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Iron Nanoparticles Supported on Chemically-Derived Graphene: Catalytic Hydrogenation with Magnetic Catalyst Separation

Mario Stein,[a] Jörg Wieland,[a] Peter Steurer,[b] Folke Tölle,[b] Rolf Mülhaupt,[b,c,*] and Bernhard Breit[a,c,*]

[a] Institut für Organische Chemie und Biochemie, Albert-Ludwigs-Universität Freiburg, Albertstrasse 21, 79104 Freiburg, Germany
Fax: (+49)-761-203-8715; e-mail: bernhard.breit@chemie.uni-freiburg.de
[b] Freiburger Materialforschungszentrum (FMF) and Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Strasse 21–31, 79104 Freiburg, Germany
Fax: (+49)-761-203-6319; e-mail: rolf.muelhaupt@makro.uni-freiburg.de
[c] Freiburg Institute for Advanced Studies (FRIAS), Soft Matter Research, Albertstrasse 19, 79104 Freiburg, Germany

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Abstract: Iron nanoparticles (Fe-NP) supported on chemically-derived graphene (CDG) were prepared and identified as an effective catalyst for the hydrogenation of alkenes and alkynes. The catalyst can easily be separated by magnetic decantation.

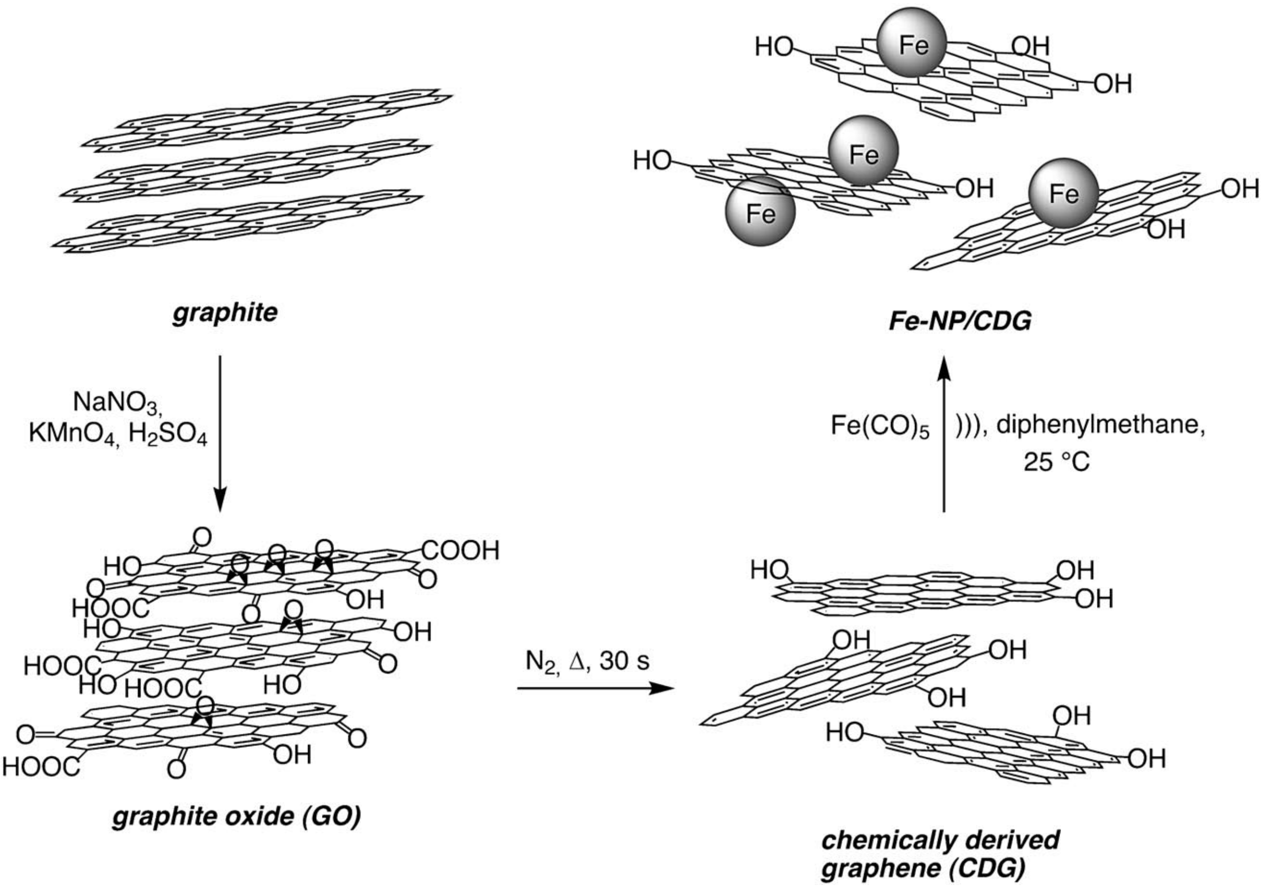
Keywords: graphene; hydrogenation; iron catalysis; magnetic separation; nanoparticles

