

Electronic Supplementary Information

Metal-Organic Framework-Templated Synthesis of γ -Fe₂O₃ Nanoparticles Encapsulated in Porous Carbon for Efficient and Chemoselective Hydrogenation of Nitro compounds

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S 1. Materials and Instrumentation.

All chemicals were from commercial and used without further purification: Iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$, 98.5%, Sinopharm Chemical Reagent Co., Ltd.), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 85%, Sinopharm Chemical Reagent Co., Ltd.), fumaric acid (99.5%, Aladdin), alcohol ($\geq 99.7\%$, Sinopharm Chemical Reagent Co., Ltd.), N,N-dimethylacetamide (DMF, $\geq 99.5\%$, Sinopharm Chemical Reagent Co., Ltd.), methanol ($\geq 99.5\%$,), nitrobenzene ($\geq 98.5\%$, Sinopharm Chemical Reagent Co., Ltd.), 1-fluoro-4-nitrobenzene (98%, Aladdin), 4-chloro-1-nitrobenzene ($\geq 99.5\%$, Aladdin), 1-chloro-2-nitrobenzene (99%, Aladdin), 1-chloro-3-nitrobenzene (98%, Aladdin), 2,4-dichloro-1-nitrobenzene (98%, Energy Chemical), 1-bromo-4-nitrobenzene (98%, Energy Chemical), 4-chloro-3-nitrobenzotrifluoride (98%, Aladdin), p-nitrotoluene (cp, Sinopharm Chemical Reagent Co., Ltd.), m-nitrotoluene (98%, Aladdin), p-nitrophenol (99%, Energy Chemical), p-nitroanisole (98%, Aladdin), 4-nitroaniline ($\geq 99\%$, Aladdin), 3-nitroaniline (98%, Aladdin), 4-nitrobenzotrifluoride (98%, Energy Chemical), p-nitrobenzaldehyde (98.0%, Energy Chemical), 3-nitroacetophenone (98%, Aladdin), 2-chloro-3-nitropyridine ($> 99.0\%$, Aladdin), 4-(4-nitrobenzyl)pyridine (98%, Aladdin), 2-hydroxy-5-nitropyridine (98%, Aladdin), acetonitrile (AR, Sinopharm Chemical Reagent Co., Ltd.), nitromethane (AR, Aladdin). De-ionized water with the specific resistance of $18.25 \text{ M}\Omega \cdot \text{cm}$ was acquired by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei). Powder X-ray diffraction patterns (XRD) were carried out on a Japan Rigaku SmartLabTM rotation anode X-ray diffractometer equipped or

Holland X'Pert PRO fixed anode X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Field-emission scanning electron microscopy (FE-SEM) was carried out with a field emission scanning electron microanalyzer (Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV). The transmission electron microscopy (TEM), high-resolution TEM observation was acquired on JEOL-2011 with an electron acceleration energy of 200 kV. The content of Fe in the catalysts was determined by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). The X-ray photoelectron spectroscopy (XPS) measurements were performed by using an ESCALAB 250 high-performance electron spectrometer using monochromatized Al K α ($h\nu = 1486.7 \text{ eV}$) as the excitation source. The conversion, purity and relative yields of the final products were determined by using a Shimadzu gas chromatograph (GC-2010 Plus with a $0.25 \text{ mm} \times 30 \text{ m}$ Rtx $^{\circledR}$ -5 capillary column) with an FID detector and high purity nitrogen as the carrier gas. The nitrogen sorption isotherms were measured by using an automatic volumetric adsorption equipment (Micromeritics ASAP 2020). Prior to nitrogen adsorption/desorption measurements, the samples were dried overnight at $120 \text{ }^{\circ}\text{C}$ under vacuum.

S2. Experiment Section

2.1 Preparation of catalysts

Synthesis of Fe-MIL-88A: Typically, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (800 mg, 2 mmol) and fumaric acid (210 mg, 1.8 mmol) were dissolved in 40 mL N,N-dimethylacetamide (DMF). The resulting solution was put in an oil bath for about 30 min under 110 °C. The mixture was cooled down at room temperature and collected by centrifuging, washing by DMF and methanol for several times. Finally, Fe-MIL-88A powder was dried in vacuum drying oven at room temperature overnight. The activated Fe-MIL-88A powder was obtained by evacuated at 120 °C for 12 h.

