CHAPTER 2

EXPERIMENTAL

2.1 CATALYST PREPARATION

The basic raw materials for the synthesis of zeolites are generally a silica source, an aluminium source, an organic quaternary ammonium salt either in the form of hydroxide or halide and inorganic bases like sodium hydroxide or potassium hydroxide depending on the choice of the zeolite to be synthesised. They are synthesised normally in a stainless steel autoclave under autogeneous pressure. In as-synthesised zeolites, the negative charge of the aluminium substituted framework is compensated by means of alkali metal cations or organic template cations. These zeolites do not exhibit Bronsted acidity. Bronsted acidity is generated upon removal of organic cations by calcination and by ion-exchange of the alkali metal cations by protons, or NH$_4^+$ or di- or trivalent cations either by liquid or solid state ion exchange followed by calcination.

2.1.1 Preparation of H-form of Zeolites

The Na-form of zeolite beta (Si/Al=15) and ZSM-5 (Si/Al=53) were obtained from Sud-Chemie India Ltd. and converted them into H-form by the following procedure: Na-form of zeolite and 1 M NH$_4$NO$_3$ solution (15 ml per gram of zeolite) were placed in a RB flask fitted with an air condenser. The slurry was stirred magnetically at 80°C for 24 h. Then the material was filtered under suction and washed with distilled water. The filtered material was dried at 120°C for 6 h. The dried material was once again treated with 1 M NH$_4$NO$_3$ by adopting the same procedure. This cycle was repeated
thrice in order to achieve the maximum removal of Na⁺ ions. The NH₄⁺-form of zeolites thus obtained were then converted into H-form by calcination in air at 550°C for 6 h. The H-form of zeolite Y (Si/Al=3) was also obtained from Süd-Chemie India Ltd. This catalyst was ion-exchanged once with 1 M NH₄NO₃ solution and again converted into H-form by following the same procedure adopted for Na-form of beta and ZSM-5 zeolites.

2.1.2 Preparation of Metal Ion-exchanged Zeolites

Zn²⁺ and Fe³⁺ containing Y and beta zeolites were obtained by ion-exchanging NH₄⁺-form of the zeolites Y and beta with 0.1 N zinc acetate (Merck, India) and ferric nitrate (Merck, Germany) solutions respectively. Zeolite and the metal ion solution (15 ml per gram of zeolite) were stirred magnetically in a RB flask at 80°C for 6 h and then the material was filtered, washed thoroughly with distilled water and dried at 120°C for 4 h. The ion-exchange process was repeated twice and then the catalysts were calcined at 550°C in dry air for 6 h. In the similar way Cs⁺ ion-exchanged beta zeolite was prepared by ion-exchanging H-beta zeolite with 0.1 N cesium nitrate (Merck, Germany) solution.

2.1.3 Dealumination of Zeolites

Thermally dealuminated H-beta zeolite (HBDA) was obtained by calcination of the parent H-beta at 850°C for 8 h in a stream of air at a high rate of heating. Acid treated samples viz., HB0.1a, HB1a, HY0.1a, HY1a were obtained by stirring the parent H-beta and HY samples with 0.1 N and 1 N HCl (10 ml of acid per gram of catalyst) respectively for 24 h at room temperature. After treatment the materials were filtered, washed with distilled water and dried at 120°C for 4 h. By adopting similar method thermally dealuminated cum acid treated sample, HBDA0.1a was obtained by treating HBDA with 0.1 N HCl.
2.1.4 Surface Passivation

Surface-passivated zeolite beta (SPHB) was obtained by following the method described by Andy et al (2000). Zeolite H-beta (0.25 g) and 3 ml of hexane were stirred under argon atmosphere into which 0.1 ml tetraethyl orthosilicate (TEOS) (Merck, Germany) was added and continued the stirring for 3 h. Then the zeolite was filtered and washed with hexane. In this method, the surface of the zeolite is coated with silica (Kunkeler et al 1997).

