Cite this: Chem. Commun., 2012, 48, 3360-3362

COMMUNICATION

Iron-iron oxide core-shell nanoparticles are active and magnetically recyclable olefin and alkyne hydrogenation catalysts in protic and aqueous media[†]

Reuben Hudson,^a Antoine Rivière,^{ab} Ciprian M. Cirtiu,^a Kylie L. Luska^a and Audrey Moores^{*a}

Received 17th October 2011, Accepted 27th December 2011 DOI: 10.1039/c2cc16438h

We report for the first time the use of iron-iron oxide core-shell nanoparticles for the hydrogenation of olefins and alkynes under mild conditions in ethanol and in an aqueous medium. This catalyst proves robust towards the presence of oxidants, such as oxygen and water, is magnetically recoverable and shows selectivity towards the less activated double bonds.

Hydrogenation is a ubiquitous reaction used in all fields of chemistry, from petrochemistry to drug synthesis.¹ Transition metals, such as Pd, Pt, Ru, Rh or Ni, both homogenous and heterogeneous, are catalysts of choice for this reaction. However, in an effort to develop a more sustainable approach,^{2,3} their cost, toxicity and potential depletion has fuelled the development of alternative hydrogenation catalysts. Very recently, several catalysts⁴⁻⁶ have been designed to avoid the use of precious metals, among which iron is a very attractive option. Iron is non-toxic, naturally abundant, cheap and potentially amenable to magnetic recovery.⁷ Iron complexes were shown to be active catalysts⁸ for the hydrogenation of olefins,⁹ carbonyl bonds^{10,11} and the selective hydrogenation of alkynes to alkenes.^{12,13} Such complexes can also hydrogenate carbonates¹⁴ and dehydrogenate formic acid.¹⁵ Besides these developments in homogenous catalysis, iron in the form of suspendable nanoparticles has been investigated as a catalyst.^{16,17} The de Vries group has evidenced that ligand-free iron nanoparticles (Fe NPs) are active catalysts for the hydrogenation of alkenes and alkynes under very mild conditions.^{4,18} These particles proved very active, however, they could not be separated from the reaction medium magnetically because of their small size. Breit and co-workers overcame this limitation by stabilizing Fe NPs made by decomposition of $Fe(CO)_5$ onto graphene sheets. Although the resulting particles were active hydrogenation catalysts,¹⁹ they were prone to oxidation in the presence of either oxygen or water. Growth of the oxide shell in the presence of an oxidant



Scheme 1 Hydrogenation of olefin catalyzed by Fe CSNPs.

was suggested to be an absolute limitation to catalysis in terms of reactivity.

Herein, we present the use of simple and stabilizer-free ironiron oxide core-shell nanoparticles (Fe CSNPs) for the hydrogenation of alkenes and alkynes. These nanoparticles represent the first iron-based catalyst in ethanol, and in water-ethanol mixtures (Scheme 1). These nanoparticles are either synthesized in an aqueous medium, or produced in large scale commercially and suspended in water.

These nanoparticles are recoverable magnetically and recyclable up to 10 times. Our results indicate that a thin shell of iron oxide surrounding the zero-valent core can protect the nanoparticles against excessive oxidation without obstructing hydrogenation reactivity, in protic and aqueous environments.

Fe CSNPs were produced by the reduction of FeSO₄ in a water/methanol mixture using NaBH₄.^{20,21} Such particles have been investigated as stoichiometric reductants for water remediation^{22–25} and also studied as magnetic seeds for Pd C–C couplings catalysts.²⁶ We were thus intrigued to see if these particles could also be active as hydrogenation catalysts. These Fe CSNPs featured an average core diameter of 44 ± 8.3 nm and a shell thickness of 6 ± 2 nm, which is comparable to what has been reported in the literature (Fig. 1).^{25,27} Alternatively, we used commercial iron core–shell nanoparticles (C–Fe CSNPs) which also presented iron oxide sheets at their surface.[†]



Fig. 1 TEM pictures of Fe CSNPs (a) before catalysis, (b) after 10 cycles.

