

## CHEMISTRY

# Hydrogenation of terminal and internal olefins using a biowaste-derived heterogeneous cobalt catalyst

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Hydrogenation of olefins is achieved using biowaste-derived cobalt chitosan catalysts. Characterization of the optimal Co@Chitosan-700 by STEM (scanning transmission electron microscopy), EELS (electron energy loss spectroscopy), PXRD (powder x-ray diffraction), and elemental analysis revealed the formation of a distinctive magnetic composite material with high metallic Co content. The general performance of this catalyst is demonstrated in the hydrogenation of 50 olefins including terminal, internal, and functionalized derivatives, as well as renewables. Using this nonnoble metal composite, hydrogenation of terminal C=C double bonds occurs under very mild and benign conditions (water or methanol, 40° to 60°C). The utility of Co@Chitosan-700 is showcased for efficient hydrogenation of the industrially relevant examples diisobutene, fatty acids, and their triglycerides. Because of the magnetic behavior of this material and water as solvent, product separation and recycling of the catalyst are straightforward.

## INTRODUCTION

Olefins constitute a central feedstock for the chemical industry and represent major platform molecules for the development of basic synthetic methodologies. Among the different reactions of alkenes, catalytic hydrogenations continue to attract significant interest from both academic and industrial researchers (1, 2). Today, they are of crucial importance for all kinds of products spanning from pharmaceuticals to food, specialty chemicals, commodity chemicals, and agrochemicals (3). More specifically, in the petrochemical industry, hydrogenation of diisobutene to isooctane (2,4,4-trimethylpentane) is of current interest, as it substitutes one of the largest organic chemicals methyl tert-butyl ether (MTBE), which has been phased out as an antiknock additive in the United States since 2006 (4).

With respect to nutrition and food additives, natural oils are hydrogenated to harden them and to obtain better processable and storable fats on million metric ton scales (5). Moreover, catalytic hydrogenations play a role in the synthesis of vitamins such as biotin (6), a vitamin K<sub>3</sub> derivative, and β-carotene, a precursor of vitamin A.

In the pharmaceutical industry selective hydrogenations of C=C double bonds are applied in the production of sertraline (antidepressant), betamethasone (glucocorticoid), and dihydroergotamine (antimigraine agent) (2). Most of the hydrogenation processes *vide supra* are based either on noble metal catalysts containing Pd and Pt or on less expensive but difficult to handle and pyrophoric Raney-Ni. Because of these disadvantages in recent years, a strong interest in catalysts using Earth-abundant base metals developed in research groups worldwide. Obviously, their main advantage in comparison with noble metals is the stable price, which makes calculations for industry more certain. However, motivations to substitute them are beyond costs. Because of their reactivity, noble metal catalysts sometimes have selectivity problems, which can be improved by poisoning (Lindlar catalyst).

Nevertheless, relatively few organometallic complexes consisting of first-row transition metals have been reported for the hydrogenation

of olefins. In this respect, apart from Fe (7–10) and Ni (11–14), Co (9, 15, 16) also offers interesting possibilities. For instance, the group of Chirik investigated Co complexes for the asymmetric hydrogenation of alkenes (17, 18). Furthermore, a bis(arylimidazol-2-ylidene)pyridine cobalt methyl complex revealed activity for the hydrogenation of unactivated and even sterically hindered alkenes, such as 2,3-dimethyl-2-butene, at comparably mild conditions (19). In addition, cobalt complexes with bidentate phosphine ligands proved to be sufficient for hydrogenation of internal and endocyclic trisubstituted alkenes through hydroxyl group activation (20). However, a downside of all these sophisticated molecular-defined catalysts is their sensitivity toward oxygen and water, as well as their general stability. Notably, although the metals in these systems are inexpensive, the ligands are precious.

Hence, the development of more stable and reusable heterogeneous cobalt catalysts offers a more attractive and practical option for selective hydrogenations. In this context, Lin and co-workers reported metal-organic framework (MOF)-based iron and cobalt catalysts for the hydrogenation of olefins at room temperature. Furthermore, imines, carbonyls, and heterocycles were hydrogenated successfully (21). Unfortunately, these materials were only active in the presence of 10 equivalent (equiv.) (with respect to metal) of NaBEt<sub>3</sub>H (22–24). In addition, the synthesis of these MOFs is rather complicated.

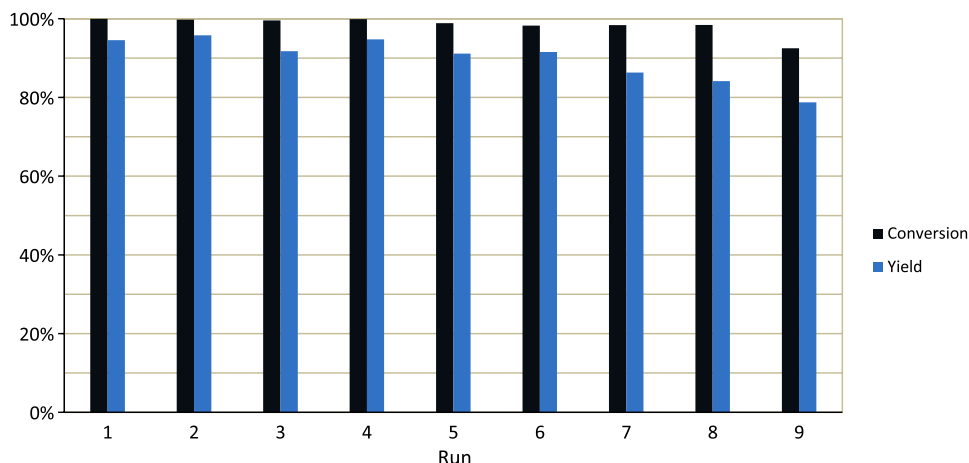
Our group (25–27) and others (28–30) have shown that simple pyrolysis of molecular-defined cobalt complexes, impregnated on inert supports, leads to materials with activity/selectivity profiles similar to homogeneous catalysts. Most recently, it was shown that the pyrolysis of a defined MOF gave a highly active reductive amination catalyst showing a broad substrate scope (31).

