CHAPTER 2

EXPERIMENTAL METHODS

2.1 INTRODUCTION

The experimental procedures employed in the present study were primarily oriented towards investigating the catalytic activity of various hydrotalcite-like compounds. The HTlcs were prepared by co-precipitation method. A detailed description of various experimental techniques used in the present study are organised in this chapter as follows:

1) Preparation of various HTlcs
2) Characterisation of these catalysts by the use of different physico-chemical techniques and
3) Evaluation of activity of the prepared catalysts towards the chosen organic reactions.

2.1.1 Materials

All the materials used in the present studies for the synthesis of hydrotalcite–like compounds (HTlcs) were of high purity (Analar Grade or equivalent) samples. Nitrates and chlorides of Mg, Co, Ni, Zn, Cu, Al, Fe, Cr and NaOH and Na₂CO₃ were obtained from E–Merck (India). Similarly the others chemicals such as toluene (Fluka AG), methanol (Aldrich),

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ethanol (E-Merck), isopropanol (Koch-Light), phenol (E-Merk), acetic anhydride and KBr (SRL) used were of extra pure quality and were used as such. The melting point/boiling point of the compounds used agreed with the values reported in the literature (Heilbron 1965).

2.1.2 Purification of Reactants

Commercial toluene (b.p 383 K) contains thiophene (b.p 385-388 K), which cannot be removed by distillation. It is removed by treating with H$_2$SO$_4$, since thiophene is more readily sulphonated than toluene. Toluene was shaken repeatedly with about 15% of its volume of concentrated sulphuric acid in a stoppered separatory funnel until the acid layer was colourless or very pale yellow on standing. After each operation, lasting a few minutes, the mixture was allowed to settle and the lower layer was drawn off. Then toluene was washed twice with water, once with 10% sodium carbonate solution, again with water and finally dried over anhydrous CaCl$_2$. After filtration it was distilled and the fraction distilling at 383 K / 760 mm Hg was collected (Vogal 1994). Its purity was better than 99% by gas chromatograph.

Methanol (purity 99.8%), formaldehyde (40% formalin solution) and acetone were used as such. Ethanol used is obtained from rectified sprit. 250 g of freshly ignited calcium oxide was added to 1 liter of ethanol. The mixture was refluxed gently for 6 h and allowed to stand overnight. It was distilled by downward distillation. Distillate boiling at 355.8 K was collected and used as absolute ethanol (99.5%). Peroxide free propan-2-ol was refluxed with calcium oxide for 4 h and then distilled. The fraction distilling between 355-356 K / 760 mm Hg was collected and used (Vogal 1994).
Nitrogen gas (Indian oxygen limited) was purified by passing successively through activated charcoal, a trap cooled in liquid nitrogen to remove hydrocarbon contaminants and a tube containing freshly reduced copper turnings kept at 673 K to remove traces of oxygen. Finally moisture and carbon dioxide were eliminated by passing it through traps containing CaCl₂, silica gel and KOH. Air used for the activation of catalysts prior to the experiments was also purified accordingly.

2.2 PREPARATION OF HT AND HTlc COMPOUNDS

The HT and HTlc were synthesized by co-precipitation techniques proposed by Cavani et al (1991). The precipitation methods involved a series of operations such as:

i) Precipitation (Co-precipitation)
ii) Hydrothermal treatment, aging
iii) Filtration
iv) Washing
v) Drying and
vi) Powdering

The single-phase formation of HTlc and their crystallinity depends on various factors such as:

i) Nature of M^{II} and M^{III} ions
ii) M^{II}/M^{III} atomic ratio
iii) Nature of precipitant
iv) Method of precipitation
2.3 CO-PRECIPITATION METHOD

In order to co-precipitate two cations it is necessary to carry out the precipitation in conditions of supersaturation at constant pH. The conditions most commonly utilized are the pH ranging from 7-10, temperature in the range of 333–353 K, washing with warm water, aging under the conditions of precipitation and the drying temperature not exceeding 393 K.

2.3.1 Preparation of Hydrotalcites

All the hydrotalcite precursors were synthesized by co-precipitation method and constant pH according to the reported experimental procedures (Cavani et al 1991, Velu and Swamy 1994). For MgAl–LDH, for instance, aqueous solutions are containing 0.09 mole of \( \text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) and 0.03 mole of \( \text{Al(NO}_3\text{)}_2 \cdot 9\text{H}_2\text{O} \) (for a composition \( \text{Mg/Al}=3 \)), and the second containing 0.33 mole of NaOH and 0.082 mole of \( \text{Na}_2\text{CO}_3 \) were slowly mixed at 338 K under vigorous stirring, maintaining the pH between 7-10. The mixture was aged at this temperature for 15 h with stirring. The precipitate was washed several times until the solution was free of nitrate ions and then dried at 383 K.

