2.1 MATERIALS AND METHODS

2.1.1 Materials

The chemicals required for the synthesis of MeAPO-5 (Me = Mg, Zn, Co and Mn) viz., aluminium isopropoxide, orthophosphoric acid (88%), magnesium acetate, zinc sulphate, cobalt nitrate and manganese acetate were used as the sources for Al, P, Mg, Zn, Co and Mn respectively. The precursors used in these studies were of Merck grade. Triethylamine (Merck) was used as the structure directing template. Other chemicals such as lanthanum nitrate (Fluka), cerium nitrate (Fluka), gallium nitrate (Aldrich) and indium nitrate (Aldrich) were used as the sources for the preparation of $\text{La}^{3+}$, $\text{Ce}^{3+}$, $\text{Ga}^{3+}$ or $\text{In}^{3+}$ ion-exchanged MeAPO-5 molecular sieves (where Me = Mg, Zn, Co and Mn). Salicylaldehyde (SRL), diethyl malonate (SRL), resorcinol (Merck), ethyl acetoacetate (Merck), ethylene glycol (Merck), anisole (Merck) and acetic anhydride (SRL) were used in the catalytic studies. All the chemicals were used as such without any further purification. All the glassware items used in the experiments were made of borosil.
2.2 SYNTHESIS OF METAL SUBSTITUTED AlPO-5 MOLECULAR SIEVES

2.2.1 Synthesis of MAPO-5

Magnesium substituted aluminophosphate (MAPO-5) was synthesised hydrothermally using the gel composition of 0.1MgO: 1TEA: 1Al\textsubscript{2}O\textsubscript{3}: 1P\textsubscript{2}O\textsubscript{5}: 40H\textsubscript{2}O. Aluminium isopropoxide (28.37 g) was soaked in distilled water (30 mL) for 24 h in a stainless steel autoclave (316 type) and stirred vigorously for 1 h using a mechanical stirrer. While stirring, magnesium acetate (1.48 g) dissolved in phosphoric acid (7.8 mL) and distilled water (20 mL) was added drop by drop and continued the stirring for additional 1 h. Then the template, triethylamine, (9.7 mL) was added drop wise to it and the pH of the gel was found to be 4.4. The autoclave was tightly closed and kept at 175 ºC under autogeneous pressure for 24 h. Then it was cooled to room temperature to obtain the solid product whose pH was found to 9.3. The product was washed several times with distilled water and dried in an air oven at 110 ºC for 12 h. It was then calcined at 550 ºC for 6 h under the flow of N\textsubscript{2} and O\textsubscript{2} for 7 h in an inert atmosphere to remove the template.

2.2.2 Synthesis of MnAPO-5

Manganese substituted aluminophosphate (MnAPO-5) was synthesised hydrothermally using the gel composition of 0.1MnO: 1TEA: 1Al\textsubscript{2}O\textsubscript{3}: 1P\textsubscript{2}O\textsubscript{5}: 40H\textsubscript{2}O. Aluminium isopropoxide (28.37 g) was soaked in distilled water (30 mL) for 24 h in a stainless steel autoclave (316 type) and stirred vigorously for 1 h using a mechanical stirrer. While stirring, manganese acetate (1.70 g) dissolved in phosphoric acid (7.8 mL) and distilled water (20 mL) was added drop by drop and continued the stirring for additional 1 h. Then the template, triethylamine (9.7 mL) was added drop
wise to it and the pH of the gel was found to be 4.2. The autoclave was tightly closed and kept at 175 °C under autogeneous pressure for 24 h. Then it was cooled to room temperature to obtain the solid product. The product was washed several times with distilled water and dried in an air oven at 110 °C for 12 h. It was then calcined at 550 °C for 6 h under the flow of N₂ and O₂ in an inert atmosphere for 7 h to remove the template.

