rates compared with the first reaction run. The authors explained that the higher reaction rates are due to the formation of B5 sites after the catalyst was exposed at 600°C. The B5 sites work in favour of the decomposition reaction, speeding up the N desorption. Sodium as a promoter had a positive effect on the performance of the catalyst preventing the sintering of the Ru particles since the catalyst before and after five runs had the same average particle size for all tested catalysts. In contrast, the un-promoted catalysts presented a slight increase in the particle size, e.g., from 1.9 nm to 2.5 nm due to the sintering of Ru particles from high temperatures. The support was either activated with carbon dioxide or doped with nitrogen and both treatments had a positive impact on the catalytic performance.

The effect of particle size was examined by El-Shafie et al. [74] using two different diameters of alumina particles size (1 and 2 mm) for the decomposition of ammonia assisted by dielectric
discharge plasma (DBD). The conversion rates and H\textsubscript{2} concentration were measured at different ammonia flow rates and plasma voltage. Conversion rates of 83.19 and 80.35 % were obtained by Al\textsubscript{2}O\textsubscript{3} particle sizes of 1 and 2 mm respectively. Moreover, particle size of 1 mm resulted in higher H\textsubscript{2} concentration. The higher conversion and H\textsubscript{2} concentration are attributed to the higher surface area in the smaller particle and thus, longer residence time for the decomposition reaction. Therefore, it was concluded that the particle size is a significant factor for this catalytic decomposition.

Cobalt catalysts in the form of cobalt oxide (II III) promoted with calcium, aluminium and potassium oxides were developed with precipitation method by Czekajlo et al. [75]. With the increase in the precipitation process temperature, it was observed that the size of Co\textsubscript{3}O\textsubscript{4} crystallites was reduced leading to a decrease of the efficiency process. The ZBAP1-C catalyst that was promoted with calcium, potassium, and aluminium oxides obtained the highest catalytic activity with a decomposition degree of 100% at 525°C. The addition of alumina had a positive effect on a shift of the maximum conversion of ammonia towards lower reaction temperatures. The ZBAP1-B catalyst had the lowest surface area value impregnated only with oxides of calcium and potassium while the ZBAP1-C catalyst showed higher resistance in sintering indicating that the addition of aluminium has a positive impact on the stability of the surface structure as well.

Fly ash (FA), a waste material, was used as support for Ru catalysts for H\textsubscript{2} production by ammonia decomposition by Li et al. [76]. The FA samples were acid treated and heat treated, and results showed that treatment enhanced the surface area and pore volume. Ru impregnation further increased the surface area and pore volume on the heat treated and untreated FA samples but decreased on the acid treated samples. From the catalysts used, Ru/FA-800 had the highest conversion of ammonia due to high Ru dispersion, less acid sites and stronger NH\textsubscript{3} adsorption.

Lendzion-Bielun et al. [77] examined the effect of different promoters (CaO, Al\textsubscript{2}O\textsubscript{3} and, K\textsubscript{2}O) and also the addition of manganese and chromium on the structure of cobalt catalysts for ammonia decomposition. Sintering of pure cobalt was noticed at a temperature of 600°C, but with the addition of the oxides as promoters the surface area of the catalysts was stabilized. The catalytic tests showed that the unpromoted Co catalyst has the lowest activity due to a very low surface area. The Co(0) catalyst that was promoted with the oxides (2.6 wt % Al\textsubscript{2}O\textsubscript{3}, 1.5 wt % CaO, 0.5 wt % K\textsubscript{2}O and 95.4 wt % Co) presented the highest activity at temperatures of 500 and 550°C with NH\textsubscript{3} conversion up to 40.1 and 50% respectively. Even though an addition
of chromium and manganese lead to an enhancement on the surface area of the catalyst, the activity was decreased.

To investigate the influence of particle size, Li et al. [78] developed Ni particles supported on MCF-17 with particle range size from 1.5 to 8.0 nm. The ammonia decomposition reaction was affected by the particle size of the catalysts especially with small Ni particles. Moreover, the particle size effect was studied at various temperatures and a volcano relationship between the particle size and the catalytic activity was obtained (Fig. 6) proving that the catalysts are structural sensitive. The Ni/MCF-17 catalyst with an average of 3.0 nm particle size exhibited excellent catalytic performance at all temperatures.

Fig. 3. Effect of the particle size at different reaction temperatures [78].

Besides the correlation between the particle size of catalysts and the catalytic activity, the structure/morphology of the support is important to be explored. Huang et al. [79] studied cobalt catalysts supported on three kinds of CeO\(_2\) supports, 3D ordered mesoporous (3DOM), nanotubes (NT) and nanocubes (NC). The Co/CeO\(_2\)-3DOM catalyst exhibited the best catalytic performance with 4.2 mmol H\(_2\) min\(^{-1}\) g\(_{\text{cat}}\) H\(_2\) production rate at 500\(^\circ\)C. According to different characterization techniques that were used in the experiment it was concluded that the particle size was not the main factor to influence the reaction but the different morphologies of the support. The morphology of the Co/CeO\(_2\)-3DOM catalyst was favourable for construction of more active sites and thus the better catalytic performance.

### 4.2 Photocatalysis and Electrocatalysis of Ammonia

Photocatalytic decomposition is considered a promising system for the H\(_2\) production because it can be operated at ambient temperature conditions, and the reaction can be easily controlled
by switching on and off the light irradiation [80]–[83]. TiO$_2$ photocatalysts were developed by Abdul Razak et al. [84] that were impregnated with Pd and Cu respectively for enhancement of the photocatalytic activity. After 3 h of light irradiation Pd/TiO$_2$ exhibited the highest activity producing 65 μmol of H$_2$ while Cu/TiO$_2$ and TiO$_2$ showed almost no production of H$_2$.

For the investigation of the stability of the photocatalysts in alkaline conditions, different NH$_3$ concentrations were investigated. With a concentration up to 19.1 g/L yield was enhanced up to 30.4 μmol but further increase of NH$_3$ resulted in a decline of the H$_2$ production rate. Dimethyl sulfoxide (DMSO) was also added as hydroxyl scavenger in ammonia further enhancing the H$_2$ yield to 121 μmol and was continuously increasing in the first cycle reaction. However, the rate of H$_2$ production was reduced with the subsequent reaction cycles and during the photocatalytic decomposition with DMSO methane gas was detected.

Apart from catalysis and photocatalysis, electrochemical decomposition of ammonia has a high potential for supply of CO$_x$-free energy. Fig. 3 demonstrates a typical ammonia electrolytic cell for hydrogen generation. The most active catalyst for this reaction is Pt and thus lots of research was carried out with Pt catalysts. However, it is very expensive so recent studies are focused on Pt-free catalysts [85]–[87]. Binary alloy electrocatalysts based on Ni such as NiCo, NiMo, NiFe, and NiCe deposited on nickel foam were synthesized by Jiang et al. [88] for the electrochemical generation of H$_2$ by ammonia. From all the electrodes investigated, NiCo in the form of nanoneedle resulted in an impressive electrochemical performance. For further improvement the NiCo catalyst was introduced to nitrogen doping and ammonia annealing treatment to obtain NiCo$_2$N electrodes. The activity was dramatically increased demonstrating a superior HER electrocatalytic performance. The NiCo$_2$N electrocatalysts also showed an excellent stability as there was no significant change after 10 h of catalytic process. Moreover, it was concluded that the electrolysis potential in ammonia (0.71 V) was much lower than the water splitting suggesting that ammonia electrolysis can replace water electrolysis for H$_2$ production. Table 2 summarises the results from photocatalysis and electrocatalysis of ammonia.
Fig. 4. A typical cell of ammonia electrolysis for hydrogen production [87].

Table 2. Photocatalysts and Electrocatalysts used for ammonia decomposition.