^a Centre for Green Chemistry and Catalysis, Department of Chemistry, McGill University, Montréal, QC H3A 2K6, Canada. E-mail: audrey.moores@mcgill.ca; Fax: +1 514 398 3797; Tel: +1 514 398 4654

^b Ecole Polytechnique (Member of ParisTech), route de Saclay, 91128 Palaiseau Cedex, France

[†] Electronic supplementary information (ESI) available: blank catalytic tests, experimental section, TEM pictures, XPS, ICP-MS and XRD analysis of Fe CSNPs. See DOI: 10.1039/c2cc16438h

Table 1 Fe CSNP^a catalyzed olefin hydrogenation



^{*a*} Reaction conditions: substrate (1 mmol), Fe CSNPs (5 mol%), EtOH (17 mL), 80 °C, H₂ (40 bars), 24 h. ^{*b*} EtOH:H₂O as solvent 99:1. ^{*c*} EtOH:H₂O as solvent 50:50. ^{*d*} C–Fe CSNP as catalyst.

Fe CSNPs proved to be an active hydrogenation catalyst for a range of substrates in ethanol, under 40 bar H₂ at 80 °C in 24 h (Table 1). Terminal alkenes were easily converted. Styrene provided ethyl benzene quantitatively (entry 1), while decene afforded decane with a conversion of 91% (entry 5). Norbornene, a strained disubstituted cis-alkene (entry 6), was converted in 96%. These Fe CSNPs were also active for alkyne hydrogenation, in which a conversion of 88% was achieved for 1-decyne. The major product of 1-decyne hydrogenation was decane (82%), (entry 7) and is in agreement with the reactivity observed for decene. Conversions of C=O bonds (entry 8, 9) and aromatic C=C bonds (entry 1) were not observed. Hydrogenation of citral (entry 9) highlighted the selectivity of this catalyst for C = Cbonds as no conversion of the aldehyde was observed. Citral also features two trisubstituted C=C double bonds. 55% of citral was hydrogenated at, at least, one of these positions. Surprisingly, the less activated, less polar bond proved more reactive, at a ratio 2.9:1. Fe CSNPs could be magnetically recovered and recycled up to 10 times with only a slight decrease in yield observed after 8 cycles (Table 2). This ease of recovery provides for a more industrially relevant system, compared to other Fe NP-based hydrogenation catalysts which could either not be separated magnetically,¹⁸ or had to employ functionalized graphene sheets to do so.19

A limitation of the use of pure FeNPs for hydrogenation resides in their sensitivity towards oxidation by either O_2 or H_2O . Even the presence of 1% water completely deactivates these catalysts.^{18,19} We found that 1% water had no effect on the hydrogenation activity of Fe CSNPs (Table 1, entry 2).

Table 2 Recycling tests performed on styrene hydrogenation to ethylbenzene a

Cycle number	Conversion (%)
1-8	100
9	94
10	89
^{<i>a</i>} Reaction conditions: substrate	(1 mmol) Fe CSNP (5 mol%) FtOH

^{*a*} Reaction conditions: substrate (1 mmol), Fe CSNP (5 mol%), EtOH (17 mL), 80 °C, H₂ (40 bars), 24 h. Magnetic recovery in air was applied between cycles.[†]

We were pleased to see that performing the reaction directly in a 50:50 water:ethanol mixture only reduced conversion to 62% (Table 1, entry 3). Performing the reaction in water as a solvent did not quench reactivity completely but led to irregular results. On the other hand, O₂ exposure was not detrimental either. Between each recycling test, the catalyst was exposed to O₂ for a few minutes, as our set up did not allow for an inert atmosphere to be completely maintained. This did not seem to adversely impact the conversion, at least for the first 8 recycling tests.

We also tested the activity of C–Fe CSNPs, commercially synthesized iron nanoparticles from Nanoiron[®] (Table 1, entry 4). We were pleased to see that despite a lower activity, still 44% of the styrene could be converted in ethanol, under the same conditions. Since these particles are produced in large scale, in water, this opens an opportunity to apply this reaction in an industrial setting.

In order to better understand the nature of the catalyst, we performed an XPS and XRD analysis of these Fe CSNPs.[†] These analyses revealed the presence of iron zero and some iron oxides, mostly FeO, which is consistent with the TEM observations.[‡] We also performed a TEM study before and after catalysis. After 5 reaction cycles, we saw no change in particle size, shape or shell thickness.[†] After 10 cycles, however, the oxide shell thickness grew and oxide build up was visible. We also witnessed the appearance of sheets of what was determined by EDAX to be crystalline FeO, beside the Fe CSNPs. These two observations correlate with a decrease in activity and can be explained by the exposure to oxygen over time, between recycling runs.

