MATERIALS AND EXPERIMENTAL METHODS

Abstract

For many years, the development and preparation of heterogeneous catalysts were considered more as alchemy than science, with the predominance of trial and error experiments. The optimum catalyst is the one that provides the necessary combination of properties (activity, selectivity, lifetime, ease of regeneration and toxicity) at an acceptable cost. The present chapter is focused on the experimental procedures for catalyst preparation, characterization and catalytic activity measurements. The textural characteristics of the catalysts were characterized using XRD, EDX, SEM, BET surface area-pore volume measurements, TGA/DTA, EPR, FT-IR, FT-Raman and DR UV-vis. Ammonia-TPD and thermogravimetric desorption of 2,6-dimethyl pyridine were done to measure the acidity. Cyclohexanol decomposition and cumene cracking were used as test reactions to understand surface acid-base property. Industrially important phenol methylation, o-cresol methylation, oxidation of ethylbenzene, benzylation of toluene and o-xylene were carried out.
2.1 Introduction

The development of novel catalytic materials is a fundamental focal point of catalysis research. After catalyst preparation, the next goal is to perform a detailed and full characterization of the solid yielded by the specific preparation method used. To do this in a systematic way one needs a diverse array of experimental techniques. This chapter gives a detailed description about the preparation of catalytic systems and the characterization techniques.

2.2 Materials

The chemicals used for the preparation of catalyst are given in Table 2.1.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Chemicals</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cerium nitrate</td>
<td>Indian Rare Earths Ltd., Udyogamandal, Kerala (99.9%)</td>
</tr>
<tr>
<td>2.</td>
<td>Zirconium (IV) propoxide</td>
<td>Sigma Aldrich Chemicals Pvt. Ltd</td>
</tr>
<tr>
<td>3.</td>
<td>Chromium nitrate</td>
<td>s.d Fine Chem. Ltd</td>
</tr>
<tr>
<td>4.</td>
<td>Manganese nitrate</td>
<td>Central Drug House P. Ltd</td>
</tr>
<tr>
<td>5.</td>
<td>Ferric Nitrate</td>
<td>Qualigens Fine Chemicals (25 %)</td>
</tr>
<tr>
<td>6.</td>
<td>Cobalt Nitrate</td>
<td>s.d Fine Chem. Ltd</td>
</tr>
<tr>
<td>8.</td>
<td>Copper Nitrate</td>
<td>s.d Fine Chem. Ltd</td>
</tr>
<tr>
<td>9.</td>
<td>Ammonia</td>
<td>s.d Fine Chem. Ltd</td>
</tr>
<tr>
<td>10.</td>
<td>Conc. HNO₃</td>
<td>s.d Fine Chem. Ltd</td>
</tr>
</tbody>
</table>
2.3 Catalyst Preparation

2.3.1 Ceria:– Sol-gel Route

Ceria was prepared via colloidal sol-gel route from aqueous inorganic precursor \( \text{Ce(NO}_3\text{)}_3.6\text{H}_2\text{O} \). Cerium nitrate was added to 1:1 NH\(_3\) to obtain cerium hydroxide, maintaining the final pH~10. The precipitate was washed to remove nitrate ions and redispersed in water following peptisation using HNO\(_3\) at 80°C. The sol obtained was heated at 90°C to obtain the gel. Gel was dried at 110°C for 12h and calcined at 500°C for 5h to get pure ceria.

2.3.2 Transition Metal modified Ceria

Transition metal (Cr, Mn, Fe, Co, Ni, Cu 2, 5 and 8 wt.%) modified ceria were prepared by the addition of corresponding metal nitrate solution to the previously prepared ceria sol. The resulting sol was stirred for 4h. Gelation and calcination was done as in the case of pure ceria catalyst.

2.3.3. Zirconia (ZrO\(_2\)):– Sol-gel Route

Zirconia sol was prepared by adding zirconium propoxide, Zr(OPr\(_n\))\(_4\), to an aqueous solution of nitric acid at a volumetric mixing ratio of 1HNO\(_3\): 50H\(_2\)O: 3.7 Zr(OPr\(_n\))\(_4\). The resulting mixture was stirred mechanically for 72h to obtain zirconia sol. For preparing pure zirconia, the sol was dried at 110°C for 24h. Then calcined at 500°C for 5h to obtain zirconia powder.

