Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary information

Facile synthesis of Fe_3O_4 nanoparticles on metal organic framework MIL-101(Cr): characterization and its catalytic activity

Mrinal Saikia[a,b], Diganta Bhuyan[a] and Lakshi Saikia*[a,b]

[a] Materials Science Division, CSIR-North East Institute of Science and Technology, Jorhat, Assam, India. Fax: +91 0376 2370011; Tel: +91 0376 2370081; E-mail: lakshi_saikia@yahoo.com

[b]Academy of Scientific and Innovative Research, New Delhi, India

Table of contents

Experimental procedure

Chemicals

Cr $(NO_3)_3.9H_2O$, terephthalic acid, $FeCl_3$, $Fecl_2.4H_2O$, Fe_3O_4 were purchased from Sigma-Aldrich, USA. C_2H_5OH, HF, NH_3, DMF were purchased from Merck, Germany. All the chemicals are used without any further purification.

Synthesis of MIL-101(C r)

MIL-101 was prepared according to the reported method by Férey et al. involving hydrothermal treatment of a mixture of 3mmol of $Cr(NO_3)_3{\cdot}9H_2O$, 3mmol of terephthalic acid (H_2bdc) and 0.6ml of 5M HF (3mmol) in 15ml H_2O at 220 ^{0}C for 8h in a Teflon-lined autoclave bomb. After equilibration at ambient temperature, the resulting Cr-MIL-101 solid was filtered to remove the unreacted colourless crystals of H_2bdc and purified by double treatment with DMF at 60 ^{0}C for 3h and then triple treatment with ethanol at 70^{0}C for 2.5h. Finally the green solid was separated by centrifugation, dried in an air oven at 70^{0}C overnight and kept it in a vacuum desiccator.

Synthesis of Fe_3O_4@MIL-101(Cr)

The nanocomposite was synthesized by adding 1mmol of $FeCl_2.4H_2O$ and 2 mmol $FeCl_3$ to an aqueous suspension (100ml) containing 0.5g of MIL-101. The suspension was then vigorously stirred and degassed with nitrogen for 1h, followed by addition of NH_3 solution (15ml) to form black suspension. The resulting black solid was filtered off, repeatedly washed with double distilled water until the P^H becomes neutral. After air dried the composite was designated as Fe_3O_4@MIL-101. The Fe content (20wt %) in the composite has been calculated from ICP-AES technique.

General procedure for Fe_3O_4@MIL-101 (Cr) catalyzed oxidation reaction of benzyl alcohol

40 mg Fe_3O_4@MIL-101 nanocomposite was added to a mixture of 1mmol of benzyl alcohol, 4mmol of *tert*-butyl hydroperoxide (TBHP, 70%). The reaction mixture was subsequently heated at 70^{0}C in a round bottom flask for 12h under solvent free condition. After completion of the reaction the catalyst was separated from the reaction mixture with the help of a magnet. The resulting mixture was analyzed by GC.

Characterization

Wide angle powder x-ray diffraction (PXRD) was performed on Rigaku, Ultima IV X-ray diffractometer from using Cu-Kα source (λ = 1.54 Å). Low angle PXRD measurement was carried out on Philips X//Pert PRO X-ray diffractometer. Thermal analysis was carried out with TA SDT Q600 machine. Specific surface area, pore volume, average pore diameter were measured with the Autosorb-1 (Quantachrome, USA). Field-emission scanning electron microscopy (FESEM, Hitachi S-4800) was applied to investigate the size and morphology of

