

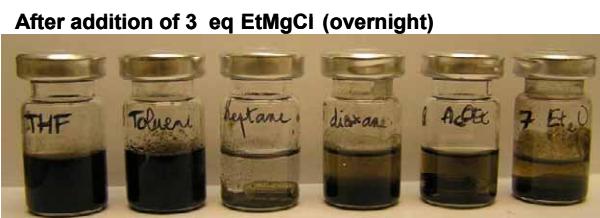
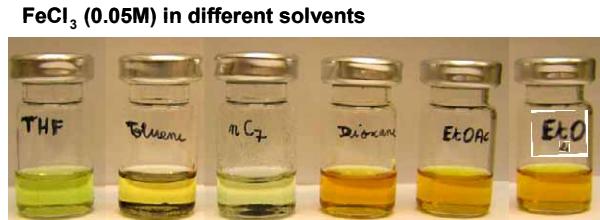
SUPPORTING INFORMATION

At the frontier between heterogeneous and homogeneous catalysis : hydrogenation of olefins and alkynes with soluble iron nanoparticles

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Screening of different solvents for the preparation of the Fe-NPs and their use in hydrogenation



Conversion in the hydrogenation of norbornene

THF	Toluene	Heptanes	Dioxane	EtOAc	Et ₂ O
100	100	47	100	6	100

Figure S1. Effect of the solvent on the activity of the catalyst in hydrogenation (Reaction conditions: 5 mol% Fe-NPs, [Alkene]=0.33M, 3 mL solvent, 10 bar H₂,

R.T.).

Kinetics for the hydrogenation of 1-octene

To a 100 ml Hastelloy C autoclave 1-octene (1.91g 17.0 mmol) and THF (17.0 ml) were added and the autoclave was subjected to three vacuum/nitrogen cycles. 17.0 ml of catalyst solution, prepared from 0.138 g of FeCl₃ (0.85 mmol) and EtMgCl (1,275 ml of a 2.0 M solution) in THF was added at once. The vessel was purged 3 times with hydrogen and kept under 10 bar of hydrogen for 4h. Samples were taken every 5minutes.

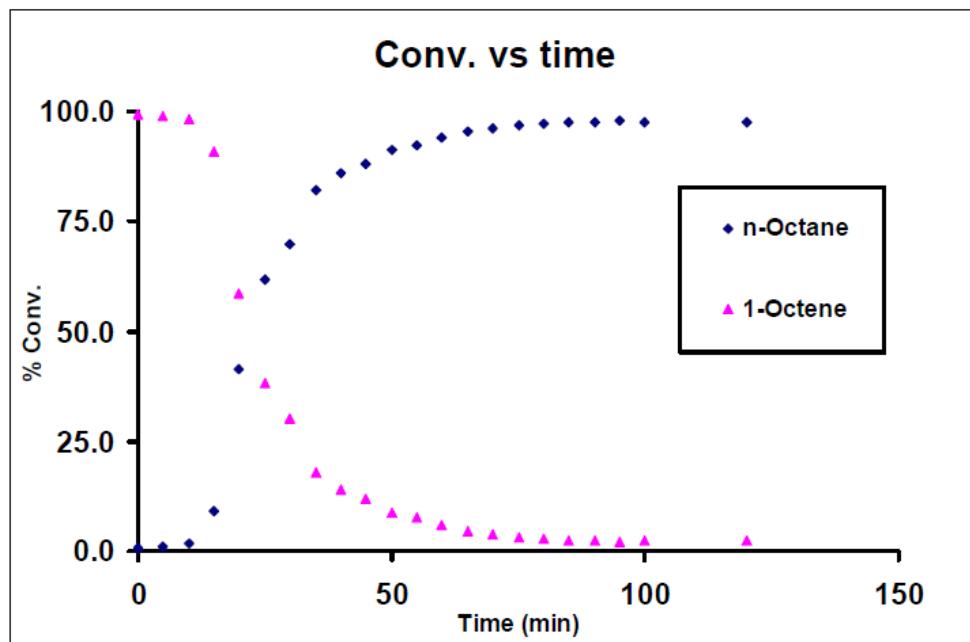
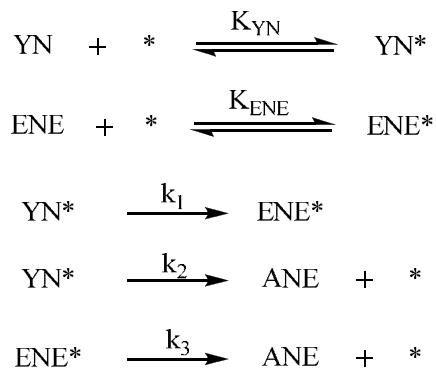


Figure S2. Hydrogenation of 1-octene

Model with Langmuir-Hinselwood type of kinetics

Adsorption of hydrogen is not included since hydrogen pressure is kept constant. Octane (ANE) is not adsorbed on catalytic sites, octene (ENE) is weakly adsorbed and octyne (YN) is strongly adsorbed at the catalyst surface.