Preparation of Fe-based NPs encapsulated in porous carbon: Generally, Fe-MIL-88A (500 mg) was placed into a porcelain boat. The boat was put in the middle of a quartz tube in a furnace, which was purged with nitrogen gas. After the air in the furnace was drained, Fe-MIL-88A was pyrolyzed from room temperature to target temperature (500~700 °C) at a heating rate of 5 °C/min under a nitrogen flow of about 40 mL/min. After the temperature reached the target temperature and maintained for a required time, the resulting product was cooling down to the room temperature naturally. Finally, the catalyst was obtained and represented as Fe-T-t (T represents the target temperature and t represents the time maintained at T). For example, Fe-500-1h represents that Fe-MIL-88A powder was pyrolyzed up at 500 °C for 1 hour.

Preparation of $\gamma\text{-Fe}_2\text{O}_3$ NPs supported on active carbon: Typically, $\text{Fe}(\text{OAc})_2$ was dissolved in a certain amount of ethanol, and was instilled into activated carbon (AC) in a quartz mortar. Then the mixture in mortar was uniformly ground. The resulting

mixture was then dried naturally and 50 mg of the mixture was placed into a porcelain boat. Then the boat was put in the middle of a quartz tube in a furnace, which was purged with nitrogen gas. After the air in the furnace was drained, the mixture was calcined from room temperature to 350 °C at a heating rate of 5 °C/min under a nitrogen flow of about 40 mL/min.

2.2 Catalytic Performance Evaluation

The reduction of nitrobenzene: Typically, the catalyst (0.025 mmol) was charged into a dried round bottom flask with 5 mL ethanol. Then 102 µL nitrobenzene (1 mmol) and 200 µL hydrazine hydrate (4 mmol) were added sequentially. Then the reflux condenser was connected to the round bottom flask and the mixture was violently stirred under refluxing at 85 °C. The conversion and selectivity were detected by GC-FID with *n*-dodecane as standard.

Recyclability investigation for Fe-500-1h catalyst: After the reduction of nitrobenzene for one hour, the catalyst (Fe-500-1h) was separated out by an external magnet. Then the recovered catalyst was washed by ethanol for several times. After that, the catalyst was used by another reduction of fresh nitrobenzene. This procedure was conducted ten times to examine the recyclability of Fe-500-1h, and the selectivity and conversion were detected by GC-FID with *n*-dodecane as standard.

Filtration test for the reduction of nitrobenzene over Fe-500-1h: The reduction of nitrobenzene catalyzed by Fe-500-1h (0.025 mmol) in two dried round flasks with the mixture of 102 µL nitrobenzene (1 mmol), 200 µL hydrazine hydrate (4 mmol) and 5 mL ethanol were conducted at the same time. The conversion of these two reactions at

every ten minutes in the starting 60 minutes was determined by GC-FID with *n*-dodecane as standard. After 30 minutes of reaction, the catalyst in one of the flasks was separated out from the reaction for comparison.

The reduction of variety of nitro compounds: In a particular reaction, Fe-500-1h (0.025 mmol) was put into a dried round bottom flask with 5 mL solvent. Sequentially, 102 μ L nitro compounds (1 mmol) and 200 μ L hydrazine hydrate (4 mmol) were added. Then the reflux condenser was connected to the round bottom flask and the mixture was violently stirred under refluxing at 85 °C. The selectivity and conversion were detected by GC-FID with *n*-dodecane as standard.