The following hydrotalcites were synthesized by this procedure: MgAl –HT with Mg/Al atomic ratios 3, 4, 5, 7 and 10. M(II)Al – HT where M(II) = Co, Ni, Cu and Zn atomic ratio 3. Mg M(III) – HT where M(III) = Fe and Cr atomic ratio 3.
2.4 PREPARATION OF CATALYSTS

These hydroxy carbonate precursors (HT samples) were decomposed in N$_2$ at 673 K overnight in order to obtain the corresponding mixed oxides (CHT samples). Calcination of HT and HTlcs at various temperatures were carried out in a muffle furnace (Indfur, India) lined with a silica tubing of 30 cm long with maximum operating temperature of 1000°C. One end of the tube was connected to the gas cylinder to maintain the required atmosphere. The muffle furnace was controlled by voltage transformer and pyrometer. During calcination 3 g of powdered LDH was loaded into a silica boat and heated at 723 K in air for 12 h and then cooled slowly to room temperature.

The calcined samples of HT and HTlcs thus prepared are considered as the required catalysts for many organic reactions. When the calcined samples are left in air, slow adsorption of atmospheric CO$_2$ occur. Hence, during each gas phase reactions the catalyst is prepared by calcination and loaded into the reactor taking care to avoid air contact.

2.5 CHARACTERISATION OF CATALYSTS

Many techniques were used to characterize HTlcs, such as ICPES, XRD, FT – IR, SEM, DSC, TGA and BET surface area measurement.

2.5.1 Chemical Composition

M(II) and M(III) composition of HT–like materials were determined by inductively coupled plasma emission (ICPE) spectroscopy (Model 3410, ARL) by dissolving about 50 mg of the sample in a minimal amount of dilute
hydrochloric acid. A calibration graph was obtained by measuring the emission intensity of standard solutions of various concentrations (in ppm). From the emission intensities, the concentration of unknown was estimated.

2.5.2 Powder X-ray Diffraction (PXRD) Studies

The X-ray diffraction (XRD) patterns of the uncalcined and calcined samples were recorded using a Philips X-ray generator (Model PW 1050/81 controlled by a 1710 unit) using Ni-filtered CuKα radiation (λ =1.5418 Å). All the X-ray patterns were obtained with the scan speed of 3°/min. For LDHs, the diffraction patterns were recorded from 2θ = 5 to 70°. The peaks were standardized with respect to elemental ‘Si’ as an external standard.

2.5.3 Calculation of Lattice Parameters

The lattice parameters of synthetic and calcined samples (723 K /12 h) in the present study were calculated employing least square fitting computer program written in a FORTRAN language. The powder X-ray diffraction (PXRD) patterns of synthetic samples were indexed to be hexagonal crystal system.

2.5.4 Fourier-Transform Infrared Spectroscopy

IR analysis is not a diagnostic tool for HTlcs but can be used to identify the presence of anions in the interlayer between the brucite-like sheets. FT-IR spectra of these samples from 4000-500 cm⁻¹ were recorded in Shimadzu FT-IR spectrometer and Perkin Elmer IR spectrometer (Model 983G) using
KBr mull technique. The powdered samples were ground with KBr in required mole ratio and pressed into pellets for recording spectra.

2.5.5 Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC)

The thermal behavior of HTlc is generally characterized by two transitions. The first one, endothermic at low temperature corresponds to the loss of interlayer water without collapse of the structure. The second one, endothermic at higher temperature is due to the loss of hydroxyl groups from the brucite-like layer as well as of the anions. TG-DSC experiments were carried out in a Perkin Elmer thermal analyzer (TGA-DSC 7) in the temperature range 323-1073 K for TG studies and 323-723 K for DSC studies under N\textsubscript{2} atmosphere with variable flow rates and different heating rates. However, a flow rate of 20 ml per minute and a heating rate of 10°C per minute were employed for most of the samples.

2.5.6 Scanning Electron Microscopy

SEM measurements were carried out using Leica stereoscan 440 scanning electron microscope (hv = 20 KV) by placing the sample on an aluminium stub. Sputter coating of the samples with gold was done in Fisons- SC 500A sputter coater, (VG microtech UK) to avoid charging effects during recording (current 5-10 mA) and accelerating voltage of 1.5 KV. The electron microphotographs of the samples were taken at various magnifications.
2.5.7 BET Surface Area Measurement

Surface of the calcined HTlcs is catalytically active and such surfaces need characterizations. Therefore, the precursors and the catalyst are subjected to the following measurements. Total surface areas were measured by flow method using Micromeritics Pulse Chemisorb 2700 instrument fundamentally adopting BET N\textsubscript{2} adsorption procedure. A steam of helium-nitrogen gas mixture of known composition at near atmospheric pressure was allowed to flow continuously over a pretreated sample cooled in liquid nitrogen. The sample adsorb the nitrogen coolant and the adsorbed nitrogen was desorbed from the surface into the flowing gas stream. The change in the concentration of the gas stream was measured with a thermal conductivity cell. The peak area was proportional to the amount of nitrogen adsorbed. The instrument was calibrated with a known volume of nitrogen so that the digital display directly gave the total surface area of the sample depending on the amount of nitrogen adsorbed. The specific surface area (m\textsuperscript{2}/g) was calculated by dividing the indicated surface area by the weight of the sample.

