Chapter 2

Materials and Methods

Abstract

The development and preparation of heterogeneous catalysts were considered more as alchemy than science with the predominance of trial and error experiments. In the production of catalysts, even a minute change in the conditions of preparation can change the quality of the catalyst. Hence they must be thoroughly characterized before use. In the present chapter the experimental procedures used for catalyst preparation, the characterization techniques and catalytic activity measurements are described in detail. The physico chemical characterization of the prepared systems are done using techniques such as XRD, EDX, SEM, BET surface area-pore volume measurements, TG/DTG, FTIR, and Diffuse Reflectance UV-vis spectroscopy. The surface acidity measurements were done using ammonia TPD, 2,6 dimethyl pyridine adsorption studies and test reactions such as cumene cracking and cyclohexanol decomposition. Reactions of industrial importance such as epoxidation of cyclohexene, hydroxylation of phenol, tert-butylation of phenol, methylation of aniline and anisole, dehydrogenation of cyclohexane and cyclohexene are chosen for the catalytic activity measurements. Photocatalytic oxidation of benzhydrol as well as photodegradation of methyl orange is carried out over the prepared systems.
2.1 Introduction

The preparation of heterogeneous catalysis has by now lost all empirical aspects. A good catalyst besides having high catalytic activity and selectivity for the desired reaction should have large specific surface area, stability and mechanical strength. These factors should be kept in mind while preparing a catalyst. The design of a catalyst covers all aspects from choice of the active phases to the method of forming particles. The catalyst surface is very complex and heterogeneous with a broad classification of structurally and chemically different sites. The nature of the active sites is the most important factor in heterogeneous catalysis. A complete knowledge on the exact location, structure and electronic ground state of the active site in the catalyst is essential to establish a basic understanding about the structure activity correlations and to improve the efficiency of the catalyst for high stability and selectivity.

2.2 Catalyst preparation

Sol-gel method is used for the preparation of the catalysts. The method is a homogeneous process, which results in a continuous transformation of a solution into a hydrated solid precursor. The sol-gel syntheses have been recognized for their versatility, which allows better control of the texture, composition, homogeneity and structural properties of the final solids. The nanoscale chemistry involved in the sol-gel methods is a more direct way to prepare highly divided materials. Particulate sol-gel route is used for the preparation of titania systems using metatitanic acid as precursor. The transition metals like molybdenum, chromium and tungsten is incorporated to titania from their soluble salts. Similarly the modification of titania is done
using rare earth metals like lanthanum, praseodymium and samarium from their nitrate salt solution. For a comparative evaluation of the properties, pure titania is also prepared.

Materials

The materials used for the preparation of catalysts are given below.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metatitanic Acid</td>
<td>Travancore Titanium Products Limited</td>
</tr>
<tr>
<td>Ammonium tungstate</td>
<td>Merck</td>
</tr>
<tr>
<td>Ammonium molybdate</td>
<td>Merck</td>
</tr>
<tr>
<td>Chromium Nitrate</td>
<td>Merck</td>
</tr>
<tr>
<td>Praseodymium Nitrate</td>
<td>Indian Rare Earth Ltd</td>
</tr>
<tr>
<td>Lanthanum Nitrate</td>
<td>Indian Rare Earth Ltd</td>
</tr>
<tr>
<td>Samarium Nitrate</td>
<td>Indian Rare Earth Ltd</td>
</tr>
<tr>
<td>Conc. Nitric Acid</td>
<td>Merck</td>
</tr>
<tr>
<td>Conc. Sulphuric acid</td>
<td>Merck</td>
</tr>
<tr>
<td>Conc. Ammonia</td>
<td>Merck</td>
</tr>
</tbody>
</table>

Methods

A detailed experimental procedure for the preparation of the catalysts is given in the flow chart in figure 2.1. The estimation of the sol is done gravimetrically before the addition of the corresponding metal solution.
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Figure 2.1 Preparation process of metal incorporated titania

