Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Fe_3O_4@ZIF-8: Magnetically Recoverable Catalysts by Loading Fe_3O_4 nanoparticles inside a Zinc Imidazolate Framework

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Materials

Iron (+3) chloride hexahydrate (Lancaster; 98%), iron (+2) sulfate heptahydrate (Aldrich; ≥ 99%), sodium citrate tribasic dihydrate (99%, Aldrich), zinc nitrate hexahydrate (98%, Aldrich), 2-methylimidazole Hmim (99%, Aldrich), benzyl bromide (≥ 98%, Fluka), sodium azide (≥ 99.5%, Aldrich), phenyl acetylene (> 98%, Alfa Aesar), sodium chloride (99-100.5%, Carlo Erba), sodium sulphate (≥ 99%, Carlo Erba), DMSO (≥ 99.7%, Fisher), ammonium hydroxide solution ca. 25% (Aldrich), ethanol (≥ 99.8%, Aldrich), and toluene (≥ 99%, Prolabo) were used as received without further purification. All solutions were prepared using Milli-Q water (18.2 MΩ.cm, Millipore) as the solvent.

Methods

Transmission electron microscopy (TEM) images were taken by placing a drop of ZIF-8 or Fe_3O_4@ZIF-8 particles dispersed in methanol onto a carbon film-supported copper grid. Samples were studied using a Philips CM20 instrument operating at 200 kV. Scanning electron microscopy (SEM) pictures were prepared using JEOL Scanning Electron

Microscope JSM-6490 LV. The X-ray powder diffraction (XRD) diagrams of all samples were measured using Panalytical X'Pert Pro MPD diffractometer using Cu Kα radiation. The X-ray powder diffraction data were collected from an X'Pert MPD diffractometer (Panalytical AXS) with a goniometer radius 240 mm, fixed divergence slit module (1/2° divergence slit, 0.04 rd Sollers slits) and an X'Celerator as a detector. The powder samples were placed on a silicon zero-background sample holder and the XRD patterns were recorded at room temperature using Cu K_{α} radiation ($\lambda = 0.15418$ nm). The textural properties of the materials were investigated with a Micromeritics ASAP 2420 instrument using liquid nitrogen (-196 °C). Prior to the analyses, the samples were out-gassed overnight in vacuum at 40°C on the degassing port followed by 4 h out-gassing on the analyse port. The resulting isotherms were analysed using the BET (Brunauer-Emmett-Teller) method while the micropore volume (V_{micro}) was determined using the Horvath-Kawazoe (HK) equation. Thermogravimetric measurements were performed on a SETARAM Setsys Evolution thermoanalyzer coupled with an Omnistar GSD301C-Pfeiffer Vacuum mass spectrometer. Samples were filled into platinum crucibles and heated in an air flow with a ramp of 5 °C.min^{-1} from room temperature up to 800°C. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 300 MHz spectrometer (Avance 300, Bruker, Bremen, Germany). The DC magnetization data were recorded using a PPMS (Quantum Design) in field up to 50000 Oe in the 5-300 K temperature range. No diamagnetism correction was applied. A VARIAN 720-ES Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used for multi-elemental analyses.

Synthesis of citrate-capped Fe_3O_4 nanoparticles

$FeCl_3.6H_2O$ (6 mmol; 1.622 g) and $FeSO_4.7H_2O$ (5 mmol; 1.39 g) were dissolved in 40 mL of water. 5 mL of a 28% ammonia solution were then added and the mixture heated at 90°C. Then 4.4 g (14.9 mmol) of sodium citrate were added to the flask and the mixture vigorously stirred for 30 min. Fe_3O_4 nanoparticles were recovered by magnetic separation, washed several times with ethanol and redispersed in water (100 mL).

Synthesis of Fe_3O_4@ZIF-8 nanoparticles

15 mL of a freshly prepared citrate-capped Fe_3O_4 particles water solution were mixed under vigorous stirring with Hmim (4.31 g, 52.5 mmol) and the mixture stirred for 5 min. Then, 15 mL of a zinc nitrate aqueous solution (0.223 g; 0.75 mmol) were added, and the solution stirred for 10 min. Fe_3O_4@ZIF-8 particles were recovered by magnetic separation and purified by washing three times with water.

