

## Supporting Information

### **Cheap and Environmentally Benign: Iron Nanoparticles as Selective Homogeneous Alkene and Alkyne Hydrogenation Catalysts.**

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## Preparation of iron nanoparticles

In a 10 ml Schlenk tube kept under argon  $\text{FeCl}_3$  (0.1622g, 1.0mmol) was dissolved in dry THF (20.0mL). A 2.0M solution of  $\text{EtMgCl}$  (2.50mL) was slowly added via syringe and the reaction mixture was vigorously stirred for 30 minutes. Iron nanoparticles are formed, indicated by the dark color of the mixture, and used without further purification. The synthesized catalyst was characterized by transmission electron microscopy coupled with EDX (Energy Dispersive X-ray Spectrometer).

## Hydrogenation of alkenes or alkynes (substrate screening)

To a 5mL reaction vial containing a stirring bar, an alkene or an alkyne (1.0mmol) in THF (1.0mL) was added. The catalyst solution prepared as described above (1.0mL,  $[\text{Fe}]=0.05\text{M}$ ,  $\text{S/C}=20$ ) was added to the reaction mixture under nitrogen. After all the ingredients had been added the vial was capped with a septum cap. The reaction mixture was vigorously stirred in the presence of hydrogen at 20 bars for 18 hours at room temperature in the Premex A96 Reactor. In this reactor it is possible to hydrogenate as many as 96 reactions in parallel. After the reaction was finished, a sample of the mixture (50 $\mu\text{L}$ ) was diluted with THF (950 $\mu\text{L}$ ) and analyzed by a Hewlett-Packard 5890 Gas Chromatography Series II using a CP-Sil-5CB Chrompack capillary column (50m x 0.32 mm x 1.2 $\mu\text{m}$ ) or CP-Sil-5CB Chrompack capillary column (25m x 0.25 mm x 0.25 $\mu\text{m}$ ). All the products, the corresponding alkanes, were known compounds.

## Hydrogenation of 1-octene in the autoclave

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  $\text{FeCl}_3$  (0.85 mmol) and  $\text{EtMgCl}$  (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 5 minutes.

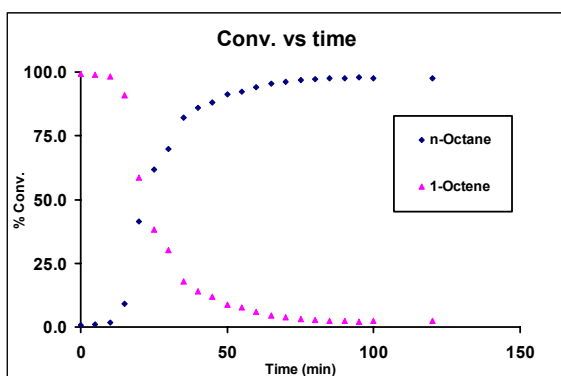


Figure 1 Hydrogenation of 1-octene

## Hydrogenation of 1-octyne in the autoclave

The hydrogenation of 1-octyne was conducted in a similar fashion as the hydrogenation of 1-octene, with the difference that only 0.5 mol% of the iron catalyst was used. During the first 2 h of the reaction the pressure was 5 bar and the temperature ambient. Thereafter the pressure was raised to 30 bar. After another hour the temperature was raised to 80 °C. After another 75 minutes acetonitrile was added. These changes in the conditions were made to observe the effect on rate and alkene/alkane ratio.

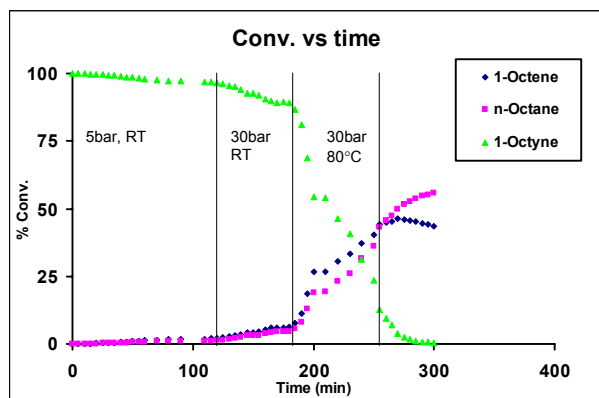


Figure 2 Hydrogenation of 1-octyne under different conditions.