<table>
<thead>
<tr>
<th>Photocatalysis</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>H₂ Yield (μmol)</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>Pt/TiO₂</td>
<td>160</td>
<td>[80]</td>
<td></td>
</tr>
<tr>
<td>Pt/Fe-TiO₂</td>
<td></td>
<td>[81]</td>
<td></td>
</tr>
<tr>
<td>Ce/TiO₂</td>
<td>80</td>
<td>[82]</td>
<td></td>
</tr>
<tr>
<td>Pd/TiO₂</td>
<td>65</td>
<td>[84]</td>
<td></td>
</tr>
<tr>
<td>Pd/TiO₂-DMSO</td>
<td>121</td>
<td>[84]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electro catalysis</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>System</td>
<td>Onset Potential</td>
<td>Current Density (mA cm⁻²)</td>
</tr>
<tr>
<td>NiCu/C</td>
<td>55mM NH₄Cl + 0.5 NaOH</td>
<td>0.47 V vs Ag/AgCl</td>
<td>52</td>
</tr>
<tr>
<td>Ni₉₈Pd₂</td>
<td>1M NaNO₃ + 200mM NH₄NO₃ + NaOH</td>
<td>1.25 V vs Hg/HgO</td>
<td>~2</td>
</tr>
<tr>
<td>NiCo₂N</td>
<td>1M KOH + 1M NH₃.H₂O</td>
<td>100x10⁻³ V vs RHE</td>
<td>100</td>
</tr>
</tbody>
</table>
Hydrous Hydrazine Decomposition as a sustainable hydrogen production method

5.1 Heterogeneous Catalysis of Hydrous Hydrazine

In recent years, the development of efficient catalysts for the decomposition of hydrous hydrazine for H₂ generation has been the focus of many studies. Ni particles were found to be a preferable choice and its alloying with noble metals such as Ir, Pt, Pd and Rh result in a noteworthy improvement on the H₂ selectivity and the catalytic performance due to the alloy synergistic effect [89]–[91]. Unfortunately, their applications are limited due to the high cost of noble metals. Therefore, it is essential to develop non noble metal containing catalysts. Until now, many studies have reported the decomposition of hydrous hydrazine with noble-metal-free catalysts. Different types of catalysts that were used for the decomposition of hydrous hydrazine are displayed in Table 3.

Noble-metal-free NiFe particles supported on CeZrO₂ were synthesized by Zoo et al. [92]. The NiFe/CeZrO₂ alloy catalyst with Ni/Fe molar ratio of 8:2 (9.11 wt % Ni and 2.41 wt % Fe) had a TOF value of 119.2 h⁻¹ and 100% H₂ selectivity in the presence of NaOH and temperature of 343 K. The catalyst exhibited high stability showing negligible decrease on the H₂ selectivity after five runs. The particle size of the NiFe/CeZrO₂ catalyst was 5.2 ± 0.8 nm while after five runs was 5.3 ± 1.2 nm. Other supports as LaZrO₂ and NdZrO₂ also presented excellent catalytic properties. NiCo, NiCu and CoFe supported on CeZrO₂ were also examined and exhibited lower selectivity towards H₂ concluding that NiFe is a highly efficient candidate for the replacement of noble metal catalysts for the hydrous hydrazine decomposition.

Liu et al. [93] synthesized NiMo particles supported on TiO₂ for the catalytic decomposition of hydrous hydrazine. The Ni₀.₁₆Mo₀.₀₄/TiO₂ catalyst with 22.6 wt % Ni and 9.23 wt % Mo exhibited a TOF value of 484 h⁻¹ and 100% H₂ selectivity. Further increase of the support content decreased the catalytic performance. After, 10 cycles the selectivity remained 100% but the TOF decreased to 138 h⁻¹. NiCu/TiO₂, NiFe/ TiO₂, and NiCo/TiO₂ catalysts were also prepared for investigation of doping other metals and results showed that the catalytic performances of these catalysts were inferior to NiMo/TiO₂ concluding that Mo doping improves the dispersion and modifies the geometric and electronic structure of the catalyst facilitating the N₂H₄ decomposition.
Mono-, bi- and tri-metallic noble and noble-metal free catalysts were prepared by Al-Thubaiti et al. [94] to investigate their catalytic activity in the dehydrogenation of hydrous hydrazine. Monometallic Ag, Ni, Pd, Fe and Cu particles were inactive while the activity of bimetallic catalysts was higher. The most active catalyst was the trimetallic Ni/Fe/Pd catalyst that contained 28.7 wt % Ni, 23.5 wt % Fe and 47.7 wt % Pd and average size of 20 nm. It exhibited excellent selectivity towards \( \text{H}_2 \) and therefore was used for further experiments. After five continuous runs the catalytic activity of the catalyst remained the same. It was concluded by the authors that adding a third metal in a bimetallic catalyst with a specific combination has a positive impact on the selectivity of \( \text{H}_2 \). Fig. 5 shows the proposed mechanism for the decomposition of ammonia on the surface of the Ni/Fe/Pd catalyst. Moreover, new catalysts can be developed with different metal plating order for the decomposition of hydrazine for \( \text{H}_2 \) production.

![Proposed mechanism for the decomposition of ammonia on the surface of the trimetallic Ni/Fe/Pd catalyst](image)

Different elements (Rh, Co, Ru, Ir, Cy, Ni, Fe, Pt, Pd NPs) were studied as catalysts for the decomposition of hydrous hydrazine for \( \text{H}_2 \) production by Sanjay et al. [95]. It was found that the catalytic activity and the selectivity were depended on the catalyst used. Rh was the most active catalyst whereas Cu, Ni, Fe, Pt and Pd were inactive for the reaction in aqueous solution even though they were active in the reaction that took place in the gas-phase. In the case of Co,
Ru and Ir the selectivity towards H\textsubscript{2} was very low. The reason this is happening is because Co, Ru and Ir nanoparticles prefer the activation of the N-N bond which is formatting ammonia. In comparison Rh particles prefer the activation of N-H bond and that’s why they are highly active. Moreover, it was observed that the catalytic activity was enhanced when the Rh particles were reduced with NaBH\textsubscript{4} in the presence of hexadecyltrimethyl ammonium bromide concluding that the modification of nanoparticles during their preparation could affect their efficiency.

Motta et al. [96] investigated the catalytic performance of Ir/CeO\textsubscript{2} as catalyst for the decomposition of hydrous hydrazine to generate H\textsubscript{2}. Parameters such as stirring speed, mass of catalyst, NaOH concentration and reaction temperature were studied to find the optimal conditions for the reaction with respect on the activity and selectivity of the catalytic decomposition. Stirring rate affected both the reaction rate and the selectivity and it was found that with lower stirring rate the H\textsubscript{2} yield was also lower. The optimum stirring rate was 1050 rpm and was used for the following tests. The mass of the catalyst did not affect the yield of the reaction but there was an increase in the activity for molar ratios between 125:1 and 250:1 and the latter were selected for the further catalytic tests. With an increase of the NaOH concentration there was an increase in H\textsubscript{2} yield and 0.5 M NaOH was chosen as the optimal value. Lastly, with an increase in the temperature the selectivity decreased in contrast with the activity of the catalyst that was increased so the value of 50\textdegree C was chosen because of the intermediate values of activity and selectivity that exhibited. The fresh catalyst had a particle size of 0.9 ± 0.2 nm and after five uses 1.2 ± 0.4 nm where the difference was in the range of the error analysis.

Kang et al. [97] developed Ni/CeO\textsubscript{2} catalysts for the decomposition of hydrous hydrazine. A solution combustion synthesis (SCS) varying different parameters was used to synthesize the catalysts and catalytic tests were run under 50\textdegree C. It was obtained that catalysts with smaller Ni size particle and larger pore size act in favour of the decomposition resulting in a good catalytic performance. 6 wt\% Ni/CeO\textsubscript{2} catalysts with 14.7 nm particle size and 18.8 nm pore size, exhibited a H\textsubscript{2} selectivity of 100 \%, N\textsubscript{2}H\textsubscript{4}.H\textsubscript{2}O conversion of 50 \% at 17.7 min corresponding to a TOF value of 34.0 h\textsuperscript{-1}. Moreover, the formation of Ni-O-Ce solid promoted the reaction for H\textsubscript{2} generation, but higher concentrations decreased the catalytic activity. A 30-fold increase of the reaction rate was obtained when increasing the temperature from 30 to 90\textdegree C but the selectivity dropped at 93 \%. Lastly, for comparison purposes, Ni-based catalysts developed
with different methods were tested and even though a high number of parameters need to be considered, it was concluded that the catalysts created by the SCS method had better catalytic performance.