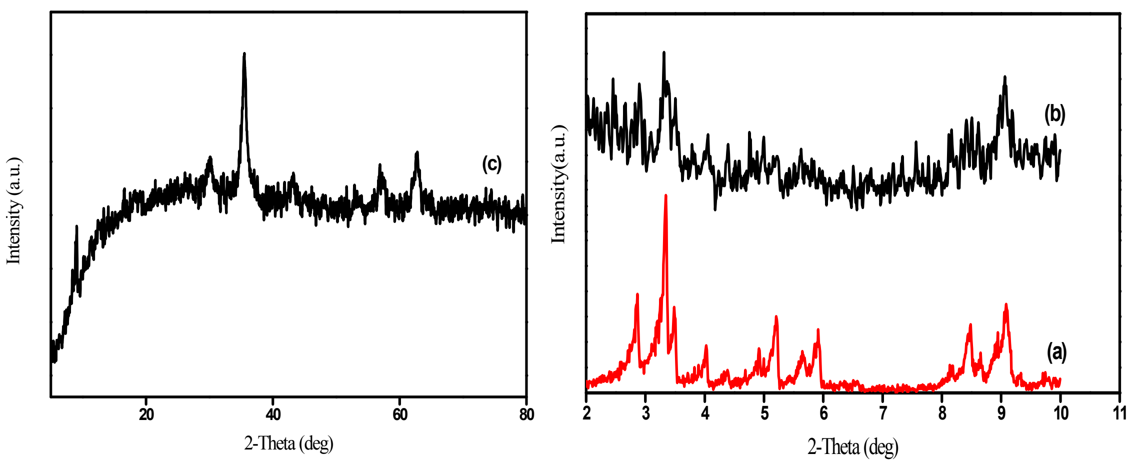

Fig. S1 PXRD patterns of (a) low angle PXRD pattern of MIL-101(Cr), (b) low angle PXRD pattern of Fe_3O_4@MIL-101(Cr), (c) wide angle PXRD pattern of Fe_3O_4@MIL-101(Cr) the sample and EDS mapping was done in Oxford XMax 20 equipment. Field–dependent magnetization of the samples was measured in ADE MAGNETICS instrument. The Fe content of the composite was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using Perkin Elmer, OPTIMA 2000 instrument. FT- IR spectra (4000–400 cm^{-1}) were recorded on KBr discs in a Perkin–Elmer system 2000 FT-IR spectrophotometer. The XPS analysis of the samples was carried out on a VG Microtech Multilab ESCA 3000.

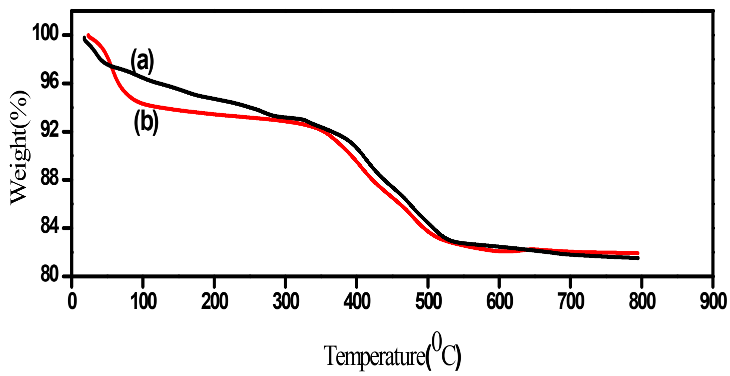

Fig. S2 Thermogravimetric curves of (a) MIL-101(Cr), (b) Fe_3O_4@MIL-101 (Cr)

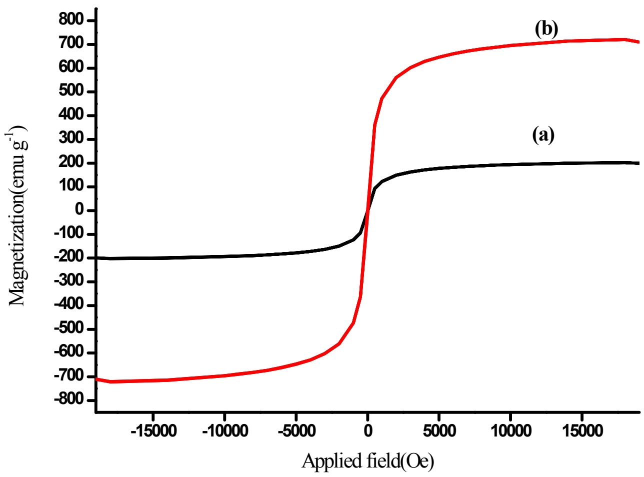

Fig. S3 Magnetization curve for (a) Fe_3O_4@MIL-101 (Cr), (b) Fe_3O_4

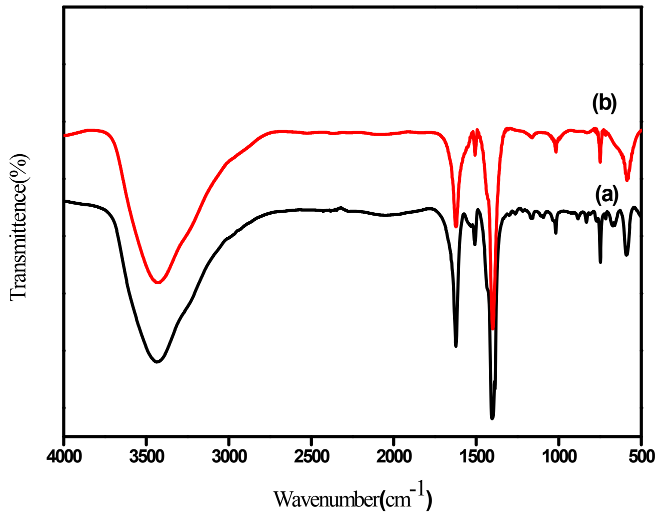

Fig. S4 FT-IR Spectra of (a) MIL-101(Cr), (b) Fe_3O_4@MIL-101(Cr)