Cochin University of Science and Technology
2.2.1 Preparation of titania

Metatitanic acid is digested with concentrated sulphuric acid above 100°C and the resultant solution is filtered to get titanyl sulphate. Titanium hydroxide is precipitated by adding concentrated ammonia dropwise to this titanyl sulphate solution until the pH rises above 10. Then the precipitate is washed several times with hot water to remove sulphate ions totally. This titanium hydroxide is suspended in hot water at 70°C and added 10% HNO₃ with continuous stirring. A clear transparent sol is obtained at a pH of ~1.5 which is stable for months. The sol is kept for ageing for 1 day and then chemical gelation is done by slightly perturbing the pH of the stable sol with the addition of ammonia. The gel is kept in contact with the mother liquor for 1 day and then decanted off. The filtered precipitate is washed with distilled water, dried overnight at 110°C in an air oven and powdered below 100 mesh size. The xerogel thus obtained was calcined at 500°C for 5h in a muffle furnace.

2.2.2 Preparation of metal incorporated titania

Titania sol is prepared as above and the incorporation of the metal is done in the sol phase. Transition metals like molybdenum, tungsten and chromium are incorporated from their respective aqueous salt solution such as ammonium molybdate, ammonium tungstate and chromium nitrate. Similarly rare earth metals like lanthanum, samarium and praseodymium is incorporated from their respective nitrate salt solution. 20ml of the sol is taken and estimated quantitatively. 2, 6 and 10 wt % of the metal is incorporated to titania by taking corresponding amounts of the salt solution. The mixed sol is stirred
again for 3h and then gelation is done by adding ammonia drop wise. Then aging of the gel is done for a day. The gel is dried overnight and calcined at 500°C for 5h.

2.3 Catalyst notations

The catalyst systems developed for the present investigation and its designation are given below.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Pure titania</td>
</tr>
<tr>
<td>TiXy</td>
<td>Ti containing metals (X) such as Cr, Mo, W, La, Pr and Sm having weight % (y) of 2, 6 and 10.</td>
</tr>
</tbody>
</table>

2.4 Characterization techniques

In heterogeneous catalysis, the reaction occurs at the surface of the catalyst. Catalysis and catalytic surfaces hence need to be characterized by reference to their physical properties and by their actual performance as a catalyst. The most important physical properties are those relating to the surface because catalyst performance is determined by surface parameters. Any characterization of a catalyst must start with knowledge of the chemical composition of the same. It is important to know the presence and the quantity of trace elements, additives, poisons etc., in a catalyst. The amount of the sample required for any characterization is relatively small and in many cases the method is non-destructive.
The prepared catalyst systems were characterized by adopting a variety of physico-chemical properties which include BET surface area and pore volume measurements, X-Ray diffraction, Energy Dispersive X-Ray analysis, Scanning electron microscopy, Fourier Transform Infrared Microscopy, UV-Vis Diffuse Reflectance Spectroscopy and TG-DTG analysis. Before each characterization except for thermogravimetric analysis, the samples were activated at 500°C for 2h.

### Materials

The materials used for catalyst characterization are

<table>
<thead>
<tr>
<th>Materials</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Nitrogen</td>
<td>Sterling gases Pvt. Ltd.</td>
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<tr>
<td>Potassium Bromide</td>
<td>Merck</td>
</tr>
<tr>
<td>Magnesium Oxide</td>
<td>Merck</td>
</tr>
</tbody>
</table>

### Methods

A brief discussion of each method of characterization technique adopted along with its experimental aspects is presented in the following sections.

#### 2.4.1 X-Ray Diffraction Analysis

X-Ray diffraction has remained the mainstay of structure determination of crystalline solids and the recent developments in technology and computing have paved the way for unequivocal determination of even macromolecular
structures with remarkable accuracy. It contains a wealth of useful information provided one can exploit and extract the same, with patience in synthesizing good materials and a healthy scientific aptitude to apply modern computational facilities.

Powder X-Ray diffraction is a long-range order technique sensitive to the basic periodic structure of a solid sample. The basic principle underlying the analysis is that the scattered waves from the atoms interfere constructively, if they are in phase (coherent), and diffracted beams are formed in specific directions. These directions are governed by the wavelength of the incident radiation and the nature of the crystalline samples. Braggs law formulated by W.L. Bragg in 1913, relates the wavelength of the X-Rays to the spacing of atomic planes by the equation,

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

where \( n \) is the order of reflection, \( \lambda \), the wavelength of X-Rays, \( \theta \), Bragg angle and \( d \), the interplanar spacing.