2.1.5 Preparation of Sulphated Zirconia

The precursor Zr(OH)$_4$ was prepared by adding simultaneously ZrO(NO$_3$)$_2$ (CDH, India) solution and concentrated ammonia to water and vigorously stirred the contents in a beaker at a flow ratio in which the pH remain at 7 ± 0.5. Calcination of Zr(OH)$_4$ at 500°C for 4 h resulted ZrO$_2$. The ZrO$_2$ thus obtained was soaked in 1 N sulphuric acid (15 ml per gram of solid) for 2 h and filtered by suction through a fritted glass filter and dried at 150°C overnight. This material was then calcined at 580°C for 5 h (Farcasiu and Li 1995). The sulphated zirconia thus obtained was stored in a desiccator.

2.2 SYNTHESIS OF 4-PHENOXYBUTAN-2-ONE

Phenol (Merck, India) (8 g, 85.2 mmol) was placed in a double necked RB flask fitted with a reflux condenser and heated at 40°C by means of an oil bath equipped with a temperature controller. To this pyridine (Merck, India) (147 mg, 1.86 mmol) was added with constant stirring and the temperature was raised to 100°C. Then methyl vinyl ketone (Merck, Germany) (1.2 g, 17 mmol) was added dropwise and the mixture was stirred at the same temperature for 24 h. The reaction mixture was then dissolved in diethyl ether and the unreacted phenol was removed by repeated washing.
with 10% NaOH solution. The evaporation of the solvent left behind a brown oil which then subjected to column chromatography (silica gel 60-120 mesh, eluent hexane: ethyl acetate 95:5). The removal of solvent using a rotary evaporator left a colourless oil of 4-phenoxybutan-2-one (1.36 g, 49% yield).

2.3 SYNTHESIS OF (PHENYLTHIO)ACETALDEHYDE DIETHYLACETAL

The freshly cut and dried sodium pieces (11.5 g) were placed in a double necked RB flask fitted with a reflux condenser. Absolute ethanol (100 ml) was added to this slowly for an hour using a pressure equivalenting funnel and stirred magnetically until all the sodium pieces were dissolved. Thiophenol (Merck, Germany) (55.1 g, 0.5 mol) in 50 ml ethanol was added dropwise and stirred for 10 minutes followed by the addition of 7.5 g of sodium iodide (Merck, India). Then bromoacetaldehyde diethylacetal (Merck, Germany) (98.5 g, 0.5 mol) was added dropwise and the contents were refluxed for 6 h. The excess ethanol was distilled off and the residue was diluted with water and extracted with diethyl ether. The solvent was then evaporated and the product was distilled under reduced pressure (120-30°C/2 mm) (Yield = 82 g, 72.5%).

2.4 CHARACTERISATION OF CATALYSTS

The catalytic property of zeolites are entirely depends on their physicochemical properties. With to a view understand their textural and chemical properties of the prepared catalysts, XRD, BET surface area measurement, FTIR, in situ DRIFTS, ICP-AES, AAS and $^{27}$Al MAS-NMR spectroscopic techniques are inevitable.
2.4.1 X-ray Diffraction

X-ray diffraction patterns were collected on Siemens D5005 X-ray diffractometer using nickel filtered CuKα radiation (\(\lambda = 0.154 \text{ nm}\)). The samples were scanned in 2θ range 1-70° in steps of 0.01° with count time of 10 s at each point. The crystallinity of the zeolites was calculated on relative basis by comparing the area under the predominant peak of the parent zeolite with that of the modified zeolites (Veda Ramaswamy 2002).

2.4.2 Surface Area (BET) Measurement

Nitrogen adsorption and desorption isotherms were obtained using Quantachrome Autosorb 1 sorption analyser. Prior to the adsorption of nitrogen at 77 K, the samples were outgased for 3 h at 250°C under 10⁻⁵ mbar. Helium was the carrier gas and TCD was used as the detector. From the monolayer volume (\(V_m\)) of the adsorbed nitrogen, BET surface area was calculated. Micro pore volume of the samples was calculated by Dubinin-Radushkevich (DR) method (Ramaswamy 2002).