An alloy of Ni-Pd nanoparticles (Ni$_{1-x}$Pd$_x$) were synthesized by Singh et al. [98] and were examined under mild reaction conditions. The Ni$_{0.60}$Pd$_{0.40}$ catalyst exhibited the highest selectivity (82 %) among the others tested. To test the effect of alloy, a physical mixture of Ni and Pd was tested and performed poor catalytic activity compared with the alloy catalyst indicating that the modified catalyst surface favours this reaction. The combination of Pd with other metals (Fe, Co and Cu) resulted poor catalytic performance (or inactive) as well as implying that the presence of Ni has a positive effect on the decomposition of hydrous hydrazine.

He et al. [99] developed Ni-based catalysts by using Ni-Al hydrotalcite-like compound as precursors. A conversion of 100 % was exhibited with a H$_2$ selectivity of 93 % at 30 °C and 70 min reaction time. The high selectivity can be attributed to the small Ni particles and strong basic sites. When the temperature increased up to 80 °C, the reaction time decreased at 5 min and the selectivity was reduced to 82 %. A Ni/Al$_2$O$_3$-IMP catalyst was also tested for the decomposition of hydrous hydrazine and compared with Ni-Al$_2$O$_3$-HT. A lower activity was noticed by the Ni/Al$_2$O$_3$-IMP catalyst with H$_2$ selectivity at 66 % and 440 min of reaction time due to the poor Ni dispersion.

Amorphous catalytic CoPt particles induced on CeOx were developed by Song-II et al. [100]. It was discovered that the CeOx plays a crucial role in the transformation of the crystalline phase to the amorphous one. The highest catalytic performance among the catalysts tested was achieved by the Co$_{0.65}$Pt$_{0.30}$(CeOx)$_{0.05}$ nanoalloy, at 25 °C with H$_2$ selectivity of 72.1 % in 3.5 min and TOF value of 194.8 h$^{-1}$ which is even higher than that of the crystalline phase catalyst. Therefore, it was concluded by the authors that Co$_{0.65}$Pt$_{0.30}$(CeOx)$_{0.05}$ exhibited the most optimum performance encouraging its practical use for the decomposition of N$_2$H$_4$.H$_2$O to produce H$_2$.

Several studies used RhNi alloy catalysts supported on different materials for the decomposition of hydrous hydrazine. Zhang et al. [101] developed CeOx-doped RhNi particles supported on reduced graphene oxide (rGO). The Rh$_{0.8}$Ni$_{0.2}$@CeOx/rGO catalyst completely decomposed N$_2$H$_4$ at room temperature in 33 min with a TOF value of 36.4 h$^{-1}$. Further increase in the temperature at 60°C, catalysed the reaction in 3.0 min giving a TOF value of 400.0 h$^{-1}$. 


Other studies used MOFs for the support of catalytic materials and therefore RhNi@MIL-101 [102] and NiRh/NPC-900 [103] were developed and tested at 50 °C and alkaline conditions 0.5 NaOH. High TOF values of 344 h⁻¹ and 156 h⁻¹ were exhibited respectively with 100 % H₂ selectivity. Other supports that were used in these studies presented inferior catalytic performance.

Dai et al. [104] synthesized bimetallic Ni-Ir alloy nano-catalysts supported on CeO₂ for the decomposition of hydrous hydrazine for H₂ production. The catalyst showed great catalytic activity and high H₂ selectivity. Further increase on the Ir content (Ni₉₁Ir₉/CeO₂) resulted in an optimal catalytic performance and was further investigated. The decomposition rate of hydrous hydrazine increased with increasing the reaction temperature. Also, the catalyst was submitted to cyclic usage, and it was found that it retains 100% H₂ selectivity even after 15 cycles but the catalytic activity was decreasing after cycle.

Nickel particles were prepared by encapsulation in the channel of TNTs (Ni@TNTs) and deposition on the surface of TNTs (Ni/TNTs) by Wang et al. [105]. Ni@TNTs exhibited high catalytic activity than the Ni/TNTs catalyst and nearly 100% H₂ selectivity at 333 K. The TOF value of this reaction was 96.0 h⁻¹. The encapsulation of Ni particles led to a small particle size of 2.7 nm, large pore size of 10.2 nm and high dispersion (28.2 %) resulting in more active sites. Moreover, after six continuous catalytic runs the catalyst did not have any significant loss in its catalytic activity due to the prevention of nickel particles leaching during the catalysis, since the particle size had a small increase of 3.5 nm. In contrary, Ni particles on Ni/TNTs increased from 2.4 to 8.9 nm indicating that aggregation is occurring without the TNTs constraining the Ni particles.

Rh nanoparticles modified with Molybdenum Oxide (MoOx) were prepared by Yao et al. [106] with different metal compositions for the catalytic decomposition of hydrous hydrazine and hydrazine borane. Various reaction temperatures were studied and at temperature of 323 K and the presence of Rh₀.₅(MoOx)₀.₅, N₂H₄ was completely decomposed to H₂ and N₂ with 100% H₂ selectivity and TOF value of 750 h⁻¹. The catalyst had an average mean size of 3.8 ± 0.8 and its composition was 10.05 wt % Rh and 8.92 wt % Mo. It was concluded that the increased catalytic performance obtained by the Rh-based catalysts might encourage the utilisation of hydrous hydrazine as H₂ storage material.
Table 3. Heterogeneous catalysts utilized for the hydrous hydrazine decomposition.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
<th>TOF (1/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{0.8}$Fe$</em>{0.2}$/CeZrO$_2$</td>
<td>70</td>
<td></td>
<td>0.033</td>
<td>[92]</td>
</tr>
<tr>
<td>Ni$<em>{0.16}$Mo$</em>{0.04}$/TiO$_2$</td>
<td>70</td>
<td>~100</td>
<td>0.134</td>
<td>[93]</td>
</tr>
<tr>
<td>Ni/Fe/Pd</td>
<td>40</td>
<td></td>
<td>0.007</td>
<td>[94]</td>
</tr>
<tr>
<td>Ir/CeO$_2$</td>
<td>50</td>
<td>~100</td>
<td>~0.028</td>
<td>[96]</td>
</tr>
<tr>
<td>6 wt% Ni/CeO$_2$</td>
<td>50</td>
<td>50</td>
<td>0.009</td>
<td>[97]</td>
</tr>
<tr>
<td>Ni$<em>{0.60}$Pd$</em>{0.40}$</td>
<td>50</td>
<td></td>
<td></td>
<td>[98]</td>
</tr>
<tr>
<td>Ni-Al$_2$O$_3$-HT</td>
<td>30</td>
<td>100</td>
<td></td>
<td>[99]</td>
</tr>
<tr>
<td>Co$<em>{0.65}$Pt$</em>{0.35}$(CeOx)$_{0.05}$</td>
<td>25</td>
<td></td>
<td>0.054</td>
<td>[100]</td>
</tr>
<tr>
<td>Rh$<em>{0.8}$Ni$</em>{0.2}$@CeOx/rGO</td>
<td>60</td>
<td>100</td>
<td>0.111</td>
<td>[101]</td>
</tr>
<tr>
<td>RhNi@MIL-101</td>
<td>50</td>
<td></td>
<td>0.095</td>
<td>[102]</td>
</tr>
<tr>
<td>NiRh/NPC-900</td>
<td>50</td>
<td>&gt;50</td>
<td>0.043</td>
<td>[103]</td>
</tr>
<tr>
<td>Ni$<em>{0.65}$Ir$</em>{0.35}$/CeO$_2$</td>
<td>50</td>
<td>100</td>
<td></td>
<td>[104]</td>
</tr>
<tr>
<td>Ni@TNTs</td>
<td>60</td>
<td>~100</td>
<td>0.026</td>
<td>[105]</td>
</tr>
<tr>
<td>Rh$<em>{0.5}$Mo$</em>{0.5}$O$_{0.5}$</td>
<td>50</td>
<td>100</td>
<td>0.208</td>
<td>[106]</td>
</tr>
</tbody>
</table>

Comparing with the temperature range of the ammonia decomposition, as seen from Table 3 that hydrous hydrazine decomposition is more favored at lower temperatures (30-70 °C). The most studied temperature is 50 °C giving almost total conversion of hydrous hydrazine [96–98], [102]–[104], [106]. Nickel is a promising catalyst for this decomposition and by alloying it with other elements, many studies give positive results [92], [93], [97], [99], [105]. However, noble metals are often used for the alloys, limiting their application [94], [98], [101]–[104]. Still research needs to be done though, considering the low TOF values.

