Supplementary Information

Magnetically separable $MnFe_2O_4$ nano-material: An efficient and reusable heterogeneous catalyst for the synthesis of 2-substituted benzimidazoles and the extended synthesis of quinoxalines at room temperature under aerobic conditions

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Catalyst (MnFe₂O₄ nano-material) preparation, characterization and magnetic evaluation

Instrumentations

The crystal structure was investigated on a powder X-ray diffractometer (Model PW1710, CuK_a radiation, $2\theta=3^{\circ}-130^{\circ}$, $\Delta 2\theta=0.03^{\circ}$). The microstructure of the catalyst was observed under Transmission Electron Microscope (TEM, Philips, Model-CM12). Magnetic measurements were carried out at room temperature using a Vibrating Sample Magnetometer (VSM), Lakeshore. Infrared spectra were recorded using a Shimadzu (FT-IR 8400S) Fourier transform infrared (FT-IR) spectrophotometer (Shimadzu, Kyoto, Japan) using KBr disc. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained at 400 & 300 and 100 & 75 MHz, respectively, using Bruker DRX spectrometer (Bruker Instruments, Billerica, MA, USA) and CDCl₃ & DMSO-*d*₆ as the solvents. Elemental analyses were performed with an Elementar Vario EL III Carlo Erba 1108 micro-analyzer instrument (*Carlo Erba Reagenti SpA, Rodano, Italy*). Melting points were recorded on a Chemiline CL725 melting point apparatus and are uncorrected. Column chromatography was carried out over silica gel (60 to 120 mesh, Merck & Co., Inc., Whitehouse Station, NJ, USA), and thin layer chromatography (TLC) was performed using silica gel 60 F₂₅₄ (Merck) plates.

Preparation of MnFe₂O₄ catalyst

 $MnFe_2O_4$ nanoparticles were produced by a simple sol-gel method. FeCl₃.6H₂O (6 mmol) and $Mn(CH_3COO)_2.4H_2O$ (3 mmol) were used in a stoichiometric ratio of 2:1. A homogeneous aqueous solution of starch was prepared by stirring it for 30 min at 90 °C. $Mn(CH_3COO)_2.4H_2O$ was then added to the starch solution under N₂ atmosphere on vigorous stirring. Subsequently,

FeCl₃.6H₂O was added to the solution; the reaction temperature was kept between 90-100 $^{\circ}$ C in an oil bath for 2 h. After then aqueous ammonium hydroxide was added into the reaction mixture to maintain the pH of 13-14, and the resulting solution was magnetically stirred for another 2 h. On completion of the reaction, the flask was allowed to cool down to room temperature. The black precipitate obtained was washed with deionised water and then dried at 100 $^{\circ}$ C for 12 h. The dried black-powder was then placed into clean alumina crucibles and annealed in the presence of air at a temperature of 900 $^{\circ}$ C for 4 h to get rid of the excess carbon and the unreacted organic residues and also to obtain a pure MnFe₂O₄ phase (yield 90% based on the calculation of FeCl₃.6H₂O).

Starch was used as a capping agent to stabilize the particles and also to prevent them from agglomeration. The influence of starch is supposed not to be restricted only to the solution and the drying step, but also affects the nucleation process of the metal ferrite nanoparticles in the calcination step. It has been reported that without a capping agent, the initially formed small nanoparticles would become larger *via* the Ostwald ripening process¹ due to their high surface energy.

XRD analysis. The crystal structure was investigated on a powder X-ray diffractometer (Model PW1710, CuK_a radiation, $2\theta=3^{\circ}-130^{\circ}$, $\Delta 2\theta=0.03^{\circ}$). The average grain diameter of the crystallites (D) were calculated from X-ray diffraction peaks widths β (= $\Delta 2\theta_{1/2}$) using Debye – Scherrer relation, D=0.9\lambda/\beta.cos θ , where λ is the wavelength and θ is the angle of diffraction. Fig. 1 shows the X-ray diffraction patterns of the sample; the spectrum shows six sharp lines corresponding to the lines of MnFe₂O₄ spinel structure and two very weak peaks, marked as '*', corresponding to the lines of FeMnO₃. All the diffraction peaks of the XRD pattern can be readily indexed to face-centred cubic phase [space group Fd3m (227)] of spinel MnFe₂O₄ with lattice constants *a* = 8.515 Å [JCPDS 00-073-1964]. This X-ray diffraction pattern indicates the purity of the nano-catalyst prepared following this present method. The (hkl) values corresponding to MnFe₂O₄ phase are also shown in fig. 1. The grain size of the crystallites in the doped specimens was estimated from the broadening of the most intense diffraction line for MnFe₂O₄ by using Debye-Scherrer formula. The particle size as obtained from XRD pattern is ~50 nm.



