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The use of ultrasmall iron(0) nanoparticles as catalysts for the selective hydrogenation of unsaturated C–C bonds[†]

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The performance of well-defined ultrasmall iron(0) nanoparticles (NPs) as catalysts for the selective hydrogenation of unsaturated C–C and C—X bonds is reported. Monodisperse iron nanoparticles of about 2 nm size are synthesized by the decomposition of $\{Fe(N[Si(CH_3)_3]_2)_2\}_2$ under dihydrogen. They are found to be active for the hydrogenation of various alkenes and alkynes under mild conditions and weakly active for C—O bond hydrogenation.

The development and application of environmentally benign nonnoble metal complexes constitutes an actual and important topic in catalysis. In this respect, iron-based catalysts are of large interest because of their low toxicity and the abundance of iron on Earth. Moreover, nanometric-sized materials show promising potential in catalysis because of the high ratio of atoms present at the surface and accessible for the catalytic reaction. Although iron-based NPs have been used for different applications, their catalytic potential has not yet been fully exploited.¹ More specifically, it has been shown that they display significant activity and selectivity in Fischer-Tropsch synthesis.² Iron nanoparticles are also widely used in the synthesis of carbon nanotubes³ and in biomedical applications such as hyperthermia agents⁴ and contrast agents for magnetic resonance imaging.⁵ Recently, the use of iron nanoparticles as catalysts for hydrogenation reactions has also emerged. Hence, iron-iron oxide core-shell nanoparticles have been described for olefin and alkyne hydrogenation.⁶ Iron nanoparticles supported on chemically-derived graphene displayed activity also in alkene hydrogenation.⁷ Notably, Morris and co-workers described the application of iron nanoparticles, supposed to be formed during the catalysis, in the asymmetric transfer hydrogenation of ketones.8 Furthermore, a general method for the synthesis of soluble iron nanoparticles active in alkene and alkyne hydrogenation has been reported.9 This latter

method involves the use of a Grignard reagent like EtMgCl to reduce the starting iron complex FeCl₃. Complementary to all these interesting developments, in the present work, we introduce the use of ultrasmall iron(0) nanoparticles synthesized by a method described previously by some of us¹⁰ as catalysts for various hydrogenation reactions. Our synthetic protocol leads to well-defined soluble nanoparticles and allows in particular the determination of the number of surface hydrides, following a method previously reported for ruthenium nanoparticles.¹¹

The synthesis of ultrasmall iron(0) nanoparticles proceeds via decomposition of $\{Fe(N[Si(CH_3)_3]_2)_2\}_2$ under 3 bar of dihydrogen at 150 °C for 12 h. In this process HN[Si(CH₃)₃]₂ (HMDS) is released and may further interact with the particles. This method provides monodisperse iron nanoparticles of 1.5 \pm 0.2 nm size (Fig. 1). The formation of air-sensitive metallic iron nanoparticles was ascertained by WAXS, SQUID and Mössbauer analysis.¹⁰ HR-TEM analysis evidenced the amorphous nature of these nanoparticles. In addition, we performed the titration of hydrides present at the surface of the nanoparticles in order to study their surface state and evaluate whether they could be interesting for applications in catalysis. The general procedure for the quantification of hydrogen atoms adsorbed onto the surface of iron nanoparticles consists of the titration of surface hydrides through the hydrogenation of 2-norbornene.^{11,12} With the percentage of conversion of olefin into alkane and the estimated percentage of surface atoms on the nanoparticles (almost 60% for nanoparticles of 1.5 nm), the number of hydrides per surface atom iron was



Fig. 1 Low magnification TEM image of iron nanoparticles.

