Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Facile Fabrication of Magnetically Recyclable Metal-Organic Framework Nanocomposites for Highly Efficient and Selective Catalytic Oxidation of Benzylic C-H Bonds

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Experimental procedures

Chemical:

Polyvinylpyrrolidone K-30 (PVP, $(C_6H_9HO)_n$, Mw: av. 40000), $Cu(OAc)_2 \cdot H_2O$ (98%), C_2H_5OH, DMF, CH_2Cl_2, trimesic acid (H_3BTC, 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd.. Carboxyl functionalized Fe_3O_4 (20 nm) was purchased from Beijing DK Nano S&T. Ltd.. All the reagents used in this work were used as received without further purification.

Synchronous Growth of HKUST-1@Fe_3O_4 Nanocomposites:

Controllable synthesis of nano-scaled core-shell HKUST-1@Fe_3O_4 with magnetic properties was achieved by one-pot strategy. First, PVP (0.200 g, 0.005 mmol), as surface capping agent, together with $Cu(OAc)_2 \cdot H_2O$ (0.100 g, 0.500 mmol) were uniformly dissolved in a mixed solution of DMF/C_2H_5OH/H_2O (1:1:1, 90 mL) in a 150 mL round-bottom flask under mechanical stirring. Then carboxyl functionalized Fe_3O_4 of 20 nm in diameter (0.200 g) were gradually added to the mixed solution with high-speed mechanical stirring of 900 r/min and kept for 10 min. After the addition of trimesic acid (0.300 g, 1.428 mmol) and another 0.100 g $Cu(OAc)_2 \cdot H_2O$ to the reaction mixture and stirred for further 12h, the product was collected by centrifugation and washed with DMF/C_2H_5OH/H_2O (1:1:1, 20 mL ×3) mixtures and C_2H_5OH (20 mL ×3). After heating at 60°C for 3h, 0.460 g black powder was collected. Then half of the product was for catalysis research, while the rest was treated repeatedly with 20 mL CH_2Cl_2 (3 times) for 24 h and the product was further centrifuged and heated in 150°C for 3h under vacuum for N_2 sorption test and elemental analysis.

***General Procedure for HKUST-1@Fe_3O_4 Catalyzed Oxidation of Diphenylmethane*:**

25 mg HKUST-1@Fe_3O_4, diphenylmethane (0.250 mmol, 42.050 mg), 70% TBHP (0.625 mmol, 130.360 mg) were added to a Schlenk Tube. And then 0.5 mL of benzonitrile was added to the mixture. The reaction mixture was subsequently heated at 80°C in a Wattecs Parallel Reactor for 14 h with stirring. After the reaction was completed, the resulting mixture was analyzed by GC-MS and GC.

Reuse Experiments:

The reuse experiments were carried out for the oxidation of diphenylmethane under the conditions listed in Table 1. After the reaction was completed, the catalyst was easily retrieved by magnet, washed and soaked with DMF (ca. 4 × 5 mL) and EtOH (ca. 3 × 5 mL), and air-dried prior to being used for the reuse experiment. The experiment of the third run was prepared in the same way as that for the second run, and finally the 92.9% conversion of diphenylmethane was also determined by GC.

Characterization:

Field-emission scanning electron microscopy (FESEM, JEOL, S-4800) was applied to investigate the size and morphology of the samples. For the detailed microstructure study, TEM and HR-TEM images were taken on a JEOL JEM-1200EX microscope. Elemental mapping were carried out under the bright field (BF) mode on a JEOLJEM-2100F microscope. The composition information was conducted by energy dispersive X-ray spectroscopy (EDS) at 20 keV on a TN5400 EDS instrument. Powder X-ray diffraction (XRD) was performed on a Bruker Foucus D8 diffractometer with a Cu-Kα X-ray radiation source (λ = 0.154056 nm). The metal content of the compound HKUST-1@Fe_3O_4 was measured by inductively coupled plasma (ICP) on a JY-ULTIMA2 analyzer. The FT-IR spectra were recorded from KBr pellets in the range 2000-400 cm^{-1} on Nicolet 170 SXFT-IR spectrometer. The GC analyses were performed on Shimadzu GC-2014C with a FID detector equipped with an HP-5ms capillary column. The GC mass spectra were recorded on Agilent 7890A-5975C at an ionization voltage of 1200 V. Field-dependent magnetization curves was performed on Lakeshore 7404 magnetic detector. Atomic absorption analysis was measured by inductively coupled plasma (ICP) on a ICP-6000 analyzer.