5.1.1 Structural and physicochemical properties of heterogeneous catalysts

While the majority of studies are focused on the structure of the catalysts there was no in-depth study of the insights of the microstructure transformations during the synthesis of catalysts which are a key point for the catalytic activity for the hydrous hydrazine decomposition. Therefore Qiu et al. [107] synthesized Ni@Ni-Ir/meso-CeO$_2$ catalysts for the investigation of the catalytic properties that may be affected by the composition of the surface. Ni@Ir/meso-CeO$_2$ resulted from the formation of the Ir surface layer on the Ni particles and with calcination treatment the targeted Ni@Ni-Ir/meso-CeO$_2$ alloy catalyst was synthesized. The post-treated alloy exhibited excellent activity with a reaction rate of 343 h$^{-1}$ and H$_2$ selectivity (100% H$_2$) at 50°C, in contrast with the as-prepared catalyst that had lower selectivity and catalytic performance. It was concluded that the calcination treatment had a positive impact since the Ni@Ir alloy enhanced both the selectivity and catalytic activity.
Shi et al. [108] studied in detail the formation mechanism of the bimetallic Ni\textsubscript{50}Pt\textsubscript{50}/CeO\textsubscript{2} alloy for the investigation of the influence of preparation process to the structure of the catalyst and thus, the impact on catalytic activity. It was discovered that during the synthesis process the formation of [(CH\textsubscript{3})\textsubscript{4}N]\textsubscript{2}PtCl\textsubscript{6} took place during the co-precipitation step. While increasing the aging time crystalline [(CH\textsubscript{3})\textsubscript{4}N]\textsubscript{2}PtCl\textsubscript{6} disappeared due to the conversion to metallic Pt which was found to have a major impact on the composition and microstructure of the catalyst. As a result, the catalytic performance of the Ni\textsubscript{50}Pt\textsubscript{50}/CeO\textsubscript{2} catalyst was different depending on the aging time. After 5-12 h of aging time the reaction rate was 465-500 h\textsuperscript{-1} at 30\degree C which was 2.5 times higher than the reaction time of the catalysts with aging time of 0-1 h.

In another study by Shi et al. [109], noble metal free Ni-W-O alloy nano-catalysts (Ni\textsubscript{4}W/WO\textsubscript{2}/NiWO\textsubscript{4}) were synthesised with a hydrothermal process and different reduction temperatures to investigate any changes in the microstructure of the catalysts. Results showed that increasing the annealing treatment temperature the catalytic properties are increased as well. The reduction at 350\degree C showed both low selectivity and reaction rate while at 400\degree C selectivity was 99\% and the reaction rate up to 33 h\textsuperscript{-1} with a complete decomposition of hydrazine at 50\degree C and reaction time of 18 min. Further increase of the annealing treatment temperature reduced the efficiency of the catalyst. Moreover, different characterization analyses were used to better understand if the increased catalytic properties were correlated with the temperature treatment. A decrease on the specific surface area was obtained with the increased reduction temperature that led to the enhanced catalytic performance.

A Ni-Pt/La\textsubscript{2}O\textsubscript{3} catalyst was synthesised by Zhong et al. [110] combining alloying and immobilization strategies. The targeted Ni@Ni-Pt/La\textsubscript{2}O\textsubscript{3} contained a Ni core and Ni-Pt alloy shell and exhibited 100 \% H\textsubscript{2} selectivity. A key factor to achieve great catalytic performance is the formation of the bimetallic alloy therefore the study was not only focused on the catalytic activity of the particles but also the physicochemical surface composition and structure. The excellent catalytic properties were correlated with the electronic and geometric structures changes during the Ni-Pt formation. Moreover, the catalysts were subjected into a second time replacement and calcination treatment under 350\degree C, and it was observed that both activity and selectivity towards H\textsubscript{2} were increased. It was found that not proper control of the calcination temperature can drastically reduce the performance of the catalyst. In general, there was a remarkable improvement after the treatment but still the reason behind the enhancement and the dependence of the treatment needs to be further studied.
5.1.2 NH₃ Formation

As it was mentioned hydrous hydrazine can be decomposed by two pathways resulting in the undesirable ammonia production. Thus is a necessity to develop effective catalyst with high selectivity towards H₂. Ni catalysts alloyed with noble metals were a preferred choice by many researchers due to their remarkable enhancement of catalytic properties that resulted from the alloy synergy effect. For example, Singh et al. [91] developed bimetallic Ni-Pt alloy nanoparticles to enhance the selectivity of Ni nanoparticles that was around 33 % at 323 K. By alloying Ni with Pt content as low as 1 mol % (Ni₀.₉₉Pt₀.₀₁), a complete conversion of N₂H₄.H₂O was obtained in 120 min at 323 K. Further increase of the temperature at 333 K caused a reduction on the reaction time at 70 min with 100 % H₂ selectivity. Authors concluded that the Ni alloying with low Pt content and moderate temperatures are promising for the development of low-cost and high efficiency catalysts for H₂ production by hydrous hydrazine decomposition.

Ni-Ir alloy catalysts supported on Al₂O₃ were investigated by He et al. [111] to compare its activity and selectivity with monometallic Ir/Al₂O₃ and Ni/Al₂O₃ catalysts. NiIr₀.₀₁₆/Al₂O₃ (2.0 wt % Ir, 36.8 wt % Ni and 6.1 wt % Al₂O₃) increased the selectivity up to 99 % and the reaction rate was 6.3 h⁻¹. Increasing the Ir molar ratio to Ni up to 0.059, the reaction rate was enhanced at 12.4 h⁻¹ and selectivity remained higher than 98%. The stability of the NiIr₀.₀₅₉/Al₂O₃ was tested at 10 consecutive cycles at 30°C. The reaction rate decreased to 9.2 h⁻¹ but the H₂ selectivity remained over 98%. Reduction of the catalyst at high temperatures resulted in a decreased selectivity and catalytic activity. Moreover, modified Au and Pt Ni/Al₂O₃ catalysts were developed for comparison purposes. NiPt₀.₀₂₇/Al₂O₃ exhibited high selectivity while NiAu₀.₀₂₀/Al₂O₃ resulted in a lower selectivity and reaction rate as low as 2.0 h⁻¹.

Furthermore, experiments showed that alkaline conditions lead to improved H₂ selectivity. Bimetallic nano-catalysts were developed by alloying Ni and Fe with different Ni/Fe molar ratios by Singh et al. [112] to investigate their catalytic performance for the decomposition of hydrous hydrazine. Even though the catalyst exhibited excellent catalytic activity, the selectivity towards H₂ was only 81%. With an addition of 0.5 M NaOH the selectivity was enhanced at 100%. The addition of NaOH also improved the selectivity of the Ni₄₅Pt₅₅ and Ni₅₀Ir₅₀ catalysts from 61 to 86% and from 7 to 95% respectively. It was suggested by the authors that the basicity of the NaOH makes the surface of the catalyst basic preventing the formation of NH₃ by the incomplete decomposition of hydrazine and thus promoting the first
pathway. Weaker bases such as ammonia and sodium acetate were also examined. Results showed that the addition of these bases had no effect on the catalytic activity and selectivity of the catalysts.

Ni particles were synthesised from the reduction of triangular Ni(HCO$_3$)$_2$ nanosheets and were used as catalysts to produce H$_2$ by hydrous hydrazine by Wang et al [113]. For the restrain of the NH$_3$ formation as a side reaction, the effect of NaOH concentration was tested. It was found that with the absence of NaOH the selectivity towards H$_2$ was 64.5%. With 0.5M of NaOH, the selectivity was up to 100% and remained unchanged with further increase of the NaOH concentration. Alkaline conditions speed up the rate determining step of the hydrous hydrazine decomposition and OH$^-$ ions inhibit the formation of ammonia obtaining 100% H$_2$ selectivity.