An ideal, industrially relevant catalyst should make use not only of base metals but also of inexpensive and renewable ligands/supports. In this context, we introduced the crab shell-derived biopolymer chitosan for catalyst preparation, both in hydrodehalogenations of alkyl and (hetero)aryl halides (32), as well as the selective hydrogenation of nitroarenes (33). Chitosan is derived by deacetylation of chitin, which represents a biowaste on a million metric ton scale (34). Despite the availability, cheap price, and known coordination to a

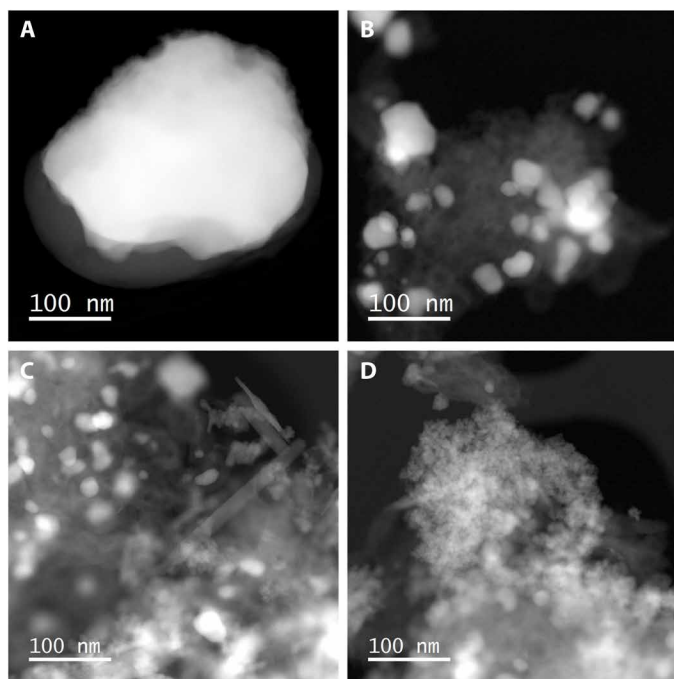
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**Scheme 1. Recycling of Co@Chitosan-700 in the hydrogenation of 1-octene.** General conditions: 1.5 mmol 1-octene, 1.5 ml of H<sub>2</sub>O, 2.9 mol % of Co@Chitosan-700, 60°C, 10 bar H<sub>2</sub>, 18 hours.



**Fig. 1. Characterization of fresh and recycled Co@Chitosan-700 by HAADF-STEM.** Images of fresh (A and B) and nine times-used (C and D) Co@Chitosan-700 catalyst, giving an overview on the general morphology.

variety of metals (35, 36) of this biopolymer, its use in heterogeneous catalysis still is narrow (37, 38). In addition, an efficient catalyst recycling is important especially for bulk chemical applications. In this respect, magnetic nanostructured materials might offer innovative potential (39).

## RESULTS

At the start of our investigations, around 25 different cobalt catalysts were synthesized by thermal treatment of cobalt(II) acetate and chitosan. Typically, these materials were prepared by stirring different ratios of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O and chitosan in ethanol at 65°C for 18 hours. Afterward, the solvent was removed and the residue