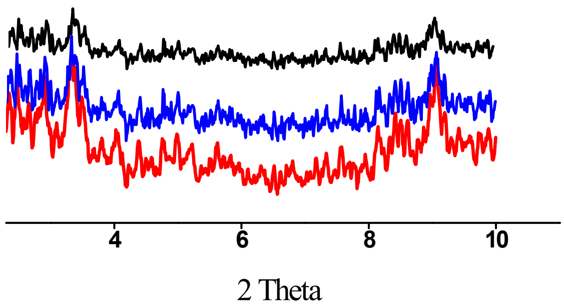

Fig. S5 Low angle PXRD pattern of recovered catalyst. Red, first cycle; blue, second cycle; black, third cycle

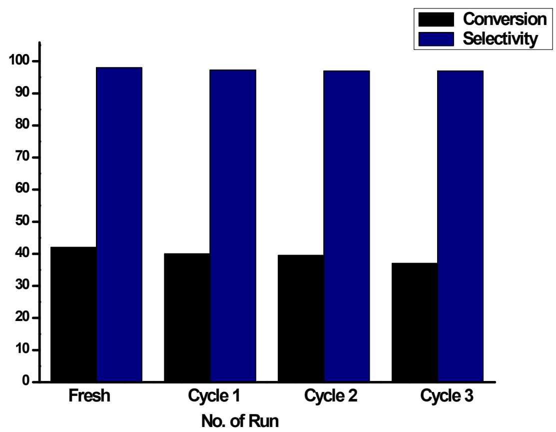

Fig. S6 Catalyst recycling tests for Fe_3O_4@MIL-101

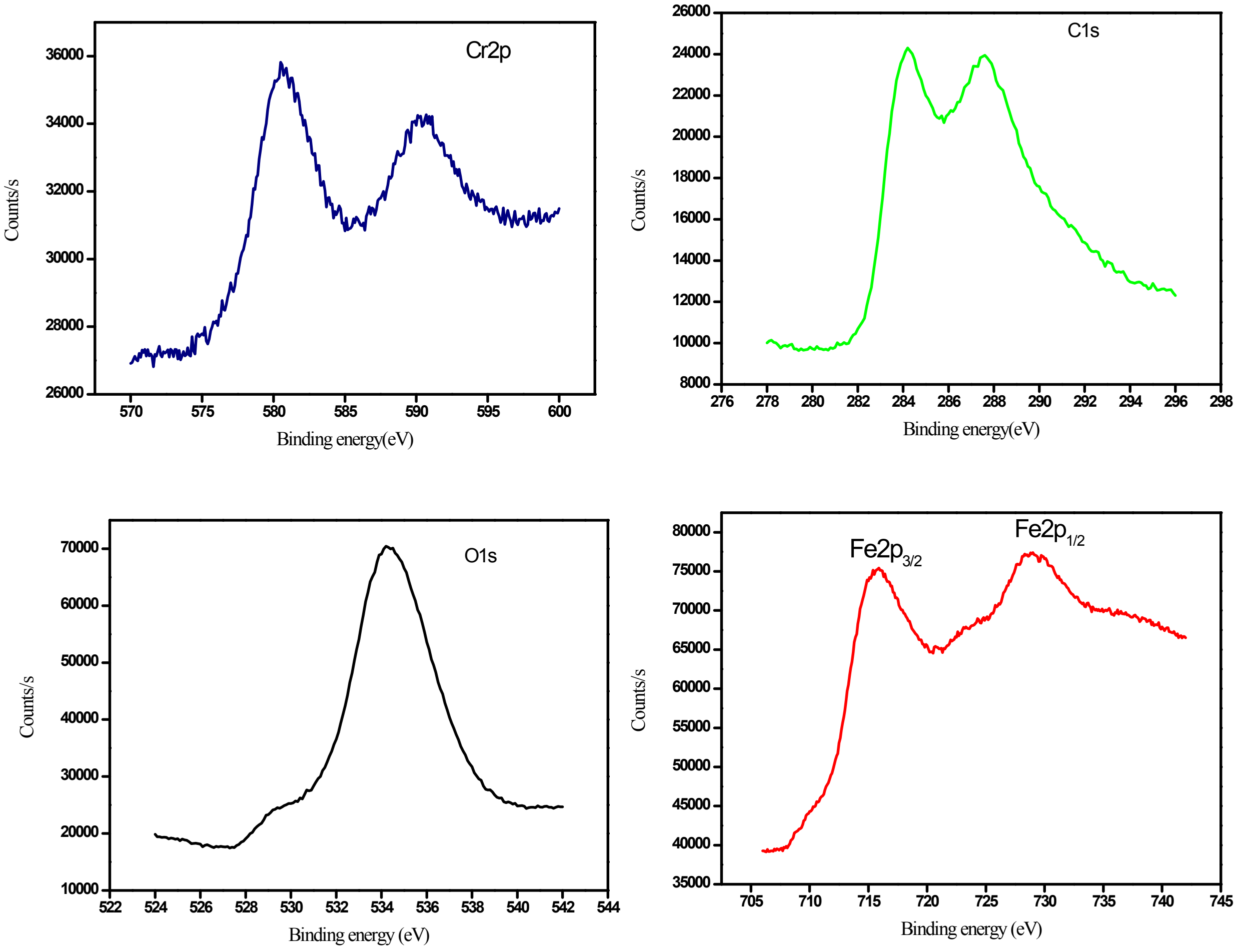

Fig. S7 XPS spectra of elements in Fe_3O_4@MIL-101(Cr), Chromium (blue), Carbon (green), Iron (red) and Oxygen (black)

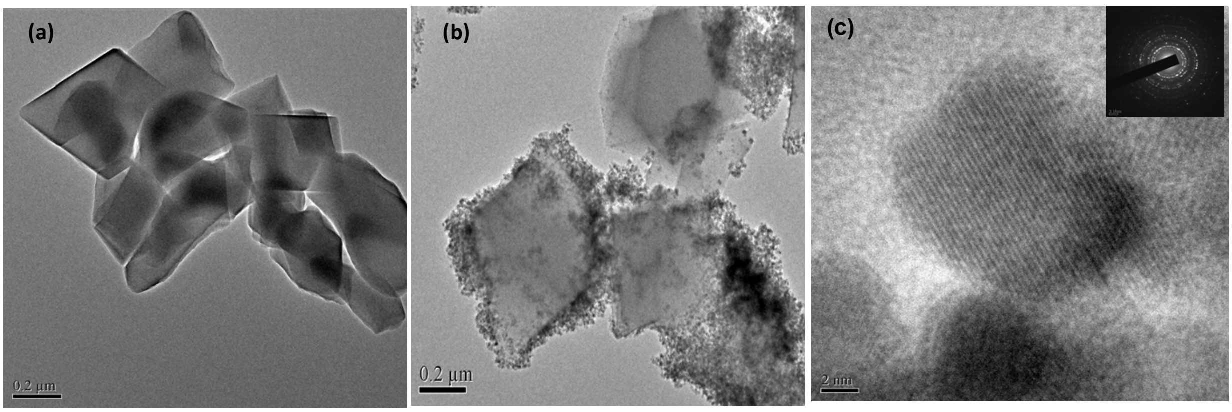

Fig. S8: TEM of (a)MIL-101(Cr), (b) Fe_3O_4@MIL-101(Cr) and (c) Individual Fe_3O_4 with SAED pattern