2.3.4 Ceria-Zirconia

To prepare ceria-zirconia mixed oxide appropriate quantity of previously estimated ceria sol and zirconia sol were mixed and stirred for 4h. Kept overnight for ageing, dried at 110°C for 12h to get gel. The gel was calcined at 500°C for 5h to get ceria-zirconia mixed oxide catalyst.
2.3.5 Transition Metal Modified Ceria-Zirconia

Transition metal (Cr, Mn, Fe, Co, Ni, Cu) modified ceria zirconia mixed oxides were prepared by adding appropriate quantity of corresponding metal nitrate solution to the mixed ceria-zirconia sol. Again stirred for 4h and dried at 90°C to get the gel. The gel was submitted to overnight night drying at 110°C and the subsequent calcination at 500°C gave transition metal modified ceria-zirconia catalyst.

2.4 Catalyst Notations

The catalyst notations assigned to the prepared catalysts are listed in Table 2.2.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Catalyst Notation</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CeO₂</td>
<td>Ce</td>
</tr>
<tr>
<td>2.</td>
<td>ZrO₂</td>
<td>Zr</td>
</tr>
<tr>
<td>3.</td>
<td>CeO₂-ZrO₂</td>
<td>CeZr</td>
</tr>
<tr>
<td>4.</td>
<td>x%M/CeO₂</td>
<td>M(x)Ce</td>
</tr>
<tr>
<td>5.</td>
<td>x%M/CeO₂-ZrO₂</td>
<td>M(x)CeZr</td>
</tr>
</tbody>
</table>

M=Cr, Mn, Fe, Co, Ni and Cu
X= 2, 5 and 8 (M in weight%)

2.5 Characterization Techniques

In heterogeneous catalysis, the reaction occurs at the surface. Catalysis and catalytic surfaces, hence, need to be characterized by reference to their physical properties and by their actual performance as a catalyst. The variety of techniques used in this work is given below.
2.5.1 Materials

Chemicals used during physico-chemical characterization of catalysts are listed in Table 2.3.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Chemicals</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>Sodium Hydroxide</td>
<td>Merck</td>
</tr>
<tr>
<td>3.</td>
<td>Oxalic acid</td>
<td>Merck</td>
</tr>
<tr>
<td>4.</td>
<td>Cyclohexanol</td>
<td>Central Drug House P. Ltd.</td>
</tr>
<tr>
<td>5.</td>
<td>Cumene</td>
<td>Sigma Aldrich Chemicals Pvt. Ltd</td>
</tr>
<tr>
<td>6.</td>
<td>2,6-dimethylpyridine</td>
<td>Sigma Aldrich Chemicals Pvt. Ltd</td>
</tr>
<tr>
<td>8.</td>
<td>Magnesium oxide</td>
<td>Merck</td>
</tr>
</tbody>
</table>

2.5.2 Powder X-ray Diffraction

X-ray diffraction (XRD) is an extremely important technique in the field of material characterization to obtain information on an atomic scale from both crystalline and noncrystalline materials. Application of X-ray diffraction to structure determination in 1913 (by W. L. Bragg and W. H. Bragg) paved the way of successful utilization of this technique to determine the crystal structure of metals and alloys, minerals, inorganic compounds, polymers and organic materials in fact all crystalline materials³. Subsequently the technique of X-ray diffraction was also applied to derive information on the fine structure of materials—crystallite size, lattice strain, chemical composition, state of ordering, etc.

The diffraction principle developed by W. L. Bragg is based on diffraction from two scattering planes that are separated by the distance d (in Å) and the intercept
X-radiation of wavelength \( \lambda \) (in Å) at the incident angle \( \theta \). Constructive interference occurs when the Bragg’s law, \( n\lambda = 2d \sin \theta \) (where \( n \) is the order of diffraction) is obeyed.

The crystallite size was calculated using Scherrer equation,

\[
L = \frac{0.9\lambda}{\beta \cos \theta}
\]

\( \beta \) = Full width at half maximum (FWHM) of the peak which have maximum intensity.

Powder X-ray diffraction data were recorded using Rigaku D-Max Ni filtered Cu K\( \alpha \) radiation (\( \lambda = 1.5418 \) Å) diffractometer equipped with a diffracted beam monochromator at a scan rate of 4°/min.

2.5.3. Energy Dispersive X-ray Analysis

Energy Dispersive X-ray analysis is referred to as EDS or EDAX analysis. It is a technique used for identifying the elemental composition of the specimen, or an area of interest thereof. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM), and cannot operate on its own without the latter. During EDX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atom’s own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray.

