CHAPTER 2

EXPERIMENTAL

2.1 SYNTHESIS OF MESOPOROUS MATERIALS

The catalytic materials, used in the present study, were synthesised as per the procedure given below,

2.1.1 Materials

Chemicals such as sodium metasilicate, aluminium sulphate, ferric nitrate, cetyltrimethylammonium bromide (structure directing agent) and sulphuric acid, were purchased from E-Merck for the synthesis of mesoporous MCM-41 molecular sieves. Ethylenediaminetetraacetic acid (EDTA) disodium salt, citric acid monohydrate and oxalic acid dihydrate, and hydrogen peroxide (6%), purchased from E-Merck were used as organic contaminants and oxidant respectively. Activated charcoal and Hβ zeolite were purchased from E-Merck and United Catalysts India Ltd respectively and were used as commercial adsorbents for adsorption studies. The glassware used in all the experiments were made of Schott Duran.

2.1.2 Synthesis of Al-MCM-41

The synthesis of mesoporous Al-MCM-41 (25, 50, 75 and 100) molecular sieves was carried out using the gel composition of SiO₂ : 0.2 CTAB : X Al₂O₃ : 0.89 H₂SO₄ : 120 H₂O (X varies with the Si/Al ratio) by
hydrothermal method. Sodium metasilicate and aluminium sulphate were used as the source for silicon and aluminium respectively. Cetyltrimethyl ammonium bromide was used as the structure-directing agent.

In a typical synthesis, 10.6 g of sodium silicate nanohydrate dissolved in 40 ml of demineralised water was combined with the appropriate amount of aluminum sulphate dissolved in 8 ml of demineralised water. The mixture was then acidified with 1M H$_2$SO$_4$ to bring down the pH to 10.5 under vigorous stirring. After 30 minutes of stirring, an aqueous solution of cetyltrimethylammonium bromide (CTAB), which was dissolved in 13 ml of demineralised water, was added and the surfactant silicate mixture was stirred for a further period of 120 minutes at room temperature. The resultant gel was autoclaved and heated for 48 h at 145 °C. The solid obtained was filtered and dried at 100 °C. The sample was then calcined at 525 °C in air for 5 h in a muffle furnace to expel the template.

2.1.3 Synthesis of Si-MCM-41

Si-MCM-41 was also synthesised by using the above mentioned procedure without aluminium source using the gel composition of SiO$_2$ : 0.2 CTAB : 0.89 H$_2$SO$_4$ : 120 H$_2$O.

2.1.4 Synthesis of Fe-MCM-41

Fe-MCM-41 (Si/Fe = 32, 55, 79 and 106) was synthesised by the above given procedure using ferric nitrate as iron source.

2.1.5 Zeolite-Hβ

The H form of commercial zeolite-β with Si/Al=15 was purchased from United Catalyst India Ltd. The surface area, pore size and pore volume of the catalyst were 583 m$^2$g$^{-1}$, 0.7 × 0.64 Å and 0.2250 cm$^3$g$^{-1}$ respectively.
2.1.5 Activated Charcoal

Activated charcoal was purchased from E-Merck. The surface area and pore volume of the catalyst were 775 m$^2$g$^{-1}$ and 0.4580 cm$^3$g$^{-1}$ respectively.

2.2 TECHNIQUES USED FOR CHARACTERISING MESOPOROUS MATERIALS

The physico-chemical characterisation of catalysts was carried out by various instrumental methods to establish the mesostructure, high surface area, and morphology and co-ordination environment of the metal containing mesoporous materials.

2.2.1 Elemental Analysis

The aluminium and the iron content in Al-MCM-41 and Fe-MCM-41 respectively was determined using ICP-AES with Allied Analytical ICAP 9000. The concentrations of elements were determined by dissolving the catalysts in hydrofluoric acid.

2.2.2 X-Ray Diffraction

The XRD powder diffraction patterns of the calcined mesoporous MCM-41 molecular sieves were obtained with a Stereoscan diffractometer using nickel-filtered CuKα radiation ($\lambda = 1.54 \text{ Å}$) and a liquid nitrogen cooled germanium solid–state detector. The diffractograms were recorded in the 2θ range of 0 -10° in the steps of 0.02° with a count time of 15 s at each point for MCM-41 molecular sieves.
2.2.3 Nitrogen Adsorption Studies

Surface area, pore volume and pore size distribution were measured by nitrogen adsorption at 77K using an ASAP-2010 porosimeter from Micromeritics Corporation, GA. The samples were degassed at 623 K and 10^{-5} torr overnight prior to the adsorption experiments. The mesopore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.4 by assuming that all the mesopores were filled with condensed nitrogen in the normal liquid state. The surface area was calculated using a multipoint Brunauer-Emmett-Teller (BET) model. Pore size distribution was estimated using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP-2010) available as built-in software from Micromeritics and the total pore volume was estimated at a relative pressure of 0.99, assuming full surface saturation with nitrogen.