Hydrogenation reactions are considered one of the most valuable synthetic transformations in organic chemistry. The hydrogenation of olefins and alkynes is typically promoted by heterogeneous catalysts based on precious metals such as palladium or platinum.[1–5] In order to render catalytic hydrogenation reactions more efficient, many efforts have been made to decrease the costs for these reactions either by obtaining highly active catalytic species or by substituting inexpensive metals such as iron for the commonly used noble metals Pd and Pt.[6–10]

The broad availability of iron makes it a desirable metal for catalysis. Furthermore, iron compounds are usually easy to handle and toxicologically inert. It is therefore not only economically but ecologically expedient to use catalysts based on iron.[11] Iron catalysts are of enormous industrial importance as they are an important part of the Haber–Bosch process[12,13] as well as the Fischer–Tropsch process[14]. Consequently, the iron-catalyzed hydrogenation of coal, carbon monoxide and carbon dioxide is heavily investigated. Progress has also been made in the transfer hydrogenation of C=O bonds including ligand-metal bifunctional catalysis.[15,16] Furthermore, direct reductive aminations of carbonyl compounds with iron were achieved employing an Fe-EDTA complex.[17]

There are only few examples known for iron catalysts that are active in the hydrogenation of C=C bonds. Chirik and co-workers used an iron complex with a tridentate N-based ligand for the hydrogenation of various alkenes under mild conditions.[18] Bhanage et al. could successfully apply the Fe-EDTA complex to the selective hydrogenation of α,β-unsaturated carbonyl compounds.[19] An interesting approach towards catalytic hydrogenation with iron nanoparticles (NP) without the need of additional ligands was reported by de Vries et al.[20] In this case the nanoparticles were homogeneously dispersed in solution. However, in order to make the catalyst easily separable, it would be rather attractive to have solid-supported iron nanoparticles.

Herein, we describe the synthesis and application of iron nanoparticles supported on chemically-derived graphene (CDG) as hydrogenation catalyst. This support features simple and inexpensive preparation as well as very high specific surface areas. Graphene-supported metal NPs were already successfully applied in different catalytic reactions.[21] The synthesis of Fe-NP/CDG is described in Scheme 1. CDG was prepared in a two-step procedure starting from graphite. The first step is an oxidation, which was first described by Hummers and Offeman, resulting in graphite oxide (GO).[22] It consists of non-planar carbon sheets due to introduced functionalities like epoxy, hydroxy, carbonyl and carboxyl groups. In the second



Scheme 1. Synthesis of Fe-NP/CDG from graphite.))) = ultrasound.

step, GO was reduced to CDG by flash heating, accompanied by exfoliation due to the release of CO, CO_2 and H_2O.[23] The deposition of iron NPs on the functionalized graphene layers was achieved by sonochemical treatment of $Fe(CO)_5$ in a suspension of CDG in diphenylmethane at room temperature. TEM images showed NPs with an average size of 4.37 ± 1.62 nm deposited on the CDG sheets (Figure 1). Diffraction patterns and ESI images indicated the presence of Fe(0). The loading of Fe-NPs was 3.66 wt%.

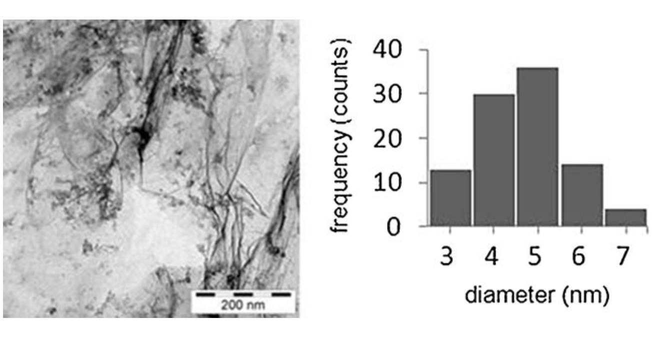
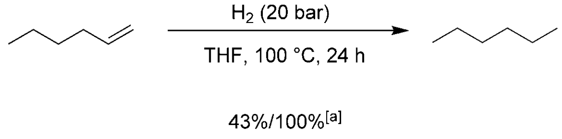


Figure 1. TEM image and histogram showing the particle size distribution.

The catalyst prepared as described above was tested in olefin hydrogenation reactions.