NiPt alloy nanoparticles supported on La$_2$O$_2$CO$_3$ were developed via an alkali assisted reduction by Yao et al [114]. Among the catalysts tested the Ni$_{0.6}$Pt$_{0.4}$/La$_2$O$_2$CO$_3$ (2.8 nm) obtained the best catalytic performance with a TOF number of 490 h$^{-1}$ and 100 % H$_2$ selectivity. After five rounds, the catalyst showed a good stability with only a slight aggregation of 3.4 nm.

Further tests were conducted for the evaluation of NaOH effect at the synthesis of the catalysts and during the catalytic process. The catalyst prepared without the addition of NaOH exhibited much lower selectivity and catalytic performance even though NaOH was added during the decomposition reaction. Moreover, the catalyst was synthesised at different NaOH concentrations (0-4 M) and results showed that the efficiency of the catalyst increased until the NaOH concentration was 3 M. These results suggest that NaOH affects both the catalytic process and the preparation of the catalysts. The effect of the NaOH addition at the preparation step of the catalyst and during the process are presented below (Fig.6).
Huang and Liu [115] examined both the synergistic effect from an Ni alloy and the addition of NaOH to generate H₂ from hydrous hydrazine. NiPt/C catalysts were synthesised with various Pt/Ni molar ratios. The optimal catalytic activity was displayed by Ni₅Pt₁/C and used for further studies with respect to different catalyst concentrations, initial N₂H₄, temperature and NaOH concentration. With an increase on the catalyst concentration and initial N₂H₄ the dehydrogenation rate also increased. The catalytic activity slightly decreased after 5 catalytic runs and characterization results showed that the average grain size of the reused catalyst increased from 2.5 nm to 3.8 nm. At higher temperatures a higher TOF value was obtained. Lastly, with an addition of 0.5 M NaOH, a TOF value of 2640.5 h⁻¹ and 100 % H₂ selectivity were obtained at 50°C, while with no addition of the alkaline solution the TOF value was 627.5 h⁻¹.

5.2 Photocatalysis and Electrocatalysis of Hydrous Hydrazine

The catalytic decomposition of hydrous hydrazine for the generation of H₂ is well investigated, but its photocatalytic decomposition still needs lots of research for the discovery of efficient photocatalysts. TiO₂ modified with deposition of noble metals is found to be very promising as for the photocatalytic oxidation of hydrazine and its derivatives [116], [117]. TiO₂
nanoparticles modified with rhodium were developed by Kumar et al. [118] for the photocatalytic decomposition of hydrous hydrazine under visible light irradiation. Unmodified TiO$_2$ particles exhibited a H$_2$ production of 83 μmol g$^{-1}$ cat and formation rate of 6.9 μmol g$^{-1}$ cat h$^{-1}$ while TiO$_2$-Rh had a H$_2$ production of 413 μmol g$^{-1}$ cat and rate formation 42.0 μmol g$^{-1}$ cat h$^{-1}$ after 12 h of visible light irradiation. The photocatalyst was still efficient after five subsequent runs and the H$_2$ yield was 384 μmol g$^{-1}$ cat but it was noticed a slight decrease in the photoactivity due to leaching of the Rh from the TiO$_2$ surface. After the five cycles, the value of Rh was 0.14 wt %, slightly lower than that of the fresh catalyst (0.16 wt %).

Noble metals such as Pt, Pd and Au were used as electrodes for the electrooxidation of hydrazine to N$_2$ and H$_2$ but their high price makes them not practical to use for further applications [119], [120]. Silver nano-catalysts Ag@C$_{60}$ were synthesised by Narwade et al. [121] to investigate the electrocatalytic activity for the oxidation of hydrazine for H$_2$ production. The electrocatalyst was also tested for its efficiency in a range of pH solutions. The best electrochemical performance and long-term stability was exhibited by the Ag@C$_{60}$ catalyst in a 0.5 M KOH solution. It was concluded that the enhanced electrocatalytic activity of the Ag@C$_{60}$ is a result of the synergistic effect of Ag nanoparticles and C$_{60}$.

A new method studied recently is the photoelectrocatalysis, a combination of photocatalysis and electrocatalysis. Thus, photoelectrochemical (PEC) H$_2$ production from N$_2$H$_4$.H$_2$O was studied by Yan et al. [122] using CdS nanorod arrays as the photoelectrode. The proposed mechanism is presented below in Fig. 7. Under visible-light irradiation the photoelectrode in electrolytes with N$_2$H$_4$.H$_2$O presented great stability after 100 h of the reaction while when there were no electrolytes the persistence of the device was less than 100 s. Moreover, the efficiency of the photoelectrode remained the same with a H$_2$ selectivity over 90%. The results that were obtained from the CdS photoelectrode promote the PEC H$_2$ production for further studies and applications. Table 4 summarises the results from the experiments mentioned above.
Fig. 7. Proposed mechanism of the photoelectrochemical decomposition on CdS nanorod catalysts [122].

Table 4. Photocatalysts and Electrocatalysts used for hydrous hydrazine decomposition.

<table>
<thead>
<tr>
<th>Photocatalysis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Reference</td>
</tr>
<tr>
<td>Au/TiO$_2$</td>
<td>[116]</td>
</tr>
<tr>
<td>Pd/SiO$_2$</td>
<td>[117]</td>
</tr>
<tr>
<td>TiO$_2$-Rh</td>
<td>[118]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrocatalysis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>System</td>
</tr>
<tr>
<td>Ni$<em>{60}$Co$</em>{40}$</td>
<td>1.0 M KOH + 0.1 M N$_2$H$_4$.H$_2$O</td>
</tr>
<tr>
<td>Ni/CB</td>
<td>0.1 M NaOH + 0.1 M N$_2$H$_4$</td>
</tr>
<tr>
<td>Ag@C$_{60}$</td>
<td>0.5 M KOH + 0.5 mL N$_2$H$_4$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Photoelectrocatalysis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>System</td>
</tr>
<tr>
<td>CdS NRs</td>
<td>0.1 M Na$_2$SO$_4$ + 0.378 M N$_2$H$_4$.H$_2$O</td>
</tr>
</tbody>
</table>
6 Reactors for NH₃ decomposition

6.1 Membrane reactors

Catalytic membrane reactors (CMRs) are frequently used for the decomposition of ammonia because they offer several advantages. They shift the thermodynamic equilibrium due to the removal of H₂ allowing the process to proceed at lower temperatures reaching full conversion. Moreover, they do not require an additional separation unit, since separation and purification occur in a single unit, lowering the cost of the system and providing pure H₂. The process is usually assisted by an inert sweep gas that might dilute H₂ stream, which is unwanted. The most suitable materials are Palladium or/and its alloys but their challenging scale-up and high cost limit this technology and therefore new materials must be explored [123].

Numerical simulations for ammonia decomposition in a catalytic membrane reactor filled with Ni/Al₂O₃ catalytic particles were studied by Di Carlo et al [124]. The focus of the study was the evaluation of the improvement of the ammonia decomposition with the use of Pd coated membranes. Firstly, a 2D study was investigated without membranes and results showed that at temperature of 550°C, pressure of 0.2 MPa and low flow velocity of 2 cm/s the ammonia conversion was extremely good with a residual NH₃ of only a few ppm. The 3D simulations were studied with the addition of Pd-membranes at 1MPa and temperature range of 500-600°C. At 550°C NH₃ conversion was 99.93% improving almost 18% the conversion rate that was obtained without the membranes.

A tube-wall catalytic membrane reactor containing a Pd membrane alloyed with Ag (Pd₇₇Ag₂₃) was developed by Itoh et al. [125] for the decomposition of ammonia at temperatures below 400°C. A Ru catalyst was used, and the optimal loading was 2 wt% due to the high dispersion on the surface area. A 2 wt% Ru/Al₂O₃ packed bed reactor was compared with the membrane reactor loaded with 2 wt% of Ru and it was found that the latter achieved a higher conversion (about 15% higher) because of the larger heat flux in the tube reactor. The reactor with 2 mm thick Pd membrane achieved 100% NH₃ conversion at 375°C and ammonia feed rate of 10 mL/min.