The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the
atom from which the X-ray was emitted can be established. The output of an EDX analysis is an EDX spectrum. The EDX spectrum is just a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. An EDX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well. For example, a peak corresponding to the amount of energy possessed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a K-Alpha peak. The peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a K-Beta peak.

The chemical compositions of catalysts were obtained from Stereoscan 440 Cambridge, UK energy dispersive X-ray analyzer used in conjunction with SEM.

2.5.4 Surface area and Pore volume measurements

The most common method of measuring surface area and one used routinely in most catalyst studies is that developed by Brunauer, Emmett and Teller. In essence, the Langmuir adsorption isotherm is extended to multilayer adsorption. As in the Langmuir approach, for the first layer the rate of evaporation is considered to be equal to the rate of condensation, and the heat of adsorption is taken to be independent of coverage. For layers beyond the first, the rate of adsorption is taken to be proportional to the fraction of the lowest layer still vacant. The rate of desorption is taken to be proportional to the amount present in that layer. The heat of adsorption for all layers except the first layer is assumed to be equal to the heat of liquefaction of the adsorbed gas. Summation over an infinite number of adsorbed layers gives the final expression as follows:
\[
\frac{P}{V} (P_o - P) = \frac{1}{V_m C} + \frac{(C - 1) P}{(C V_m P_o)}
\]

where 
- \( V = \) Volume of gas adsorbed at pressure \( P \)
- \( V_m = \) Volume of gas adsorbed in monolayer, same units as \( V \)
- \( P_o = \) Saturation pressure of adsorbate gas at the experimental temperature.
- \( C = \) a constant related exponentially to the heats of adsorption and liquefaction of the gas.

A graph of \( \frac{P}{V}(P_o - P) \) versus \( P/Po \) should give a straight line, the slope and intercept of which can be used to evaluate \( V_m \) and \( C \). The surface area of the catalyst can be calculated from \( V_m \) if the average area occupied by an adsorbed molecule is known.

Liquid nitrogen is a readily available coolant, and nitrogen is usually used as the adsorbate since it is relatively cheap and readily available in high purity. The surface area is then calculated using:

\[
S_{BET} = \frac{V_m A_m N_a}{V_{mol}}
\]

where;
- \( N_a \): Avogadro’s number \((6.0238 \times 10^{23})\), \( V_{mol} \): molar volume of absorbate gas at STP \((22.41 \text{ mol}^{-1})\) and \( A_m \): Cross sectional area of adsorbed gas \((A_m (N_2) = 0.162 \text{ nm}^2)\).

When nitrogen is the adsorbing gas, this reduces to:

\[
S_{BET} = 4.353 V_m
\]

BET surface areas and pore volume values of the catalysts were acquired by nitrogen adsorption and subsequent desorption at liquid nitrogen temperature \((77K)\) with a Micromeritics Flow Prep-060 Gemini 2360 instrument.

**2.5.5 Scanning Electron Microscopy**

The fundamental principles of Scanning Electron Microscopy (SEM) were discovered in the 1930s. Generally speaking, the signals from the interaction between
electrons and sample are used to obtain the information of the sample, either
topographical, or compositional, or elemental, or structural images, depending on
which signal is used. The scanning electron microscope generates a beam of electrons
in a vacuum. That beam is collimated by electromagnetic condenser lenses, focused
by an objective lens, and scanned across the surface of the sample by electromagnetic
deflection coils. The primary imaging method is by collecting secondary electrons
that are released by the sample. The secondary electrons are detected by a
scintillation material that produces flashes of light from the electrons. The light
flashes are then detected and amplified by a photomultiplier tube. By correlating the
sample scan position with the resulting signal, an image can be formed that is
strikingly similar to what would be seen through an optical microscope. The
illumination and shadowing shows a quite natural looking surface topography.

SEM pictures were obtained on Cambridge Oxford 7060 scanning electron
microscope connected to a 4-quadrant backscattered electron detector under a
resolution of 1.38 eV coated with a layer of gold to minimum charge effects.