The three main types of information in a diffraction pattern include the position, the intensity and the shape of diffraction peaks. The positions of the diffraction peaks are determined by the geometry of the crystal lattice i.e., the size and shape of the unit cell. The intensities of the peaks in a profile are related to the specific atoms in a crystal and their arrangement in the unit cell of the crystal. The diffraction profile is related to the size and perfection of the crystallites and various instrumental parameters. Most of the analytical methods used for diffraction profile studies, emphasize the position variables (d spacing) as they can be accurately determined and the other two parameters
are considered when quantitative analysis/structure refinement and crystallite size are required.

Crystallite size \((L)\) can be determined from the corrected line broadening \((\delta)\) in the sample using Scherrer equation.

\[
L = K \lambda / \beta \cos \theta
\]

Where \(L\), \(\lambda\) and \(\theta\) have their usual meanings, \(L\) is the mean dimension of the crystallites composing the powder sample or the thickness of the crystal in a direction perpendicular to the diffracting planes, \(K\) is a constant approximately equal to 0.9-1.0 and related both to the crystallite shape and to the way in which \(\delta\) and \(L\) are related.

XRD patterns were recorded in a Rigaku D-max C X-Ray diffractometer using Ni filtered CuK\(\alpha\) radiation \((\lambda = 1.5406\text{Å})\). The crystallite phases were identified by comparison with the standard JCPDS data file.

2.4.2 Diffuse Reflectance UV-Vis Spectroscopy

The diffuse reflectance UV-Vis spectroscopy is known to be a very sensitive probe for the identification and characterization of metal ion coordination. It is a non-invasive technique that uses the interaction of light, absorption and scattering, to produce a characteristic reflectance spectrum, providing information about the structure and composition of the medium. It gives information regarding electronic transition between orbitals or bands in the case of atoms, ions and molecules in gaseous, liquid or solid state. Electronic transition of transition elements are of two types, namely, metal centered transitions \([d-d\ or\ (n-1)\ d-ns]\) and charge transfer (CT) transitions. d-d transitions gives information about the oxidation state and the coordination.
environment of transition metal ion. (n-1) d-ns transitions are often too high in energy to be observed in the spectrum. The CT transitions are intense since they are Laporte allowed and are sensitive to the nature of donor and acceptor atoms.\(^{10-11}\). Diffuse reflectance UV-Vis spectra of the samples were recorded at room temperature between 200 and 800 nm using magnesium oxide as standard in *Ocean optics AD 2000* instrument with a CCD detector.

### 2.4.3 Thermogravimetric Analysis

Thermal analysis is a widely used analytical technique for material research\(^ {12}\). Thermogravimetry or thermogravimetric analysis (TGA) provides a quantitative measurement of any weight changes associated with thermally induced transitions. The rates of these thermally induced processes are often a function of the molecular structure. TGA provides information on the thermal stability of the material. Thermal stability of a compound depends on the constituent elements present and on the type of linkages between the different elements.\(^3\) Changes in weight result 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 of weight of the samples.

Thermal analysis techniques have great potential in the development of catalysts especially for the control and generation of active systems. They can also be successfully employed for determining the surface properties of the catalysts under favorable conditions. The application of thermal analysis methods for catalyst development is reaching a mature status and can be
expected to be exploited by many others for even studying the surface
transformations that take place on catalyst surface.

In thermo gravimetric analysis, the loss of weight of a sample is being
continuously recorded over a period of time under controlled heating rate. The
first derivative of the thermogram (DTG) gives a better understanding of the
weight loss and can also be used to determine the thermal stability of the
samples. TGAQ V2.34 thermal analyzer was used for carrying out
thermogravimetric studies. About 20mg of the samples was used at a heating
rate of 20°C/min from 20 to 700°C in N₂ atmosphere. The TG data were
computer processed to get thermograms. Any decomposition of the sample is
indicated by a dip in the curve. These dips correspond to the weight loss due to
decomposition and hence provide an idea about the species lost during the
heating step. This method cannot distinguish the actual nature of the material
evolved in the course of the process and is also handicapped in resolving
overlapped thermal analysis. So it is seldom able to describe the process under
study completely.