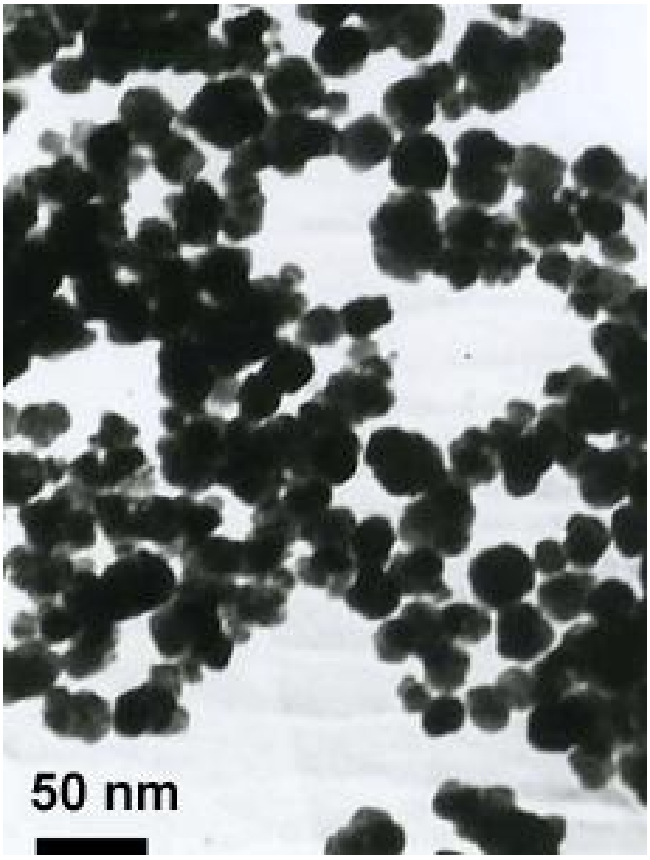
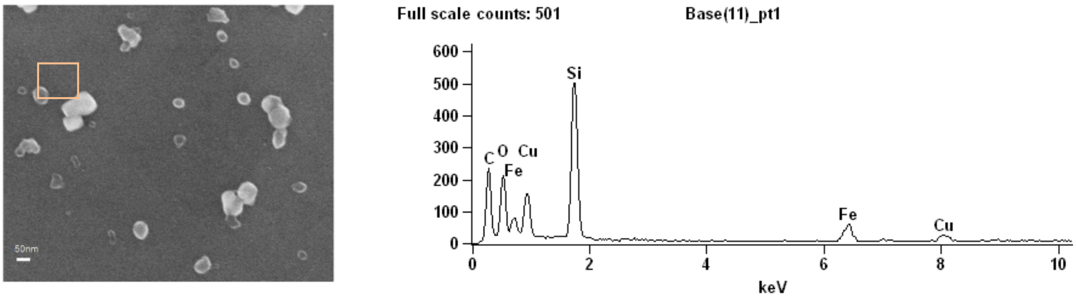


Figure S1. TEM of carboxyl functionalized Fe_3O_4.



Element	Fe	Cu	C	O	Si
Percentage (%)	11.30	9.60	15.56	19.61	41.94

Figure S2. The EDS element analysis of HKUST-1@Fe_3O_4, the scale bar is 50 nm.

