**SUPPORTING INFORMATION**

**Fe₃O₄@ZIF-8: Magnetically Recoverable Catalysts by Loading Fe₃O₄ nanoparticles inside a Zinc Imidazolate Framework**

Aleksandra Schejn,a Thomas Mazet,b Véronique Falk,a Lavinia Balan,c Lionel Aranda,b Ghouti Medjahdi,b Raphaël Schneidera

a Laboratoire Réactions et Génie des Procédés (LRGP), UMR CNRS 7274, Université de Lorraine, 1 rue Grandville 54001 Nancy, France.
b Institut Jean Lamour (IJL), Université de Lorraine, CNRS, UMR 7198, CNRS, BP 70239, 54506 Vandoeuvre-lès-Nancy Cedex, France
c Institut de Science des Matériaux de Mulhouse (IS2M), UMR 7361, CNRS, 15 rue Jean Starcky, 68093 Mulhouse, France

**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 Fe₃O₄@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 Kα radiation (λ = 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. ¹H and ¹³C NMR spectra were recorded in CDCl₃ 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 Fe₃O₄ nanoparticles**

FeCl₃.6H₂O (6 mmol; 1.622 g) and FeSO₄.7H₂O (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. Fe₃O₄ nanoparticles were recovered by magnetic separation, washed several times with ethanol and redispersed in water (100 mL).

**Synthesis of Fe₃O₄@ZIF-8 nanoparticles**

15 mL of a freshly prepared citrate-capped Fe₃O₄ 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. Fe₃O₄@ZIF-8 particles were recovered by magnetic separation and purified by washing three times with water.
Synthesis of Fe₃O₄@Cu₂5%/ZIF-8 nanoparticles

10 mL of a freshly prepared citrate-capped Fe₃O₄ 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. Fe₃O₄@Cu₂5%/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 Fe₃O₄@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 Fe₃O₄@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 ¹³C NMR.
Fig. S1. Size distributions of ZIF-8 and Fe3O4@ZIF-8 particles.
Fig. S2. (a) TEM image of citrate-capped Fe₃O₄ 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$_3$O$_4$@ZIF-8 crystals (reactions were conducted in toluene at room temperature).
Fig. S4. Recycling performance of Fe₃O₄@ZIF-8 particles in the Knoevenagel condensation between malononitrile and benzaldehyde.
Fig. S5. Recycling performance of Fe₃O₄@Cu_{25%}/ZIF-8 particles in the Huisgen cycloaddition between benzylazide and phenylacetylene.
**Fig. S6.** XRD patterns of (a) Fe$_3$O$_4$@ZIF-8 and (b) Fe$_3$O$_4$@Cu$_{25\%}$/ZIF-8 catalysts before and after five recyclings.