2.5.6 Thermogravimetric Analysis

A generally accepted definition of thermal analysis is: “A group of
techniques in which a physical property of a substance and/or its reaction products is
measured as a function of temperature whilst the substance is subjected to controlled
temperature programme”. Thermogravimetric analysis (TGA) provides a quantitative
measurement of any weight changes associated with thermally induced transitions. For example, TG can record directly the loss in weight as a function of temperature or
time for transitions involve dehydration or decomposition. Thermogravimetric curves
are characteristic of a given compound or material due to the unique sequence of
physical transitions and chemical reactions that occur over definite temperature range.
Changes in weight results from physical and chemical bonds forming and breaking at
elevated temperatures. These processes may evolve volatile products or form reaction products that result in a change in weight of the sample\textsuperscript{2}.

Differential thermal analysis (DTA) is a technique in which the difference in temperature between a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program. Thermogravimetry, a valuable tool in its own right, is perhaps most useful when it complements differential thermal analysis studies, virtually all weight change processes absorb or release energy and are thus measurable by DTA, but all energy change processes are accompanied by changes in weight. This difference in two techniques enables a clear distinction to be made between physical and chemical changes when samples are subjected to both DTA and TGA.

TGA/DTA analysis were done on a Perkin Elmer Pyris Diamond thermogravimetric/differential thermal analyzer instrument under nitrogen atmosphere at heating rate of $20^\circ\text{C/ min}$ from room temperature to $800^\circ\text{C}$ with samples mounted on an alumina sample holder.

2.5.7 FT-Infrared Spectroscopy

Infrared (IR) spectroscopy undoubtedly represents one of the most important tools in catalysis research\textsuperscript{7,8}. It is the most widely used, and usually most effective, spectroscopic method for characterization of the surface chemistry of heterogeneous catalysts. Vibrational spectroscopy has become a very powerful tool for characterizing the molecular structures of these supported metal oxides. Infrared spectroscopy has been used to study the interactions of the surface metal oxide species with the surface hydroxyls of the support. It can also be used to measure the distribution of surface Bronsted and Lewis acid sites by adsorption of pyridine. The number of surface sites on these catalysts can also be estimated by measuring the
amount of chemisorbed CO₂. IR can also be used to detect the terminal metal-oxygen stretches (M=O) on supported metal oxides.

Infrared spectra were recorded with KBr pellets on an ABB BOMEM (MB Series) FT-IR spectrometer model in the range 400-4000 cm⁻¹.

2.5.8 UV-vis Diffuse Reflectance Spectroscopy

In surface chemistry, the UV–Vis spectroscopic method is usually used in its diffuse reflection modification. The radiation reflected from a powdered crystalline surface consists of two components, i.e. (i) that reflected from the surface without any transmission (mirror or specular reflection), and (ii) that absorbed into the material and which then reappears at the surface after multiple scattering. Modern spectrometers minimize the first component, and the term 'reflectance' is thus used for diffusely reflected radiation. Since only a part of the diffuse radiation is returned to the detector, measurement of the diffused intensity is difficult. For this purpose, a special integrative sphere, coated inside with a highly reflecting layer, such as MgO or BaSO₄, is used. Such a sphere increases the part of the diffused intensity that reaches the detector (30-50%). Spectra are recorded 'in ratio' with a sample which has similar diffusion characteristics to the sample under investigation, but without any absorption losses. The evaluation of the intensities of diffuse reflectance spectra is based on the theory of Kubelka and Munk.

DR UV-vis spectroscopy may be used to determine the local symmetry and oxidation state of a transition metal, and thus it is a sensitive probe for the type of site in which such an ion exists. The applicability of this method is not limited to transition-metal-containing systems. It can be also used to measure the electronic spectra of adsorbed molecules and to obtain direct information about the excited and ground states of such species.
Chapter 2

DR UV-vis spectra were taken in the range 200-800 nm on an Ocean Optics, Inc. SD 2000, Fiber Optic Spectrometer with a charged coupled device detector. The spectra were recorded at room temperature using MgO as a reference. Prior to measurement, the samples were pretreated for 1h at the calcination temperature.

2.5.9 FT-Raman Spectroscopy

Raman spectroscopy (FT-Raman) can provide molecular-level structural information about the nature of the active surface sites, especially in highly dispersed catalyst systems, and the surface reaction intermediates. Surface metal oxide species typically vibrate in the 100-1100 cm\(^{-1}\) region. Common oxide supports, such as alumina and amorphous silica, absorb strongly below approximately 1000 cm\(^{-1}\). Consequently, the IR bands of the surface metal oxide species are usually masked by the strong IR bands of the oxide support. In contrast, the Raman bands of these oxides support are weak or Raman inactive in the same region. Because of this, Raman spectroscopy is preferred over IR spectroscopy for measuring the vibrational spectra of supported metal oxides. Since the Raman spectrum of each molecular structure is unique, Raman spectroscopy can discriminate between different molecular structures of the supported metal oxides\(^{10}\).