We also investigated the heterogeneous nature of the catalyzed reaction. Upon magnetic removal of the nanoparticles, the reaction supernatant was exposed to styrene under the exact same conditions and no conversion of styrene was observed. ICP-MS analysis of this same supernatant indicated the presence of 35 μ M of dissolved iron. As a blank test, we used an equivalent amount of soluble FeSO₄ as catalyst and observed no hydrogenation of styrene. Tests in absence of H₂ led to no conversion.†

Overall, Fe CSNPs feature a scope that is similar to that of the pure Fe NPs described before, ^{18,27} namely a good activity for olefin and alkyne hydrogenation and no activity towards C=O double bonds. This suggests a mechanism in which Fe(0) surface acts as the catalysis, indicating that the nanoparticle iron oxide shell is sufficiently porous to allow substrate access to the surface of the Fe(0) core. While the porosity of the Fe CSNPs is under investigation, porosity in iron oxide shells caused by a Kirkendall effect, as an oxide shell is formed onto a reduced core, has been reported.²⁸ Indeed, the formation of the oxide shell around both Fe CSNPs and C-Fe CSNPs results directly from the presence of water during their synthesis. This contrasts with the previously reported examples of Fe NPs, relying on either reduction of iron salt in THF by Grignard reagents,¹⁸ or Fe(CO)₅ decomposition.¹⁹ Fe CSNPs were less active than Fe NPs, but their oxide shell does provide protection to allow reaction in an aqueous environment and under ligandfree conditions. Water, as a main poison to a pure Fe(0) surface, may interact strongly with this shell and migrate more slowly than the lipophilic substrates. The selectivity of the hydrogenation of citral (Table 1, entry 9) is of interest. Of the two available C=C double bonds, the isolated double bond was converted more quickly than the traditionally more active conjugated C=C bond.^{29,30} This, perhaps, could be due to an orienting affect of the iron oxide shell-directing the less polar double bond to the zero valent core, thus leaving the more polar aldehyde (along with its conjugated partner) to interact with the oxide shell and polar solvent environment.

We have described the first water-stable catalytic hydrogenation system based on iron nanoparticles. Specifically, we have identified iron-iron oxide core-shell nanoparticles as robust, magnetically recoverable catalysts for hydrogenation of olefins and alkynes, in ethanol and aqueous ethanol. The system is active towards many substrates and strictly selective for alkenes and alkynes over carbonyl and aromatic groups. These results suggest that the presence of an oxide shell is not an obstacle to activity and does provide protection against oxidation by oxygen and water. Commercially prepared particles were also active, opening an opportunity to apply this reaction under more realistic conditions.

We thank the Natural Science and Engineering Research Council of Canada (NSERC), the Canada Foundation for Innovation (CFI), the Canada Research Chairs (CRC), the Fonds de Recherche sur la Nature et les Technologies (FQRNT), the Center for Green Chemistry and Catalysis (CGCC) and McGill University for their financial support. Ecole Polytechnique (France) financially supported AR. Nanoiron[®] is thanked for providing C–Fe CSNPs to test. We are grateful K. Wilkinson and M. Hadioui for their help with ICP-MS, and to F. Qi, A. Lacasse and T. Friscic for XRD. CJ Li, N. Braidy, T. Friscic and Y. Feng are acknowledged for fruitful discussions.

Notes and references

 \ddagger Although we observed the presence of 3.3 wt% of boron by ICP in Fe CSNPs, XPS was consistent with a complete absence of iron boride. This is consistent with catalysis performed by the Fe(0) phase \ddagger^{31}