### 2.2.3 Synthesis of ZAPO-5

Zinc substituted aluminophosphate (ZAPO-5) was synthesised hydrothermally using a gel composition of 0.1ZnO: 1TEA: 1Al₂O₃: 1P₂O₅: 40H₂O. Aluminium isopropoxide (28.37 g) was soaked in distilled water (30 mL) for 24 h in a stainless steel autoclave (316 type) and stirred vigorously for 1 h using a mechanical stirrer. While stirring, zinc sulphate (1.99 g) dissolved in phosphoric acid (7.8 mL) and distilled water (20 mL) was added drop by drop and continued the stirring for additional 1 h. Then the template, triethylamine (9.7 mL), was added drop wise to it and the pH of the gel was found to be 4.4. The autoclave was tightly closed and kept at 175 °C under autogeneous pressure for 24 h. Then it was cooled to room temperature to obtain the solid product whose pH was found to be 9.6. The product was washed several times with distilled water and dried in an air oven at 110 °C for 12 h. It was then calcined at 550 °C for 6 h under the flow of N₂ and O₂ in an inert atmosphere for 7 h to remove the template.

### 2.2.4 Synthesis of CoAPO-5

Cobalt substituted aluminophosphate (CoAPO-5) was synthesised hydrothermally using a gel composition of 0.1CoO: 1TEA: 1Al₂O₃: 1P₂O₅: 40H₂O. Aluminium isopropoxide (28.37 g) was soaked in distilled water (30 mL) for 24 h in a stainless steel autoclave (316 type) and stirred
vigorously for 1 h using a mechanical stirrer. While stirring, cobalt nitrate (2.01 g) dissolved in of phosphoric acid (7.8 mL) and distilled water (20 mL) was added drop by drop and continued the stirring for additional 1 h. Then the template, triethylamine (9.7 mL), was added drop wise to it and the pH of the gel was found to be 4.2. The autoclave was tightly closed and kept at 175 °C under autogeneous pressure for 24 h. Then it was cooled to room temperature to obtain the solid product whose pH was found to be 9.8. The product was washed several times with distilled water and dried in an air oven at 110 °C for 12 h. It was then calcined at 550 °C for 6 h under the flow of N₂ and O₂ for 7 h in an inert atmosphere to remove the template.

2.3 MODIFICATION OF MeAPO-5

2.3.1 Preparation of Lewis acid Metal Ion-exchanged MeAPO-5 Molecular Sieves

The calcined MeAPO-5 (Me = Mg, Zn, Co and Mn) molecular sieves were ion-exchanged with La³⁺, Ce³⁺, Ga³⁺ or In³⁺ using the respective metal nitrate as the source. The ion-exchange was carried out by wet method. About 2 g of calcined material was taken in a round bottom flask. The corresponding metal nitrate solution (30 mL, 0.1 M) was added to the flask. The solution was stirred for 12 h at 80 °C. The solid sample was filtered, washed thoroughly with distilled water to remove the excess metal nitrate from the surface of MeAPO-5 and dried at ambient temperature. The same procedure was repeated thrice. The sample was then calcined at 550 °C for 6 h.

2.4 PHYSICO-CHEMICAL CHARACTERISATION

The basic relationship between structure and activity of a catalyst has been predicted by several techniques. The following analytical techniques
viz., XRD, FT-IR, TGA, TPD (ammonia), ESR and SEM were employed in the present study with a view to correlate the physico-chemical properties of the synthesised catalysts and their catalytic activities.

2.4.1 X-Ray Diffraction

The powder X-ray diffraction patterns of as-synthesised, calcined and ion-exchanged catalysts were recorded using a X-ray diffractometer (X’ pert PRO PANalytical) equipped with nickel-filtered CuKα (λ = 1.54 Å) radiation and a liquid nitrogen-cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range 5-40° in steps of 1.2° with a count time of 10 s at each point. The peaks were identified with reference to compilation of simulated XRD powder patterns. The unit cell parameters were calculated using the standard least square refinement technique. The d spacing values were calculated using the Bragg’s equation (2.1)

\[ n\lambda = 2d \sin\theta \]  

where \( n \) = order of reflection, \( \lambda \) = wavelength of the incident X-ray beam, \( d \) = spacing between reflecting crystal planes and \( \theta \) = angle between incident and reflecting planes .

