Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information:

The use of ultrasmall Iron(0) nanoparticles as catalysts for the selective hydrogenation of unsaturated C-C bonds

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Synthesis of ultrasmall Iron(0) nanoparticles

The Iron precursor $\{Fe(N[Si(CH_3)_3]_2)_2\}_2$ (376.5 mg) (from Nanomeps) was dissolved in dried and degassed mesitylene (20 mL) (from VWR Prolabo, 99%) and stirred magnetically overnight at 150°C under 3 bar of dihydrogen. The solution turned from green to black and was then dried under vacuum to remove the solvent. A black shiny powder (112 mg) was obtained and kept under Argon in a glove box. A drop of colloidal solution was deposited on a carbon coated copper grid for the observation of the nanoparticles by Transmission Electronic Microscopy (TEM) (JEOL-1011 microscope). Crystallographic characterization was performed by Wide Angle X-ray Scattering (WAXS) on a dedicated two-axis diffractometer (λ_{Mo} = 0.71Å) (Figure S1).

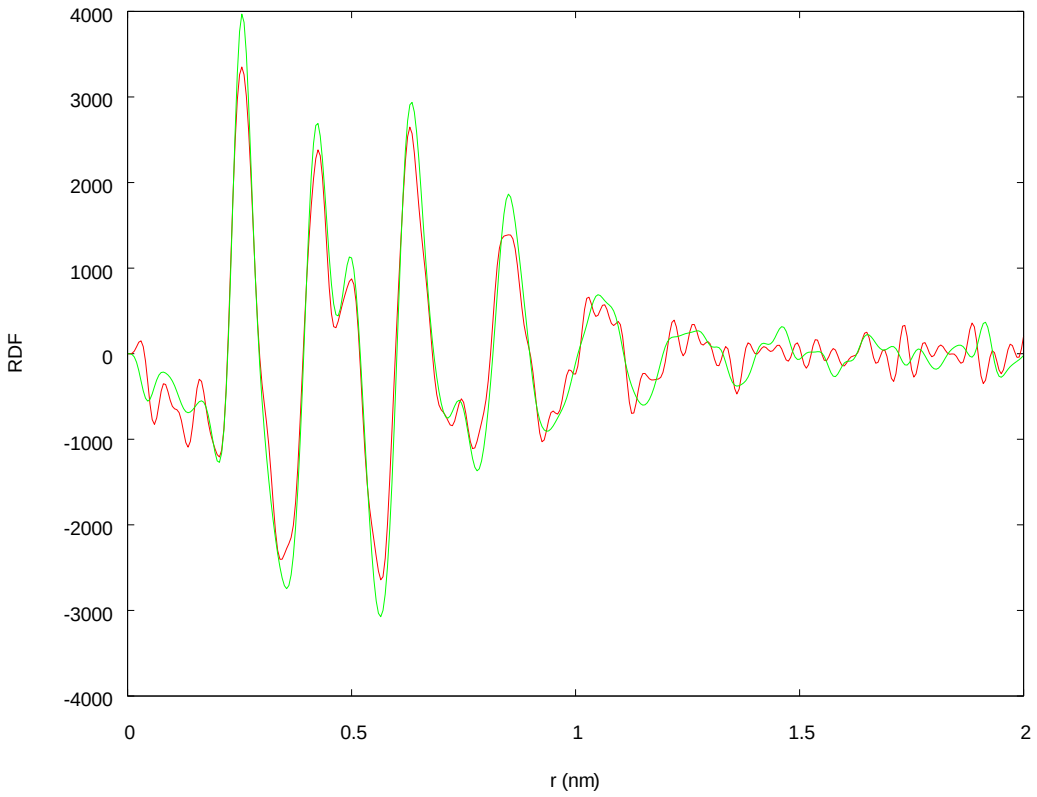


Figure S1. WAXS analysis of Iron(0) nanoparticles before (green line) and after (red line) the hydrogenation reaction.

Experimental procedure for the hydride titration

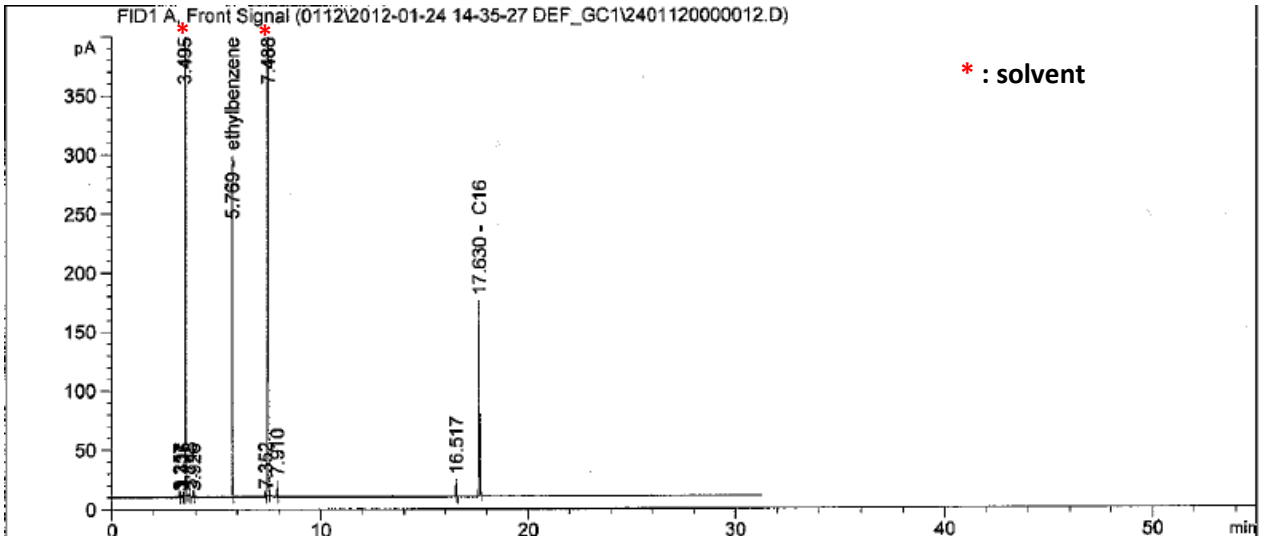
On a colloidal solution of nanoparticles in mesitylene, three freeze-pump cycles were performed in order to remove the dihydrogen solved into the solvent. Then, 1 or 5 equivalents of 2-norbornene were added. After stirring during 24h at room temperature, the samples were analyzed by CPG. Note that pumping will eliminate some coordinated hydrides. The value obtained is therefore the minimum amount of hydrogen on the surface.