S 3. Characterization Section

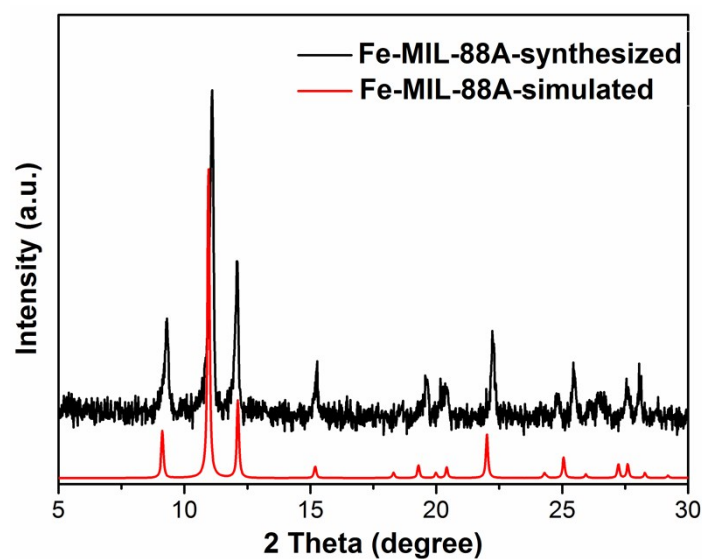


Figure S1. Powder XRD patterns of as-prepared Fe-MIL-88A, in good agreement with the simulated one.

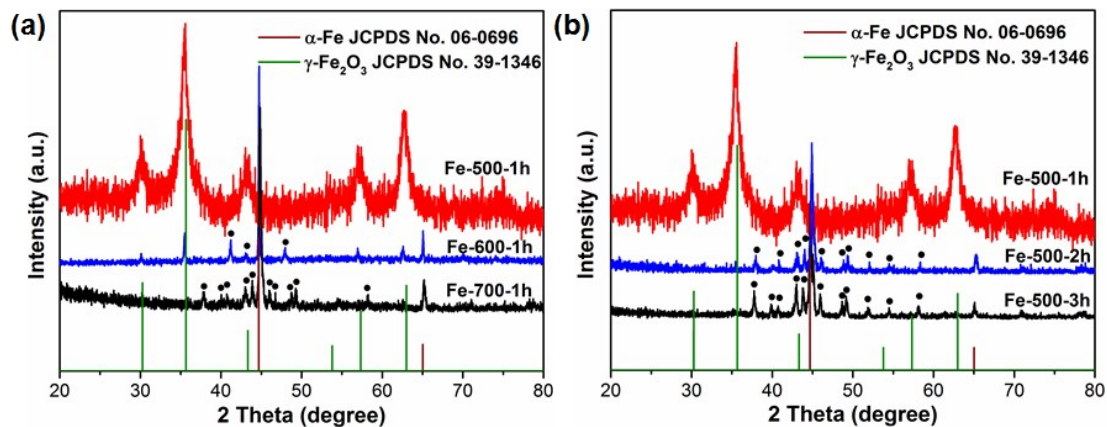


Figure S2. Powder XRD patterns of MOF-templated Fe-based NPs encapsulated in porous carbon via pyrolysis of Fe-MIL-88A in N_2 atmosphere (a) for 1 h at different temperature: 500 °C, 600 °C, 700 °C (named as Fe-T-1h), and (b) at 500 °C for different time: 1 h, 2 h, 3 h (named as Fe-500-t). Peaks marked with ● are assigned to Fe_3C (JCPDS card no. 35-0772).

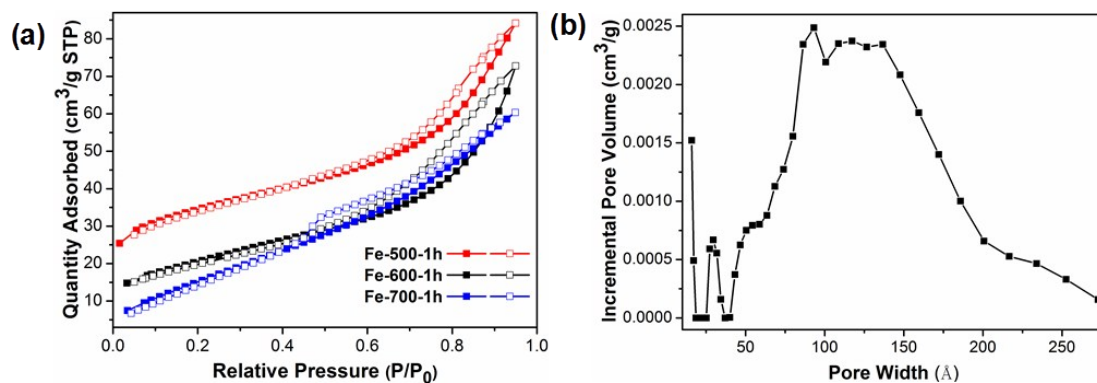


Figure S3. (a) Nitrogen adsorption and desorption isotherms of MOF-templated nanocomposites (Fe-T-1h) at 77 K. The BET surface areas are 114, 73, and 67 m²g⁻¹, respectively for Fe-500-1h, Fe-600-1h, and Fe-700-1h. (b) Pore size distribution analysis based on the DFT model for Fe-500-1h, indicating the presence of hierarchical pores.