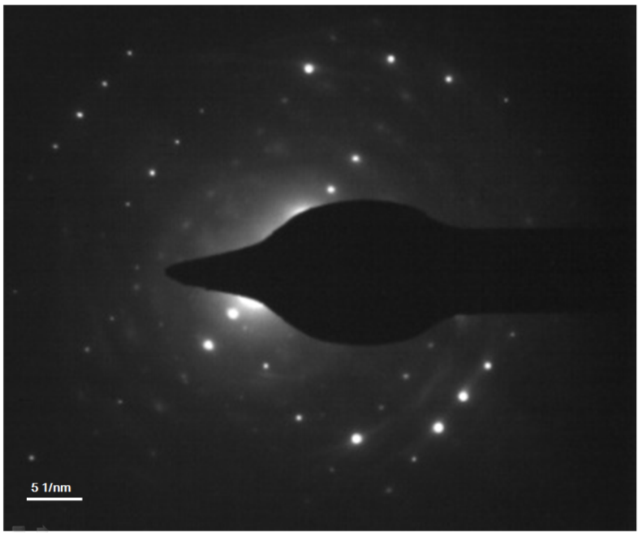


Figure S3. Selected-area electron diffraction of the shell.

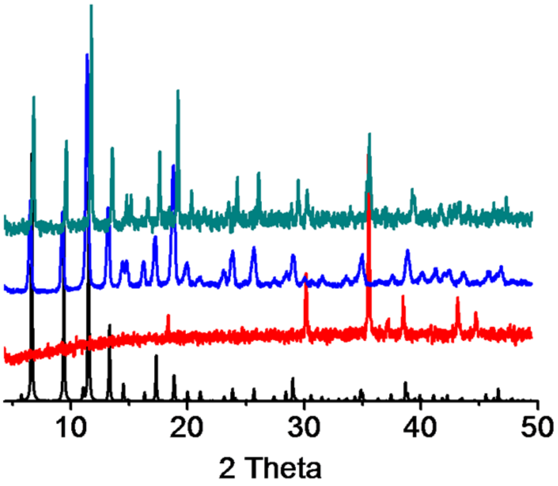


Figure S4. PXRD patterns of simulated HKUST-1 (black), Fe_3O_4 (red), HKUST-1 (blue) and HKUST-1@Fe_3O_4 (cyan).

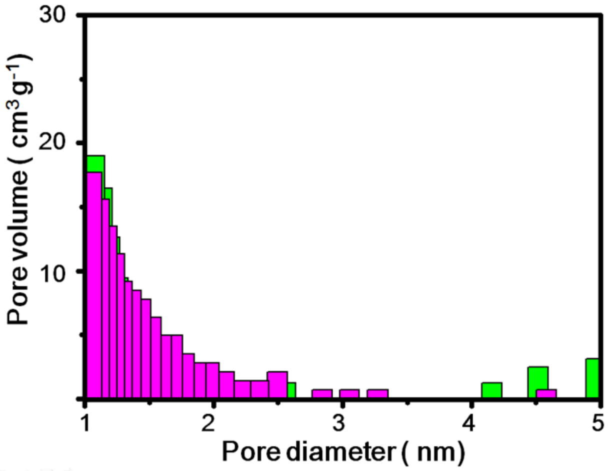


Figure S5. Pore size distributions of HKUST-1 (green) and HKUST-1@Fe_3O_4 (pink).

S6. The elemental analysis of HKUST-1@Fe_3O_4

Element	Cu	Fe	C	H
Mass Percentage (%)	19.34	28.63	21.72	3.41
Calculated Data	18.98	28.78	21.35	1.86