2.4.4 Surface Area and Pore Volume Measurements

The surface area calculated from the use of BET equation is perhaps
the most popular and widely used in the literature, ever since Brunauer,
Emmett and Teller (BET) derived the equation for physical adsorption of gases
on solid surfaces that lead to multilayer adsorption¹³. The phenomenon of
higher concentration of any molecular species at the surface than in the bulk of
the solid or liquid is known as adsorption. The assumptions are that the surface
is energetically uniform, that the condensation of layers of gas can proceed to
multilayers and that the adsorbed molecules do not interact laterally. The simple form of this equation that forms the basis of the BET method for the determination of surface area of solids can be written as:

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

where \( V \) is the volume of gas adsorbed at equilibrium pressure, \( P \) and \( P_0 \) is the saturated vapour pressure of the adsorbate at liquid nitrogen temperature and \( C \) is the isothermal constant. By plotting \( P / [V (P_0 - P)] \) vs \( P / P_0 \) and determining \( V_m \) from the slope and the resultant straight line in the partial pressure range of 0.05 to 0.35, the surface area can be calculated. The specific surface area can be found out using the relation,

\[
A = V_m N_o A_m / W \times 22414
\]

Where \( N_o \) is the Avogadro number, \( A_m \) the molecular cross sectional area of the adsorbate and \( W \) the weight of the sample (g).

The method is based on the phenomenon of adsorption. Nitrogen is commonly used as the adsorbate at liquid nitrogen temperature. Here we determine the volume of nitrogen gas adsorbed by a known weight of the sample at liquid nitrogen temperature. Since the area occupied by single adsorbed molecular nitrogen can be estimated, the total surface area can be calculated by multiplying the area of one molecule by the number of molecules required forming the monolayer. Adsorption varies directly with pressure and inversely with temperature. Here the temperature is held constant and the amount of nitrogen adsorbed at liquid nitrogen is measured at different relative pressures. \( P_o \) will depend on the temperature and hence the purity of liquid nitrogen.
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Simultaneous determination of surface area and total pore volume of the samples were achieved in a Micromeritics Gemini – 2360 surface area analyzer by the low temperature nitrogen adsorption method. Previously activated samples at 500°C were degassed at 400°C under nitrogen atmosphere for 4h prior to each measurement. The pore volume is measured by the uptake of nitrogen at a relative pressure of 0.9.

2.4.5 Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectroscopy has been extensively used for identifying the various functional groups on the catalyst itself, as well as for identifying the adsorbed species and reaction intermediates on the catalyst surface.\textsuperscript{14-15} It is one of the few techniques capable of exploring a catalyst, both in its bulk and its surface, and under the actual reaction conditions. Infrared spectrum originates from the transitions between discrete vibrational and rotational energy levels of the molecules. The IR spectrum of the compound is the characteristic of that compound and may be used for identification just like melting point, boiling point optical rotation etc. The analysis of the spectrum was done by comparing with the reported values. The most commonly used region for this purpose is the fingerprint region (4000 – 600cm\textsuperscript{-1}).

Infrared spectroscopy has been widely used for characterizing the acid sites of the catalyst, which are responsible for their catalytic properties. The measurement of the intensity of IR bands due to adsorbed pyridine at a particular temperature enables one to calculate the concentration of the individual Bronsted and Lewis acid sites in a catalyst sample. It also finds
applications to identify the intermediate species in heterogeneous catalytic reactions.

The FTIR spectrum of the sample was recorded on a Nicolet Impact 4000 spectrometer using the KBr pellet method. The measured quantity of the sample was mixed with spectroscopic grade KBr and ground well. The mixture was compacted to a disc by pressing. The percentage transmittance is plotted against the wave number.

2.4.6 Energy Dispersive X-Ray (EDX) fluorescence Analysis

Energy dispersive X-Ray fluorescence analysis is one of the successful analytical methods for the qualitative and quantitative analysis of the solid samples. It allows non destructive elemental analysis of the sample\textsuperscript{16}. The principle of EDX is based on the strong interaction of electrons with matter. When electrons of appropriate energy impinge on a sample, they cause emission of X-Rays whose energies and relative abundance depend on the composition of the sample.