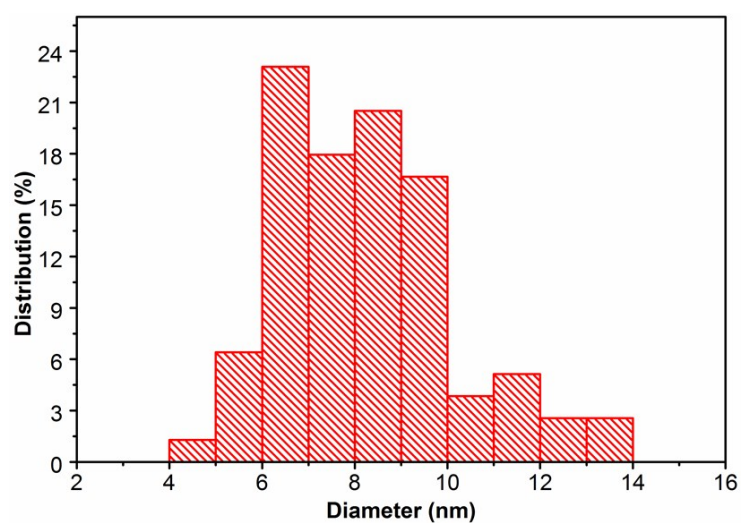


Figure S4. Size distribution of γ -Fe₂O₃ NPs, showing the average sizes of 6-10 nm.

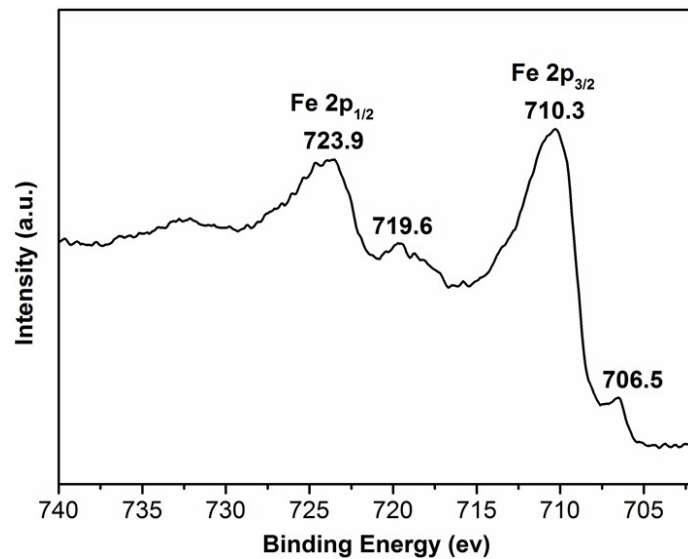


Figure S5. XPS survey spectrum for Fe-500-1h with two main broad peaks at 723.9 and 710.3 eV, assigned to Fe 2p_{1/2} and Fe 2p_{3/2}, respectively.