Abashar et al. [126] simulated multi-stage Pd-Ag membrane reactors for the generation of ultra-pure H₂. In comparison with a single stage reactor that achieved 29.49% ammonia conversion the seven-stage membrane reactor exhibited complete conversion of ammonia at 40 bar.
Moreover, a multi-stage fixed bed reactor was modelled under the same conditions and the exit ammonia conversion was 92.37% suggesting that a multi-stage membrane reactor is superior. The numerical results demonstrated a promising performance of the membrane reactor and even though they were not confirmed experimentally they might have fundamental importance for further design and optimization of the reactor and the process.

Co-based catalysts combined with Pd-Au alloy membranes were demonstrated by Cerrillo et al. [127] for the decomposition of ammonia to the production of high purity H\textsubscript{2}. Experiments were carried out with and without the addition of the membrane and results showed that the membrane drastically enhances the conversion of NH\textsubscript{3}. The purity of H\textsubscript{2} was > 99.97% for over 1000 h of running stream. Moreover, the ammonia conversion increased when the temperature, pressure and contact time increased.

Cechetto et al. [128] experimentally demonstrated ammonia decomposition in a catalytic membrane reactor (Fig.8). The catalyst was Ru-based with double-skin Pd-based membranes. The main focus of the experiments was the purity of H\textsubscript{2} produced in the membrane reactor technology. Results showed that with an increase of the thickness of the membrane above 6 μm ultra-pure H\textsubscript{2} can be generated. Also, a small purification unit can be installed as a more economic feasible solution in contrast with the increase of the membrane thickness. More specifically, a bed of 13X zeolite was tested and it was concluded that it’s a suitable sorbent for H\textsubscript{2} purification.
Fig. 8. Process flow diagram of the experimental setup [128].

In addition to that, membranes are required to be free of defects to achieve high H₂ purity. Alternative materials to Pd that have been already used are Vanadium, and Ni alloys. A 3D CFD model was developed by Shwe Hla and Dolan [129] for the examination of the performance of a Vanadium-based alloy membrane reactor for H₂ generation and separation by ammonia decomposition. At 30 L/min NH₃ inlet flow rate, pressure of 7.8 bar, and 300°C, a conversion of 90% NH₃ was achieved and H₂ yield over 95% within a shorter distance along membrane tubes. As expected, at lower inlet flow rates, H₂ yield was higher due to a longer residence time. The effects of the membrane permeability on the H₂ yield were tested under different percentages of the original value. At only 50% functionality the H₂ yield was similar with that obtained at 100% membrane permeability.

A double layered Nd₅.₅Mo₀.₅W₀.₅O₁₁.₂₅₋δ (NMW)/Nd₅.₅Mo₀.₅W₀.₅O₁₁.₂₅₋δ-Ni (NMW-Ni) membrane was synthesized by Cheng et al. [130] for the on-site H₂ production by catalytic ammonia decomposition. NMW-NiO layer served as the catalytic reaction site while the NMW layer provided the separation of H₂. A sweep gas of N₂ was used and NH₃ conversion of 99% was obtained at 750°C, 24% higher than that of a packed bed reactor that was achieved under the same conditions, given to the simultaneous removal of the H₂. Moreover, the highest conversion may be attributed to the longer length of the membrane reactor. It was noticed that NH₃ conversion was higher at lower NH₃ flow rates in the feed stream due to a higher residence time of ammonia in the reactor, whereas H₂ production was small due to a slower composition rate, indicating the need to improve ammonia decomposition at high feed flow rates. After 75 h of reaction at 750°C, the membrane reactor maintained a high conversion of 91% achieving high long-term stability.

Ru particles dispersed on yttria-stabilized zirconium (YSZ) coated by a Pd film, were developed by Zhang et al. [131] to utilize them for H₂ production by the decomposition of NH₃. The reaction took place in a catalytic membrane reactor. Different parameters such as temperature, pressure and inlet flow were tested to evaluate the reactor performance. An addition of Cs promoter caused complete decomposition of NH₃ at temperatures of 400°C and volumetric H₂ productivity of 31.6 mol m⁻³ s⁻¹. Both the catalyst and the membrane were found to eliminate any transport resistances resulting in a decreased operation temperature, reduced catalyst content and higher H₂ productivity in contrast with a PBMR. Also, a reactor model was developed to better understand the performance of the reactor. The experimental results
were in a great agreement with the model at all conditions, validating the first-order kinetics and the efficiency of the CMR.

### 6.2 Fixed Bed Reactors

Fixed bed reactors (FBRs) have many large-scale applications in the industry. One great advantage is that the catalyst is immobilized, and the reactant mixture is technically forced to be in contact with it. Though, due to its poor mixing properties large temperature gradients occur and therefore, the extent of the ammonia decomposition can be reduced [132].

Commercial 5 wt% Ru/C catalyst on different promoter Cs loadings was studied experimentally by Chen et al. [133] in a fixed bed reactor for the decomposition of ammonia. The experimental setup that was used in this work is demonstrated in Fig.9. The optimum Cs/Ru molar ratio was 4.5 and further increase than that resulted in a decrease on the conversion of ammonia. At 400°C ammonia conversion was nearly 100%.

Fig.9. Schematic diagram of the process for ammonia decomposition in a fixed bed reactor [133].

Gu et al. [134] developed Ni-based catalysts supported in porous alumina (Ni@Al₂O₃) via a simple one-pot method for the decomposition of ammonia. The Ni content was adjusted from 5 at.% to 25 at.% and the reaction took place in a fixed bed reactor. The catalyst with the highest nickel content (25 at.%) exhibited the highest ammonia conversion of 93.9 % at 600°C and almost full conversion (99.1%) at 650°C. H₂ formation rate reached up to 7.8 mmol gcat⁻¹ min⁻¹.
at 450°C. There was an increase in the crystallite size of Ni particles from 1 nm (fresh) to 6 nm (used) due to high reaction temperature. The high catalytic performance could be attributed by the strong interaction amongst the mesoporous alumina matrix and nickel particles that can prevent the metallic Ni from sintering into large aggregates and the high dispersion of Ni particles.

A fixed bed plug flow reactor was used by Morlanés et al. [135] for the decomposition of ammonia by Ba-CoCe catalysts with various Co/Ce molar ratios. When catalysts were prepared by impregnation it was noticed that above 20% of Co loading decreased the conversion of ammonia, while when they were prepared via coprecipitation the opposite trend was found since 30% Co content catalysts showed higher activity. The high activity could be attributed to the coprecipitation method that allowed higher amounts of Co incorporated in the catalyst. The optimum performance was from the 0.5Ba/CoCe(80/20) catalyst with 41.4 wt% Co, 23.5 wt% Ce and 0.45 wt% Ba, whose catalytic activity was comparable with Ru-based catalysts. At 450°C it exhibited a conversion little bit lower than 80%. Ce as a promoter, increased Co dispersion and prevented sintering and aggregation.

Ru nanoparticles were supported on alkali silicates (Ru/A₂SiO₃, A = Li, Na and K) by Zhiqiang et al. [136] The catalytic reaction occurred in a fixed bed reactor at atmospheric pressure. Ru/K₂SiO₃ (3.21 wt% Ru) showed the best catalytic performance with an NH₃ conversion of 60.5%, H₂ formation rate of 20.3 mmol g⁻¹cat⁻¹min⁻¹ and TOF value of 2.03 s⁻¹ at 450°C. A series of K-promoted catalysts were prepared to evaluate the effect of the K content but results showed that the highest ammonia conversion was the one already exhibited by Ru/K₂SiO₃. In comparison with other works that used Ru particles supported on other silicon materials at the same conditions, Ru/K₂SiO₃ achieved higher performance due to a better promotion effect of the alkali metal silicates. It was concluded by the authors that the formation of oxygen vacancies on the alkali metal silicates can stabilize the Ru nanoparticles with strong metal support interactions that results in an increase of the number of active sites.