Catalytic testing

In general, 1 mmol of substrate, 2.4 mol% of iron nanoparticles and 1 mL of mesitylene were mixed together in a 6 vials-autoclave (4760 Parr pressure vessel). Then, the autoclave was pressurized with 10 bar of H_2 (from Air Liquide, Alphagaz 99.999%) and stirred at room temperature for 20 hours. At the end of the reaction, the autoclave was depressurized and the internal standard (*n*-hexadecane) was added to each vial to be analyzed by Gas Chromatography (GC).

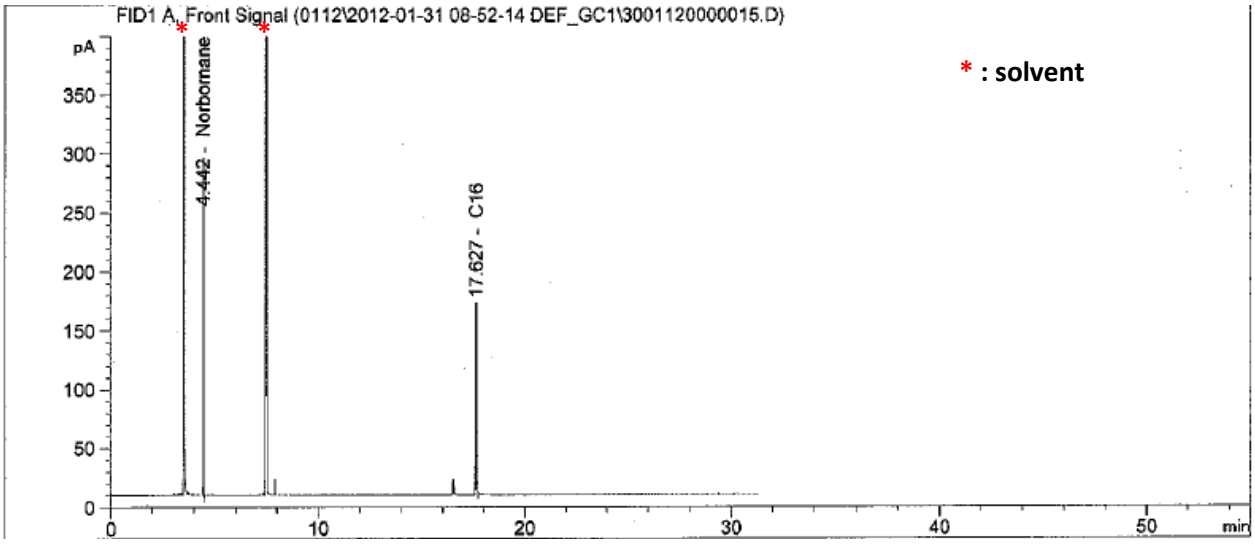
GC analyses

GC analyses were performed on an Agilent 7890 A apparatus. The column used was a "HP-5" from Agilent (30 m length; 0.32 mm diameter; 0.25 µm film thickness). The general oven program started with 50°C, ramped with 8°C/min to 260°C and held during 5 min. The flow of Argon was of 1 mL/min, the split of 100/1, the injector at 260°C and the detector at 320°C (Figure S2 and S3).



RetTime [min]	Type	ISTD used	Area [pA*s]	Amt/Area ratio	Amount [mg]	Grp	Name
5.769	BB	1	459.66379	1.00975	94.46662		ethylbenzene
6.219		1	-	-	-		styrene
17.630	BB	I 1	398.96060	1.00000	81.20000		C16

Figure S2. GC chromatogram of the sample resulting from the hydrogenation of phenylacetylene.



RetTime [min]	Type	ISTD used	Area [pA*s]	Amt/Area ratio	Amount [mg]	Grp	Name
4.161		1	-	-	-		Norbornene
4.442	BB	1	383.25830	1.33481	101.33469		Norbornane
17.627	BB I	1	401.34604	1.00000	79.50000		C16

Figure S3. GC chromatogram of the sample resulting from the hydrogenation of 2-norbornene.