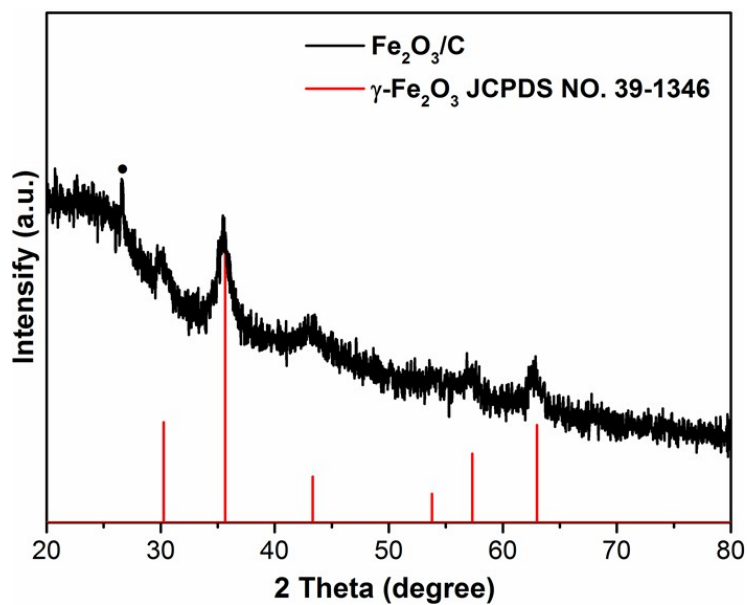


Figure S6. Powder XRD patterns for Fe₂O₃ supported on activated carbon, the peaks of γ-Fe₂O₃ were associated with standard JCPDS card no. 39-1346. The peak marked with ● is assigned to active carbon.

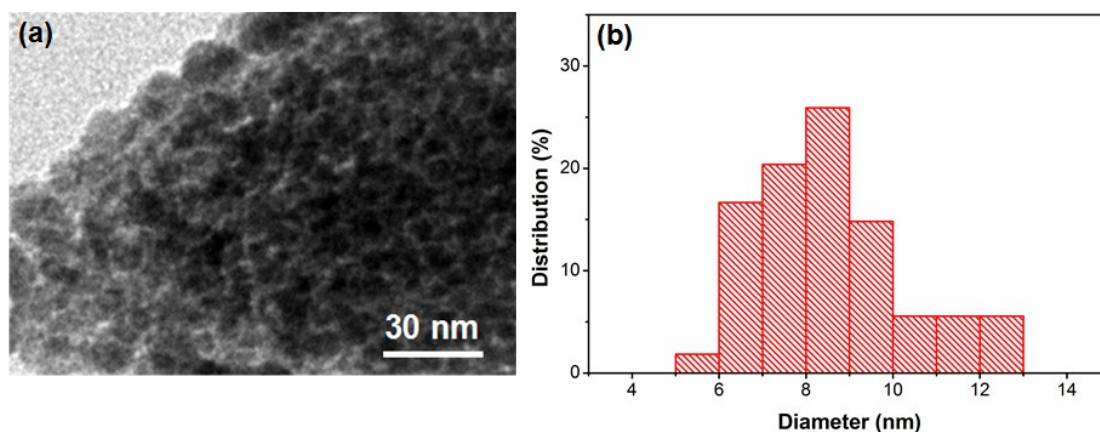
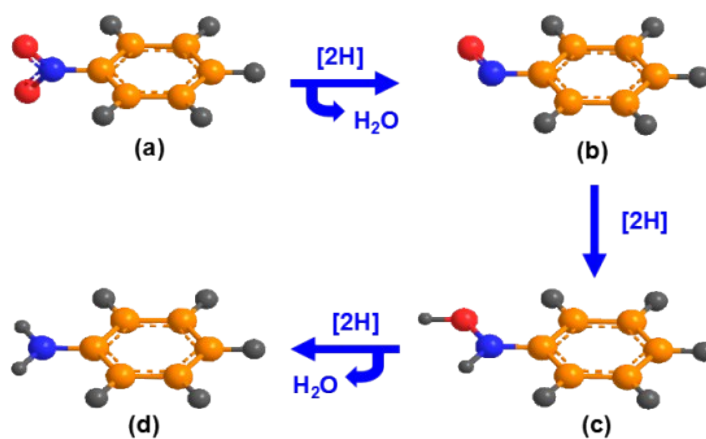


Figure S7. TEM image for Fe-500-1h after catalysis, showing the encapsulation of dispersed γ -Fe₂O₃ NPs inside porous carbon, no obvious agglomeration was observed.



Scheme S1. A proposed mechanism for the reduction of (a) nitrobenzene to (d) aniline in the presence of Fe-500-1h nanocatalyst, where (b) nitrosobenzene and (c) phenylhydroxylamine are reaction intermediates.

Table S1. ICP-AES and element analysis results for the contents of Fe in catalyst of Fe/Fe₂O₃ doped on porous carbon.

Fe/Fe ₂ O ₃ doped on porous carbon	The content of Fe (%)
Fe-500-1h	21.99
Fe-600-1h	25.99
Fe-700-1h	30.92