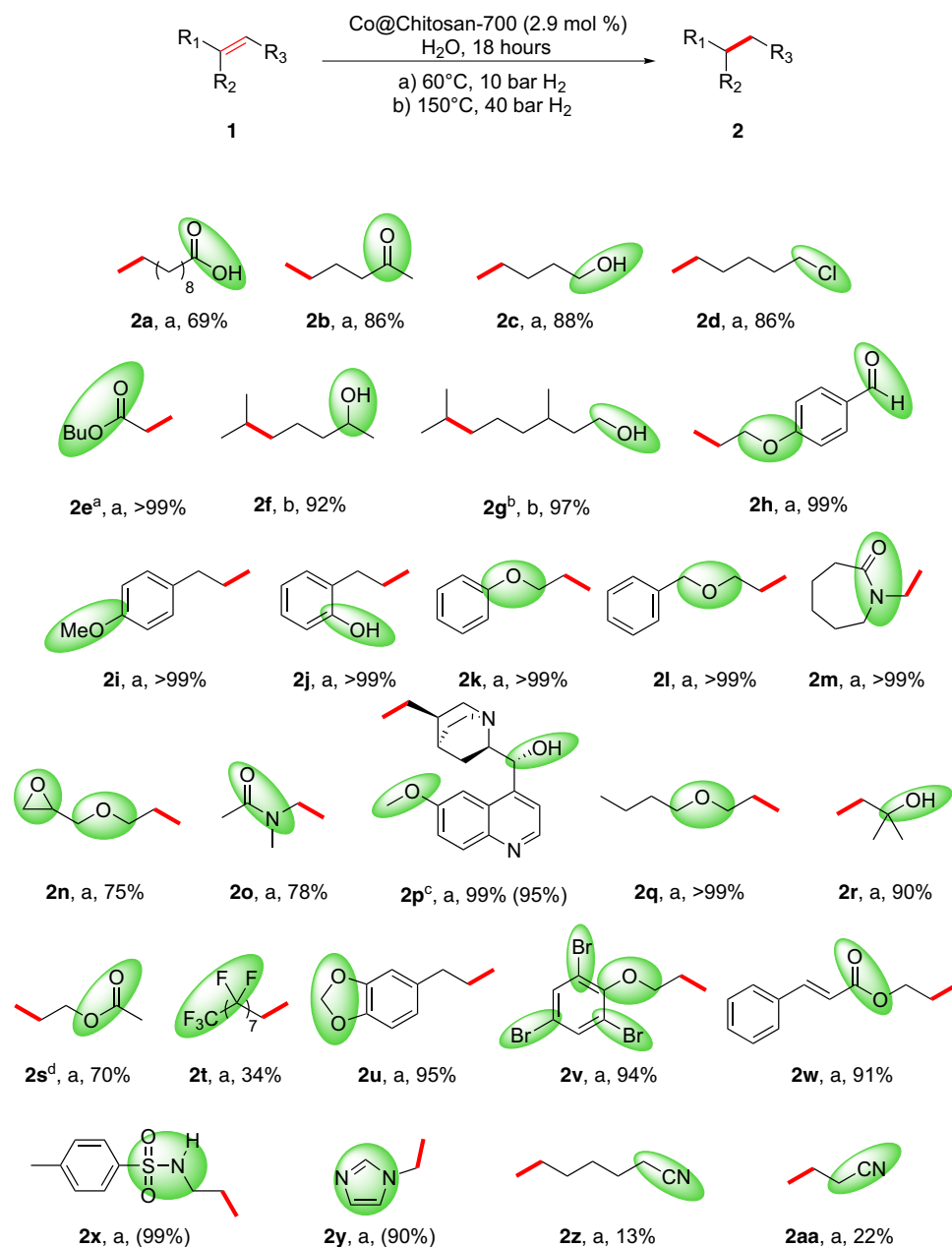
was dried overnight at 65°C by applying high vacuum. The resulting samples were ground in an agate mortar, pyrolyzed in between 700° and 1000°C, and ground again.

As a benchmark catalytic test, the hydrogenation of 1-octene was investigated under mild conditions (40°C). Among all the prepared materials, Co@Chitosan-700 (cobalt/chitosan ratio of 1:2; pyrolysis temperature: 700°C) resulted in the most active catalyst for this hydrogenation (table S1). As shown in table S2, this system is active in the presence of several solvents at 40°C and 10 bar hydrogen without any other additives. Near-quantitative conversion and best yields (>88%) were obtained in heptane, methanol, and water (table S2, entries 1, 5, and 13). Other solvents such as propylene carbonate (PC), acetonitrile (MeCN), and tetrahydrofuran (THF) were not suitable for this system, most likely due to a preferential adsorption on the catalyst's surface with respect to the olefin (table S2, entries 3, 4, and 7).

In general, for industrial applications, neat conditions are desirable. Gratifyingly, excellent conversion and product yield were obtained without any solvent present (table S2, entries 15 and 16). To illustrate the activities of the catalyst Co@Chitosan-700 in water, MeOH, and under neat conditions, we plotted a conversion-time graph for the best reaction media (scheme S1).

These investigations revealed that neat conditions seem to be most suitable for this system (60% yield after 2 hours), while in the case of water and methanol, significantly lower yields (19% and traces of *n*-octane, respectively) were observed. Nevertheless, for several applications, the use of a solvent is advantageous: For example, improved heat exchange is desirable for exothermic hydrogenations. Moreover, for the synthesis of fine chemicals, the required substrate amount can be minimized. Hence, the recyclability of this catalyst was investigated under aqueous conditions (40).

In general, the reusability of a given material is an important aspect of heterogeneous catalysis. For this purpose, such catalysts are typically separated by filtration. In contrast, Co@Chitosan-700 can be simply magnetically separated due to the high metal content (see Supplementary Materials). After washing the catalyst three times with acetone and once with water, new substrate and solvent were added. No significant drop of the activity of the catalyst was noticed for hydrogenation of 1-octene (1.5-mmol scale) for six runs (Scheme 1). After that, a slight deactivation is observed. It should be mentioned that in each decanting procedure, a small amount of catalyst was