2.4.3 FTIR Spectroscopy

The changes due to the modification of zeolites can be seen by analysing the frame work vibrations. Hence frame work vibration spectra were recorded using Nicolet Avatar 360 FTIR spectrophotometer. The samples were diluted (7 times) with IR spectral grade KBr, ground well and made into pellets of 13 mm diameter and used for the analysis. The pellets were scanned 50 times at 4 cm⁻¹ resolution.

2.4.4 DRIFT Spectroscopy and Acidity Measurements

The acid properties of the catalysts were analysed by in situ DRIFTS-pyridine adsorption and desorption technique. Nicolet Avatar 360
FTIR spectrophotometer with provision for DRS analysis and equipped with a high temperature vacuum chamber was used for this purpose. The inlet of the chamber was connected to a flask containing pyridine through a shut down valve. The outlet of the chamber was connected to a high vacuum pump. Water was circulated around the chamber using a peristaltic pump to prevent over heating. The typical experimental procedure is as follows: About 10 mg of the well ground sample was taken in the sample holder and dehydrated at 500°C for 6 h under vacuum (10⁻⁵ mbar). The sample was then cooled to room temperature and the spectrum was recorded (600 scans, 4 cm⁻¹ resolution) in order to obtain the hydroxyl vibration bands. Then pyridine vapours were let into the chamber and allowed to equilibrate for 10 minutes. The physically adsorbed pyridine was removed by heating the sample at 110°C under vacuum (10⁻⁵ mbar) for 30 minutes. The material was then cooled to room temperature and the spectrum was recorded. In a similar manner the temperature was increased stepwise to 200, 300 and 400°C to desorb pyridine and the spectra were recorded at each temperature after cooling the sample to room temperature every time.

2.4.5 ²⁷Al MAS-NMR Spectroscopy

²⁷Al MAS-NMR spectra were recorded in order to ascertain the nature of aluminium present in the catalysts. The spectra were recorded on a Bruker DSX-300 solid state NMR spectrometer at 104.25 MHz. The spinning frequency was 3.5 KHz. Aluminium chloride was used as the external standard.

2.4.6 Chemical Analysis

The amount of Si, Al, Zn and Fe present in the catalysts were obtained by chemical analysis. About 0.5 g of the sample was weighed into a platinum crucible of known weight. The crucible was heated to red hot using electrical bunsen burner for 3 h to remove moisture content and
volatile matter. The exact weight of volatile and moisture free sample was noted. The sample was then treated with a mixture of 1 ml concentrated sulphuric acid and 10 ml hydrofluoric acid (40% solution) and evaporated to dryness. The treatment was repeated thrice. Silica was estimated from the loss of weight. The residue was dissolved in 1:1 mixture of con. HCl and con. HNO$_3$ and diluted with 250 ml water. The solution was analysed quantitatively for aluminium using an ARL 3410 ICP atomic emission spectrometer. The same solution was analysed for the amount of zinc and iron using Analytik Jena AAS-6 Vario atomic absorption spectrometer. Zinc and iron metal wire dissolved in 1:1 mixture of con. HCl and con. HNO$_3$ and diluted in distilled water was used as standards.

2.5 CHARACTERISATION OF 4-PHENOXYBUTAN-2-ONE AND (PHENYLTHIO)ACETALDEHYDE DIETHYLACETAL

The purity and mass spectra of the compounds were obtained by GC-MS analysis employing a Perkin Elmer auto system XL gas chromatograph (Perkin Elmer elite series PE-5 capillary column, 30 m x 0.25 mm x 1 µm) connected to a turbo mass spectrometer.