The electron beam from a scanning electron micrograph used in this technique can eject an electron from the inner shell of the sample atom. The resulting inner shell electron vacancy is filled by another electron from a high energy shell in the atom. While moving from a high energy state to a lower one, this vacancy filling electrons give up some of its energy (equal to the difference in the energy between the two electronic energy levels involved) in the form of electromagnetic radiation. Since this electronic energy is fairly larger for inner shells, the radiation appears as X-rays. As all elements have a unique configuration of electronic energy levels, the X-ray pattern spectrum
will be unique for a particular element. Furthermore, under the given analysis conditions, the number of X-rays emitted by each element will be directly proportional to the concentration of that element in the sample\textsuperscript{17}.

The X-ray peak position along with the energy scale identify the element present in the sample, while the integrated peak areas after application of appropriate correction factors, can give us percentage composition of each of the elements\textsuperscript{8}. Powdered sample is put on a double-sided carbon tape on a metal strip before analysis. EDX spectra of the samples were recorded in an EDX-JEM-3S instrument (JEOL Co. link system AN-1000-Si-Li detector).

2.4.7 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy is a well-established technique in the realm of materials science for the determination of structure. It allows the imaging of the topography of a solid surface by using back scattered or secondary electrons with good resolution of about 5nm. In this technique, a fine probe of electrons is scanned over the sample surface using deflection coils. The interaction between the primary beam and the specimen produces various signals, which are detected, amplified and displayed on a cathode ray tube screened synchronously with the beam. They can also be conveniently deflected and focused by electronic or magnetic field so that magnified real space images can be formed. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The
combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today. This make the technique suitable for producing very impressive, in focus images from a highly irregular structure typical of catalyst specimens. This technique is of great interest in catalysis because of its high resolution\textsuperscript{18}. The scanning electron microscope can be used to measure not only the composition profile of a surface, but also the geometric profile of its magnetic structure.

Scanning electron micrographs of the samples were taken using Cambridge Oxford 7060 scanning electron microscope with a resolution of 1.38eV. The powdered sample is put on a double sided carbon tape on a metal strip. It is further sputter coated with gold to minimize the charging effect and to protect the material from thermal damage by the electron beam. A film of uniform thickness, about 0.1mm, was maintained for all the samples. A serious draw back of the analysis is the charging of the particles and also the result need not be the representative of the whole sample.

2.5 Surface acidity measurements

Solid acid catalysts in many commercial processes have proved to be more economical and often produce better quality products. Being stronger acids, they have a significantly higher catalytic activity compared to conventional acid catalysts\textsuperscript{20}. Determining the quantity and strength of the acid sites is crucial to understanding and predicting the performance of a catalyst. Therefore the main task of catalyst technologists lies in the surface acidity measurements. Quantitative analysis of model surfaces using temperature
programmed desorption technique was developed in the early 1960s. The problem of finding the most relevant method for acidity measurement is an evolutionary process. Various methods have been used to find out the nature, strength and concentration of acid centers on the surface. Some techniques can distinguish between the Lewis acidity and Bronsted acidity. A large variety of probe molecules have been utilized to ascertain the surface acidity. Similarly model reactions such as cumene cracking and cyclohexanol reaction are carried out to evaluate surface acidity.

**Materials**

The materials used for the acidity determination of the prepared catalysts are given below.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Sulphuric Acid</td>
<td>Merck</td>
</tr>
<tr>
<td>2 Sodium Hydroxide</td>
<td>Merck</td>
</tr>
<tr>
<td>3 Cumene</td>
<td>Aldrich</td>
</tr>
<tr>
<td>4 Cyclohexanol</td>
<td>CDH</td>
</tr>
<tr>
<td>5 2,6 dimethyl pyridine</td>
<td>Merck</td>
</tr>
<tr>
<td>6 Ammonia</td>
<td>Merck</td>
</tr>
<tr>
<td>7 Phenolphthalein</td>
<td>Merck</td>
</tr>
</tbody>
</table>

**Methods**

2.5.1 **Temperature Programmed desorption of ammonia**

The temperature programmed desorption technique is one of the most widely used and flexible techniques for characterizing the acid sites on oxide...
surface. The method is based on desorbing ammonia adsorbed on the solids by heating it at a programmed rate. Ammonia is an excellent probe molecule for the measurement of acid property by TPD, because it can be stabilized on acid sites. Its small molecular size allows ammonia to penetrate into all pores of the solid where larger molecules commonly found in cracking and hydrocracking reactions only have access to large micropores and mesopores. Also, ammonia is a very basic molecule, which is capable of titrating weak acid sites, which may not contribute to the activity of the catalyst. The strongly polar adsorbed ammonia is also capable of adsorbing additional ammonia from the gas phase.