Ni-Ru/CeO₂ catalysts with several metal loadings were prepared by Lucentini et al. [137] and tested for the H₂ generation from the decomposition of ammonia. The catalytic tests were carried in a fixed bed reactor and results showed that the best catalytic performance was observed by 0.4-0.6 wt% Ru and 2.4-5.0 wt% Ni. After 100 h of continuous operation the catalysts exhibited excellent long-term stability. At 400°C, TOF values exceeding 2 s⁻¹ were obtained. With the use of Langmuir-Hinshelwood-Hougen-Watson approach, a kinetic model
was developed for the simulation of the H₂ production rate under different parameters. Lastly, it was concluded that the limiting step for the reaction is the dehydrogenation of ammonia adsorbed on the surface of the catalysts.

In addition to the previous research Lucentini et al. [138] continued the investigation on the decomposition of ammonia on Ni-Ru catalysts supported on 3D-printed CeO₂ structures in a fixed bed reactor. The 0.5Ni0.1Ru catalyst achieved the best catalytic performance and therefore was used for the rest of the study. Moreover, a 1D mathematical model was developed over the 3D-printed catalytic structure loaded with Ni-Ru catalysts. A comparison between the experimental results and the simulation validated the model that was developed. For the optimisation of the catalytic structure, a series of simulations were performed with different geometric parameters to examine their effect on the catalytic performance in ammonia decomposition. Specifically, the geometric parameters that were optimized were the wall thickness, the number and width of channels for better and more efficient usage of the reactor with the intention of on-site generation H₂ and usage in a PEM-type fuel cell.

Co₃Mo₃N and γ-Mo₂N catalysts were synthesised with the use of citric acid as a chelating agent by Jolaoso et al. [139]. The catalytic tests were performed in a fixed bed quartz tube reactor at atmospheric pressure, a temperature range of 300-600°C and constant GHSV of 6000 h⁻¹. At 550°C, γ-Mo₂N catalyst gave 71.9 % NH₃ conversion while Co₃Mo₃N gave 97.3 % resulting in a better catalytic performance indicating that Co particles promote the ammonia decomposition. Characterization tests showed that Co₃Mo₃N catalyst contained 33.72 wt %, 54.41 wt % and 4.03 wt % Co, Mo and N respectively. After 35 h of a continuous test the catalyst showed no deactivation. This was validated by measuring the crystallite size of the fresh catalyst (6.20 nm) and the used catalyst (6.19 nm) whereas no significant decrease was obtained. Conversion of 100 % was obtained by both catalysts at 600°C.

Another study conducted in a fixed bed reactor, implemented three Ru-supported catalysts (Ru/Al₂O₃, Ru/La₂O₃-Al₂O₃ and Ru/La₂O₃CO₃-Al₂O₃). Kim et al. [140] examined their catalytic activity at a low temperature range of 350-500°C. The best catalytic activity was established by Ru/La₂O₃CO₃-Al₂O₃ (11.5 wt % La and 0.95 wt % Ru) with 80.1 % NH₃ conversion at 500°C. Even though characterization tests showed that Ru/Al₂O₃ had higher Ru dispersion (27.3 %) than Ru/La₂O₃-Al₂O₃ (20.6 %) it resulted in a lower catalytic activity suggesting that the La addition promoted electron donation from La to Ru particles due to their electronegativity difference and therefore increasing the kinetics of the reaction. Moreover, the
La oxycarbonate-rich surface favoured the formation of Ru particles on the surface of the catalyst preventing the particles to leave from the surface into the bulk phase. Thus, it was concluded that the La$_2$O$_2$CO$_3$ surface coating might be beneficial for catalyst synthesis when an increased surface metal concentration is needed.

6.3 Microreactors

Microreactors gained attention in the early 1990s marking them as a relatively new field. Microreactor technology offers better control, high surface area ratios, high heat and mass transfer rates and enhanced conversion efficiency. Compared with conventional reactors, microstructured reactors exhibited higher activity towards NH$_3$ ammonia decomposition [141].

An autothermal microchannel reactor was evaluated for the decomposition of ammonia to generate H$_2$ and provide it for power generation systems. Engelbrecht, Chiuta and Bessarabov [142] studied the effects of different parameters such as NH$_3$ decomposition flow rate and oxidation flow rate and fuel-oxygen equivalence ratio to find the optimal operation parameters. The catalyst for decomposition was 8.5 wt% Ru/Al$_2$O$_3$ and for the oxidation was 5 wt% Pt/Al$_2$O$_3$. A conversion up to 99.8% was observed with a H$_2$ equivalent fuel power of 0.71 kWe, when the decomposition flow rate was 6 NL min$^{-1}$, the oxidation flow rate was 4 NL min$^{-1}$ and the fuel-oxygen ratio was 1.4. A stability test was also carried out for 24 h in demanding reactor conditions to determine any inconsistencies in the catalyst where results showed that no deactivation of the catalyst occurred during reaction. It was concluded that the performance of the reactor was good and further research might be able to up-scale this system for multi-kW power generation systems.

Based on the experimental results obtained from Engelbrecht, Chiuta and Bessarabov [142], a 3D CFD model was developed by Schumacher et al. [143] to study both steady-state and transient regimes in a microchannel reactor to provide a suitable mathematical model. In consideration of the wide range of ammonia decomposition and oxidation flow rates and temperature profiles, the simulation fitted the experimental data with an acceptable accuracy. It was found that at the microreactor inlet the highest temperature was obtained and therefore a different solution needed to be developed to solve the model with regard in the distribution of heat transfer. Therefore, any future reactor designs should be focused on the optimization of the heat transfer rate.
3D printed SiCN monolithic ceramic microreactors and Ru catalysts were used by Gyak et al. [144] for ammonia decomposition at high temperature. A temperature range of 500-1000°C and different flow rates of 2, 4 and 8 mL min⁻¹ were the conditions for the catalytic reaction. At 2 mL min⁻¹ and 1000°C, ammonia was completely decomposed due to an increased residence time. After 48 h of exposure to ammonia and 1000°C, the ceramic microreactors demonstrated excellent chemical resistance and heat tolerance.

Maleki, Fulton and Bertola [145] designed a microreactor, both experimentally and numerically for H₂ production via low temperature ammonia decomposition over Co₀.₅Ce₀.₁Al₀.₄O(sa) catalyst. The geometries of the microchannel are presented in Fig.10. Two kinetic models were used to describe the reaction, a pseudo-first order model and a modified Temkin-Pyzhev model that were compiled in a CFD model. The model then was solved at a various NH₃ flow rates and temperatures and exhibited good agreement with the experimental data. At a lower temperature range the Temkin-Pyzhev model had better accuracy than the first model and therefore was selected for further study. Higher conversion rates were obtained while increasing the temperatures whereas over 99 % was observed at temperatures of 550°C.

Bimetallic Ru-Fe alloy catalysts were synthesised and impregnated with carbon nanotubes by Chen et al. [146] The experiments took place in a fixed bed microreactor at a temperature range of 300-500°C and atmospheric pressure. The Ru₃Fe/CNTs catalyst (1.67 wt % Ru, 0.31 wt % Fe) presented the best catalytic performance in contrast with the Ru/CNTs catalyst. At 500°C both catalysts resulted in a 100 % ammonia conversion. After 60 h of reaction, the activity of Ru/CNTs was decreased by 30 % while that of Ru₃Fe/CNTs decreased only 10 % exhibiting superior stability with the addition of Ru. It was concluded that the alloy synergistic effect...
between Ru and Fe enhanced the catalytic activity and furthermore the addition of the non-
noble metal Fe reduces the content of Ru resulting in a lower catalyst cost.