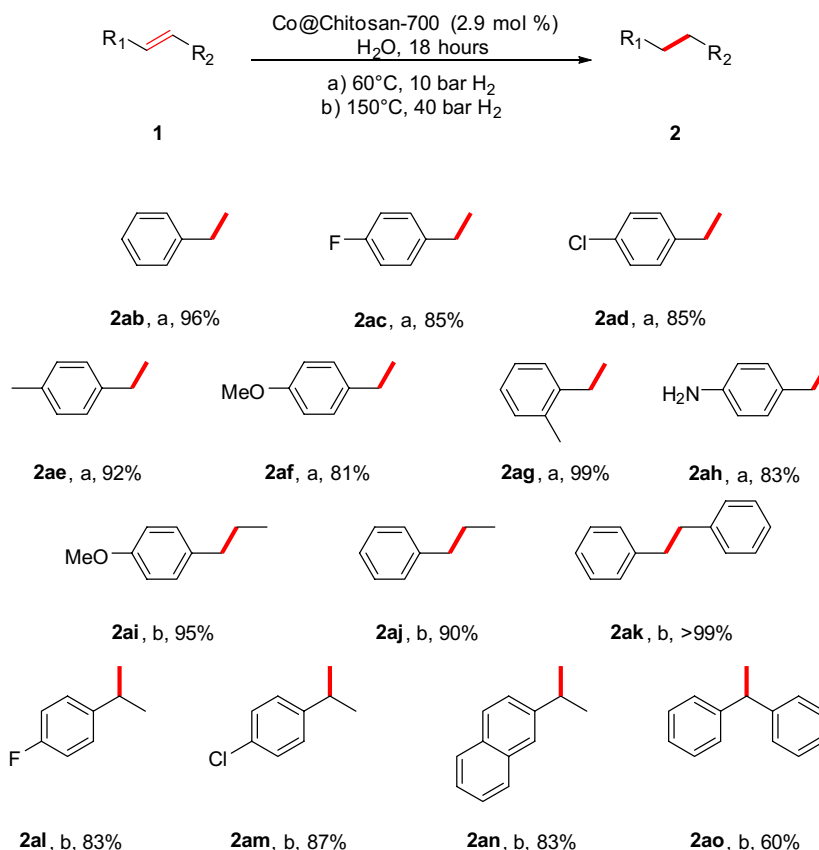


**Scheme 2. Olefin hydrogenation with Co@Chitosan-700: Investigation of functional group tolerance.** General conditions: 1.5 mmol substrate, 2.9 mol % (8.8 mg) of catalyst with respect to Co, 1.5 of ml  $\text{H}_2\text{O}$ . Yields were determined via  $^1\text{H}$  NMR using mesitylene as internal standard. Isolated yields are given in parentheses. <sup>a</sup>Yield was determined via gas chromatography (GC) using hexadecane as internal standard. <sup>b</sup>Yields were determined via  $^{13}\text{C}$  NMR using mesitylene as internal standard. <sup>c</sup>Reaction was conducted in methanol. <sup>d</sup>Reaction was conducted neat.

lost, which explains the decrease in activity. Atomic absorption spectroscopy (AAS) experiments revealed extremely low cobalt leaching of 0.055% [0.14 parts per million (ppm); 0.053% of the initial cobalt was found in the aqueous and 0.002% in the product phase].

Elemental analysis (EA) of the fresh catalyst revealed high cobalt content of 29.31%, which is the reason for the magnetic behavior of the material. The nitrogen content is relatively low with 2.53%, whereas carbon is dominant with 58.94%. To get more insight into the catalyst structure, we conducted powder x-ray diffraction (XRD) and scanning transmission electron microscopy (STEM) analyses.

XRD was measured to gain knowledge about the cobalt and carbon phases present in the composite materials. After pyrolysis at 700°C (Co@Chitosan-700), the cubic phase of metallic cobalt and graphitic carbon was indexed (fig. S9) from the received powder pattern. In contrast to related known cobalt catalysts (32, 33), no crystalline cobalt oxides ( $\text{Co}_3\text{O}_4$  or  $\text{CoO}$ ) were observed. Aberration-corrected STEM analysis was conducted from the fresh catalyst, as well as from the eight-times-recycled one. Before use, the catalytic material consisted mainly of metallic cobalt particles with graphitic carbon attached to the surface and with a rather wide range of sizes



**Scheme 3. Olefin hydrogenation with Co@Chitosan-700: Investigation of aromatic mono- and disubstituted substrates.** General conditions: 1.5 mmol substrate, 2.9 mol % (8.8 mg) of catalyst with respect to Co, 1.5 ml of H<sub>2</sub>O. Yields were determined via <sup>1</sup>H NMR using mesitylene as internal standard.

(roughly 10 to 300 nm observed; Fig. 1, A and B, and figs. S2 to S4). Cobalt oxide could be found as some very small crystallites on the surface of the metallic particles, which is in contrast to previous systems, in which cobalt was mostly present as oxides, rather than metallic (32, 33). In addition, electron energy loss spectroscopy (EELS) suggests the presence of nitrogen located in an amorphous carbon phase accompanying the graphitic carbon structures. In/on both carbon structures, bright contrast spots could be observed in the high-angle annular dark-field (HAADF) images. These might be a hint for single cobalt surface atoms; however, this could not be ensured spectroscopically because of their low density on the carbon. The small cobalt oxide particles might consist of CoO; however, the noisy oxygen K-edge in the energy loss spectrum of the small Co oxide crystallites makes comparison to literature data (41) difficult (figs. S4 and S8).