TPD experiment describes not only the number and strength of chemisorption sites, but it may also describe the surface heterogeneity of the surface sites. In principle, any chemical interaction between the adsorbate and adsorbent can be studied by the TPD technique.

The assumption in TPD is that the desorption energy is primarily the deprotonation energy of the solid acid\(^1\). Thus, a stronger acid requires a higher energy to deprotonate, but this direct relationship may be modified by the type of acid sites. This technique then could provide a relative amount of weak, medium and strong acidity in a solid, depending upon the temperature in which the desorption of an adsorbed base takes place. It may be noted that the temperature range associated with weak, medium or strong acid sites is rather arbitrary. Still the information and classification of the acid sites is useful. It has also been the practice to collect the desorbing base in a medium and then titrate against a standard acid to quantify the desorbed base, according to the temperature range in which it desorbs.
Ammonia TPD measurements were carried out in the range 100-600°C in a conventional flow type apparatus using a stainless steel reactor of 30 cm length and 1 cm diameter kept in a cylindrical furnace. The catalyst is pelletized and put in the reactor under nitrogen flow at 300°C. After cooling to room temperature, ammonia was injected in the absence of carrier gas flow and allowed to attain equilibrium. The excess and physisorbed ammonia was flushed out using a current of nitrogen for half an hour. Under a controlled temperature programme, the amount of chemisorbed ammonia leached out for each 100°C was absorbed in a known volume of dilute sulphuric acid. The desorbed ammonia is estimated volumetrically by titrating with sodium hydroxide solution. The amount of ammonia desorbed in the temperature ranges 100-200, 200-400 and 400-600°C was assigned as measures of weak, medium and strong acid sites respectively.

2.5.2 Thermodesorption Studies of 2,6-dimethyl pyridine

2,6-dimethyl pyridine is a useful probe molecule for the selective determination of the Bronsted acid sites\textsuperscript{22}. Due to steric hindrance of the methyl groups, 2,6-DMP gets selectively adsorbed at the Bronsted acid sites and thus the percentage weight loss during thermal treatment will correspond to the Bronsted acidity of the sample. Previously activated catalysts were kept in a desiccator saturated with vapours of 2,6-DMP for 48h for the effective and uniform adsorption. After this, the weight loss of the adsorbed samples was measured by thermogravimetric analysis in nitrogen atmosphere at a heating rate of 20°C/minute. The fraction of weight loss in the range of 300-600°C was found out and taken as a measure of the Bronsted acidity of the sample\textsuperscript{23}.
2.5.3 Cumene cracking reaction

Cumene cracking reaction is generally used as the probe reaction to characterize the acid properties of the solid acid catalyst. Cumene cracking mainly depends on Bronsted acid sites whereas dehydrogenation occurs on Lewis acid sites\textsuperscript{24}. The major reactions taking place during the cracking of cumene are dealkylation to give benzene and propene and dehydrogenation to give \( \alpha \)-methyl styrene. Thus it is possible to compare both Lewis and Bronsted acid sites in a catalyst through cumene conversion reaction. The vapour phase cumene cracking reaction is carried out in a fixed bed down flow vertical glass reactor. The reaction conditions are optimized and the product distribution of all the prepared systems is compared under the optimized conditions. The product analysis was achieved by using a gas chromatograph, comparing with authentic samples.