2.2.4 Fourier Transform Infrared Spectroscopy

Mid-infrared spectra of the catalysts were recorded on a Nicolet (Avatar 360) instrument by KBr pellet technique. About 4 mg of the sample was ground with 200 mg of the spectrochemical grade KBr to form a mixture, which was then made into a pellet using a hydraulic press (under a pressure of 5 ton/ cm^2) into a self-supported wafer of 13 mm diameter. This pellet was used to record the infrared spectra in the range 4000-400 cm^{-1}.

2.2.5 ²⁹Si MAS-NMR

²⁹Si MAS-NMR spectra were recorded using a DRX-500 FT-NMR spectrometer at a frequency of 59.64 MHz, having spinning speed of 8 KHz, pulse length of 2.50 _s (45° pulse), delay time of 10 s, and spectral width of 335 ppm. Two thousand scans were acquired with reference to the trimethylsilylpropene sulfonic acid (TSP).
2.2.6  $^{27}$Al MAS-NMR

Solid-state $^{27}$Al MAS-NMR spectra were recorded at a frequency of 104.22 MHz, spinning rate of 8 KHz, a pulse length of 1.0 s, delay time of 0.2 s, and a spectral width of 330 ppm. The total scans were 150 and the line broadening was 50 Hz. The $^{27}$Al chemical shifts were reported in relation to the solution of aluminum nitrate.

2.2.7  Diffuse Reflectance UV-Visible Spectroscopy

The co-ordination environment of Fe in Fe-MCM-41 samples was examined by diffuse reflectance UV-Visible spectroscopy. The spectra were recorded from a Shimadzu, UV-Visible spectrophotometer (Model 2101 PC) in the wavelength range of 200 to 400 nm.

2.2.8  Electron Paramagnetic Resonance Spectroscopy

The co-ordination environment of Fe in Fe-MCM-41 samples was further confirmed by the EPR analysis recorded on a JEOL EPR spectrometer (JES-REIXM) operating in the X-band region. The microwave power employed was 3.0 mW and the amplitude of magnetic field modulation at 100 kHz was 0.03 mT. All the readings were taken at room temperature. 40 mg of the sample, taken in a quartz tube with 4mm outer diameter, was evacuated to $10^{-5}$ torr. The tube was then sealed under vacuum and then set in the quartz Dewar vessel fitted in the EPR cavity. Diphenylpicrylhydrazene (DPPH) (g=2.0037) was used as a reference to get the g value.

2.2.9  Scanning Electron Microscopy

The size and morphology of the mesoporous MCM-41 molecular sieves samples were examined by the scanning electron microscope of model JEOL 640. Samples were gold coated using an Instrumental Scientific Instrument PS-2 coating unit. The SEM pictures were developed on a thin photographic paper.
2.2.10 Transmission Electron Microscopy (TEM)

TEM was performed using a Philips CM 30 ST electron microscope operated at 300 kV. Samples for TEM were prepared by placing droplets of a suspension of the sample in methanol on a polymer micro grid supported on a Cu grid. Melting points were determined using a WRS-1 digital melting point apparatus in open capillaries.

2.3 ANALYSIS OF ORGANIC CONTAMINANTS

The following instruments/equipments were used for the analytical work.

2.3.1 pH Meter

The pH of the solution was measured using a calibrated pH meter (ELICO, model – LI 120 with electrode).

2.3.2 High Performance Liquid Chromatography (HPLC)

The concentration of the organic contaminants were determined by HPLC (Reversed phase ion-pair liquid chromatography, Model – Perkin Elmer Series 200, SPHERI-5, RP-18 column, Isocratic elution)

2.3.3 Total Organic Carbon (TOC) Analyser

Total Organic Carbon (TOC) of the samples were analysed using SHIMADZU, TOC-V CPN analyser by a Non-Purgeable Organic Carbon method through catalytic oxidation at 680 ºC. Zero air gas was used as carrier gas to carry the sample to furnace and was heated upto 680 ºC in the presence of platinum catalyst. The resulting CO₂ was detected by a Non-Dispersive Infrared Detector.
2.4 ADSORPTION STUDIES

2.4.1 Experimental Procedure

Mesoporous Al-MCM-41 with various ratios (Si/Al = 25, 50, 75 and 100), Si-MCM-41 molecular sieves, microporous Hβ zeolite and microporous and mesoporous activated charcoal were used as adsorbents, whereas EDTA, citric acid and oxalic acid were used as adsorbates. All the adsorbents were ground into small particle size and were kept at 125 °C for 3 h in oven to expel the water molecules present in the adsorbent and stored in desiccator to attain room temperature. The particle size of the Al-MCM-41 was in the range of 5 – 7.5 micron.