Figure 1 X-ray diffraction patterns of the MnFe₂O₄ nanoparticles.

TEM analysis. The microstructure of the catalyst was observed under Transmission Electron Microscope (TEM, Philips, Model-CM12). The typical TEM image shown in figure 2(a) reveals that the average size of $MnFe_2O_4$ nanocrystal is in the range 50-100 nm. Thus the results from the analysis of both XRD and TEM data support the creation of nanoscale regions of ferrites. For investigation under TEM, the powder samples were dispersed in an acetone medium by ultrasonic vibrator. The dispersed samples were placed drop-wise on a carbon coated Cu grid. After drying for a few hours, these grids were placed inside the TEM.



Figure 2 (a) Bright field Transmission Electron Micrographs and (b) EDAX obtained by HRTEM of MnFe₂O₄ nanoparticles.

EDAX analysis. The nano-grains were chemically analyzed with Energy Dispersive Absorption (EDAX) spectra. To investigate the chemical composition of the catalyst, EDAX by High Resolution Transmission Electron Microscope was carried out. Figure 2(b) shows a typical EDAX pattern of the catalyst. The matrix of the EDAX shows strong Mn, Fe and O peaks. No trace of other element is evident. The molar ratios of Mn : Fe : O is 1 : 1.75 : 3.27. This is almost in accordance with the theory formula of MnFe₂O₄. Slight deviation from formula ratio arises due to the existence of small amount of secondary phase of FeMnO₃ as evidenced from XRD analysis.

VSM analysis. Magnetic measurements were carried out at room temperature using a Vibrating Sample Magnetometer (VSM), Lakeshore. The magnetic hysteresis loops of MnFe₂O₄ nanoparticles treated at 900 °C were characterized by VSM as shown in the fig. 3(a) and the maximum applied magnetic field is 20000 G. The samples were measured at room temperature and the measured magnetization was divided by the total mass of the samples. At room temperature the, samples showed symmetric hysteresis curves. The coercive fields (H_c) and saturation magnetizations (M_s) were calculated from the curves. The MnFe₂O₄ nanoparticles possess saturation magnetization of 30.03 emu/g and coercivity of 168 (–193) G. At 900 °C calcinations temperature, the MnFe₂O₄ sample may be characterized as a mixture of normal and inverse spinel ferrite.² The interactions between the A and B sub-lattices in the spinel lattice system (AB₂O₄) consist of two fundamental process: (i) inter-sub-lattice (A-B) super-exchange interactions (ii) intra-sub-lattice (A-A) and (B-B) exchange interactions. The magnetic interactions. In a

mixed spinel structure of $MnFe_2O_4$,³ Mn^{2+} and Fe^{3+} ions coexist in the two sublattices. At higher calcination temperature, the occupation ratio of Fe^{3+} ions at the octahedral sites decreases and hence net magnetic moment increases.⁴ The spin disorder may occur on the surface of the $MnFe_2O_4$ nanoparticles due to vacant sub-lattice disorder sites and poor crystal structure.⁵ The values of saturation magnetization of our sample are lower than those reported for the bulk $MnFe_2O_4$ (80 emu/g).⁶ Such behaviour is ascribed to the surface effects in nanoparticles. The surface effect may be developed due to the existence of an inactive magnetic layer or a disordered layer on the surface of nanoparticles and/or the heating rate of calcinations.



Figure 3: (a) The magnetic hysteresis loops of of MnFe₂O₄ nanoparticles at room temperature. (b) Magnetic separation of the prepared MnFe₂O₄ nano-material by an external magnet

References

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