Soluble iron nanoparticles as cheap and environmentally benign alkene and alkyne hydrogenation catalysts†

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Iron nanoparticles prepared by reducing $FeCl_3$ with three equivalents of EtMgCl in THF are effective catalysts for the hydrogenation of alkenes and alkynes under moderate conditions.

For the hydrogenation of olefins and alkynes, palladium or nickel-based heterogeneous catalysts are state-of-the-art. Homogeneous catalysts are almost exclusively used for asymmetric hydrogenation reactions. We were interested in the development of new non-chiral homogeneous hydrogenation catalysts to enable continuous hydrogenation processes in microreactors. In principle, it would be possible to use Pd, Pt, Rh, Ru or Ni nanoparticles (NPs) as catalysts, since these have been used extensively for hydrogenation reactions.[1] However, the first four metals are rather expensive, and most transition metals are highly toxic, necessitating the removal of the catalyst to very low ppm levels for pharmaceutical applications. In view of the above, we wanted to explore the use of a homogeneous iron catalyst. In the past, $Fe(CO)_5$ has been used as a poorly active hydrogenation catalyst.[2] More recently, the groups of Budzelaar,[3] Chirik[4] and Casey[5] have developed homogeneous iron complexes that show interesting properties as hydrogenation catalysts. Beller *et al.* have developed the use of iron complexes as transfer hydrogenation[6] and asymmetric hydrosilylation catalysts.[7] Morris and co-workers recently reported an iron-based asymmetric transfer hydrogenation catalyst.[8] Fe-NPs have been used for different applications, including magnetic fluids,[9] catalysts for carbon nanotube formation,[10] magnetic resonance imaging (MRI) contrast agents,[11,12] nickel–iron batteries, catalysts and sorbents for environmental remediation,[13,14] and as catalysts for C–C bond formation.[15,16] A number of synthetic methods for their preparation have been reported, such as the thermal decomposition of iron carbonyl complexes,[17] the hydrogenation of iron amides[18] and the chemical reduction of iron salts.[19,20] Commonly used $NaBH_4$ leads to a colloidal material containing some boron.[21] Heterogeneous iron catalysts are well-known and used industrially in the Haber–Bosch and in Fischer–Tropsch reactions. There are also several publications on the use of heterogeneous iron catalysts for the hydrogenation of olefins, dienes, and alkynes at high temperatures and pressures.[22]

In addition, a finely divided iron catalyst, prepared according to the Raney® method by leaching away aluminum, has been used for the hydrogenation of alkynes.[23] However, hydrogenation with soluble Fe-NPs has not been reported to date.

Herein, we report the use of Fe-NPs as catalysts for the selective hydrogenation of alkenes and alkynes using molecular hydrogen. The Fe-NPs were prepared, as reported by Bedford *et al.*, by reducing a solution of $FeCl_3$ with 3 equiv. of EtMgCl in Et_2O or THF.[15b]‡ TEM showed the presence of NPs with an average size of 2.67 ± 0.60 nm (Fig. 1). EDX showed the presence of iron, magnesium and chlorine. Presumably, the NPs are stabilised by $MgCl_2$ and possibly by THF. Finke[24] recently revealed that even BF_4^- is a better stabiliser of NPs than ethereal solvents. It thus seems highly likely that the chloride ions of $MgCl_2$ will bind to the outer rim of the Fe-NPs. The Fe-NPs prepared in this manner were tested in the hydrogenation of olefins. The conversions under various reaction conditions are listed in Table 1.

The results indicate that Fe-NPs in THF are active catalysts for the hydrogenation of norbornene (Table 1, entries 1, 2 and 4),

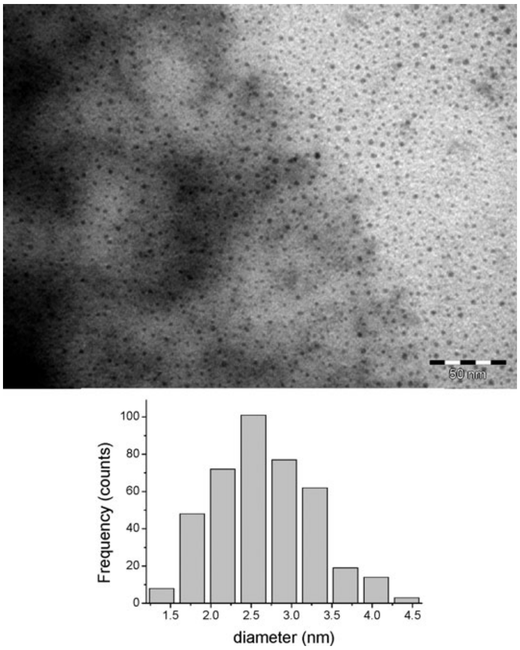

Fig. 1 A TEM micrograph of Fe-NPs and a histogram showing their particle size distribution.

