

Supplementary Information to:

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

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- **Blank catalytic runs**

Comparison of Fe CSNP^a catalyzed olefin hydrogenation with H₂, Ar, or no additional gas.

Entry	Gas	Substrate	Product	Conversion (%)
1	40 bar H ₂			100
2 ^b	None			0
3 ^c	40 bar Ar			0

^a Reaction conditions: substrate (1 mmol), Fe CSNPs (5 mol%), EtOH (17mL), 80°C, 24 hour.

Hydrogenation of styrene proceeds quantitatively in the presence of 40 bar H₂ (entry 1), though not in the absence of an external gas (entry 2) or in the presence of the same pressure of Ar (entry 3). The dependence of hydrogenation on H₂ refutes the possibility of EtOH as a transfer hydrogenation agent in this system. Blank test with no catalyst under H₂ pressure (40 bars) resulted in no conversion.

- **Experimental section:**

Chemicals

NaBH₄ (99.99%) was purchased from and FeSO₄·7H₂O from AlfaAesar, 99+%. High-purity water (18.2 MΩ·cm from a Nanopure Diamond unit, Barnstead) was used to prepare the solutions. Methanol (HPLC grade) was purchased from Fischer Scientific and used with no further purification. Ethanol (anhydrous) was purchased from GreenField Ethanol and used only after being passed through an Innovative Technologies Pure Solve solvent purification system. All the hydrogenation substrates tested were purchased from Aldrich and used as received. All Solvents were deoxygenated prior to reaction by bubbling nitrogen gas for 1 hour. Unless specified otherwise, all reactions were carried out in an inert atmosphere in either a glovebox or using the Schlenk technique.

Analytical Methods

High-pressure experiments were performed employing a Parr Instruments 5000 Series Multiple Reactor System equipped with 45 mL reaction vessels. TEM images of bare-NZVI nanoparticles were taken with a Philips CM200 instrument operated at 200 kV. High resolution TEM images presented in the supplementary information were taken with a FEI Tecnai G2 F20 instrument. X-ray photoelectron spectrometry (XPS) was

performed on a VG ESCALAB 3 MKII spectrometer (VG, Thermo Electron Corporation, UK) equipped with an MgK α source. X-ray diffraction (XRD) was achieved on a Bruker AXS D8 Discover using Cu K α radiation at 40kV & 40 mA.

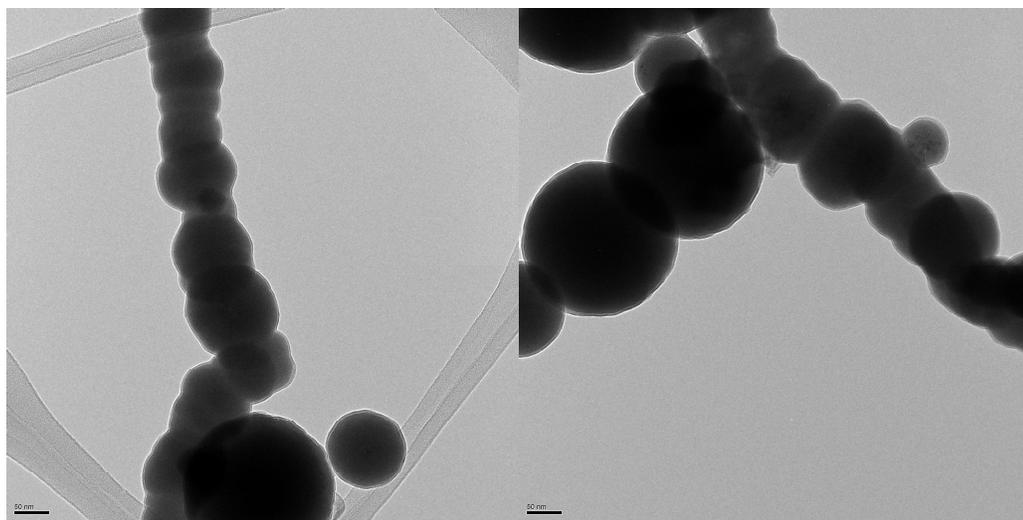
Synthesis of Fe CSNPs

This synthesis is adapted from ref 20 of the article. 8.4 g of FeSO₄·7H₂O was dissolved in a 480 mL methanol/water solution (30% methanol, v/v). An aqueous solution NaBH₄ (2.4 g in 60 mL) was added at a constant flow of 3 mL/min using a syringe pump. Once all of the NaBH₄ solution was added, the mixture was stirred for an additional 30 min. Magnetic collection followed by solvent removal and three ethanol washes (200 mL each) yielded an ethanol dispersion of Fe CSNPs used directly in catalysis.