SUPPORTING INFORMATION

Synthesis of Fe_3O_4@$Cu_{25\%}$/ZIF-8 nanoparticles

10 mL of a freshly prepared citrate-capped Fe_3O_4 particles water solution were mixed under vigorous stirring with Hmim (2.873 g, 35.03 mmol) and the mixture stirred for 5 min. Then, 10 mL of a zinc nitrate (0.111 g; 0.38 mmol) and copper nitrate (0.029 g; 0.12 mmol) aqueous solution were added, and the solution stirred for 10 min. Fe_3O_4@$Cu_{25\%}$/ZIF-8 particles were recovered by magnetic separation and purified by washing three times with water.

Knoevenagel condensation

Benzaldehyde (0.5 mmol) was dissolved in 5 mL of toluene, the Fe_3O_4@ZIF-8 catalyst (11.45 mg, 0.04 mmol) added and the mixture stirred for 5 min. Malononitrile (3 mmol) was then injected in the flask and the reaction was conducted with bubbling of Ar gas through the mixture for 3 h at room temperature. After magnetic separation of the catalyst and concentration of the toluene phase, the crude reaction mixture was purified using silica gel column chromatography (petroleum ether – ethyl acetate (v/v), 95:5) and the product analyzed by ^1H NMR.

Huisgen 1,3-dipolar cycloaddition

The 1,3-dipolar cycloaddition of the benzylazide with phenylacetylene was conducted as follows. The Fe_3O_4@ZIF-8 catalyst (5 mol%) in ethanol (6 mL) was placed inside a round bottom flask connected to a reflux condenser and the temperature was set to 70 °C under argon. Azide (1 mmol) and alkyne (1.2 mmol) were then added and the reaction mixture maintained at 70°C for 3 h. After cooling, the catalyst was magnetically separated, washed with ethanol and water, and finally dried. The triazole product was purified by flash chromatography and analyzed with ^1H and ^{13}C NMR.

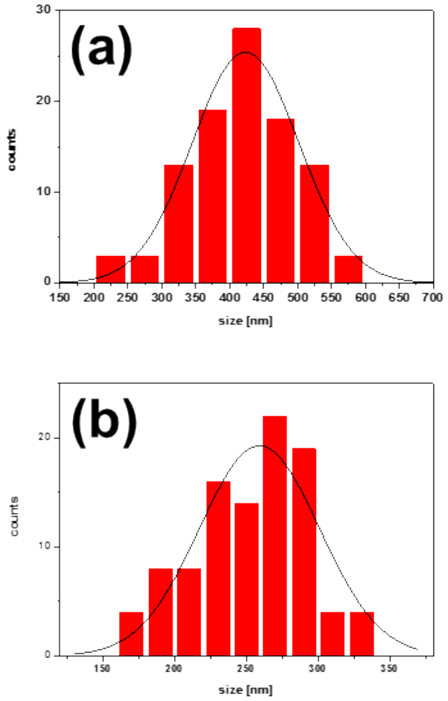

Fig. S1. Size distributions of ZIF-8 and Fe3O4@ZIF-8 particles.