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Table 1 The hydrogenation of olefins catalysed by Fe-NPs[a]

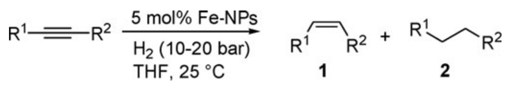
Entry	Olefin	Olefin/Fe (mol/mol)	t/h	Conv.[d] (%)
1	Norbornene	20	0.5	100
2[b]	Norbornene	20	0.5	100
3[c]	Norbornene	20	0.5	3
4	Norbornene	200	15	100
5	1-Hexene	20	15	100
6	*cis*-2-Hexene	20	15	100
7	*trans*-2-Hexene	20	15	22
8	1-Octene	20	15	100
9	2-Methyl-1-pentene	20	15	100
10	2,3-Dimethyl-2-butene	20	15	0 (0)
11	Cyclohexene	20	15	22 (100)
12	Cyclooctene	20	15	11 (100)
13	1-Methyl-1-cyclohexene	20	15	0 (0)
14	1-Phenyl-1-cyclohexene	20	15	0 (0)
15	*trans*-Stilbene	20	15	6 (100)

[a] Reaction conditions: 5 mol% Fe-NPs, 1 mmol olefin, THF (3 mL), r.t. All hydrogenation products are known, were identified by GC, and characterised by comparison with authentic samples and spectral data. [b] Pressure of H_2 was 1 bar. [c] Presence of 1% (v/v) of H_2O. [d] Values in parentheses were obtained at 100 °C.

terminal olefins (Table 1, entries 5 and 8), *cis*-disubstituted olefins (Table 1, entry 6) and 1,1′-disubstituted olefins (Table 1, entry 9), even at room temperature and hydrogen pressures as low as 1 bar. *trans*-Olefins (Table 1, entry 7 and 15) and *cis*-cyclic olefins (Table 1, entries 11 and 12), other than norbornene, could be hydrogenated, but at a lower rate; full conversion was nevertheless obtained at 100 °C. At room temperature, tri- (Table 1, entries 13 and 14) and tetra- (Table 1, entry 10) substituted olefins did not react. Increasing the temperature to 100 °C did not change this to a large extent; only non-cyclic tri-substituted olefins could be hydrogenated under these conditions. This clearly offers possibilities for the selective hydrogenation of substrates containing more than one differentially-substituted double bond.

To substantiate the involvement of Fe-NPs as active hydrogenation catalysts, we performed a number of control experiments. Thus, when using any of the following as catalysts: $MgCl_2$, EtMgCl, $FeCl_3$, EtMgCl/MgCl and $FeCl_3/MgCl_2$, no reaction was obtained. In fact, the addition of an extra equivalent of $MgCl_2$ to the pre-formed Fe-NPs only served to retard the hydrogenation of norbornene.

Table 2 The hydrogenation of alkynes catalysed by Fe-NPs[a]



Entry	Olefin	$p(H_2)$/bar	t/h	Conv. (%)	Select. (**1** : **2**)
1	1-Hexyne	20	15	100	0 : 1
2	1-Octyne	20	15	100	0 : 1
3	1-Hexyne	10	0.5	100	1 : 0.6
4	1-Octyne	10	0.5	100	1 : 0.6
5	3-Hexyne	10	0.5	100	0 : 1
6	3-Octyne	10	0.5	100	0 : 1
7	3-Hexyn-1-ol	10	0.5	0	—
8	3-Hexyn-1-ol	20	15	100	0 : 1
9	4-Pentyn-1-ol	20	15	43	1.3 : 1
10	2-Methyl-3-butyn-2-ol	20	15	56	2 : 1

[a] Reaction conditions: 5 mol% Fe-NPs, 1 mmol alkyne, THF (3 mL), r.t. All hydrogenation products are known, were identified by GC and characterised by comparison with authentic samples and spectral data.

The catalyst is very sensitive to water (Table 1, entry 3). The presence of even 1% of water in the reaction mixture strongly retarded the reaction. We assume that water oxidises the NPs to Fe(II) or Fe(III) species. Similarly, the presence of air completely inhibited the reaction, presumably for similar reasons. The catalyst loading could be reduced to 0.5 mol%, but a longer reaction time was required to achieve full conversion (Table 1, entry 4).

Experiments were also carried out to investigate the fate of the catalyst after the hydrogenation had finished. Thus, norbornene was added successively to the reaction mixture after the previous hydrogenation had finished. It was found that up to five consecutive additions of substrate resulted in full conversion without compromising the activity of the catalyst. This bodes well for continuous applications.

Interestingly, traces of positional isomers were observed, along with the hydrogenated product, in the hydrogenation of *trans*-2-hexene. Since we also found that the Fe-NPs serve as an isomerisation catalyst for 1-octene in the absence of molecular hydrogen, it appears that the isomerisation proceeds *via* an allylic mechanism rather than *via* the β-hydride elimination of an iron alkyl complex.