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 Table 1
 Investigation of the reactivity of ultrasmall iron(0) nanoparticles as catalysts for the hydrogenation of different functional groups^a

	,X Iron(0) NPs (2.4	mol%)	ХН		
	$\acute{C'}$ mesitylene, H ₂ (10 bar), rt, 20h \acute{CH}				
Entry	Substrate	$\operatorname{Conv.}^{b}(\%)$	Yield ^{b} (%)		
1	1-Octene	>99	>99		
2	Phenylacetylene	>99	89 (ethylbenzene)		
3	Acetophenone	$4(4)^{c}$	$2(2)^{c}$		
4	2-Butanone	$7(31)^{c}$	$7(31)^{c}$		
5	Benzaldehyde	$0 (0)^{c}$	$0 (0)^{c}$		
6	<i>N</i> -(1-Phenylethylidene)aniline	$0(16)^{c}$	$0 (11)^{c}$		

^{*a*} Reaction conditions: 1 mmol substrate, 2.4 mol% iron(0) nanoparticles, 1 mL mesitylene, 10 bar H₂, r.t., 20 h. ^{*b*} Determined by GC using *n*-hexadecane as internal standard. ^{*c*} Values in brackets are obtained by increasing the temperature to 80 °C.

estimated to be between 0.4 and 0.6. Notably, this is the first direct evidence for the presence of surface hydrides on iron nanoparticles and hence demonstrates the absence of surface oxidation in the present case.¹²

Next, the catalytic reactivity of the iron nanoparticles was investigated for the hydrogenation of several functional groups. As shown in Table 1, alkenes, alkynes, ketones, aldehydes and imines were explored. In general in this study, 1 mmol of substrate, 2.4 mol% of iron nanoparticles and 1 mL of mesitylene were mixed together in an autoclave under an inert atmosphere. Then, the autoclave was pressurized with 10 bar of H₂ and stirred at room temperature for 20 hours. Under these conditions excellent yields for the hydrogenation of 1-octene and phenylacetylene (Table 1, entries 1 and 2) were obtained. Isomerization does not occur in the case of 1-octene. Phenylacetylene was totally converted into ethylbenzene, while no hydrogenation of the phenyl ring was observed. In addition, the iron nanoparticles displayed a weak activity for the hydrogenation of ketones (Table 1, entries 3 and 4). Yields below 10% were obtained for acetophenone and 2-butanone at room temperature. However, the yield of 2-butanone increased to 31% at a higher temperature (80 °C), while keeping the same reaction time. Ketone hydrogenation reactions have recently been found to be catalyzed by iron nanoparticles⁸ but the mechanism is proposed to involve a hydrogen transfer in this case. However, our nanoparticles were inactive in the hydrogenation of aldehydes and imines (Table 1, entries 5 and 6). Only a small amount of the imine was converted to amine at 80 °C.

Due to the activity in the hydrogenation of 1-octene and phenylacetylene various other alkenes and alkynes were tested in the presence of the ultrasmall iron particles. The scope of the catalyst is presented for both alkenes and alkynes in Tables 2 and 3. For this study, we generally used 2.4 mol% of catalyst, although even 0.5 mol% of catalyst was sufficient for the 1-octene and 2-norbornene hydrogenation (*vide infra*).

Concerning the hydrogenation of alkenes, terminal aliphatic alkenes (Table 2, entries 1, 3 and 4) were completely hydrogenated at room temperature. In the case of 1,7-octadiene both double bonds are reduced under these conditions. For internal aliphatic olefins (Table 2, entries 2 and 5), a peculiar result was observed: while 2-pentene was fully hydrogenated, no reaction Table 2 Iron nanoparticle-catalyzed reduction of alkenes^a

	$\begin{array}{c} R \\ HC \overset{\wedge}{} CH \\ R \end{array} \xrightarrow{\text{Iron(0) NPs (2.4 mol%)}}_{\text{mesitylene, H}_2 (10 \text{ bar), rt, 20h}} \begin{array}{c} R \\ H_2C \\ CH_2 \\ R \end{array}$			
Entry	Substrate	$\operatorname{Conv.}^{b}(\%)$	$\operatorname{Yield}^{b}(\%)$	
1	1-Octene	>99 (>99) ^c	>99 (>99) ^c	
2	Trans-4-octene	0	0	
3	1,7-Octadiene	>99	>99	
4	2-Methyl-1-heptene	>99	>99	
5	Trans-2-pentene	>99	95	
6	Styrene	>99	87	
7	3-Chlorostyrene	>99	98	
8	3-(Trifluoromethyl)styrene	>99	97	
9	Trans-stilbene	>99	>99	
10	Cyclohexene	>99	>99	
11	Cyclopentene	>99	>99	
12	2-Norbornene	>99 (>99) ^c	>99 (>99) ^c	