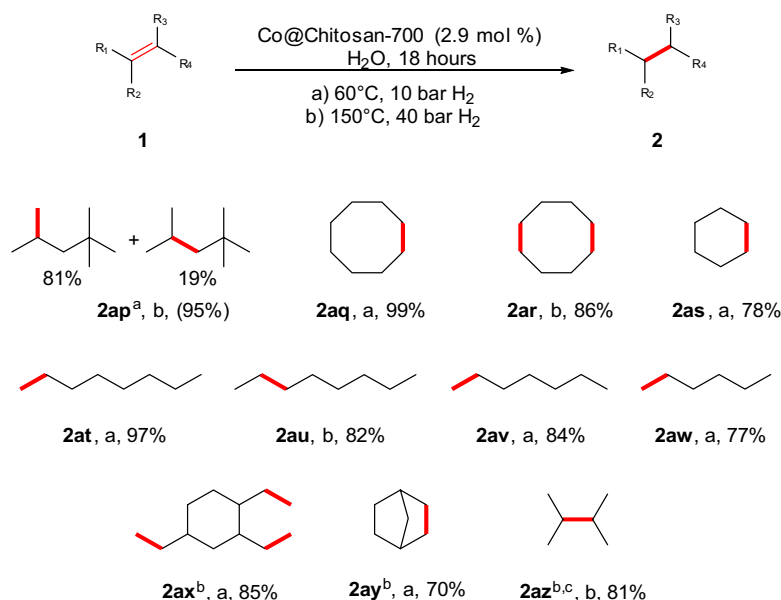
The recycled catalyst consisted in part of metallic cobalt, generally covered by graphitic carbon, but as a major difference, also big structures of cobalt oxide were present (Fig. 1, C and D, and figs. S5 to S7). Here, the fine structure of the oxygen K-edge of the EELS data (fig. S6) compares well with Co<sub>3</sub>O<sub>4</sub> data from the literature (41). Also, an amorphous carbon structure containing nitrogen is still present. These data are in good accordance with the results of XRD from the recycled catalyst, which indicate the formation of Co<sub>3</sub>O<sub>4</sub> (fig. S10).

To demonstrate the general utility of Co@Chitosan-700, we performed catalytic hydrogenations of >25 functionalized olefins. The following substrate scope was carried out in water to reduce the

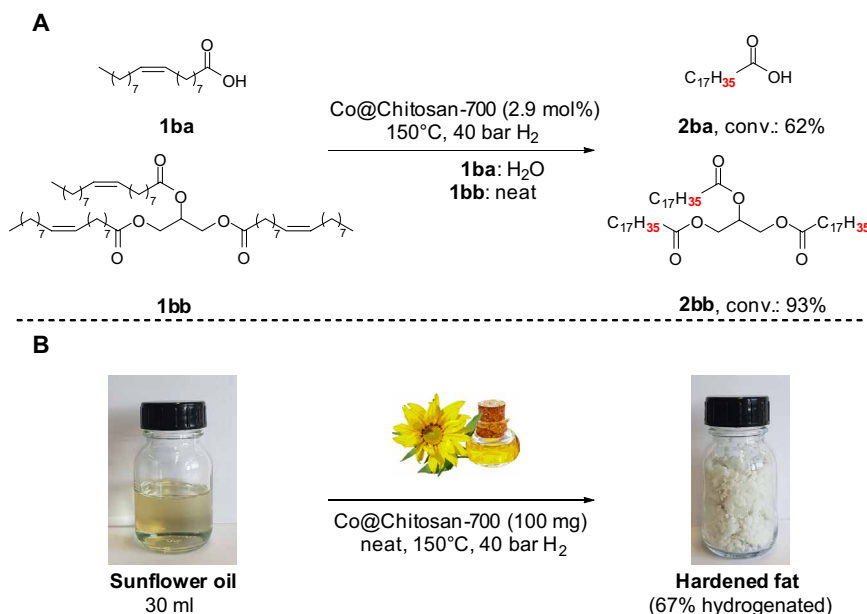
amounts of catalyst and substrate. As shown in Scheme 2, the system tolerates well several functional groups, that is, carboxylic acids (2a), alcohols (2c, 2f, 2g, 2j, 2p, and 2r), halides including bromides (2d and 2v), esters (2e, 2s, and 2w), ethers (2h, 2i, 2k, 2l, 2n, 2p, 2q, and 2v), amides (2m and 2o), methylenedioxy groups (2u), sulfonamides (2x), and coordinating heterocycles (2p and 2y). Nitriles give lower yields (2z and 2aa), possibly due to a competitive coordination of the nitrile group, which partially deactivates the catalyst. This is in accordance with the results obtained using acetonitrile as the solvent (vide supra). Our catalyst allows for selective olefin hydrogenation even in the presence of sensitive ketones (2b), aldehydes (2h), and epoxides (2n). In recent years, there is an increasing interest in fluorinated building blocks (42, 43). However, apparently simple hydrogenation of perfluoroalkenes is rather challenging (44). Nevertheless, a highly fluorinated substrate (2t) was hydrogenated under these mild conditions, albeit to a lesser extent.

Furthermore, the rather complex natural compound quinine was successfully converted to dihydroquinine 2p in excellent isolated yield. In the past, these dihydrocinchona alkaloid derivatives have been used as organocatalysts and ligands in asymmetric catalysis (45, 46). Notably, because of solubility problems, in this case, methanol was chosen as solvent. The same strategy was used for the hydrogenation of solid 2,4,6-tribromophenyl allyl ether 1v to give 2v in 95% yield.

Apart from terminal olefins, which react easily (10 bar H<sub>2</sub>, 60°C), internal ones also can be hydrogenated. For example, trisubstituted



**Scheme 4. Olefin hydrogenation with Co@Chitosan-700: Investigation of industrially relevant unsaturated hydrocarbons.** General conditions: 1.5 mmol substrate, 2.9 mol % (8.8 mg) of catalyst with respect to Co, 1.5 ml of  $\text{H}_2\text{O}$ . Yields were determined via GC using hexadecane as internal standard. <sup>a</sup>Reaction was carried out on a 10-ml scale (7.2 g, 64 mmol) without additional solvent. Isolated yield is given. <sup>b</sup>Yields were determined via  $^1\text{H}$  NMR using mesitylene as internal standard. <sup>c</sup>Reaction was carried out on a 5-ml scale (3.5 g, 42.1 mmol) without solvent.