In initial attempts, 1-hexene was chosen as a test substrate for the catalytic hydrogenation with Fe-NP/CDG (Scheme 2). At 100 °C, a hydrogen pressure of 20 bar, and a comparatively low catalyst loading of 0.9 mol%, a conversion of 43% towards *n*-hexane was observed. Complete conversion was achieved by addition of a small amount of Grignard reagent (EtMgCl) under otherwise identical conditions. Presumably, the Grignard reagent acts as a surface activator and reduces remaining oxide shells of the Fe-NPs which may form *via* remaining oxidic functions on CDG. In order to have the most active catalyst in hand, in all



Scheme 2. Catalytic hydrogenation of 1-hexene.[a] Addition of 5 mol% EtMgCl.

further experiments the catalyst was preactivated in this manner.

To demonstrate the involvement of Fe-NP/CDG as catalytically active species in the hydrogenation, several control experiments were performed. Thus, attempted hydrogenation on CDG in the absence of Fe-NPs and in the presence of EtMgCl or $MgCl_2$ did not furnish even traces of hydrogenated products.

It was recently published that metal contaminants of the iron source such as copper may act as the real catalyst.[24] Consequently, we checked the presence of all relevant metals for hydrogenation catalysis in Fe-NP/CDG as well as in the magnesium source by AAS. In all cases, all concentrations were below the detection limits. Hence, it can be assumed that Fe-NP/CDG acts as the real catalyst and other metals have no influence on the catalytic activity.

Different olefins were hydrogenated with Fe-NP/CDG in order to define the scope of substrates (Table 1). Complete or almost complete conversion was obtained with terminal olefins (Table 1, entries 1 to 4 and 6). 1-Hexene and 1-octene were also tested under milder reaction conditions. 1-Hexene was quantitatively hydrogenated at 25 °C (Table 1, entry 3) while for 1-octene, the yield dropped to 11% (Table 1, entry 5). However, it was shown that a further increase of the hydrogen pressure led to full conversion again (Table 1, entry 6). Furthermore, Fe-NP/CDG gave good results in the hydrogenation of cyclic olefins (Table 1, entries 7 to 10). Unfortunately, this catalyst revealed to be inapplicable in the hydrogenation of internal double bonds of acyclic systems (Table 1, entries 11 to 14). Little to no product was identified with tri- and tetrasubstituted olefins (Table 1, entries 12 and 13).

The catalyst was also active in the hydrogenation of alkynes (Table 1, entries 15 to 18). Surprisingly, disubstituted alkynes gave better results than the terminal 1-octyne. Full conversion in the hydrogenation of 1-phenyl-1-propyne to *n*-propylbenzene (Table 1, entry 17) raised the speculation that electron-withdrawing groups favor the reaction. However, tolane was hydrogenated with rather moderate yield (Table 1, entry 18). This might be caused by the steric hinderance of the triple bond and the stability of the fully conjugated substrate.

Subsequent to the hydrogenation reactions the catalyst was recovered by centrifugation. Fe-NP/CDG was washed twice with degassed H_2O and CH_2Cl_2, dried under vacuum and reapplied in a second cycle of hydrogenation of 1-hexene. Again, complete conversion to *n*-hexane was observed.

A rather simple and attractive way of catalyst separation was the magnetic decantation (Figure 2).[25] Therefore, a constant magnetic field of a Nd-Fe-B based magnet was applied to the reaction mixture after hydrogenation on homogeneous catalyst slurries. Induced by magnetic separation, the catalyst remained at the wall of the glass tube and the clear solution was ready for decantation. The recovered catalyst was again successfully recycled without any loss of activity and without renewed activation with ethyl magnesium chloride reagent.

In principal, the catalysis with Fe-NP/CDG could proceed in either a heterogeneous or homogeneous manner, which should be clarified by a three-phase

Table 1. Hydrogenation of different olefins and alkynes with H_2 using Fe-NP/CDG.[a]

Entry	Substrate	Yield [%][b]
1	styrene	99
2	1-hexene	100
3[c]	1-hexene	100
4	1-octene	100
5[c]	1-octene	11
6[c,d]	1-octene	100
7	norbornene	100
8	cyclopentene	73
9	cyclohexene	79
10	cyclooctene	99
11	*trans*-2-hexene	0
12	2-methyl-1-butene	0
13	2,3-dimethyl-2-butene	0
14	*trans*-stilbene	7
15	1-octyne	0
16	4-octyne	7[e]
17	1-phenyl-1-propyne	100[e]
18	tolane	24[f]

[a] Olefin (1 mmol) in THF (1 mL), Fe-NP/CDG (0.9 mol%), EtMgCl (2M/THF, 5 mol%), H_2 (20 bar), 100 °C, 24 h.