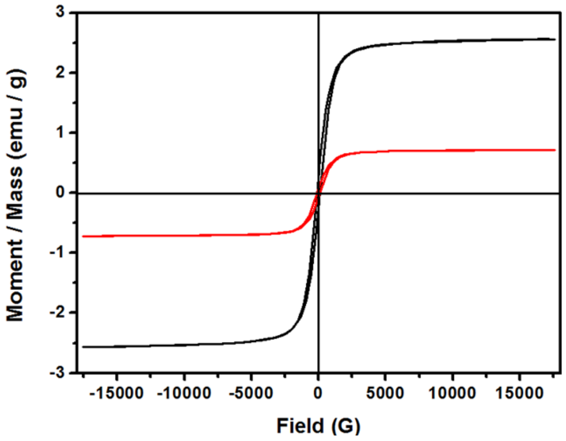


Figure S7. Field-dependent magnetization curves of Fe_3O_4 (black) and HKUST-1@Fe_3O_4 (red) at 293 K.

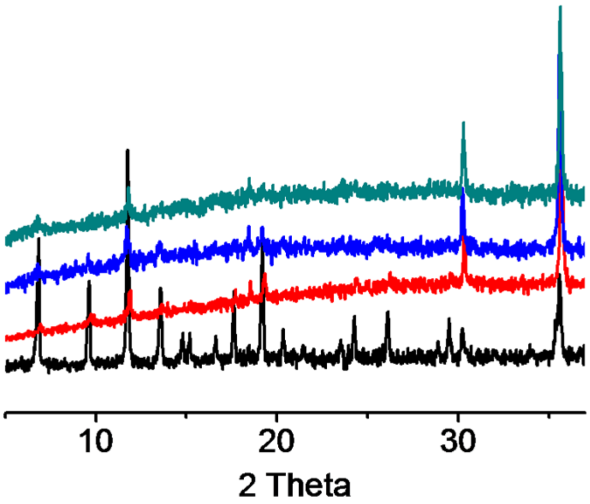


Figure S8. PXRD patterns of HKUST-1@Fe_3O_4 after catalysis. Black, as-synthesized HKUST-1@Fe_3O_4; red, first cycle; blue, second cycle; cyan, third cycle.

S9. Atomic absorption analysis of product solution after three catalytic cycles

The detection limit of the inductivelyvcoupledvplasma (ICP) analyzer (ICP-6000) is 1 mg/L and the analysis results of copper and iron ions are both below the detection limit.

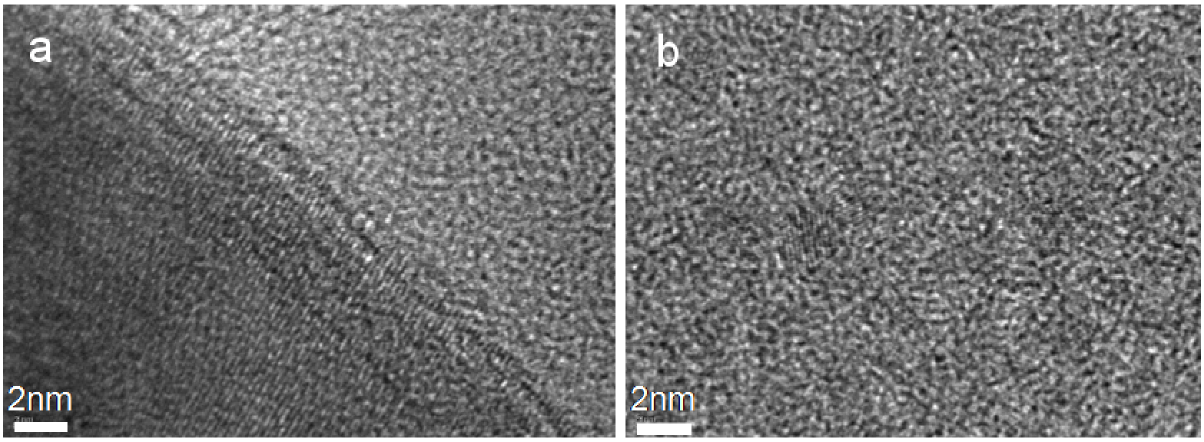


Figure S9. The high-resolution TEM images of HKUST-1@Fe_3O_4 (a) and Fe_3O_4 (b).