1 J. G. de Vries and C. J. Elsevier, *Handbook of Homogeneous Hydrogenation*, Wiley-VCH, Weinheim, 2007.

- View Article Online
- 2 P. T. Anastas and M. M. Kirchhoff, Acc. Chem. Res., 2002, 35, 686–694.
- 3 P. T. Anastas, M. M. Kirchhoff and T. C. Williamson, *Appl. Catal.*, *A*, 2001, **221**, 3–13.
- 4 P. A. Chase, T. Jurca and D. W. Stephan, *Chem. Commun.*, 2008, 1701–1703.
- 5 P. A. Chase and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2008, **47**, 7433–7437.
- 6 B. Dudle, K. Rajesh, O. Blacque and H. Berke, J. Am. Chem. Soc., 2011, 133, 8168–8178.
- 7 S. Enthaler, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2008, **47**, 3317–3321.
- 8 R. H. Morris, Chem. Soc. Rev., 2009, 38, 2282-2291.
- 9 S. C. Bart, E. Lobkovsky and P. J. Chirik, J. Am. Chem. Soc., 2004, 126, 13794–13807.
- 10 A. Mikhailine, A. J. Lough and R. H. Morris, J. Am. Chem. Soc., 2009, 131, 1394–1395.
- 11 C. Sui-Seng, F. Freutel, A. J. Lough and R. H. Morris, Angew. Chem., Int. Ed., 2008, 47, 940–943.
- 12 S. Enthaler, M. Haberberger and E. Irran, *Chem.–Asian J.*, 2011, 6, 1613–1623.
- 13 M. Haberberger, E. Irran and S. Enthaler, Eur. J. Inorg. Chem., 2011, 2797–2802.
- 14 C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 9777–9780.
- 15 A. Boddien, D. Mellmann, F. Gaertner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig and M. Beller, *Science*, 2011, **333**, 1733–1736.
- V. Polshettiwar and R. S. Varma, *Green Chem.*, 2010, **12**, 743–754.
 R. B. Bedford, M. Betham, D. W. Bruce, S. A. Davis, R. M. Frost
- and M. Hird, Chem. Commun., 2006, 1398-1400. 18 P.-H. Phua, L. Lefort, J. A. F. Boogers, M. Tristany and
- J. G. de Vries, *Chem. Commun.*, 2009, 3747–3749.
- 19 M. Stein, J. Wieland, P. Steurer, F. Toelle, R. Muelhaupt and B. Breit, *Adv. Synth. Catal.*, 2011, **353**, 523–527.
- 20 C. M. Cirtiu, T. Raychoudhuty, S. Ghoshal and A. Moores, *Colloids Surf.*, A, 2011, **390**, 95–104.
- 21 Y. Q. Liu, H. Choi, D. Dionysiou and G. V. Lowry, *Chem. Mater.*, 2005, **17**, 5315–5322.
- 22 G. E. Hoag, J. B. Collins, J. L. Holcomb, J. R. Hoag, M. N. Nadagouda and R. S. Varma, J. Mater. Chem., 2009, 19, 8671–8677.
- 23 Y. Q. Liu, S. A. Majetich, R. D. Tilton, D. S. Sholl and G. V. Lowry, *Environ. Sci. Technol.*, 2005, **39**, 1338–1345.
- 24 J. T. Nurmi, P. G. Tratnyek, V. Sarathy, D. R. Baer, J. E. Amonette, K. Pecher, C. M. Wang, J. C. Linehan, D. W. Matson, R. L. Penn and M. D. Driessen, *Environ. Sci. Technol.*, 2005, **39**, 1221–1230.
- 25 W.-X. Zhang, J. Nanopart. Res., 2003, 5, 323-332.
- 26 S. Zhou, M. Johnson and J. G. C. Veinot, *Chem. Commun.*, 2010, 46, 2411–2413.
- 27 B. Schrick, B. W. Hydutsky, J. L. Blough and T. E. Mallouk, *Chem. Mater.*, 2004, 16, 2187–2193.
- 28 S. Peng and S. Sun, Angew. Chem., Int. Ed., 2007, 46, 4155-4158.
- 29 G. Guo, F. Qin, D. Yang, C. Wang, H. Xu and S. Yang, *Chem. Mater.*, 2008, **20**, 2291–2297.
- 30 M. Steffan, F. Klasovsk, J. Arras, C. Roth, J. Radnik, H. Hofmeister and P. Claus, *Adv. Synth. Catal.*, 2008, 350, 1337–1348.
- 31 J. Vanwonterghem, S. Morup, C. J. W. Koch, S. W. Charles and S. Wells, *Nature*, 1986, **322**, 622–623.