Next, we examined the hydrogenation of alkynes (Table 2). The catalyst was found to be active for the hydrogenation of a variety of alkynes, with good to excellent conversion under mild reaction conditions. Terminal alkynes were easily converted to the corresponding alkanes within 15 h at 20 bar pressure (Table 2, entries 1 and 2). The selectivity to the alkene increases by decreasing the reaction time and H_2 pressure (Table 2, entries 3 and 4).

The hydrogenation of internal alkynes only furnished alkanes (Table 2, entries 5 and 6). Introducing a hydroxyl group onto the alkynes seemed to retard the hydrogenation reaction (Table 2, entry 7), although 3-hexyn-1-ol was completely converted to the corresponding alkane at high pressure after a long reaction time (Table 2, entry 8). Under these conditions, 4-pentyn-1-ol and 2-methyl-3-butyn-2-ol were also converted by 43 and 56%, respectively. In these cases, more alkene than alkane was formed (Table 2, entries 9 and 10).

As we wanted to gain more insight into the selectivity change to the *cis*-alkene over time, we monitored the progress of the hydrogenation of 1-octyne over a 5 h period (Fig. 2).

Interestingly, we observed an induction period of about 10 min. Thus far, we have no explanation for this. Disappointingly, almost immediately after the hydrogenation commenced, 1-octene and octane were produced in a fixed ratio of 1 : 0.6. Only after 2 h did this ratio diminish. In a similar experiment performed at substrate/catalyst = 200, the alkene/alkane ratio did not improve (Fig. 3).

In this experiment, we also explored the effects of pressure and temperature on the rate of the hydrogenation. Increasing the pressure from 5 to 30 bar raised the turnover frequency (TOF) from 5 to 14 h^{-1}. Raising the temperature from r.t. to

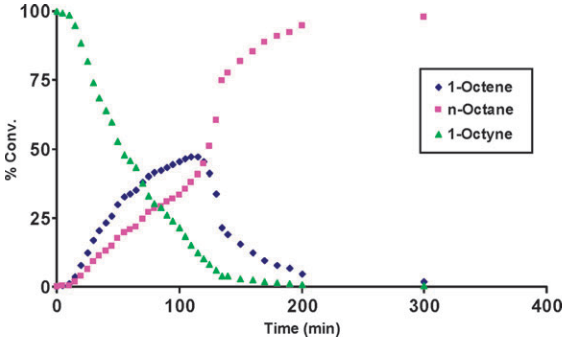


Fig. 2 The conversion of 1-octyne into 1-octene and octane.

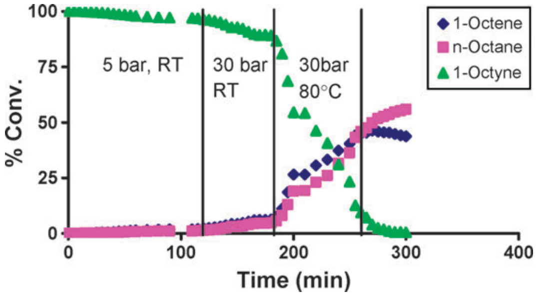


Fig. 3 The effect of pressure and temperature on the rate and selectivity of 1-octyne hydrogenation.

80 °C at 30 bar had a stronger effect on the rate and led to an increase in the TOF to 118 h^{-1}. Although the rate was somewhat lower than that achievable with currently used palladium- and nickel-based catalysts, the catalyst cost is significantly reduced.

In conclusion, Fe-NPs prepared from $FeCl_3$ and EtMgCl in THF are an economic and non-toxic catalyst for the hydrogenation of olefins and alkynes. Work is in progress to expand the application of this catalyst to the hydrogenation of other substrates.

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Notes and references

‡ Bedford used 5 equiv. of EtMgCl. We find no difference in catalytic activity between the material prepared with 3 or 5 equiv. of EtMgCl. For a discussion on the possible presence of iron in the −2 oxidation state upon addition of 5 equiv. of EtMgCl, see ref. 20.