Table 5. A summary of the type of reactors used for ammonia decomposition

<table>
<thead>
<tr>
<th>Type of reactor</th>
<th>Catalyst</th>
<th>Temperature</th>
<th>Conversion</th>
<th>Yield</th>
<th>TOF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd membrane reactor</td>
<td>Ni/Al₂O₃</td>
<td>550</td>
<td>99.93</td>
<td></td>
<td></td>
<td>[124]</td>
</tr>
<tr>
<td>Pd membrane reactor</td>
<td>2%Ru/Al₂O₃</td>
<td>375</td>
<td>100</td>
<td></td>
<td></td>
<td>[125]</td>
</tr>
<tr>
<td>Pd-Ag membrane reactor</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td>[126]</td>
</tr>
<tr>
<td>Pd-Au membrane reactor</td>
<td>Co</td>
<td></td>
<td>99.97</td>
<td></td>
<td></td>
<td>[127]</td>
</tr>
<tr>
<td>Double-skin Pd membrane reactor</td>
<td>Ru</td>
<td></td>
<td>93.2</td>
<td></td>
<td></td>
<td>[128]</td>
</tr>
<tr>
<td>Vanadium alloy membrane reactor</td>
<td></td>
<td>300</td>
<td>90</td>
<td>&gt;95</td>
<td></td>
<td>[129]</td>
</tr>
<tr>
<td>NMW/NMW-NiO</td>
<td>NMW-NiO powder</td>
<td>750</td>
<td>99</td>
<td></td>
<td></td>
<td>[130]</td>
</tr>
<tr>
<td>YSZ/Pd membrane reactor</td>
<td>Ru</td>
<td>400</td>
<td>93</td>
<td>90</td>
<td></td>
<td>[131]</td>
</tr>
<tr>
<td>Fixed bed reactor</td>
<td>5%Ru/C</td>
<td>400</td>
<td>~100</td>
<td></td>
<td></td>
<td>[133]</td>
</tr>
<tr>
<td>Fixed bed reactor</td>
<td>25%Ni@Al₂O₃</td>
<td>650</td>
<td>99.1</td>
<td></td>
<td></td>
<td>[134]</td>
</tr>
<tr>
<td>Fixed bed reactor</td>
<td>0.5Ba/CoCe(80/20)</td>
<td>450</td>
<td>74</td>
<td>0.602</td>
<td></td>
<td>[135]</td>
</tr>
<tr>
<td>Fixed bed reactor</td>
<td>Ru/K₂SiO₃</td>
<td>450</td>
<td>60.5</td>
<td>2.03</td>
<td></td>
<td>[136]</td>
</tr>
<tr>
<td>Fixed bed reactor</td>
<td>Ni-Ru/CeO₂</td>
<td>400</td>
<td>93</td>
<td>90</td>
<td></td>
<td>[137]</td>
</tr>
<tr>
<td>Fixed bed reactor</td>
<td>Ni-Ru/CoO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[138]</td>
</tr>
<tr>
<td>Fixed bed reactor</td>
<td>Co₃Mo₂N</td>
<td>550</td>
<td>97.3</td>
<td></td>
<td></td>
<td>[139]</td>
</tr>
<tr>
<td>Fixed bed reactor</td>
<td>Ru/La₂O₃₂Al₂O₃</td>
<td>500</td>
<td>80.1</td>
<td></td>
<td></td>
<td>[140]</td>
</tr>
<tr>
<td>Microreactor – Experimental</td>
<td>8.5%Ru/Al₂O₃</td>
<td>651</td>
<td>99.8</td>
<td></td>
<td></td>
<td>[142]</td>
</tr>
<tr>
<td>Microreactor – Experimental</td>
<td>Ru/Al₂O₃</td>
<td>300</td>
<td>99.86</td>
<td></td>
<td></td>
<td>[143]</td>
</tr>
<tr>
<td>Microreactor – Simulation</td>
<td>Ru/Al₂O₃</td>
<td>300</td>
<td>99.94</td>
<td></td>
<td></td>
<td>[143]</td>
</tr>
<tr>
<td>Microreactor</td>
<td>Ru</td>
<td>1000</td>
<td>100</td>
<td></td>
<td></td>
<td>[144]</td>
</tr>
<tr>
<td>Microreactor</td>
<td>Co₃Ce₇Al₁₀₄O₈(sa)</td>
<td>550</td>
<td>99</td>
<td></td>
<td></td>
<td>[145]</td>
</tr>
<tr>
<td>Microreactor</td>
<td>Ru/Fe/CNTs</td>
<td>500</td>
<td>100</td>
<td>86.21</td>
<td></td>
<td>[146]</td>
</tr>
</tbody>
</table>

As seen from Table 5 membrane reactors and microreactors are superior to fixed bed reactors. Even though membrane reactors are well studied, the most common membrane used is Pd and its alloys [124]–[128], [131], which is rare and expensive and needs to be replaced with other elements that give off such high catalytic activity and selectivity. Regarding fixed bed reactors, a number of studies give promising results but most of them presented low conversion of ammonia [135]–[137], [140]. The need for high temperatures for the decomposition makes these reactors unsuitable. Studies on microreactors operating experimentally and theoretically...
in a large range of temperatures are limited mostly for Ru-based catalysts as they present high catalytic activity giving the opportunity for further development of a cost-effective reactor system [143], [144], [146].

7 Conclusions

Green energy carriers have the potential to solve the current issues related with climate change. An emerging energy resource is H₂ as an alternative to non-renewable sources such as conventional fuels. Its physical storage though, is limiting its application. Therefore, this review provides information about ammonia and hydrous hydrazine as possible chemical hydrogen storage compounds. Moreover, heterogeneous catalysts utilized for the decomposition reactions of the compounds mentioned above are reviewed in contrast with their efficiency. An issue occurring with hydrous hydrazine decomposition is ammonia formation that can lead to corrosion and lower selectivity regarding H₂. The most promising catalytic system for ammonia decomposition is ruthenium and its alloys but it’s not methodical due to its high price and scarcity. For hydrous hydrazine, the most active catalytic system is nickel catalysts alloyed with noble metals that are some of the most expensive metals in the world. Thus, there is a great need for the development of cost-effective catalytic systems for both ammonia and hydrous hydrazine, using more abundant metals instead of precious metals with lower metal loading and higher atom efficiency. Reactor technology used for NH₃ decomposition has also been presented in this review. The most common catalyst used for this reaction is the catalytic membrane reactor. Due to the membrane, separation and purification can occur in a single step, giving pure H₂ and lowering the operation cost. Palladium membranes were found to be the most suitable materials, but future works need to take into consideration their high cost and therefore, explore and develop other materials with the same efficacy. Microreactors are also an attractive option due to a high activity towards NH₃ with different types of catalysts, especially ruthenium and its alloys. In contrast, fixed bed reactors presented lower activity and further research is needed for future applications and up-scaled production of H₂. In conclusion, for on-site hydrogen production by NH₃ and N₂H₄·H₂O future research must give attention to the development of low-cost catalyst with optimum catalytic performance and great selectivity towards H₂. Furthermore, it’s important to consider the reactor technology and develop systems with low operation cost and high efficiency.
References


B. Robert Matt air, H. H. Sisler, F. Raschig, and V. Chemie GmbH, “Hydrazine from Chlorine with Anhydrous Ammonia The Production of Hydrazine by the Reaction of Chlorine with Anhydrous Ammonia1.”


V. A. Matyshak and O. N. Silchenkova, “Catalytic Decomposition of Hydrazine and
Hydrazine Derivatives to Produce Hydrogen-Containing Gas Mixtures: A Review,”

L. Zhou, X. Luo, L. Xu, C. Wan, and M. Ye, “Pt-Ni nanoalloys for H2 generation from


J. Zheng, X. Liu, P. Xu, P. Liu, Y. Zhao, and J. Yang, “Development of high pressure


manufacturing for hydrogen storage applications,” Energies, vol. 14, no. 24, 2021, doi:
10.3390/en14248513.

D. P. Broom and M. Hirscher, “Irreproducibility in hydrogen storage material
research,” Energy Environ. Sci., vol. 9, no. 11, pp. 3368–3380, 2016, doi:
10.1039/c6ee01435f.

A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J.

in Graphite Nanofibers,” vol. 102, 1998.


44


[103] B. Xia, K. Chen, W. Luo, and G. Cheng, “NiRh nanoparticles supported on nitrogen-doped porous carbon as highly efficient catalysts for dehydrogenation of hydrazine in...


S. Shwe Hla and M. D. Dolan, “CFD modelling of a membrane reactor for hydrogen production...