2.5.6 Cyclohexanol decomposition reaction

Cyclohexanol decomposition reaction may be used to characterize the acidity of solid acid catalyst. The amphoteric nature of cyclohexanol permits their interaction with acidic and basic sites resulting in dehydration and dehydrogenation. The reaction usually gives two types of products; cyclohexene and cyclohexanone. The selectivity to a particular product is determined by the acid base properties of the catalyst\textsuperscript{25}. The reaction was carried out in a fixed bed down flow glass reactor and the reaction conditions are optimized. The catalyst samples are compared under the optimized reaction conditions and the liquid products were analyzed by using a gas chromatograph.
2.6 Catalytic activity measurements

The role of a catalyst in bringing about a chemical reaction is a stimulating one. In order to test the catalytic activity of the prepared systems, reactions are carried out both in liquid as well as vapour phase. In the present case, epoxidation of cyclohexene and hydroxylation of phenol is carried out in the liquid phase. Alkylation of aromatics to give various industrially important products can be successfully carried out in vapour phase over the prepared catalytic systems. All the systems are effective in dehydrogenating cyclohexane and cyclohexene. Titania, being a well known photocatalyst, the influence of modified metals on its photocatalytic activity is studied in detail. Photocatalytic oxidation of benzhydrol and photodegradation of methyl orange were done over the prepared catalysts.

Materials

The materials used for the catalytic activity measurement is as follows.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>2 Cyclohexane</td>
<td>Merck</td>
</tr>
<tr>
<td>3 TBHP in water</td>
<td>Aldrich</td>
</tr>
<tr>
<td>4 Phenol</td>
<td>Merck</td>
</tr>
<tr>
<td>5 Hydrogen peroxide</td>
<td>SD Fine-Chem Ltd</td>
</tr>
<tr>
<td>6 Tert-butanol</td>
<td>Qualigens</td>
</tr>
<tr>
<td>7 Aniline</td>
<td>Merck</td>
</tr>
<tr>
<td>8 Methanol</td>
<td>SD Fine-Chem Ltd</td>
</tr>
</tbody>
</table>
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9 Anisole Merck
10 Benzhydrol SD Fine-Chem Ltd
11 Methyl orange Merck
12 Acetonitrile Merck

Methods

A brief description of the experimental procedure for the different types of reactions studied is given below. The catalytic activity was expressed as the percentage conversion and the selectivity for a product is expressed as the amount of the particular product divided by the total amount of products multiplied by 100.

2.6.1 Liquid Phase Reactions

Epoxidation of cyclohexene and hydroxylation of phenol was carried out in liquid phase. The reactants in the required molar ratio and a definite amount of the catalyst were taken in a 50ml round bottom flask fitted with a water condenser. The whole set up is placed in an oil bath put on the top of a magnetic stirrer. The temperature of the oil bath can be adjusted according to the requirement for a particular reaction and kept constant with the help of a dimmerstat. The product analysis was done using gas chromatograph (Chemito) equipped with Flame ionization detector and a capillary column.

2.6.2 Gas Phase Reactions

Applicability of the liquid phase reaction is often limited by low temperature requirement below the boiling point of the least boiling
component of the reaction mixture. Reactions can be done at much higher temperatures in the vapour phase set up where the reactants will be in the gas phase, which undergo reaction over the catalyst surface. Tert-butylation of phenol, methylation of aniline and anisole, dehydrogenation of cyclohexane and cyclohexene were done in vapour phase. These reactions were conducted at atmospheric pressure in the presence of $N_2$ in a fixed bed, vertical, down flow reactor inserted into a double zone furnace. A temperature controller was used to maintain the temperature of the reaction. The reactant was fed into the reactor with the help of a syringe pump at a controlled flow rate. The condensed reaction mixture was collected downstream from the reactor in a receiver connected through a cold water circulating condenser. The products were collected at regular intervals and analyzed gas chromatographically.

2.6.3 Photochemical reactions

The photocatalytic cativity of the prepared systems towards the oxidation of benzhydrol as well as the degradation of methyl orange is intensively studied. The reactions were carried out in a Heber photoreactor (multilamp type, model HML-MP88) containing concentrically arranged eight numbers of 8W mercury lamps of 365nm wavelength. In the methyl orange degradation, the extent of degradation was determined by using a Shimadzu UV-Vis spectrophotometer (UV-160A) at $\lambda_{\text{max}}$ of 660nm. The product analysis of the photooxidation of benzhydrol was done gas chromatographically.
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