**Scheme 5. Hydrogenation of fatty acids and esters.** Hydrogenation of (A) oleic acid and its triglyceride triolein and (B) sunflower oil. General conditions: (A) 1.5 mmol substrate, 2.9 mol % (8.8 mg) of catalyst with respect to Co, 0.5 ml of solvent if used,  $150^\circ\text{C}$ , 40 bar  $\text{H}_2$ , 18 hours; (B) 30 ml (25.68 g) of substrate, 100 mg of catalyst,  $150^\circ\text{C}$ , 40 bar  $\text{H}_2$ , 19 hours. Conversions were determined via  $^1\text{H}$  NMR using mesitylene as internal standard. Photo Credit: Florian K. Scharnagl, Leibniz-Institut für Katalyse e.V. an der Universität Rostock.

double bonds (**2f** and **2g**) were reduced at  $150^\circ\text{C}$  and 40 bar  $\text{H}_2$  in 97 and 92% yield, respectively. Obviously, this opens the possibility of selective hydrogenation of an easily accessible double bond in the presence of a less reactive one (47), as was shown for the formation of **2w**. At  $60^\circ\text{C}$ , the terminal double bond was selectively hydrogenated, while the internal was not.

As another important class of unsaturated compounds, several aromatic olefins were investigated (Scheme 3). Again, both terminal and internal olefins were effectively converted to the saturated al-

kanes in high yields. Styrene (**2ab**) and derivatives with either electron withdrawing (**2ac**, **2ad**) or electron donating groups (**2ae–2ah**), respectively, were converted to the corresponding ethylbenzenes in 81 to 99%. It is noteworthy that primary amines (**2ah**) also were tolerated by the system.

Next, apart from terminal olefins, also 1,2- and 1,1-disubstituted substrates (**2ai–2ak** and **2al–2ao**, respectively) were investigated. The yields for the latter were, in general, lower than those for 1,2-disubstituted olefins, indicating a reduced catalytic activity. For



instance, *trans*-stilbene was quantitatively hydrogenated to **2ak**, whereas the 1,1-disubstituted diphenylethylene gave 60% yield of **2ao**.

An exemplary industrial application for hydrogenation catalysts is the saturation of diisobutene. Since the ban of MTBE as an anti-knock additive in gasoline in the United States in 2006, isooctane (2,4,4-trimethylpentane) represents an attractive alternative in the petrochemical industry because of its high octane number, aliphatic character, and low vapor pressure (4). Furthermore, it is the primary component of aviation gasoline. It is produced via dimerization of isobutene to diisobutene, a mixture of two isomers, followed by hydrogenation. Many of the known catalysts for this latter reaction are based on noble metals, that is, Pd (48) and Pt (49). In addition, also Ni (50) and scarcely Co (51) gained some attention. Hence, we investigated the performance of Co@Chitosan-700 in the hydrogenation of diisobutene. As can be seen in Scheme 4, this novel material is able to fully hydrogenate diisobutene to give **2ap** on a 10-ml scale. With a metal loading of only 0.08 mole percent (mol %), the desired product was obtained in 95% yield after 5 hours. Using 0.4 mol % of catalyst, the reaction was finished within ~1 hour, which makes Co@Chitosan-700 an interesting candidate in the petrochemical industry.

Similarly, several other nonfunctionalized, aliphatic, unsaturated hydrocarbons were converted well, including terminal (**2at**, **2av**, **2aw**, and **2ax**), internal cyclic (**2aq**, **2ar**, **2as**, and **2ay**), and internal acyclic substrates (**2au**). Notably, even the tetrasubstituted olefin 2,3-dimethyl-2-butene was hydrogenated to **2az** under neat conditions on a 5-ml scale. The reaction was conducted directly in a 25-ml stainless steel autoclave with mechanical stirring to achieve proper mixing. Commonly, such olefins are challenging substrates for hydrogenation (52).

Hydrogenation experiments using 1-octene with D<sub>2</sub> in H<sub>2</sub>O and with H<sub>2</sub> in D<sub>2</sub>O, respectively, showed that H<sub>2</sub> and D<sub>2</sub> are the hydrogen sources in each case, and not H<sub>2</sub>O or D<sub>2</sub>O (see Supplementary Materials). Internal octene derivatives were observed when D<sub>2</sub> was used, whereas for H<sub>2</sub> in H<sub>2</sub>O or D<sub>2</sub>O, respectively, only *n*-octane and traces of 1-octene were detected. This indicates a large kinetic isotope effect of the hydrogenation step, which makes isomerization more likely.

Besides the synthesis of isooctane, the hydrogenation of vegetable oils is another important industrial process, for instance, in the production of margarine (vide supra) (5). These oils consist mainly of triglycerides of fatty acids, which can be either saturated, mono, or multiple unsaturated. In general, a higher degree of saturation increases the melting point of the acids and triglycerides. By altering the degree of hydrogenation, the melting point can be adjusted and tailored for applications. Therefore, we investigated the behavior of Co@Chitosan-700 in the hydrogenation of oleic acid [**1ba**, (9Z)-octadec-9-enoic acid] and its triglyceride triolein (**1bb**) (Scheme 5A).

Both substrates were hydrogenated to the corresponding products stearic acid (**2ba**) and tristearin (**2bb**) in good to very good yields. Tristearin is generally recognized as safe (GRAS) food additive (53). It has many applications, for instance, as hardening agent in the manufacture of soap and candles. The fact that the degree of hydrogenation is lower for oleic acid than for triolein might be due to coordination of the acid functionality to cobalt on the catalyst surface. This would be consistent with the yield for the carboxylic acid **2a** (Scheme 2), which was comparable (69%). Furthermore, in the case of **2ba**, the reaction solution became slightly

pinkish, indicating complexation of cobalt. This was not the case for the triglyceride.