Batch adsorption experiments were carried out by shaking 0.5g of the adsorbent with 100ml of the aqueous solution of organic contaminant, which was prepared by dissolving with distilled water, at different concentration ranging from 100 – 900 ppm in glass stoppered conical flask of 250ml capacity at the speed of 200 RPM (Revolution Per Minute) in agitator (Mechanical shaker) for equilibrium time at room temperature (30 – 32 ºC). At different intervals of time, the samples were drawn out from flask and centrifuged. The supernatant solutions were analysed by Reversed–phase ion-pair high performance liquid chromatography

2.4.2 Analytical Procedure

2.4.2.1 Analysis of EDTA

The concentration of EDTA in the supernatant solution was determined by HPLC (Reversed phase ion-pair liquid chromatography, model – Perkin Elmer Series 200, SPHERI-5, RP-18 column, Isocratic elution, flow rate = 1.5 ml/min, detector wavelength = 254 nm) as per the literature procedure (Bergers and de Groot 1994). The mobile phase was prepared by dissolving 2.5 g water free sodium acetate in approx. 800 ml water. The pH
was adjusted to 4.0 by adding acetic acid. After adding 20 ml tetrabutyl ammonium hydroxide (20% aqueous solution), the final volume was adjusted to 1 litre with water.

The $\text{Fe}^{3+}$ solution was added to the supernatant solution. Iron (III) chloride solution (1.75 g/l) was prepared by dissolving 175 mg iron (III) chloride hexahydrate in 30 ml glacial acetic acid and subsequently diluting it with water to a final volume of 100ml. Quantitation of EDTA was determined based on its peak area measurements. The retention time of EDTA was found to be around 5.2 min.

**2.4.2.2 Analysis of Citric acid and Oxalic acid**

The concentration of citric acid and oxalic acid in supernatant solution was determined by HPLC (Reversed phase ion-pair liquid chromatography, model – Perkin Elmer Series 200, SPHERI-5, RP-18 column, Isocratic elution, mobile phase = water ($(\text{H}_3\text{PO}_4) = 6 \times 10^{-3} \text{ mol/L}, \text{pH} = 2.10 – 2.15$), flow rate = 1ml/min, detector wavelength = 210 nm) as per the procedure reported in the literature (Kordis-Krapez et al 2001). Quantitation of citric acid and oxalic acid was determined based on their peak area measurements and their retention time was found to be 5.5 and 1.0 min respectively.

**2.5 OXIDATION STUDIES**

**2.5.1 Experimental Procedure**

Organic contaminants such as EDTA, citric acid and oxalic acid oxidation with hydrogen peroxide were carried out in a glass batch reactor of 100 ml capacity equipped with a condenser, stirrer, thermocouple etc., under air atmosphere using Fe-MCM-41 (Si/Fe=25, 50, 75 and 100) as catalyst. 50 ml (1 mM) of aqueous solution of organic contaminants was prepared by dissolving them in distilled water and brought to required pH with sulphuric
acid and then it was added to the reactor together with 0.2 g of the Fe-MCM-41 catalyst. Then the solution was heated up to the required temperature ranging from 30 – 70 °C. Required stoichiometric amount of H₂O₂ was also added to that mixture 17 mM, 9 mM and 1 mM of H₂O₂ was required to oxidise 1mM of EDTA, citric acid and oxalic acid as per stoichiometric calculation to oxidise the organic molecules completely to CO₂ and H₂O. At different intervals of time, the samples were drawn out from flask and one drop of hydrazine was also added to prevent H₂O₂ from reacting with organic substrates and centrifuged. Then the supernatant solution was analysed for total organic carbon using a TOC analyser.

2.5.2 Leaching Tests

Leaching tests were carried out in two ways. In the first method, the aim was to establish whether small amounts of the dissolved iron were responsible for the observed catalytic activity. After the wet oxidation with H₂O₂, the Fe-MCM-41 was filtered at the temperature of the catalytic tests, in order to prevent the possible readsorption of the leached iron during the cooling of the solution. Then, the substrate and H₂O₂ were added to the solution in the same concentrations as before the catalytic tests. Then the TOC of the substrate was measured at the same temperature of the catalytic tests as a function of time, but in the absence of the solid Fe-MCM-41. If dissolved iron ions were responsible for the catalytic behaviour, a reactivity similar to that shown in the presence of the Fe-MCM-41 would be expected.

The second method to check the potential of leaching of the iron from the Fe-MCM-41 involved analysis of the solution by ICP-AES. In this case also, the solid was filtrated at the temperature of the catalytic reaction, in order to prevent the possible readsorption. This method allowed direct determination of the presence of iron ions in solution.