1.1 INTRODUCTION
Catalysis involves the interaction of the reactant molecules with the active sites of the catalysts. The texture of the catalyst particles and their surface properties largely influence the catalytic activity of these systems. Many experimental parameters such as metal oxide preparation procedure, sulphate and metal oxide loading method, temperature of calcination before reaction, etc, have been observed to affect the strength and nature of the active sites of sulphate modified metal oxides. The physico-chemical analysis gives a picture about the texture, phase and chemical composition of the catalyst. Thus, a methodological preparation and catalyst characterisation becomes highly essential. This chapter covers the preparation methods and characterisation techniques employed in the present work.

2.2 CATALYST PREPARATION

2.2.1 MATERIALS

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stannous chloride</td>
<td>Qualigens</td>
</tr>
<tr>
<td>Conc. HNO₃</td>
<td>Merck</td>
</tr>
<tr>
<td>Conc. HCl</td>
<td>Merck</td>
</tr>
<tr>
<td>Conc. H₂SO₄</td>
<td>Merck</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Merck</td>
</tr>
<tr>
<td>Ferric nitrate</td>
<td>Qualigens</td>
</tr>
<tr>
<td>Ammonium heptamolybdate</td>
<td>Merck</td>
</tr>
<tr>
<td>Tungstic acid</td>
<td>Merck</td>
</tr>
</tbody>
</table>
2.2.2 METHODS

i) Tin hydroxide

Hydrous tin oxide was prepared by the hydrolysis of stannic chloride using ammonium hydroxide (1). Stannic chloride solution was prepared from stannous chloride by oxidation with conc. HNO₃. Conc. HNO₃ was added to stannous chloride taken in a beaker until a pasty material was formed. It was then dissolved in minimum amount of aqua-regia on a sand bath to get stannic chloride solution. It was diluted with distilled water and heated to 80°C and 1:1 ammonia solution was added dropwise to this solution with constant stirring to complete the precipitation. The final pH of the solution was maintained as 4. The solution was boiled for 10 minutes and kept overnight. The precipitate was then washed several times with deionised water, until it was free from chloride and nitrate ions, filtered and dried in an air oven at 110°C for 12 hours. The dried sample was then sieved to get particles of 75-100 microns mesh size.

ii) Metal oxide loaded sulphated tin oxide

Metal oxide loaded sulphated tin oxide systems were prepared from tin oxide by single step wet impregnation using metal salt solution and 1N H₂SO₄. Iron, molybdenum and tungsten oxide loaded samples were prepared using ferric nitrate, ammonium heptamolybdate and tungstic acid solution respectively. The systems prepared are represented in Table 2.1.

To pure tin hydroxide, sulphuric acid and metal salt solution were added and stirred for four hours and then the solution was dried off. The samples thus obtained were subjected to overnight drying at 110°C. Then these were sieved to get particles of size < 100 microns. After sieving the samples were calcined. The calcination temperature employed for pure, sulphated and iron oxide modified systems was 550°C and that for molybdenum and tungsten series was 700°C. Pure and sulphated tin oxides were designated as S and SS respectively.
Table 2.1 Catalyst systems used for the present study

<table>
<thead>
<tr>
<th>% of metal oxide loaded</th>
<th>Notation for iron systems</th>
<th>Notation for molybdenum systems</th>
<th>Notation for tungsten systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>F₄</td>
<td>M₄</td>
<td>W₄</td>
</tr>
<tr>
<td>8</td>
<td>F₈</td>
<td>M₈</td>
<td>W₈</td>
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<tr>
<td>12</td>
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<td>M₁₂</td>
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<td>M₂₀</td>
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</tr>
<tr>
<td>24</td>
<td>F₂₄</td>
<td>M₂₄</td>
<td>W₂₄</td>
</tr>
</tbody>
</table>

2.3 CATALYST CHARACTERISATION

The catalyst systems prepared were characterised using various physico-chemical techniques such as X-ray diffraction (XRD), BET surface area and pore volume measurements, infrared spectroscopy, energy dispersive X-ray analysis, thermal analysis (TG), scanning electron microscopy and Laser Raman Spectroscopy. The acidic properties of the samples were determined by ammonia TPD and thermodesorption study using pyridine. The electron accepting properties of the catalyst systems were studied by adsorption studies using perylene, which provide a measure of the Lewis acidity of the catalysts.