[b] Yields determined by GC and NMR analysis.

[c] Reaction temperature was 25 °C.

[d] H_2 pressure was 30 bar.

[e] Only the corresponding alkane was identified as product.

[f] 21% stilbene, 3% dibenzyl.

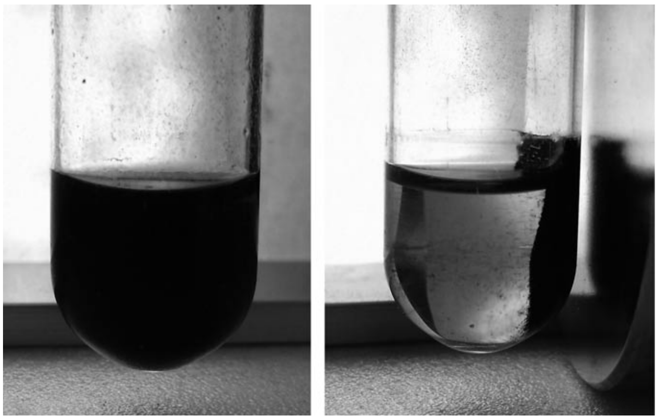
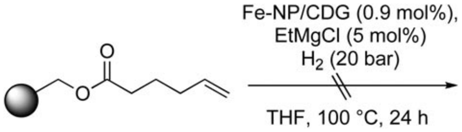


Figure 2. Fe-NP/CDG after hydrogenation reaction dispersed (*left*); magnetic separation of the catalyst at ambient temperature with a Nd-Fe-B based magnet (*right*).



Scheme 3. Three-phase hydrogenation control experiment with an alkenyl-functionalized Wang resin.

experiment (Scheme 3). For this reason, 1-hexenoic acid attached *via* esterification to a Wang resin was subjected to our hydrogenation conditions. The spatial separation of the substrate from the catalyst will prohibit the reaction if the catalyst acts heterogeneously. Indeed, after cleavage from the solid support only starting material was detected and no hydrogenation product was observed. Contrary to former similar experiments with Pd/CDG catalysts,[20a] iron nanoparticles supported on CDG appear to be truly heterogeneous catalysts without noteworthy leaching of Fe-NP.[26]

In conclusion, we have established a simple, cheap and rapid synthesis for Fe nanoparticles supported on chemically derived graphene by decomposition of $Fe(CO)_5$ with ultrasound. The obtained material (Fe-NP/CDG) was highly active in the hydrogenation of terminal and cyclic olefins. Furthermore, the catalyst was separated in an elegant manner by simple magnetic decantation and recycled without loss of activity. Work is in progress to enhance catalytic activities and to expand the application to other substrates.

Experimental Section

Preparation of Fe-NP/CDG

CDG (920 mg) was suspended in a solution of $Fe(CO)_5$ (447 mg, 2.28 mmol) in diphenylmethane (200 mL). The reaction mixture was ultrasonicated three times for 10 min at room temperature with an ultrasonic lancet (Bandelin, Sonoplus HD 2200, lancet KE76).

General Procedure for Hydrogenation Reactions at Atmospheric Pressure

In a dry and argon-flushed Schlenk tube, Fe-NP/CDG (14 mg, 9.1 μmol, 0.009 equiv.) was suspended in THF (1 mL). EtMgCl (25 μL, 2M in THF, 0.05 mmol, 0.05 equiv.) and olefin (1 mmol, 1.0 equiv.) were added. The Schlenk tube was purged 5 times with H_2 from an H_2 gas filled balloon. The reaction mixture was stirred for 24 h at a pressure of 1 bar H_2 and a temperature as specified in the text. The catalyst was removed by one of the following procedures: (a) Fe-NP/CDG was separated by condensation of all other compounds with a flask cooled to −196 °C in high vacuum (10^{-2} mbar); (b) A constant magnetic field was applied to the reaction vessel. The liquid was removed by syringe while Fe-NP/CDG remained on the inner wall of the reaction tube. The residue was washed with THF (2×1 mL). All hydrogenation products were known and identified by GC, GC/MS and NMR. Conversion was determined by GC.

General Procedure for Hydrogenation Reactions at High Pressure

The reaction mixture was prepared as described above, and was transferred *via* syringe into a stainless steel autoclave containing a glass inlet. The autoclave was purged three times with H_2. The reaction mixture was stirred for 24 h at the temperature and H_2 pressure as specified in Table 1. The pressure was relieved and the catalyst was separated from the reaction mixture as described above. The hydrogenation products were known and identified by GC, GC/MS and NMR.

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