Table S1: [a]Performance of different catalyst in the oxidation of benzyl alcohol to benzaldehyde in presence of TBHP under solvent free condition

Entry	Catalyst[a]	Conversion (%)	Selectivity (%)
1	Au/CoO_x	34.0	85.2
2	Au/CaO	40.8	85.9
3	Au/Fe_2O_3	29.6	88.7
4	Mg–Al–HT[b]	20.2	99.3
5	Mg–Fe–LDH[c]	19.4	97.7
6[d]	Fe_3O_4@MIL-101(Cr)	44	98

[b]HT=hydrotalcite phase

[c]LDH= layered double hydroxides

[d]Present study

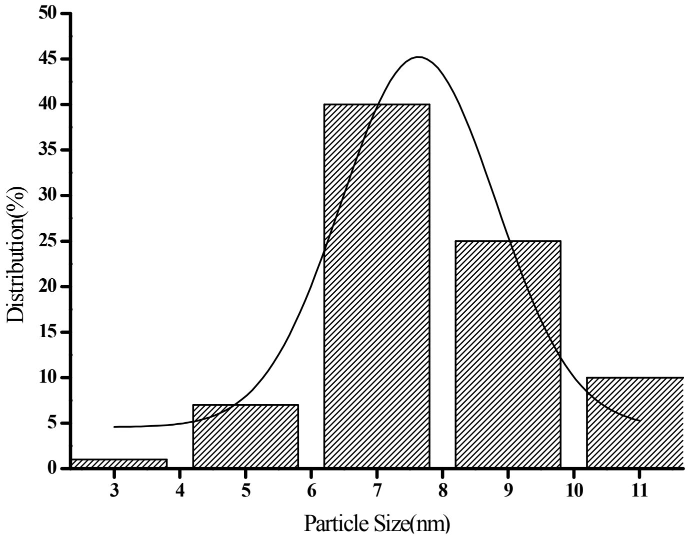

Fig. S9: Distribution and size of magnetite nanoparticles on MIL-101(Cr)