1 (*a*) A. Roucoux and K. Philippot, in *Handbook of Homogeneous Hydrogenation*, ed. J. G. de Vries and C. J. Elsevier, Wiley-VCH, Weinheim, 2007, vol. 1, pp. 217–256; (*b*) A. Roucoux, A. Nowicki and K. Philippot, in *Nanoparticles in Catalysis*, ed. D. Astruc, Wiley-VCH, Weinheim, 2008, pp. 349–388.
2 B. R. James, *Homogeneous Hydrogenation*, John Wiley & Sons, New York, 1973, pp. 64–72.
3 Q. Knijnenburg, A. D. Horton, H. Van der Heijden, A. W. Gal, P. H. M. Budzelaar, to Stichting voor de Technische Wetenschappen, *Int. Pat. Appl.*, WO03/042131, 2003.
4 S. C. Bart, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2004, **126**, 13794–13807.
5 C. P. Casey and H. Guan, *J. Am. Chem. Soc.*, 2007, **129**, 5816–5817.
6 S. Enthaler, B. Hagemann, G. Erre, K. Junge and M. Beller, *Chem.–Asian J.*, 2006, **1**, 598–604.
7 N. S. Shaikh, S. Enthaler, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2008, **47**, 2497–2501.
8 C. Sui-Seng, F. Freutel, A. J. Lough and R. H. Morris, *Angew. Chem., Int. Ed.*, 2008, **47**, 940–943.
9 K. T. Wu, Y. D. Yao, C. R. C. Wang, P. F. Chen and E. T. Yeh, *J. Appl. Phys.*, 1999, **85**, 5959–5961.
10 E. W. Wong, M. J. Bronikowski, M. E. Hoenk, R. S. Kowalczyk and B. D. Hunt, *Chem. Mater.*, 2005, **17**, 237–241.
11 Y. W. Jun, Y. M. Huh, J. S. Choi, J. H. Lee, H. T. Song, S. Kim, S. Yoon, K. S. Kim, J. S. Shin, J. S. Suh and J. Cheon, *J. Am. Chem. Soc.*, 2005, **127**, 5732–5733.
12 S. Mornet, S. Vasseur, F. Grasset and E. Duguet, *J. Mater. Chem.*, 2004, **14**, 2161–2175.
13 F. Li, C. Vipulanandan and K. K. Mohanty, *Colloids Surf., A*, 2003, **223**, 103–112.
14 W. X. Zhang, *J. Nanopart. Res.*, 2003, **5**, 323–332.
15 (*a*) A. Fürstner, A. Leitner, M. Méndez and H. Krause, *J. Am. Chem. Soc.*, 2002, **124**, 13856–13863; (*b*) R. B. Bedford, M. Betham, D. W. Bruce, S. A. Davis, R. M. Frost and M. Hird, *Chem. Commun.*, 2006, 1398–1400; (*c*) G. Cahiez, V. Habiak, C. Duplais and A. Moyeux, *Angew. Chem., Int. Ed.*, 2007, **46**, 4364–4366.
16 For recent reviews on iron-catalysed reactions, see: (*a*) C. Bolm, J. Legros, J. Le Paih and L. Zani, *Chem. Rev.*, 2004, **104**, 6217; (*b*) A. Fürstner and R. Martin, *Chem. Lett.*, 2005, **34**, 624; (*c*) A. Correa, O. G. Mancheno and C. Bolm, *Chem. Soc. Rev.*, 2008, **37**, 1108–1117; (*d*) D. Farrell, S. A. Majetich and J. P. Wilcoxon, *J. Phys. Chem. B*, 2003, **107**, 11022–11030.
17 D. Farrell, S. A. Majetich and J. P. Wilcoxon, *J. Phys. Chem. B*, 2003, **107**, 11022–11030.
18 O. Margeat, F. Dumestre, C. Amiens, B. Chaudret, P. Lecante and M. Respaud, *Prog. Solid State Chem.*, 2005, **33**, 71–79.
19 H. Bönnemann, W. Brijoux, R. Brinkmann, R. Fretzen, T. Joussen, R. Koppler, B. Korall, P. Neiteler and J. Richter, *J. Mol. Catal.*, 1994, **86**, 129–177.
20 A. Fürstner, R. Martin, H. Krause, G. Seidel, R. Goddard and C. W. Lehmann, *J. Am. Chem. Soc.*, 2008, **130**, 8773–8787.
21 G. N. Glavee, K. J. Klabunde, C. M. Sorensen and G. C. Hadjipanayis, *Inorg. Chem.*, 1995, **34**, 28–35.
22 (*a*) Z. Lu, C. Wang, D. Liang and L. Lin, *Shiyou Huagong*, 1991, **20**, 454–457; (*b*) Y. Nitta, S. Matsugi and T. Imanaka, *Chem. Express*, 1989, **4**, 547–550; (*c*) Y. M. Bondarev, Y. S. Mardashev, A. D. Mokrushin, V. F. Blokhin and I. V. Razumovskaya, *Zh. Fiz. Khim.*, 1985, **59**, 2343–2345.
23 A. F. Thompson, Jr. and S. B. Wyatt, *J. Am. Chem. Soc.*, 1940, **62**, 2555–2556.
24 (*a*) L. S. Ott and R. G. Finke, *Inorg. Chem.*, 2006, **45**, 8382–8393; (*b*) L. S. Ott and R. G. Finke, *Coord. Chem. Rev.*, 2007, **251**, 1075–1100.