2.4.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of the materials were performed using a high-resolution thermogravimetric analyser (Perkin Elmer TG-DTA diamond series). About 15 mg of the sample was used in each experiment. The sample was heated under nitrogen atmosphere at a heating rate of 10 °C min\(^{-1}\) in the temperature range 50-800 °C.
2.4.3 Fourier-Transform Infrared (FT-IR) Spectroscopy

FT-IR spectroscopy is useful for the investigation of structural features and acidic properties as well as the nature of adsorbate-molecular sieves interaction (Flanigen et al 1971 and 1976). This spectroscopy constitutes a key technique for the characterisation of molecular sieves in the vibrational (1300-400 cm\(^{-1}\)) and hydroxyl group regions (3750-3400 cm\(^{-1}\)). The FT-IR spectra were recorded on a FT-IR spectrometer (Nicolet Avatar 360) using KBr pellet technique. About 15 mg of the sample was ground with 200 mg of spectral grade KBr and made into a pellet using a hydraulic press (Model: Kimaya) under a pressure of 2 ton cm\(^{-2}\) into a self-supported wafer of 15 mm in diameter. Then the spectra were recorded in the range 4000-400 cm\(^{-1}\). The pellets were scanned 50 times at 4 cm\(^{-1}\) resolution. The spectra were recorded as % transmittance against wavenumber.

2.4.4 Electron Spin Resonance (ESR) Spectroscopy

ESR technique is very sensitive to environmental symmetry of transition metal cations as long as they are paramagnetic. The co-ordination environment of Co in CoAPO-5 and Mn in MnAPO-5 sample was confirmed by this technique. ESR spectra were recorded using Varian E 112 spectrophotometer at room temperature with microwave power of 20 MW and modulation frequency of 100 KHz. The sample (40 mg) was taken in a quartz tube with 4 mm outer diameter and then evacuated to approximately 10\(^{-3}\) Torr. The tube was sealed under vacuum and then set in a quartz Dewar vessel fitted in the EPR cavity. Diphenylpicrylhydrazine (DPPH) was used as the reference to mark the g value.
2.4.5 **Scanning Electron Microscopy (SEM)**

The size and morphology of the samples were recorded using a scanning electron microscope (SEM) (JEOL 640). The sample was suspended in methanol and the specimen stub was dipped into the liquid and removed. The sample powder got deposited evenly onto the surface of the stub when methanol evaporated. The SEM pictures were developed on a thin photographic paper.

2.4.6 **Temperature Programmed Desorption (TPD) of Ammonia**

Temperature programmed desorption (TPD) is commonly used to determine both concentration and strength of acid sites (Cvetanovic and Amenomiya 1972) in solid acid catalysts. The probe molecules most frequently used were ammonia, isopropylamine, n-butylamine and pyridine. Semiquantitative information regarding the concentration of acid sites can be obtained either by gravimetric or volumetric technique. Continuous monitoring by spectrometry or titration is required for quantitative information (Kerr and Chester 1971 and Tospe et al 1981). Hedge et al (1987) determined the acidity of AlPO-5 and SAPO-5 by TPD (ammonia) technique.

The density and strength of acid sites were determined by temperature programmed desorption (TPD) of ammonia (Micromeritics chemisorb 2750 pulse chemisorption system). Approximately 50 mg of the sample was placed in a U shaped, flow-through, quartz microreactor. The surface of the sample was cleaned by heating the sample at 500 °C for 2 h with helium flow of 20 mL min\(^{-1}\). The sample was cooled to 100 °C. Ammonia was then exposed to the sample. The sample was again flushed with helium for half an hour to remove the excess and physisorbed ammonia. The desorption profile was then recorded by increasing the sample temperature from 100 to 600 °C at a rate of 5 °C min\(^{-1}\). The desorption was monitored by thermal conductivity detector.
2.5 EXPERIMENTAL SET-UP FOR CATALYTIC REACTIONS

2.5.1 Liquid Phase Reactions

The liquid phase reaction was carried out in an oil bath set-up. The reactants were taken in a round bottom flask fitted with a reflux condenser. The flask with its content was heated to a constant temperature by keeping the flask in an oil bath and stirred magnetically. In order to monitor the progress of the reaction, aliquots of the hot mixture were withdrawn at regular intervals, centrifuged and the clean centrifugate was analysed. The schematic diagram of the reactor set-up for the liquid phase reaction is shown in Figure 2.1.