Reaction scheme (* indicates an Fe catalytic site)



Absorption equilibria:

$$K_{\text{YN}} = \frac{\theta_{\text{YN}}}{c_{\text{YN}} \cdot \theta_*} \Rightarrow \theta_{\text{YN}} = K_{\text{YN}} \cdot c_{\text{YN}} \cdot \theta_*$$

$$K_{\text{ENE}} = \frac{\theta_{\text{ENE}}}{c_{\text{ENE}} \cdot \theta_*} \Rightarrow \theta_{\text{ENE}} = K_{\text{ENE}} \cdot c_{\text{ENE}} \cdot \theta_*$$

Surface coverage of all absorbing components and free sites are constant in time, then

$$1 = \theta_{\text{YN}} + \theta_{\text{ENE}} + \theta_*$$

Substitution for the 2 components gives:

$$\theta_* = \frac{1}{1 + K_{\text{YN}} \cdot c_{\text{YN}} + K_{\text{ENE}} \cdot c_{\text{ENE}}}$$

Since the adsorption constants can not be determined separately from the small number of experiments two values have been arbitrarily chosen: $K_{\text{ENE}} = 1$ and $K_{\text{YN}} = 10^4$.

Reaction rates are linearly dependent on the surface coverage of intermediates:

$$r_1 = k_1 \cdot \theta_{\text{YN}}$$

$$r_2 = k_2 \cdot \theta_{\text{YN}}$$

$$r_3 = k_3 \cdot \theta_{\text{ENE}}$$

Substitute equilibria and adsorption summation:

$$r_1 = \frac{k_1 \cdot K_{\text{YN}} \cdot c_{\text{YN}}}{1 + K_{\text{YN}} \cdot c_{\text{YN}} + K_{\text{ENE}} \cdot c_{\text{ENE}}}$$

$$r_2 = \frac{k_2 \cdot K_{\text{YN}} \cdot c_{\text{YN}}}{1 + K_{\text{YN}} \cdot c_{\text{YN}} + K_{\text{ENE}} \cdot c_{\text{ENE}}}$$

$$r_3 = \frac{k_3 \cdot K_{ENE} \cdot c_{ENE}}{1 + K_{YN} \cdot c_{YN} + K_{ENE} \cdot c_{ENE}}$$

Component reaction rates:

$$R_{YN} = -r_1 - r_2$$

$$R_{ENE} = r_1 - r_3$$

$$R_{ANE} = r_2 + r_3$$

Reactor equation (batch liquid):

$$\frac{dc_i}{dt} = w_{kat} \cdot R_i \text{ with initial conditions } c_i = c_{i,0} \text{ at } t = 0$$

System of non-linear differential equations was solved using Aspen Custom Modeler (ACM). Also parameter estimations for k_1 to k_3 have been performed within ACM (heteroscedasticity method, standard settings, equal weights for all datapoints).

Results of parameter estimations

[cat]	[octene]_0	[octyne]_0	k1	k2	k3
g/l	mole/l	mole/l			
0.93	0.00	0.33	0.088 ± 0.002	0.040 ± 0.002	4.29 ± 0.55
0.18	0.00	0.07	0.037 ± 0.001	0.019 ± 0.001	0.20 ± 0.04
0.93	0.33	0.33	0.055 ± 0.003	0.027 ± 0.002	2.31 ± 0.18

Intervals indicated are calculated for 95% confidence.

c_i concentration in mole/l

$c_{i,0}$ initial concentration in mole/l

k_i reaction rate constant, mole/g(cat)/s

K_i adsorption constant, l/mole

r_i reaction rate, mole/g(cat)/s

R_i component reaction rate, mole/g(cat)/s

w_{kat} concentration of catalyst, g(cat)/l

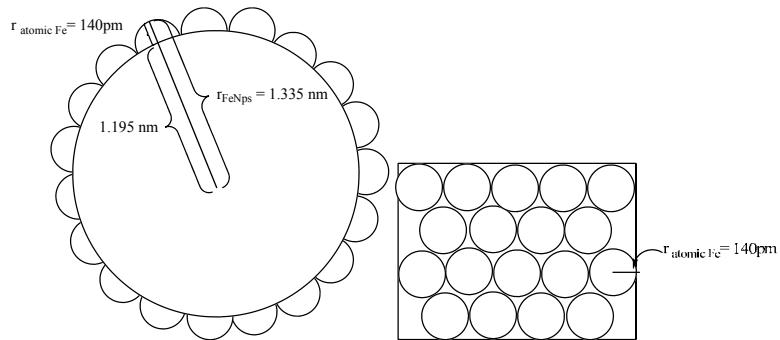
θ_i fraction of the total number of sites covered with species i

Calculation of the number protons per surface iron atoms:

Iron nanoparticles average size $d = 2.67 \pm 0.60$ nm so $r_{FeNps} = 1.335$ nm

Fe atomic radius = 140pm (Atomic radii in crystals, J. C. Slater, J. Chem. Phys. 1964, 41, 3199)

