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Supplementary Information

β-Cyclodextrin Coated Fe_3O_4 Nanoparticles: a Simple Preparation and Application for Selective Oxidation of Alcohols in Water

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Experimental

Ethanol and acetone used in the work were previously distilled. The other organic compounds of analytical grade were obtained from commercial sources and used without further treatment. Catalysts were characterized by IR spectroscopy recorded on NICOLET NEXUS870. Raman spectra were recorded on JY HR800. XRF was detected by ARL-9800. TEM images were taken by JEM-2100. Thermogravimetric analysis (TGA) was performed on TGA/SDTA851e under N_2 atmosphere from 50 to 800 °C, with a heating rate of 20 °C *per* min and an air flowing rate of 30 mL *per* min. Products were identified using a 6820 gas chromatograph (GC) with an Agilent Technologies HP-Innowax (30 m × 0.32 mm × 0.5 μm). XRD data were collected with Cu_{Ka} radiation on Bruker C8 ADVANCE.

The Fe_3O_4/SiO_2 coated β-CD was synthesized according to the method proposed by Ghosh (reference 25 in paper) with some modifications.

General procedure for the synthesis of bare magnetic nanoparticles (bare MNPs)

A Nanosized magnetic particles were synthesized by chemical coprecipitation method[1] under alkaline condition. To a solution of $FeCl_2$ (0.86 g) and $FeCl_3$ (2.35 g) in 40 mL ultrapure water, aqueous ammonia (25%, 40 mL) was added slowly over 20 min to the mixture under N_2 atmosphere at 80 °C and the reaction was continued for another 30 min with mechanical stirrer. Fe_3O_4 nanoparticles were separated by external magnet and washed three times with deionized water and ethanol. The final product was obtained after drying under vacuum.

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General procedure for the synthesis of silica coated magnetic nanoparticles (Fe_3O_4/SiO_2 SMNPs)

The procedure of silica coating follows a method reported in the literature.[2] An amount of 1g of the synthesized Fe_3O_4 was suspended in 35 mL ethanol and 6 mL deionized water and sonication for 15 min was carried out to maintain proper dispersion. Tetraethyl orthosilicate (TEOS) (1.5 mL) was added slowly to the mixture and sonicated for another 10 min. Then aqueous ammonia (10%, 1.4 mL) was added slowly over 10 min under mechanical stirrer. The reaction was allowed to proceed at 40 °C for 12 h.

General procedure for the synthesis of carboxymethyl–β-cyclodextrin (CM–β-CD)

A derivative of β-CD, carboxymethyl–β-CD (CM–β-CD) was prepared according to a method reported in the literature.[3] Briefly, a mixture of β-CD (5.675 g, 5 mmol) and sodium hydroxide (5 g, 0.125 mol) in 20 mL of distilled water was treated with 0.4725 g (5 mmol) of chloroacetic acid at 50 °C for 5 h. After neutralization, the obtained product was precipitated with excess amount of acetone and dried at 40 °C under vacuum.

General procedure for the synthesis of Fe_3O_4/SiO_2 MNPs Coated CM–β-CD (Fe_3O_4/SiO_2/CM–β-CD)

Grafting of CM–β-CD on Fe_3O_4/SiO_2 MNPs was done via modified carbodiimide activation method.[4] Dry Fe_3O_4/SiO_2 MNPs (1 g) were mixed with 20 mL sodium phosphate buffer (0.003 mol L^{-1}, pH ca. 6) and sonicated for 15 min. Then 125 mg of cyanamide was dissolved in 5 mL of the same buffer solution and added to the previous mixture. Further sonication was done for another 15 min and finally 25 mL of CM–β-CD solution (50 mg *per* mL

in same buffer solution) was added and the reaction was continued for 2 h. The final product of CM−β-CD coated magnetic silica nanoparticles (Fe_3O_4/SiO_2/CM−β-CD MNPs) were washed several times with sodium phosphate buffer. Some of the synthesized particles were dried under vacuum at 60 °C. The quality of Fe_3O_4/SiO_2/CM−β-CD was 1.15 g on average of 5 times experiments, and the fluctuation was no more than 3%.

General procedure for the oxidation reaction

Fe_3O_4/SiO_2 MNPs coated CM−β-CD (1 mmol) was dissolved in deionized water (25 mL) and sonicated for 15 min. To the mixture was added alcohol (1mmol) at 50 °C, followed by the addition of NaOCl (10%, 5 mL) dropwisely over 20 min. When the reaction was finished, the mixture was extracted by ethyl acetate and dried over anhydrous sodium sulfate. Then ethyl acetate was removed in vacuum. The crude product was analyzed by GC.

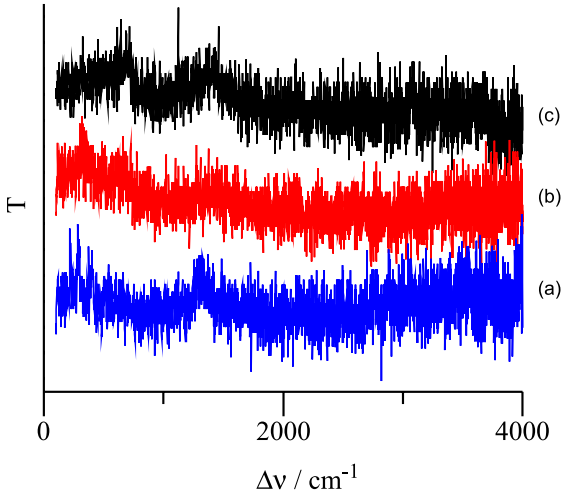

Figure S1. Raman spectrum of (a) Fe_3O_4; (b) Fe_3O_4/SiO_2 MNPs and (c) Fe_3O_4/SiO_2/CM−β-CD MNPs.

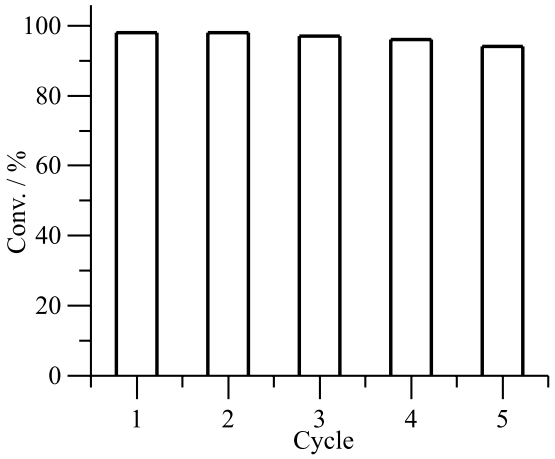

Figure S2. Recycling study of Fe_3O_4/SiO_2/CM−β-CD MNPs.

Table S1. XRF analyze of Fe_3O_4/SiO_2/CM−β-CD MNPs (wt.%)

Items	contents	Items	contents
Fe_2O_3	50.16	Al_2O_3	0.082
SiO_2	47.54	CaO	0.063
Na_2O	1.24	ZnO	0.040
P_2O_5	0.54	PbO	0.039
Cl	0.17	Cr_2O_3	0.015
MnO	0.12		

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