For the Raman spectra measurements the catalysts calcined at 773K were introduced into a metallic sample holder. FT-Raman spectra were collected on Bruker FRA 106 FT-Raman Accessory and the RES 100 FT-Raman spectrometer.

2.5.10 Electron Paramagnetic Resonance Spectroscopy

Electron paramagnetic resonance (EPR) spectroscopy has long been recognized as a powerful tool for the catalytic chemist, as the high sensitivity of the techniques permits the detection of low concentrations of active sites, even under in situ conditions. EPR techniques are widely used to study paramagnetic centers on
various solid surfaces. These centres may be surface defects, inorganic or organic radicals, metal cations or supported metal complexes and clusters. Each of these paramagnetic species will produce a characteristic EPR profile with well defined spin-Hamiltonian parameters. However the magnetic properties, stability and reactivity of these centres can vary dramatically depending on the nature of the support. In some case, radicals, which are stable on one surface will be transient on another, while variations in the EPR spectra of these radicals may be observed simply by altering the pretreatment conditions of the support. EPR techniques provide a deeper understanding of catalyst preparation, the nature of surface-active sites and the types of reaction intermediates as well as details of the catalytic reaction mechanisms\textsuperscript{14}. When the molecules of solid exhibits paramagnetism, transitions can be induced between spin states by applying magnetic filed and then supplying electromagnetic energy, usually in the microwave frequencies. The resulting EPR spectra provide information about the material.

The EPR measurements were determined on a VARIAN E-line Century Series instrument at X-band at liquid nitrogen temperature.

2.6 Surface Acidity measurements

2.6.1 Temperature Programmed Desorption of Ammonia

Temperature programmed desorption of basic molecules such as ammonia (TPD-NH\textsubscript{3}), pyridine, n-butylamine, etc. is frequently used to characterize the acid strength as well as acid amount on a solid surface. However, ammonia and n-butylamine in which hydrogen atoms are attached to the nitrogen atom have a tendency to dissociate (e.g., \(\text{NH}_3 \rightarrow \text{NH}_2^+ + \text{H}^+\)) and adsorb on both acidic and basic sites depending on the kinds of solids and the adsorption condition. Methods utilizing adsorption and desorption of gaseous bases have the advantage that the acid amount
for a solid at high temperatures, or under its actual working conditions as a catalyst, can be determined\textsuperscript{11}.

Prior to the experiment, the catalysts were activated inside the reactor at 300°C for 30 min with continuous flow of nitrogen. After cooling to the room temperature, a specific volume of ammonia was injected in the absence of the carrier gas and allowed to attain equilibrium. Excess physisorbed ammonia was removed by the flow of nitrogen. Then the temperature program is done from room temperature to 600°C in a stepwise manner. The ammonia desorbed at each interval of 100°C was collected in a known volume of dilute sulfuric acid and estimated volumetrically by titration with standardized NaOH.

2.6.2 Thermodesorption of 2,6-dimethyl pyridine

The thermodesorption of study of 2,6-dimethyl pyridine (2,6-DMP) adsorbed catalyst samples to get an idea about Bronsted acid sites present on the catalyst surface. 2,6-dimethyl pyridine adsorbs strongly on Brönsted acid sites and forms weak bonds with Lewis acid sites. The 2,6-dimethyl pyridine weakly bound to the Lewis acid sites get desorbed below 300°C. Hence thermodesorption study of 2,6-dimethyl pyridine adsorbed sample beyond 300°C can give the measure of Bronsted acid sites. The samples were activated at 500°C for 1h and kept in a dessicator saturated with 2,6-dimethyl pyridine for 48 h. Further subjected to TG analysis at a heating rate of 20°C/min. in nitrogen atmosphere. The percentage of weight loss in the temperature region 300-600°C is divided in to weak (300-400°C), medium (400-500°C) and strong (500-600°C) acid sites.

2.6.3 Cumene Cracking

Cumene cracking has been used extensively as a test reaction to investigate the characteristics of any newly developed catalyst. Bronsted acid sites catalyse
cracking of cumene to Benzene and propylene and Lewis acid sites catalyze dehydrogenation to \( \alpha \)-methylstyrene. The relative amounts of benzene and \( \alpha \)-methylstyrene in the product mixture can therefore be a good indication of the types of acidities possessed by catalyst\(^{12}\). All the prepared catalysts were subjected to cumene cracking in vapor phase at optimized reaction conditions.