Typical catalytic run

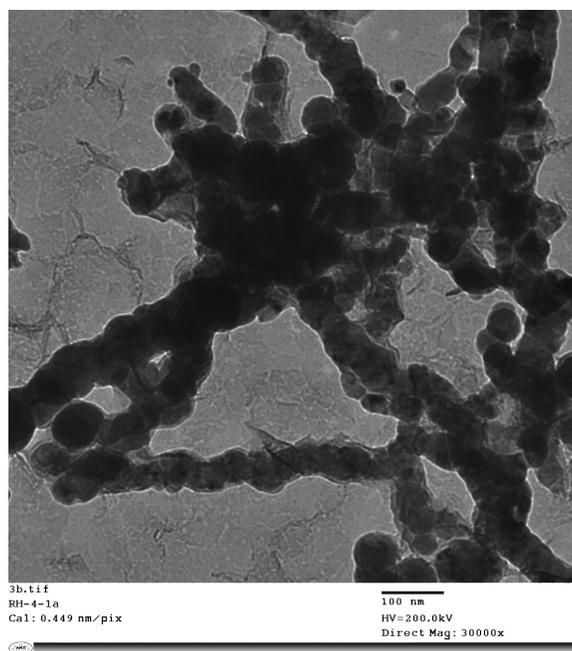
In a general reaction procedure, Fe CSNPs or C-Fe CSNPs (5 mol%- assuming all the sample is composed of iron) were loaded in the high pressure reactor liner, as a suspension, followed by application of an external magnet to pull the nanoparticles out of suspension. Then the excess solvent could be removed. 1mmol of substrate and 0.5 mmol dodecane as an internal standard were then loaded. with 17 mL of EtOH and a magnetic stirbar. The reaction proceeded for 24 hour. After the reaction, the reactor was open to air for a few minutes, the catalysts was recovered magnetically, washed three times with 10-15 mL EtOH and reused on another catalytic run as is. The conversion was monitored by GC-FID.

- **High resolution TEM pictures of Fe CSNPs:**

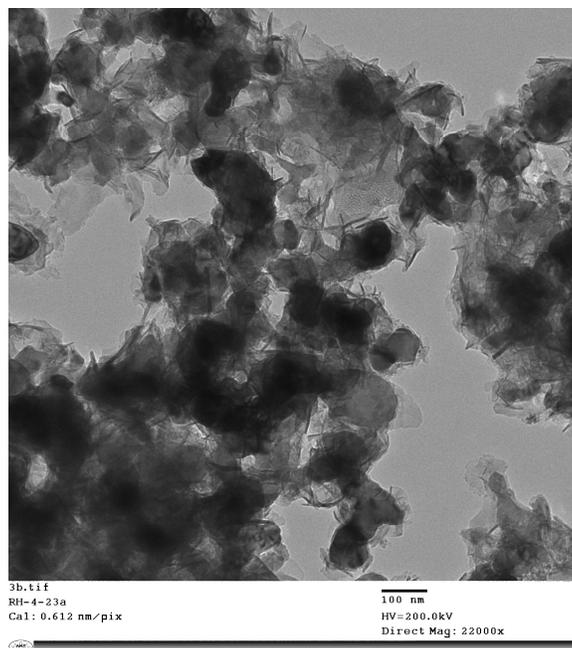


The scale bar represents 50 nm.

- TEM picture of Fe CSNPs after 5 cycles:



- TEM picture of C-FeCSNPs:

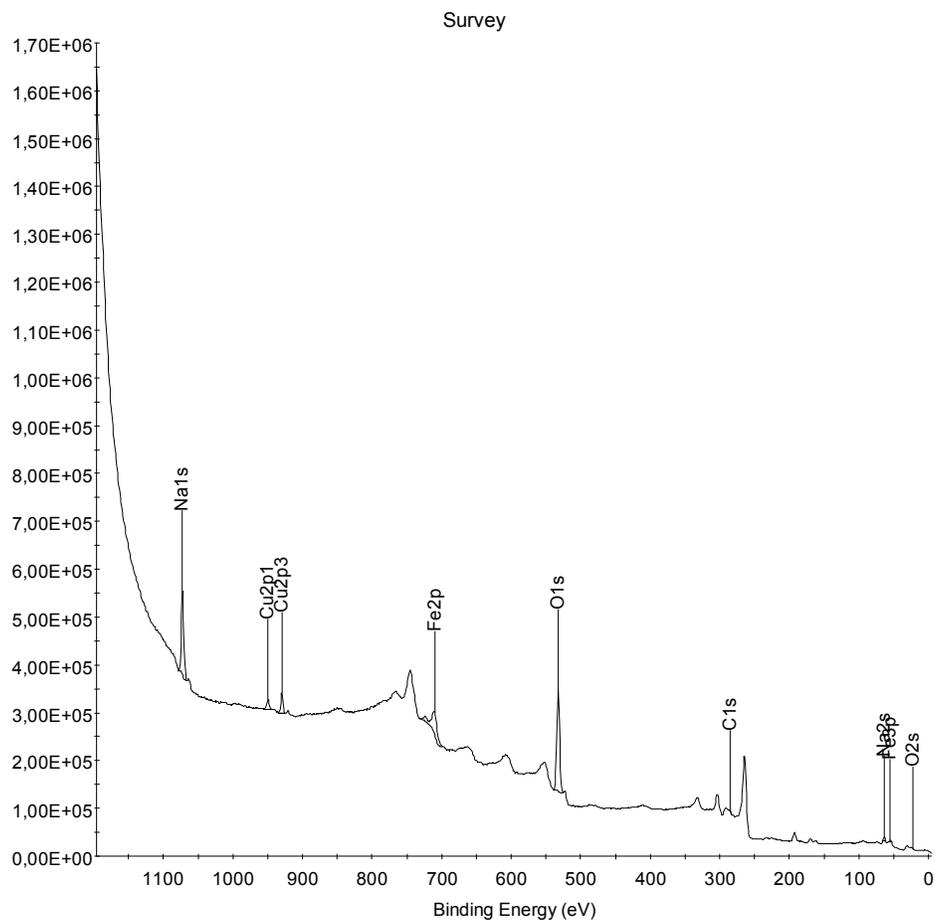


- **Estimated Fe:FeO ratio from TEM data**

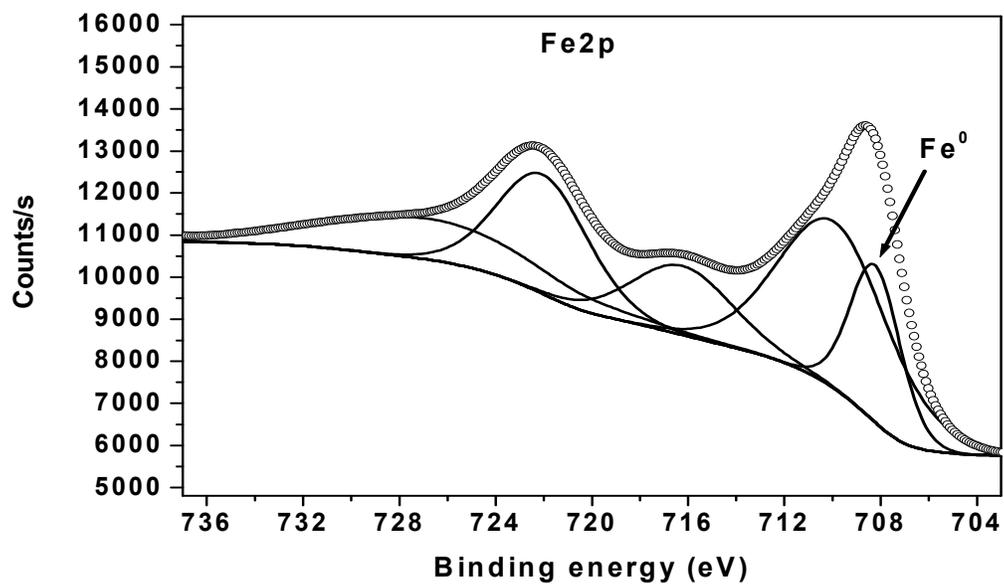
The average nanoparticle (44 nm core, 6 nm shell) should have 3.5×10^{-19} g Fe and 1.2×10^{-19} g FeO (for a molar ratio of 3.75:1 Fe:FeO).

- **XPS analysis of Fe CSNPs:**

Full spectrum (note that the presence of copper is caused by the type of holder used during analysis)



High resolution XPS for Fe2p

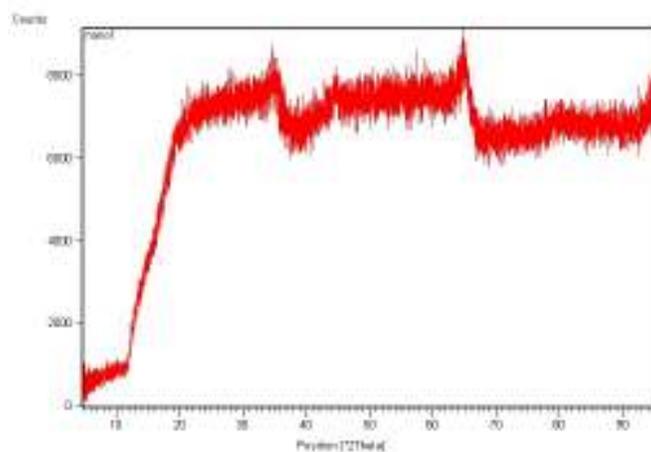


- **ICP-MS analysis of Fe CSNPs:**

Performed by digesting 100 mg of Fe CSNPs in 10mL aqueous nitric acid.

Element	Quantity detected	Quantity detected / Quantity of iron detected
Fe	6867184.97	1
B	226309.718	3.30 %
Co	55.1642745	8 ppm
Cu	175.839891	25 ppm
Ru	0.06552416	9 ppb
Rh	0.03524121	5 ppb
Pd	0.05011601	7 ppb

- **XRD analysis of Fe CSNPs**



The signal was very noisy due to iron interferences. The peak around 36° 2θ can be associated with FeO.