^{*a*} Reaction conditions: 1 mmol substrate, 2.4 mol% iron(0) nanoparticles, 1 mL mesitylene, 10 bar H_2 , r.t., 20 h. ^{*b*} Determined by GC using *n*-hexadecane as internal standard. ^{*c*} Values in brackets are obtained by using 0.5 mol% of catalyst.

 Table 3
 Reduction of alkynes catalyzed by ultrasmall iron(0) nanoparticles^a

	R C C R Iron(0) NPs (mesitylene, H ₂ ((2.4 mol%) 10 bar), rt, 20h	H_2C R		
Entry	Substrate	$\operatorname{Conv.}^{b}(\%)$	Yield ^b (%)		
1	1-Octyne	>99	>99		
2	3-Octyne	0	0		
3	Phenylacetylene	>99	89		
4	4-Phenyl-1-butyne	>99	>99		
5	4-Fluorophenylacetylene	>99	>99		
6	4-Methoxyphenylacetylene	>99	>99		
7	4-Acetylphenylacetylene	>99	90		
8	3-Hydroxyphenylacetylene	>99	12 (3-ethylphenol)		
			88 (3-vinylphenol)		
9	Diphenylacetylene	>99	>99		
^a Reaction conditions: 1 mmol substrate, 2.4 mol% iron(0) nano-					

particles, 1 mL mesitylene, 10 bar H_2 , r.t., 20 h. ^b Determined by GC using *n*-hexadecane as internal standard.

occurred in the case of 4-octene. We explain this difference in reactivity by the increased steric hindrance of 4-octene, which displays a trans configuration. In the case of 2-pentene, a mixture of cis/trans olefins was used, displaying a lower steric hindrance in comparison with 4-octene. On the other hand, the more reactive trans-stilbene was totally converted into the corresponding diphenyl ethane (Table 2, entry 9). In the case of iron nanoparticles synthesized with the Grignard reagent,^{9b} a temperature of 100 °C was necessary to reach a full conversion. In our case, the reduction proceeded smoothly at room temperature. We explain the increased reactivity of this internal olefin by the coordination of the aromatic rings of stilbene to the easily accessible surface of the small nanoparticles. Similar to stilbene, styrene showed good reactivity and is converted to ethylbenzene in excellent yield (Table 2, entry 6). The hydrogenation of the double bond occurred even with halide-substituted styrenes (Table 2, entries 7 and 8). Here, no reduction of the C-X bond or the phenyl ring was observed. Concerning cyclic olefins (Table 2, entries 10–12), the hydrogenation of the C–C double bond was complete giving cyclic alkanes in high yields without increasing the temperature of the reaction. The reactivity of our iron nanoparticles was further tested by decreasing the loading of catalyst to 0.5 mol% (Table 2, entries 1 and 12). Gratifyingly, full conversion of 1-octene and 2-norbornene was achieved under these conditions proving the efficiency of iron nanoparticles as catalysts for hydrogenation reactions. Lowering the pressure to 3 bars H_2 , almost full conversion of 1-octene was observed after 20 h at 2.4% Fe loading but only 5% conversion at 1% Fe loading. This result nevertheless demonstrates the ability of this catalyst to work under very mild conditions.