The FTIR spectra of the samples were recorded on a Nicolet Avatar 360 FTIR spectrophotometer. The neat liquids were pressed in between two KBr discs. The film thickness was maintained as 0.025 mm employing a teflon spacer. The samples were scanned 50 times at 4 cm$^{-1}$ resolution. The $^1$H NMR spectra of the samples were recorded on a Bruker DPX-200 NMR instrument using CDCl$_3$ as solvent and TMS as standard.

2.6 CATALYTIC STUDIES

The reactions were carried out in a 50 ml double necked round bottom flask fitted with a reflux condenser and equipped with a magnetic stirrer. The flask was heated by means of an oil bath fitted with a
temperature controller. All the catalysts were preactivated at 300°C for 3 h except sulphated zirconia.

2.6.1 Alkylation of Phenol

The known amount of catalyst was added to phenol (5.34 g, 56.7 mmol) at 40°C and then the mixture was stirred for 10 min. The temperature was raised to the desired value and then 11.3 mmol of 4-hydroxybutan-2-one (Lancaster, England) (1 g) or methyl vinyl ketone (Merck, Germany) (800 mg) was added dropwise. This reaction mixture was stirred at the same temperature for 48 h. Aliquots were withdrawn from the reaction mixture periodically and analysed using a gas chromatograph (Shimadzu GC-17A) equipped with a flame ionisation detector (DB-5 capillary column, 30 m x 0.25 mm x 0.25 μm). Nitrogen was used as the carrier gas. The product identification was carried out by comparing its retention time with that of the commercial sample of raspberry ketone or synthesised sample of 4-phenoxybutan-2-one. The product identification was also carried out using GC-MS (Perkin Elmer auto system XL gas chromatograph (Perkin Elmer elite series PE-5 capillary column, 30 m x 0.25 mm x 1 μm) connected to a turbo mass spectrometer. Raspberry ketone was separated from the reaction mixture by adopting the following procedure: After filtering the catalyst from the reaction mixture, phenol was distilled off using a rotary evaporator. Then the residue was dissolved in 20 ml diethyl ether. The filtered catalyst was washed with diethyl ether and the washings were combined with the ether solution of the residue. The combined ether solution was washed 4 times with 20 ml 10% NaOH solution, 5 ml each time. The NaOH extract was then neutralised with dil.HCl and extracted with diethyl ether. The ether extract was then subjected to column chromatography (silica gel 60-120 mesh, eluent:hexane:ethyl acetate 95:5). The removal of the solvent with a rotary evaporator gave light yellow needles of raspberry ketone.
2.6.2 Rearrangement of 4-Phenoxy-2-butanone

To 26.6 mmol of phenol or toluene, 0.5 g of the catalyst was added at 40°C with constant stirring magnetically. The temperature of the mixture was raised to 100°C and the mixture was then stirred for 15 min. To this, 4-phenoxybutan-2-one (400 mg, 2.44 mmol) was added and the mixture was stirred at the same temperature for 24 h. The products were analysed using gas chromatograph (Shimadzu GC-17A) equipped with a flame ionisation detector and DB-5 capillary column.

2.6.3 Cyclisation of (Phenylthio)acetaldehyde Diethylacetal

To the refluxing solution of (phenylthio)acetaldehyde diethylacetal (500 mg, 2.2 mmol) in 15 ml of solvent (chlorobenzene or 1,2-dichloroethane or dichloromethane), the catalyst was added and continued the heating for 4 h. Aliquots were withdrawn from the reaction mixture periodically and analysed using a gas chromatograph (Shimadzu GC-17A) equipped with a flame ionisation detector and DB-5 capillary column. The product identification was carried out by comparing the retention time of the commercial sample of benzo[b]thiophene and by GC-MS (Perkin Elmer auto system XL gas chromatograph (Perkin Elmer elite series PE-5 capillary column, 30 m x 0.25 mm x 1 μm) connected to a turbo mass spectrometer.)