As another application, the hydrogenation of sunflower oil was investigated on a 30-ml scale under neat conditions using 100 mg of catalyst. The oil consists mainly of triglycerides of unsaturated fatty acids (89%), which are oleic acid (monounsaturated, 30%) and linoleic acid (double unsaturated, 59%) (54). To our delight, hydrogenation leads to a white solid, and <sup>1</sup>H NMR revealed a conversion of 67% (Scheme 5B).

For the food industry, it is crucial that the product does not contain significant amounts of metal. Determination of the cobalt content of the product via AAS revealed no metal contamination. This analysis was carried out three times, and in each case, the amount of cobalt was below the detection limit of 0.04 ppm.

## CONCLUSION

In conclusion, we have developed a versatile, biowaste-derived, and easily prepared catalyst, which permits olefin hydrogenation in water under mild conditions and does not require any additives. A variety of more than 50 terminal and internal alkenes were hydrogenated with broad functional group tolerance. In the presence of Co@Chitosan-700, industrially important processes can be successfully carried out, that is, hydrogenation of diisobutene and fatty acids and their esters, including sunflower oil. Recycling studies demonstrated the simplicity of reusing the catalyst, as well as its stability during several consecutive runs. Compared to established metallic nanoparticles, the present system is highly stable toward air and water for months. Hence, we believe that the here reported material is one of the most promising nonnoble metal-based heterogeneous catalysts for olefin hydrogenations including industrial applications.

## MATERIALS AND METHODS

### Unsupported catalysts—Preparation

Unsupported catalysts were prepared by stirring Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.00 g, 4.01 mmol, 1.0 equiv.) and chitosan (1.29 g, 8.03 mmol, 2.0 equiv.) in 80 ml of ethanol at 65°C for 18 hours. Afterward, the solvent was removed at the rotary evaporator and the residue was dried overnight at 65°C by applying high vacuum. The dried sample was ground in an agate mortar, pyrolyzed at temperatures between 700° and 1000°C, and ground again in an agate mortar. The catalysts were stored in glass vials in air without special protection. The catalysts were labeled as Co@Chitosan-temperature (for example, Co@Chitosan-700).

### Supported catalysts—Preparation

One gram of supported catalyst was prepared by stirring Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (126.8 mg, 0.51 mmol, 1.0 equiv.) and chitosan (164.4 mg, 1.02 mmol, 2.0 equiv.) in 80 ml of ethanol at 65°C for 18 hours. Afterward, inorganic support (708.8 mg) was added and the mixture was stirred for 2 hours. The solvent was removed at the rotary evaporator and the residue was dried overnight at 65°C by applying high vacuum. The dried sample was ground in an agate mortar, pyrolyzed at temperatures between 700° and 1000°C, and ground again in an agate mortar. The catalyst was stored in glass vials in the air without special protection. The catalysts were labeled as Co/Chitosan@support-temperature (for example, Co/Chitosan@BN-1000).

### General catalytic procedure

A 4-ml screw cap vial was charged with catalyst (8.8 mg, 2.9 mol %), substrate (1.5 mmol), 1.5 ml of solvent, and a glass-coated stirring bar. The vial was closed by polytetrafluoroethylene (PTFE)/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was fixed in an alloy plate and put into a Parr 4560 series autoclave (300 ml). At room temperature, the autoclave was flushed with H<sub>2</sub> three times and H<sub>2</sub> was charged at the required pressure. The autoclave was placed in an aluminum block on a heating plate equipped with magnetic stirring. The reaction was heated for 18 hours. Afterward, the autoclave was cooled in an ice bath and the pressure was carefully released. For GC analysis, hexadecane (32  $\mu$ l) was added into the reaction mixture as an internal standard. The mixture was diluted with ethyl acetate, stirred properly, and the organic fraction was analyzed by GC. For <sup>1</sup>H and <sup>13</sup>C NMR, instead of hexadecane, mesitylene (20  $\mu$ l) was added into the reaction mixture as an internal standard, and 2 ml of CDCl<sub>3</sub> was added. After proper stirring, the organic fraction was filtered through a 0.2- $\mu$ m PTFE syringe filter, and both NMR and GC were measured. The obtained NMR spectra were compared with the ones reported in the literature.

Isolation of products was done by extraction with dichloromethane (DCM) or ether, followed by filtration through a 0.2- $\mu$ m PTFE syringe filter. 1,1-Diphenylethane (**2ao**) was purified by column chromatography over silica using hexane as an eluent.

### Upscale procedure for diisobutene

A 25-ml stainless steel autoclave with mechanical stirrer was loaded with 50 mg of catalyst and 10 ml (7.0584 g, 62.9 mmol) of substrate, which was dried over Na and freshly distilled. The autoclave was closed and flushed with H<sub>2</sub> three times. H<sub>2</sub> (40 bar) was charged, and the autoclave was heated to 150°C with an aluminum block and stirred properly. When the pressure dropped to around 5 bar, it was readjusted to 40 bar. After the denoted reaction time, the autoclave was cooled with an ice bath and the pressure was carefully released. The mixture was filtered through a filter paper into a round bottom flask (6.843 g, 59.9 mmol, 95%). Mesitylene was added as internal standard, and <sup>1</sup>H NMR was measured.