The hydrogenation of different alkynes was achieved by applying the same reaction conditions (1 mmol substrate, 2.4 mol% of catalyst, 1 mL mesitylene, 10 bar H₂, r.t., 20 h; Table 3). Except for 3-hydroxyphenylacetylene, in all the tested substrates the C-C triple bond was selectively reduced to give the corresponding alkanes. Similarly to octenes, the terminal aliphatic alkyne (1-octyne) (Table 3, entry 1) was fully converted into octane with high yield, whereas no hydrogenation was observed for the internal one (3-octyne) (Table 3, entry 2). Diphenylacetylene (Table 3, entry 9) was also successfully hydrogenated as well as stilbene in the case of alkenes. Moreover, different substituted phenylacetylenes were tested (Table 3, entries 3 and 5-8). In each case up to 99% conversion was obtained. High yields of alkanes were achieved with phenylacetylenes bearing halide, methoxy- or carbonyl groups (Table 3, entries 5-7). However, in the case of 3-hydroxyphenylacetylene, partial hydrogenation was observed yielding 12% of 3-ethylphenol and 88% of vinylphenol (Table 3, entry 8). Interestingly, De Vries et al. reported the need for high pressure and longer reaction time to hydrogenate 3-hexyn-1-ol into the corresponding alcohol but did not mention partial hydrogenation.^{9b} These results suggest a coordination between the oxygen of the hydroxyl group and the nanoparticle, which leads to a decrease in the reaction rate of the hydrogenation, and therefore may favour the formation of unsaturated species.

Finally, we explored the possibility of recycling the ultrasmall iron(0) nanoparticles in the hydrogenation of 1-octene. After each run, the reaction mixture was analyzed by CPG. Then, the solvent, substrate and product were removed by evaporation in order to keep only the nanoparticles for the next run. To our delight no decrease in the activity of the nanoparticles was observed after 3 runs under the same experimental conditions. In all cases 1-octene was completely converted to the corresponding alkane. WAXS analysis of the nanoparticles after the catalytic reactions showed that the structure of nanoparticles remained unchanged.

In conclusion, ultrasmall iron(0) NPs are active for alkene and alkyne hydrogenation under mild conditions. These nanoparticles are well-defined and were completely spectroscopically characterized. They initially possess at their surface around 0.5 hydrides per atom of iron which is an indication of high reactivity and absence of surface oxidation. Furthermore, they display a highly accessible surface which should be beneficial in catalysis. The catalytic performance of our iron nanoparticles should be compared to that of the nanoparticles synthesized by the method of Bedford.⁹ Both hydrogenate terminal aliphatic alkenes and alkynes but iron nanoparticles prepared from FeCl₃ and EtMgCl allow the hydrogenation of some internal C–C double and triple bonds whereas our nanoparticles are not good candidates for this reaction. However, the ultrasmall nanoparticles can completely hydrogenate cyclic olefins and *trans*-stilbene at room temperature while in the works of De Vries significantly higher temperature of 100 °C is needed.^{9b,c} Concerning the hydrogenation of styrene and its derivatives, in the work of Jacobi von Wangelin, a H₂ pressure of 30 bar is needed to avoid the competitive styrene polymerization reaction.^{9d} Under our experimental conditions, *i.e.* at 10 bar of H₂, no polymerization occurred and styrenes are selectively converted into the corresponding ethylbenzenes.

Partial hydrogenation of 3-hydroxyphenylacetylene proved the possibility of modulating the hydrogenation properties of the nanoparticles presumably through the coordination of the hydroxo group. Interestingly, our nanoparticles are very selective for the hydrogenation of terminal alkenes and alkynes. They are inactive for internal olefins except for aryl substituted ones. This may result from the steric bulk at the surface of the nanoparticles arising from the presence of amido groups or from HMDS. Phenyl rings may compete for coordination and allow the hydrogenation of aryl substituted species. Finally, the nanoparticles prepared by our method also display a weak activity in the direct hydrogenation of C—O bonds which further demonstrates the catalytic potential of these nanoparticles.

It should be noted that our ultrasmall iron(0) nanoparticles are good models for the intrinsic reactivity of iron because they are well-defined and do not present oxides at their surface. Further work is in progress to enlarge the scope of catalytic reactions and to dope iron nanoparticles with other metals.

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