2.3.1 MATERIALS

- Liquid nitrogen: Manorama Oxygen Pvt. Ltd.
- Potassium bromide: Merck
- Perylene: Merck
- Pyridine: Merck
- Benzene: Merck
2.3.2 METHODS

i) Surface area and pore volume measurements

Gas adsorption isotherm measurements are widely used for determining the surface area of various solids (2-4). N\textsubscript{2} is the usually recommended adsorbate for determination of surface areas higher than 5\text{m}^{2}\text{ g}^{-1}. N\textsubscript{2} adsorption is usually carried out at liquid nitrogen temperature (77 K). BET method is generally used for analysing the surface area of the catalysts. The BET equation can be represented as

\[
P/ [V(P_0-P)] = [1/V_m C] + [(C-1)/V_m C] (P/P_0)
\]

where, C is a constant for a given system and is dependent on adsorbent - adsorbate interaction

P - adsorption equilibrium pressure
P\textsubscript{0} - saturation vapour pressure of the adsorbate
V - volume of nitrogen adsorbed at equilibrium pressure, P
V\textsubscript{m} - volume of adsorbate required for monolayer coverage

A plot of \(P/ [V(P_0-P)]\) against \(P/P_0\) gives a straight line with slope \((C-1)/V_m C\) and intercept \(1/V_m C\). From these two, surface area can be obtained by applying the value of \(V_m\) in the equation

Surface area = \(V_m N_A A_m / 22414\)

where, \(N_A\) is the Avagadro number and \(A_m\) the molecular cross sectional area of the adsorbate (0.162 nm\textsuperscript{2} for N\textsubscript{2})

In the present study Micromeritics Gemini surface area analyser was used for determining the surface area and total pore volume of the samples simultaneously. Prior to the measurement, the samples were activated for two hours at the appropriate temperature and then degassed at 200°C under nitrogen flow. The degassed samples were then subjected to N\textsubscript{2} adsorption at 77 K maintained using liquid nitrogen.
**ii) X-Ray diffraction studies**

X-ray diffraction analysis is the most frequently employed method for the structural analysis of the solids. It helps to identify the crystalline phases present in the analysed material, by comparing the experimental results with the XRD data banks. Analysis of diffraction patterns allows the determination of the XRD detectable phases, unit cell parameters, degree of structural order, size and shape of crystallites, purity of the substance, randomness and imperfections in the lattice and composition of solid solutions.

XRD analysis is based on the interaction of X-rays with the crystalline phases of the solid samples, which leads to the scattering of the X-rays in different directions. A monochromatic X-ray beam is allowed to fall on the powdered sample and the diffraction pattern is obtained by plotting the intensity of the scattered radiation as a function of scattering angle $\theta$. Bragg’s equation $n\lambda = 2d \sin \theta$, gives the value of interplanar spacing ($d$), where $n$ is the order of diffraction, $\lambda$ is the wavelength of the monochromatic X-ray used, $\theta$ is the angle between the crystal plane and X-ray. The crystallite size of the sample can be determined from the broadening of the diffraction peak, using the Scherrer's equation, $t = \lambda / B \cos \theta$, where $B$ is the Full-Width - Half Maximum of the strongest peak, $t$-crystal diameter, $\theta$-Bragg angle. In the present study XRD patterns of the samples were recorded using Rigaku D-max C X-ray diffractometer using Ni filtered Cu- $K_{\alpha}$ radiation ($\lambda = 1.5406 \ \text{Å}$). The data obtained were compared with the standard data file (Joint Committee on Powder Diffraction Standards).

**iii) Energy dispersive X-Ray analysis**

Energy dispersive X-ray analysis is used for the qualitative and quantitative elemental analysis of solid samples. This method is based on the fact that when electrons of appropriate energy strike a sample surface it causes emission of X-rays. The principle of this emission is that electron beam striking a solid surface ejects an electron from the inner shell of the sample atom. Electron from a higher energy
level will fill the resulting vacancy. When the electron falls from a higher to a lower energy level it will emit some amount of energy, which will be equal to the energy difference between the two electronic levels involved. Due to the large energy difference of the inner shells, the resulting radiation will be in the form of X-rays. Each element will have a unique electronic configuration; hence the energy and the intensity of the X-rays emitted will be dependent on the composition of the solid sample. EDX of the samples were analysed using a Stereo scan 440 apparatus.

**iv) Infrared spectroscopy**

Infrared spectroscopy is another important technique used for the structural analysis of samples. This spectral analysis gives information about the metal-support interactions, metal-metal interactions and the functional groups present on the catalyst surface. It also identifies the adsorbed species on the catalyst surface, which makes this method useful for the surface acidity determination of catalyst using suitable probe molecules such as ammonia and pyridine. The IR analysis of the samples adsorbed with pyridine helps to identify both the Lewis and Brönsted acid sites.