Surface area of Fe-NPs:



$$r = 1.335 - 0.140 = 1.195 \rightarrow \text{area} = 4\pi(1.95)^2 = 17.9451 \text{ nm}^2$$

$$\text{Plane compact stacking of circles : } d = \frac{\pi}{2\sqrt{3}} = 0.9069$$

$$17.9451 \times 0.9096 = 16.2744 \text{ nm}^2 \text{ (surface area of Fe-NPs really occupied by Fe atoms)}$$

Surface area of middle section of one iron atom

$$\pi \times (0.14)^2 = 0.06157 \text{ nm}^2$$

$$\text{Number of surface atoms} = \frac{16.2744}{0.06157} = 264.3$$

Number of Fe atoms in one NPs:

$$\text{Volume nanoparticles} = \frac{4\pi(1.335)^3}{3} = 9.9663 \text{ nm}^3$$

$$\text{Spheres compact stacking: volumic density: } d = \frac{\pi}{3\sqrt{2}} = 0.74048$$

$$9.9663 \times 0.74048 = 7.398 \text{ nm}^3 \text{ (volume of Fe-NPs really occupied by Fe atoms)}$$

Volume of one Fe atm:

$$\frac{4\pi(0.14)^3}{3} = 0.01149 \text{ nm}^3$$

$$\text{Number of Fe atoms in Np: } \frac{7.3798}{0.01149} = 643$$

We previously showed that there should be one atom of hydrogen per atom of iron. If we supposed that only the iron surface atom supports protons then there are $\frac{643}{264} = 2.45$ H per surface Fe atom

Influence of the ageing time in absence and in presence of 1-octyne and of the concentration of the precursors FeCl_3 on the activity of the Fe-NPs in the hydrogenation of 1-octyne.

We performed kinetic studies for the hydrogenation of 1-octyne at room temperature using the same catalyst concentration and substrate to catalyst ratio as described in the first kinetic studies (Conditions of Figure 2). In this new set of experiments, a number of parameters were varied, such as the FeCl_3 solution concentration ($[\text{Fe}]_i$) used to form the Fe-NPs but also the ageing time of the Fe-NPs alone (t_1) or in the presence of 1-octyne (t_2) prior to hydrogenation (Figure S3).

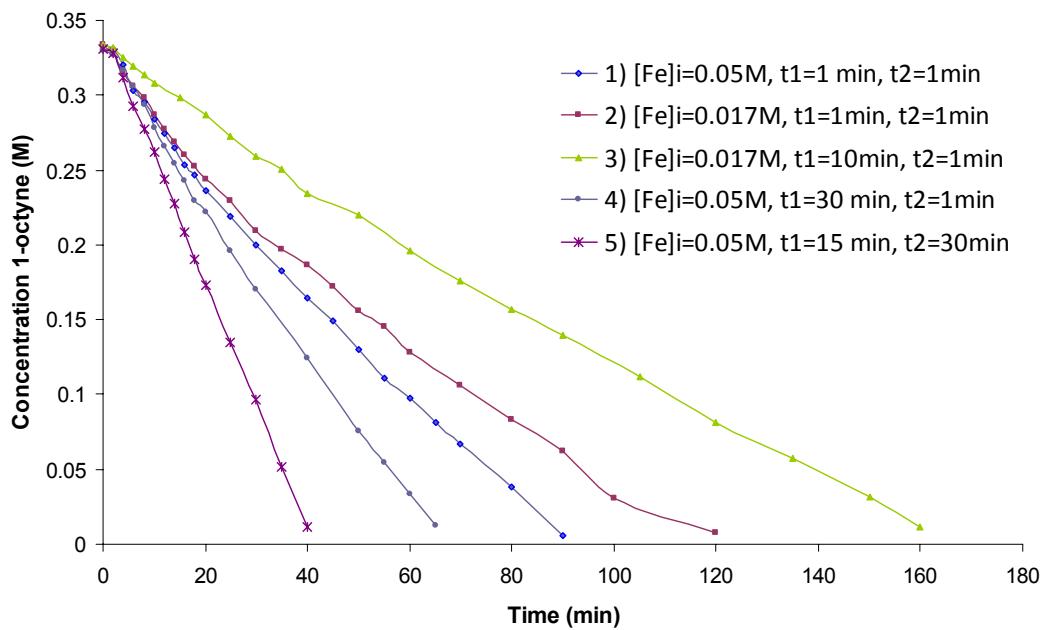


Figure S3. Concentration 1-octyne vs time at high catalyst concentration (Reaction conditions: 5 mol % Fe, [1-Octyne]=0.33M, THF, 5 bar H_2 , R.T.)

At room temperature, no induction period occurs. Within experimental error, hydrogenation performed with Fe-NPs freshly synthesized from a diluted iron

precursor solution displays a similar reaction rate as the reaction performed with standards Fe-NPs (curve 1, 2). However the use of aged NPs made from a diluted FeCl_3 solution slowed down the reaction (curve 3) while the rate was increased with aged Fe-NPs formed from a concentrated FeCl_3 solution (curve 4). In all cases, the same 1-octyne, 1-octene and *n*-octane concentration profiles as described previously were observed. The reaction order in 1-octyne follows zero-order behavior. The formation of *n*-octane and 1-octene from 1-octyne is simultaneous and the ratios of the formation rates are constant and identical for all reactions.