![Figure 2.1 Schematic model of catalytic reactor-set up for liquid phase reaction](image-url)
2.5.1.1 Synthesis of 3-ethylcoumarin carboxylate (Knoevenagel Condensation)

Knoevenagel condensation of salicylaldehyde (5 mmol) and diethyl malonate (15 mmol) was performed in a 25 mL round bottom flask fitted with a reflux condenser. Nitrogen gas was purged into the flask in order to avoid oxidation of salicylaldehyde. After attaining the requisite temperature appropriate amount of the catalyst was added to the mixture and stirred simultaneously with a magnetic stirrer. Aliquots of the reaction mixture were withdrawn at regular intervals and subjected to gas chromatographic analysis.

2.5.1.2 Synthesis of 7-hydroxy-4-methylcoumarin (Pechmann Reaction)

The liquid phase batch reactor consists of a three-necked round bottom flask fitted with a condenser, a connector for nitrogen purge and a sampling apparatus. The reaction mixture viz., resorcinol (10 mmol) and ethyl acetoacetate (10 mmol) was taken in the reactor and heated in an oil bath to the requisite temperature with simultaneous stirring using a magnetic stirrer. Prior to each experiment the empty reactor was purged with nitrogen to remove oxygen to avoid oxidation. Aliquots of the reaction mixture were withdrawn at regular intervals and subjected to gas chromatographic analysis.

2.5.1.3 Synthesis of fructone (Acetalisation Reaction)

The liquid phase batch reactor consists of a 100 mL round bottom flask fitted with Dean-stark apparatus to remove the water formed in situ. The reaction mixture viz., ethyl acetoacetate (5 mmol), ethylene glycol (10 mmol) and solvent toluene (5 mL) was added to the flask and heated in an oil bath to the requisite temperature and stirred simultaneously with magnetic
stirrer. Aliquots of the reaction mixture were withdrawn at regular intervals and subjected to gas chromatographic analysis.

2.5.1.4 Friedel-Crafts acylation

Acylation of anisole (10 mmol) with acetic anhydride (20 mmol) was performed in a 25 mL round bottom flask fitted with a reflux condenser. The flask was kept in an oil bath and heated to the requisite temperature. After attaining the requisite temperature appropriate amount of the catalyst was added to the mixture and stirred simultaneously with a magnetic stirrer. Aliquots of the reaction mixture were withdrawn at regular intervals and subjected to gas chromatographic analysis.

2.6 PRODUCT ANALYSIS AND IDENTIFICATION

The liquid products were analysed using a gas chromatograph (Shimadzu GC-17A) using DB-5 capillary column (30m×0.25m×0.25μm) equipped with flame ionisation detector (FID). Nitrogen was used as the carrier gas. The products were further confirmed by gas chromatograph (Perkin-Elmer Auto System XL elite series PE-5 capillary column 30m×0.25mm×1μm) coupled with mass spectrometer (Turbo) (EI, 70 eV). Helium was used as the carrier gas at a flow rate of 1 mL min⁻¹. The components present in the products were identified from the m/e values and mass fragmentation patterns.

2.6.1 Method of Calculation of Conversion and Selectivity

In a typical catalytic reaction, reactants are converted into feasible products through possible pathways. Reactants conversion is an important parameter to know the catalytic activity of a catalyst. In a chemical reaction,
the reactant may undergo several reactions to give various products. A good catalyst is a material that could increase the rate of the reaction and leads to the formation of a desired product. The reactant conversion and products selectivity were calculated using the following Equations 2.2 and 2.3.

\[
\text{Conversion (\%)} = \frac{\text{weight of the feed} - \text{weight of the product formed}}{\text{weight of the feed}} \times 100 \quad (2.2)
\]

\[
\text{Selectivity (\%)} = \frac{\text{weight of the desired product}}{\text{sum of the weight of the products formed}} \times 100 \quad (2.3)
\]