The IR spectrum is produced during the change in dipole moment of the molecule due to the vibrations in the molecule. IR analysis helps to identify the surface sulphate species of the modified tin oxide systems. FTIR spectra of the activated powdered samples were determined using Shimadzu DR 8001 spectrophotometer by KBr pellet method.

**v) Thermogravimetric analysis**

Thermogravimetric analysis helps to determine the phase transformations, decomposition temperature, drying ranges, etc. of the solid samples. In TGA, the weight of the sample subjected to controlled linear heating was recorded as a function of time or temperature. The weight of the sample was plotted against temperature to get a thermogram. The dips in the thermogram indicate the weight loss due to decomposition, and the horizontal portions in the graph indicate that the
sample is thermally stable at that temperature range. The thermogravimetric analysis of the samples was performed using Shimadzu TGA-50 equipment. The analysis was done in nitrogen atmosphere using a heating rate of 10°C/minute.

vi) **Scanning electron microscopy**

The scanning electron microscopy allows the imaging of the topology of a solid surface (5). In SEM, a fine probe of electrons is used to scan the catalyst surface with the help of deflection coils. This technique gives an idea about the morphology and crystal size of the samples. The main disadvantage of this analysis is that the result represents only a spot in the sample and not of the entire sample. In order to overcome this disadvantage we should take the images of various spots on the catalyst surface. The scanning electron micrographs of the samples were recorded using Stereoscan 440 scanning electron microscope.

vii) **Acidity determination**

The surface acid-base properties play an important role in determining the activity and selectivity of the catalysts. Sulphation improves the surface acidity of tin oxide, so only the acidic properties of the samples were analysed. Acidity of the samples were obtained by different methods such as temperature programmed desorption of ammonia, thermodesorption of pyridine, perylene adsorption studies and test reactions like cumene cracking and decomposition of cyclohexanol.

a) **Temperature programmed desorption studies**

Conventional Hammett method for acidity determination is not useful for the coloured samples. Temperature programmed desorption of base molecule is found to be an efficient method for determining the acidity of the catalysts (6,7). NH$_3$- TPD is now widely used for evaluating the surface acidity of the solid catalysts. This method gives the total acidity and acid strength distribution of the catalyst since NH$_3$ molecules can bind to acid sites of any strength and type.
Chapter 2-Experimental

For the TPD analysis, 0.5 g of the pelletised and subsequently activated catalyst was loaded into a steel reactor of 30 cm length and 1 cm diameter kept in a cylindrical furnace. The pellets were degassed at 300°C for half an hour under nitrogen atmosphere. It was then brought to room temperature and a fixed amount of ammonia was injected into the reactor in the absence of nitrogen flow and the pellets were allowed to adsorb the ammonia for 20 minutes. Excess ammonia was then flushed off by passing nitrogen. The temperature was then raised in a stepwise manner and the ammonia desorbed in the temperature range 100-600°C at intervals of 100°C was trapped in dilute sulphuric acid of known normality. It was then back titrated with NaOH to get the amount of ammonia desorbed at that particular temperature.

b) Perylene adsorption studies

Perylene molecule readily donates an electron to form a radical since the radical formed is stabilised by resonance. Hence perylene adsorption analysis gives the amount of Lewis acid sites present in the catalyst (8,9). For the adsorption studies, perylene solutions of varying concentrations were prepared using benzene as solvent. Definite weight of preactivated samples were stirred with 5 ml of these solutions then get adsorbed on the catalyst surface as radical cation, by donating its electron to the Lewis acidic center. The amount of perylene adsorbed was obtained by measuring the absorbance of the solution before and after adsorption. The absorbance was measured using Shimadzu UV-160 A UV-Vis spectrophotometer. By plotting equilibrium concentration of the electron donor against amount of perylene adsorbed, limiting amount of perylene adsorbed is calculated.

c) Thermodesorption of pyridine

Thermodesorption of probe molecules is another method used for determining the acidity of catalyst systems. The probe molecules used includes pyridine, \(n\)-butyl amine, 2,6-dimethylpyridine, etc. Pyridine has affinity to both Brönsted and Lewis acid sites so thermodesorption study using pyridine as probe
helps to determine the total acidity of the system (10). The activated samples were
kept in a dessicator containing pyridine for 48 hours, for the equilibrium adsorption
of the probe molecule on the catalyst surface. The samples were then subjected to
thermogravimetric analysis in N₂ atmosphere at a linear heating rate of 20°C/min.
The amount of pyridine desorbed gives the measure of the total acidity of the
system. These data can be compared with the TPD results.