2.6 ACIDITY – BASICITY DETERMINATION

In the present investigation the acid-base properties of a series of calcined hydrotalcites (CHTs) with Mg/Al atomic ratio 3-10 have been evaluated employing non-aqueous titration techniques and catalytic test reactions like conversion of cyclohexanol. In the non-aqueous titration method, slurry of the sample in dry toluene (100 ml/g) with small amount of indicator was titrated against 0.1N solution of benzoic acid in dry toluene. The indicators used, their pka and their colour change in acidic and basic medium are presented in Table 2.1. As the colour change in these systems are insignificant
and are slow in forming, quantitative determination of number of acidic/basic sites was not possible. However, a qualitative comparison of basic sites has been made from the colour change in the presence of indicators.

**Table 2.1 Indicators used for basicity determination of Mg\textsuperscript{II} - Al\textsuperscript{III} CO\textsubscript{3}-HT calcined at 723 K / 12 h**

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pka</th>
<th>Colour(acidic)</th>
<th>Colour(basic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromo methyl blue</td>
<td>7.1</td>
<td>Yellow</td>
<td>Purple</td>
</tr>
<tr>
<td>4-nitroaniline</td>
<td>18.4</td>
<td>Yellow</td>
<td>Yellow orange</td>
</tr>
<tr>
<td>4-Chloroaniline</td>
<td>26.5</td>
<td>Colourless</td>
<td>Pink</td>
</tr>
</tbody>
</table>

It can be seen from Table 2.2 that except with Mg-Al 10.0 CHT whose basicity lies around pka = 18.0-26.4, while all other samples showed a very wide distribution of basicities (pka 14.3-26.0). The basicity of pure MgO is in the range 16.5-26.5, while pure Al\textsubscript{2}O\textsubscript{3} is 7.0-13.6. These results indicate that the basicity of CHT is similar to that of pure MgO and higher than that of pure Al\textsubscript{2}O\textsubscript{3}.

**Table 2.2 Acid-base properties of MgAl CO\textsubscript{3}-HT Calcined at 723K/12h**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Basicity range (pka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl 3.0 CHT</td>
<td>14.3–26.0</td>
</tr>
<tr>
<td>MgAl 4.0 CHT</td>
<td>14.1–26.2</td>
</tr>
<tr>
<td>MgAl 5.0 CHT</td>
<td>14.4–26.1</td>
</tr>
<tr>
<td>MgAl 7.0 CHT</td>
<td>14.5–26.1</td>
</tr>
<tr>
<td>MgAl 10.0 CHT</td>
<td>18.0–26.4</td>
</tr>
<tr>
<td>MgO</td>
<td>16.5–26.5</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>7.0–13.6</td>
</tr>
</tbody>
</table>
2.7 CATALYTIC STUDIES

2.7.1 Vapour Phase Reaction

The success of vapour phase alkylation reaction lies primarily on the design and choice of various possible reactors. In the present work, it has been decided to adopt vertical flow type reactor made up of borosil glass tube of 40 cm length and 2 cm internal diameter. The schematic diagram of the reactor is shown in Figure 2.1. The reactor was heated to the requisite temperature with the help of a tubular furnace controller cum indicator. The chromel-alumel thermocouple was used to measure the temperature of the catalyst bed. About 1.5 g of calcined hydrotalcite (723 K / 12 h) was packed inside the reactor and supported on either side with a thin layer of quartz wool and ceramic beads. A continuous supply of the reactant mixtures at desired flow rates with accuracy was maintained by a syringe model infusion pump. The bottom of the reactor was connected to a coiled condenser and a receiver to collect the products. The products obtained in the first 10 minutes were discarded. After each catalytic run the catalyst was regenerated by passing moisture and CO$_2$ free air through the reactor at 450°C for 3 h. The liquid products were analyzed using a Hewlett Packard gas chromatograph 5890 equipped with a flame ionisation detector (FID) and OV 17 column. Nitrogen was used as the carrier gas at a flow rate of 20 ml per minute.

2.7.2 Liquid Phase Reaction

For acylation of phenol, phenol (0.028 mole), acetic anhydride (0.028 mole), mole ratio (1:1) and catalyst (0.5 g) were taken in a 25 ml round bottomed flask fitted with a reflux condenser. The flask with its contents were heated in a constant temperature oil bath and stirred magnetically. The
Fig. 2.1 Schematic model of catalytic reactor set-up for vapour phase reaction
schematic diagram of the reaction set up used for this reaction is shown in Figure 2.2. In order to monitor the progress of the reaction, aliquots of the hot mixture were withdrawn at regular intervals and centrifuged. The clean centrifuge was analysed by Hewlett Packard 5890 gas chromatograph equipped with carbowax column and FID detector. Nitrogen was used as the carrier gas at a flow rate of 20 ml per minute.

For acylation of salicylaldehyde, salicylaldehyde (0.023 mole), acetic anhydride (0.023 mole), mole ratio (1:1) and catalyst (0.5 g) were taken and the reaction was carried out in the same procedure as in the case of acylation of phenol. The reaction was carried out in the nitrogen atmosphere, the samples were collected for different feed ratios and temperature and analysed using the GC. The products obtained were confirmed by GC-MS analysis.
Fig. 2.2  Schematic model of reactor set-up for liquid phase reaction