Superparamagnetic mesoporous Mg-Fe bi-metal oxides as efficient magnetic solid-base catalysts for Knoevenagel condensations

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Supporting Information

Experimental

1. Catalyst synthesis

Three Mg-Fe bi-metal oxalate precursors with different Mg/Fe ratios were synthesized in the present study: these are labeled hereafter as M2F, MF and MF2, corresponding to the Mg/Fe atomic ratio = 2/1, 1/1 and 1/2, respectively, in the precursors. In a typical procedure, 20 mmol $MgCl_2 \cdot 6H_2O$ and 10 mmol $FeSO_4 \cdot 7H_2O$ were dissolved in 100 mL deionized water. 30 mmol $Na_2C_2O_4$ was dissolved into 100 mL water at 80 ^oC under stirring for at least 1 h. Then this solution was slowly dropped into the former solution. Precipitates yielded during the process. The precipitated products were separated by centrifugation, subsequently washed with deionized water, and dried at 60 ^oC overnight.

All of the six mesoporous Mg-Fe bi-metal oxides were obtained by calcining the three Mg-Fe oxalate precursors at 400 and 500 ^oC for 2 h, labeled as M2F-400, MF-400 and MF2-400; M2F-500, MF-500 and MF2-500, respectively.

2. Characterization

The chemical compositions (metal contents) of all precursors were determined by ICP-AES. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2200PC diffractometer using Cu Ka radiation at 40 kV and 40 mA. The N_2 sorption measurements were performed using Micromeritics Tristar 3000 at 77 K for mesoporosity, and the mesoporous specific surface area and the pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Transmission electron microscopy (TEM) images were obtained on a JEOL-2010 electron microscope operated at 200 kV. A vibrating-sample magnetometer (PPMS Model 6000 Quantum Design, San Diego, USA) was used to study the magnetic properties. The basicities of the catalysts were determined using the temperature-programmed desorption of carbon dioxide (CO_2-TPD) as follows. The catalysts (50 mg) were treated by heating at 500 °C under N_2 and then exposed to the probe gas stream at room temperature. Physically adsorbed CO_2 was removed by flushing N_2 at room temperature for 1 h. Then the TPD analysis was run under N_2 flow at a heating rate of 10 ^oC/ min up to 600 ^oC and the amount of CO_2 desorbed was detected by a gas chromatography.

3. General procedure for the Knoevenagel reaction

Aldehyde (5 mmol) and 0.1 g catalyst were stirred in 10 mL of ethanol for 5 min. Then the active methylene compound (5.5 mmol) was added and stirring was continued at room temperature until the completion of the reaction. After the reaction, the magnetic catalyst was separated with a magnet and dried for the next reuse. The pure product was isolated and confirmed with gas chromatographic mass spectrometry (GC–MS) (Agilent, 6890N/5973N). The reusability of the M2F-400 catalyst was carried out using *p*-nitrobenzaldehyde and malononitrile as substrates by adopting the similar experimental conditions as described above.
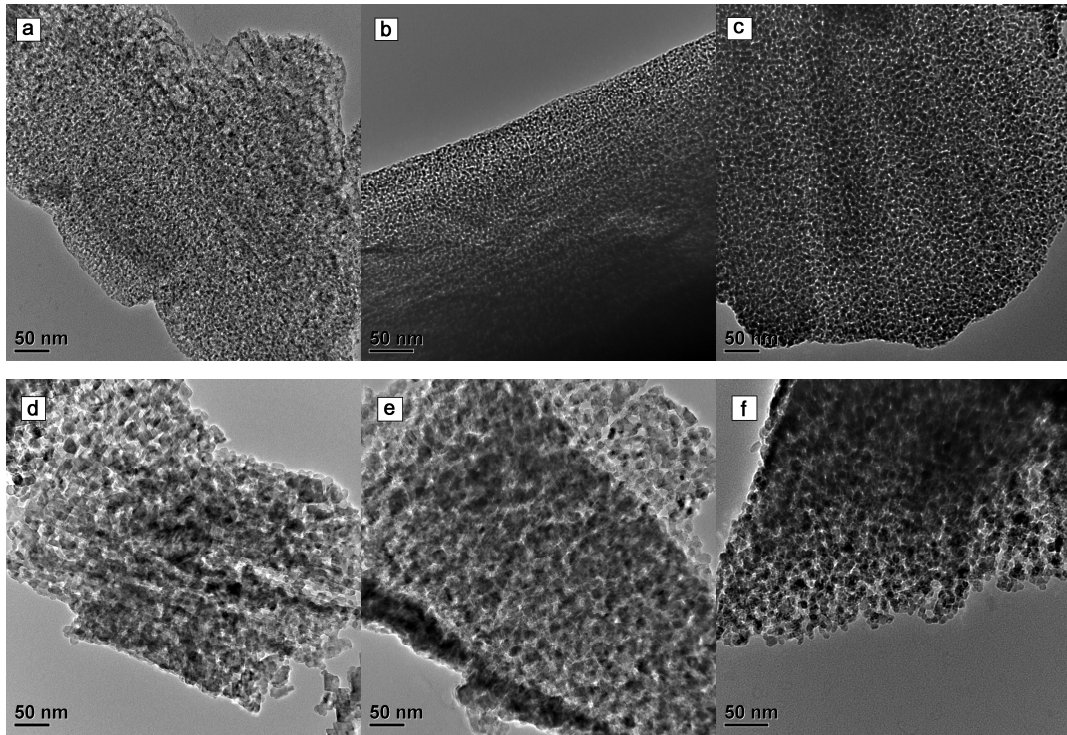
Figure S1. TEM images of samples M2F-400 (a), MF-400 (b), MF2-400 (c), M2F-500 (d), MF-500 (e) and MF2-500 (f).
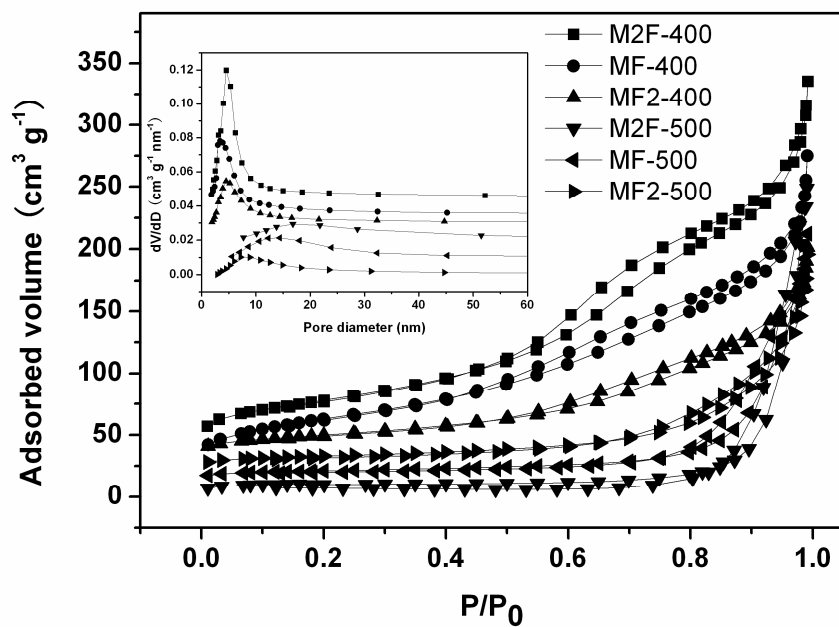
Figure S2. Nitrogen adsorption-desorption isotherms and corresponding BJH desorption pore size distribution plots (inset) of all synthesized Mg-Fe bi-metal oxide samples.