2.4 CATALYTIC ACTIVITY STUDIES

The catalytic activity of the systems was tested by carrying out some
industrially important reactions. The reactions can be carried out either in liquid or
in vapour phase. The main drawback of liquid phase reactions is that the maximum
reaction temperature attained is limited to the refluxing temperature of the reaction
mixture, whereas in vapour phase we can easily carry out the reaction at higher
temperatures. The liquid phase reactions carried out in the present study are Friedel­
Crafts benzylation and benzoylation. Vapour phase reactions carried out include
methylation of aniline and oxidative dehydrogenation of ethylbenzene. Cumene
cracking and decomposition of cyclohexanol were done in vapour phase, as test
reactions for acidity.

2.4.1 MATERIALS

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
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<tbody>
<tr>
<td>Benzene</td>
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</tr>
<tr>
<td>Toluene</td>
<td>Merck</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>Merck</td>
</tr>
<tr>
<td>Benzyl chloride</td>
<td>Merck</td>
</tr>
<tr>
<td>Benzoyl chloride</td>
<td>Merck</td>
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</tr>
<tr>
<td>Cumene</td>
<td>Merck</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>Qualigens</td>
</tr>
</tbody>
</table>
2.4.2 METHODS

i) Liquid phase reactions

a) Friedel-Crafts benzylation

Friedel-Crafts benzylation of toluene and o-xylene using benzyl chloride was carried out in batch wise manner. The reaction mixture containing the substrate and benzylating agent in a definite molar ratio was added to 50 mL double-necked round bottomed flask fitted with a spiral condenser containing 0.1 g catalyst. It was then placed in an oil bath maintained at a selected temperature and the reaction mixture was stirred magnetically. The product analysis was done using Chemito 8610 Gas Chromatograph equipped with flame ionisation detector and SE-30 column.

The reaction was carried out using excess substrate and the yield was calculated based on the amount of benzyl chloride. The selectivity for a particular product is expressed as the amount of that product divided by the total amount of all the products multiplied by 100. The catalytic activity was studied by varying different parameters such as reaction temperature, reaction time and molar ratio between the substrate and benzyl chloride. The effect of metal leaching and moisture was also investigated.

b) Friedel-Crafts benzoylation

Reaction mixture containing o-xylene and benzoyl chloride in the required molar ratio was taken in a 50 mL RB flask (mounted on a magnetic stirrer) containing 0.1 g of catalyst maintained at a definite temperature using an oil bath. Influence of reaction parameters like substrate to benzoyl chloride molar ratio, reaction temperature and time was studied in detail. The effect of moisture and metal leaching on catalytic activity was also scrutinised. The product analysis was done using Chemito 8610 Gas Chromatograph equipped with FID and SE-30 column.
ii) Vapour phase reactions

The vapour phase reactions were carried out in a vertical, fixed bed, flow type, quartz reactor of 2.5 cm diameter and 30 cm length mounted in a cylindrical furnace vertically. The preactivated catalyst powder (0.5 g) was placed in a glass wool bed in the middle of the reactor, packed with silica beads. A thermocouple placed near the catalyst bed monitored the reaction temperature. A temperature controller was used to maintain the temperature of the furnace. The reactants were introduced into the reactor by means of a syringe pump. The circulation of cold water in the condenser connected to the reactor cooled the reaction mixture eluting out of the reactor. The condensed reaction mixture was collected in the receiver. This mixture was then analysed at definite time intervals with the help of Gas Chromatograph.

a) Methylation of aniline

A mixture of aniline and methanol in a definite molar ratio was fed into the reactor maintained at the required temperature. The products were analysed using Chemito 8610 Gas Chromatograph containing an SE-30 column. The change of catalytic activity with feed rate, time on stream, reaction temperature and aniline to methanol molar ratio was also investigated.

b) Oxidative dehydrogenation of ethylbenzene to styrene

The ethylbenzene feed was introduced at the top of the reactor maintained at a fixed temperature at a particular flow rate. The reaction was carried out in presence of air, for certain selected samples catalytic activity was analysed in the absence of air also. The effect of reaction parameters such as feed rate and reaction temperature was studied in detail. Deactivation studies were carried out for few systems. The products were analysed using FFAP column.
b) Decomposition of cyclohexanol and cumene cracking

Decomposition of cyclohexanol and cumene cracking were done as test reactions for acidity. In the case of cumene cracking the product analysis was done in FFAP column, while for cyclohexanol, carbowax column was used.
REFERENCES