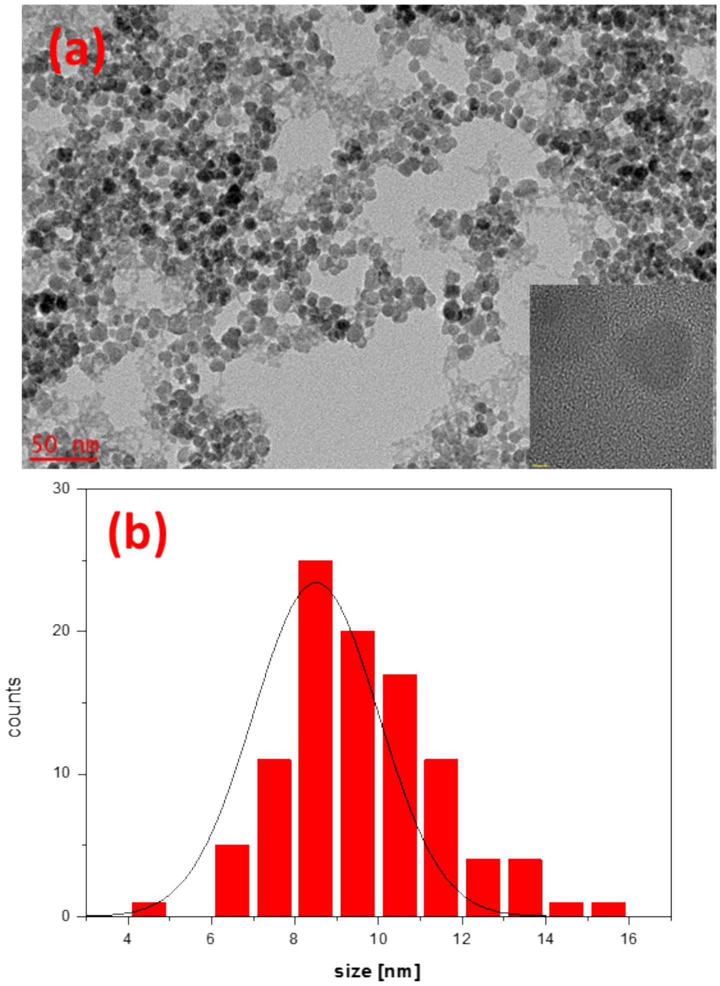

Fig. S2. (a) TEM image of citrate-capped Fe_3O_4 nanoparticles (the inset shows a HR-TEM image of the crystals) and (b) the corresponding size distribution.

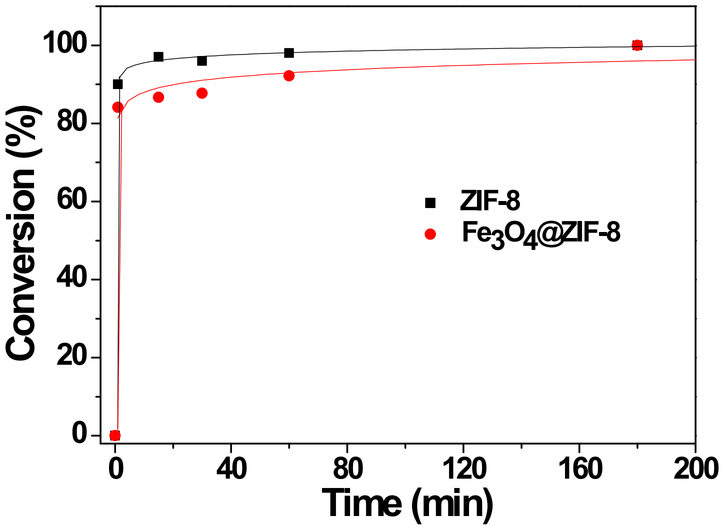

Fig. S3. Time-dependent conversion plots for the Knoevenagel reaction between 4-bromobenzaldehyde and malononitrile catalyzed by ZIF-8 crystals and Fe_3O_4@ZIF-8 crystals (reactions were conducted in toluene at room temperature).

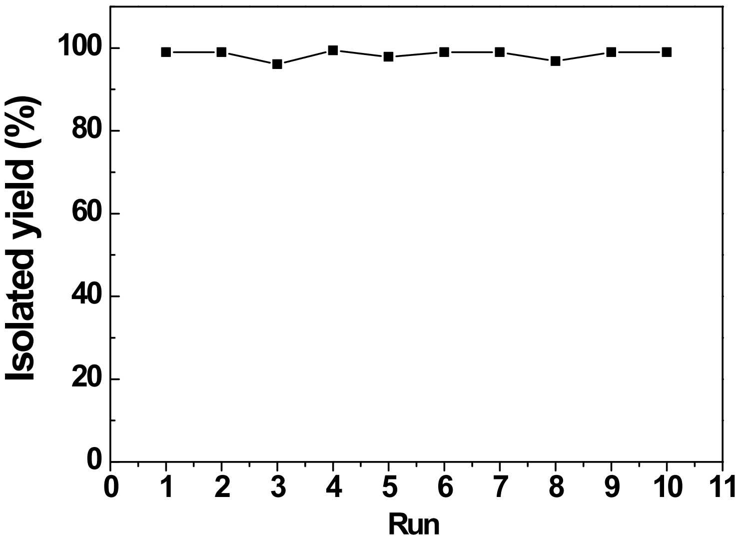

Fig. S4. Recycling performance of Fe_3O_4@ZIF-8 particles in the Knoevenagel condensation between malononitrile and benzaldehyde.