### 2.6.4 Cyclohexanol Decomposition

Cyclohexanol decomposition was carried out to study the acid-base properties of the catalyst systems. Being amphoteric in nature, cyclohexanol can interact with both the acidic and basic sites on the catalyst surface resulting in dehydration and dehydrogenation reactions. Dehydration activity is linked to the acidic property and dehydrogenation activity to the combined effect of both acidic and basic properties of the catalyst\(^{13}\). Vapour phase cyclohexanol decomposition was done using the prepared catalysts under optimized conditions.

### 2.7 Catalytic Activity

The chemicals used for catalytic activity studies are presented in the following Table 2.4.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Chemicals</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Toluene</td>
<td>s.d Fine Chem. Ltd.</td>
</tr>
<tr>
<td>2.</td>
<td>( o )-xylene</td>
<td>s.d Fine Chem. Ltd.</td>
</tr>
<tr>
<td>4.</td>
<td>Phenol</td>
<td>Merck</td>
</tr>
<tr>
<td>5.</td>
<td>( o )-cresol</td>
<td>Merck</td>
</tr>
<tr>
<td>6.</td>
<td>methanol</td>
<td>s.d Fine Chem. Ltd.</td>
</tr>
<tr>
<td>7.</td>
<td>Ethylbenzene</td>
<td>s.d Fine Chem. Ltd.</td>
</tr>
</tbody>
</table>
2.7.1 Ethylbenzene Oxidation

Ethyl benzene oxidation was conducted in a 50mL Glass round bottom flask placed in a thermostated oil bath fitted with a magnetic stirrer and water cooled condenser. In a typical oxidation, required quantity of ethyl benzene, solvent and catalyst were taken in the R.B and after attaining the reaction temperature tertiary butyl hydroperoxide was added in drops. The products were identified by GC-MS and conversion and product selectivity were monitored using a Chemito 8610 GC using a FID detector and an SE-30 column.

2.7.2 Benzylation of Toluene and o-xylene

Liquid phase benzylation of toluene and o-xylene was carried using benzyl chloride as the benzylation agent. The reactants in the required mole ratio and definite amount of the catalyst were taken in a 50mL double necked round bottom flask and refluxed in an oil bath using water condenser. The temperature of the oil bath was adjusted according to the requirement of the reaction studied and kept constant by means of a dimmerstat. The reaction mixture was stirred magnetically and the products were analyzed using a Chemito 8610 GC using a FID detector and an SE-30 column.

2.7.3 Methylation of Phenol and o-cresol

Methylation was carried out in a vertical down flow glass reactor. All the reactions were carried out using 0.5 g charge of the catalyst. Prior to the reaction the
catalysts were activated in the muffle furnace for 1h at 500°C. The catalyst was packed between the layers of quartz wool, and the upper portion of the reactor was filled with glass beads, which served as pre-heaters for the reactants. The reactor was placed inside a temperature-controlled furnace with a thermocouple placed at the centre of the catalyst bed for measuring the reaction temperature. In a typical reaction, a mixture of phenol or cresol and methanol in required molar ratio was fed into the reactor at pre-determined flow rate through a syringe pump at a particular reaction temperature. The products were condensed and collected in an ice trap. The products were identified by GC-MS and were analyzed by a Chemito 8610 GC using a FID detector and an OV-17 column. The conversion was expressed in terms of o-cresol reacted and the product selectivity was obtained as the amount of the particular product divided by the total amount of products multiplied by 100.

Gas chromatographic analysis conditions are given in Table 2.6.

**Table 2.6 GC analysis conditions of various reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Column</th>
<th>Temperature (°C)</th>
<th>Programme of Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Injector</td>
<td>Detector</td>
</tr>
<tr>
<td>Cumene cracking</td>
<td>BP-1</td>
<td>230</td>
<td>230</td>
</tr>
<tr>
<td>Cyclohexanol decomposition</td>
<td>Carbowax</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Ethylbenzene oxidation</td>
<td>SE-30</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Toluene/o-xylene benzylaation</td>
<td>SE-30</td>
<td>230</td>
<td>230</td>
</tr>
<tr>
<td>Phenol/o-cresol methylation</td>
<td>OV-17</td>
<td>250</td>
<td>250</td>
</tr>
</tbody>
</table>
References