### Upscale procedure for 2,3-dimethyl-2-butene

A 25-ml stainless steel autoclave with mechanical stirrer was loaded with 2.9 mol % of catalyst (245.2 mg) and 5 ml (3.5 g, 42.1 mmol) of substrate, which was filtered over a plug of basic Al<sub>2</sub>O<sub>3</sub> prior to the reaction. The autoclave was closed and flushed with H<sub>2</sub> three times. H<sub>2</sub> (40 bar) was charged, and the autoclave was heated to 150°C with an aluminum block and stirred properly. After 18 hours, the autoclave was cooled with an ice bath and the pressure was carefully released. The mixture was filtered through a 0.2- $\mu$ m PTFE syringe filter. Mesitylene was added as internal standard, and <sup>1</sup>H NMR was measured.

### Upscale procedure for sunflower oil

A 100-ml stainless steel autoclave with mechanical stirrer was loaded with 100 mg of catalyst and 30 ml of sunflower oil. The autoclave was closed and flushed with H<sub>2</sub> three times. H<sub>2</sub> (40 bar) was charged, and the autoclave was heated to 150°C with a heating system and stirred properly. After 19 hours, the autoclave was cooled with an ice bath and the pressure was carefully released. The solid was taken up in DCM and sucked with a PTFE tube into a big round bottom

flask. It was dissolved in DCM completely and filtered off the catalyst with a PTFE tube, wrapped with filter paper. The volatiles were removed in vacuo, and the remaining oil became solid at room temperature. For further drying, it was heated and melted with an oil bath (bath temperature, 65°C) and connected to high vacuum for several hours. The degree of hydrogenation was determined by measuring <sup>1</sup>H NMR with mesitylene as internal standard. From both the product and the starting material, the mol % of double bonds was calculated with mesitylene as internal standard, and the amounts before and after the reaction were compared and the conversion was calculated with respect to that difference.

### Procedure for hydrogenation of 1-octene with D<sub>2</sub>

A 25-ml stainless steel autoclave with mechanical stirrer was loaded with 2.9 mol % of catalyst (46.6 mg), closed, and set under argon carefully. In a flow of argon, 8.0 mmol 1-octene and 12 ml of H<sub>2</sub>O were added. The autoclave was connected to a D<sub>2</sub> bottle, and the connection was put under argon. Then, 10 bar D<sub>2</sub> was introduced into the reactor, and the autoclave was heated to 60°C with an aluminum block and stirred properly. After 18 hours, the autoclave was cooled with an ice bath and the pressure was carefully released. The organic phase was diluted with ethyl acetate, filtered through a 0.2- $\mu$ m PTFE syringe filter, and GC–mass spectrometry (MS) was measured.

### Recycling procedure

A 4-ml screw-cap vial was charged with Co@Chitosan-700 (8.8 mg, 2.9 mol %), 1-octene (1.5 mmol, 168.3 mg, 237  $\mu$ l), 1.5 ml of H<sub>2</sub>O, and a glass-coated stirring bar. The vial was closed by a PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was fixed in an alloy plate and put into a Parr 4560 series autoclave (300 ml). At room temperature, the autoclave was flushed with H<sub>2</sub> three times, and 10 bar H<sub>2</sub> was charged. The autoclave was placed in an aluminum block on a heating plate equipped with magnetic stirring. The reaction was heated at 60°C for 18 hours. Afterward, the autoclave was cooled with an ice bath, and the pressure was carefully released. For GC analysis, hexadecane (32  $\mu$ l) was added into the reaction mixture as an internal standard. The mixture was diluted with ethyl acetate, stirred properly, and the organic fraction was analyzed by GC. Then, a magnet was placed at the outer wall of the vial, in a way that as much catalyst as possible was attracted by it. The liquids were decanted off, and the catalyst was washed with acetone three times and once with deionized water. Then, new substrate was added, along with 1.5 ml of H<sub>2</sub>O, and the vial was closed by a new PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a fresh needle. The next reaction was started analogously to the first one.

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/4/9/eaau1248/DC1>

Table S1. Screening of different supports, substrates, solvents, conditions, and temperatures of pyrolysis.

Table S2. Solvent screening for the hydrogenation of 1-octene.

Table S3. Content of C, H, N, and Co before and after pyrolysis.

Table S4. Leached metal content in different reaction media detected by AAS.

Scheme S1. Plot of conversions (top) and yields (bottom) against time in different solvent conditions of Co@Chitosan-700.

Fig. S1. Recycling of Co@Chitosan-700.

Fig. S2. High-resolution (HR)-STEM images of Co@Chitosan-700.

Fig. S3. EELS and energy-dispersive x-ray spectroscopy (EDXS) elemental distributions of carbon, nitrogen, oxygen and cobalt, along with the overlay put onto the annular dark-field (ADF) survey image of Co@Chitosan-700.

Fig. S4. ADF survey image, EELS, and EDX spectra of fresh Co@Chitosan-700.

Fig. S5. HR-STEM images of nine-times-used Co@Chitosan-700.

Fig. S6. ADF survey image, EELS, and EDX spectra of recycled Co@Chitosan-700.

Fig. S7. EELS and EDXS elemental maps of carbon, oxygen, and cobalt, and the overlay on the corresponding ADF survey image of nine-times-used Co@Chitosan-700.

Fig. S8. Comparison of O-K edge from Co oxide particles of fresh and nine-times-used Co@Chitosan-700 showing the difference in edge fine structure.

Fig. S9. Powder pattern of fresh Co@Chitosan-700.

Fig. S10. Powder pattern of nine-times-used Co@Chitosan-700.

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