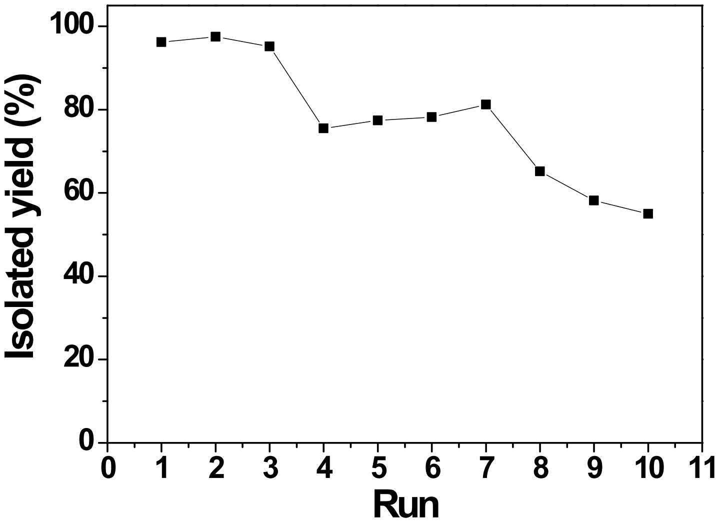

Fig. S5. Recycling performance of Fe_3O_4@$Cu_{25\%}$/ZIF-8 particles in the Huisgen cycloaddition between benzylazide and phenylacetylene.

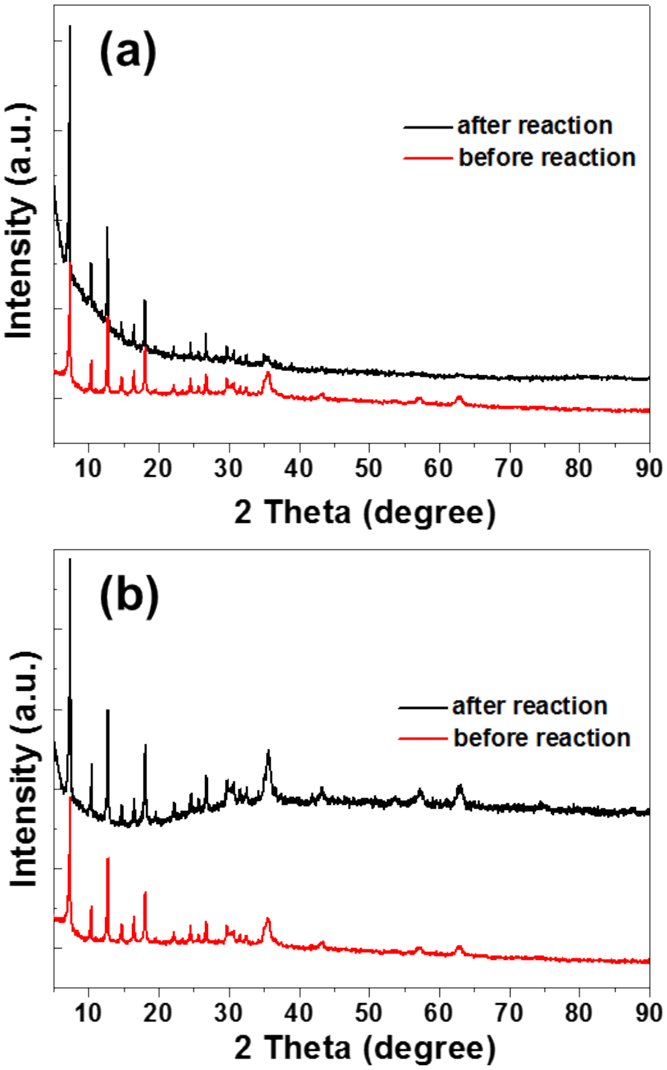

Fig. S6. XRD patterns of (a) Fe_3O_4@ZIF-8 and (b) Fe_3O_4@$Cu_{25\%}$/ZIF-8 catalysts before and after five recyclings.