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The performance of a catalyst depends on the method of preparation and catalyst pretreatment condition along with the reaction parameters. The materials and the experimental procedures used for catalyst preparation, surface acidity and catalytic activity measurements are described in this chapter. The structural and morphological characteristics of the prepared samples were investigated by the techniques like wide and low angle XRD, BET surface area and pore volume measurements, BJH sorption studies, TEM, FT-IR, TG-DTA, SEM, EDX, ICP-AES, TPR in H₂ and UV-Vis DRS. These techniques are expected to be powerful tools to study the changes of the local environment and nature of ceria species. Ammonia TPD and vapour phase cumene cracking as the test reaction for acidity are adopted for the surface acidity determination. For the activity study of the prepared systems, liquid phase reactions like oxidation of ethyl benzene using TBHP to get acetophenone as the main product, Friedel Crafts benzylation of toluene, o-xylene and anisole using benzyl chloride, acetalization and deacetalization of cyclohexanone for the protection of ketone functional group and vapour phase reaction of methylation of phenol are done.

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2.1 Introduction

Catalysis is a complex surface phenomenon occurring on the surface of a catalyst. The adsorption of the reactant molecules and their interaction to give product on the active phase of the catalyst depend not only on the reaction variables, but also on the nature of sites on the catalyst surface, which in turn determines the quality of the catalyst [1]. In the preparation of the commercial catalysts even a minute change in the conditions of preparation, changes the quality of the catalyst. Hence utmost care should be taken during the preparation of systems. When designing and making reliable catalysts, it is necessary to take into account process parameters such as temperature, pressure, reactant concentration and space velocity, as well as variable factors such as feed composition and unpredictable or unsuspected factors such as impurities and poisons in the feed [2].

We have prepared six series of ceria catalysts modified with chromium, manganese, iron, cobalt, nickel and copper. The experimental procedures used to prepare the pure and supported catalysts are given in this chapter. All the prepared catalyst systems were characterized and tested for catalytic activity with various techniques. The materials used and the methodologies adopted are described in the following sections.

2.2 Catalyst Preparation

The metal oxide was prepared via templated method (surfactant assisted route) [3] using cerium nitrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] as the precursor.

2.2.1 Materials

The materials used for the catalyst preparations are given below

Table 2.1 Chemicals used for catalysts preparations

Materials	Suppliers
Cerium nitrate hexahydrate	Indian Rare Earth Ltd.
Nitric acid	Merck
Ammonia	Qualigens
Chromium nitrate	S. D. Fine Chemicals Ltd
Manganese Acetate	Merck
Ferric Nitrate	Qualigens fine Chemicals
Cobalt Nitrate	S. D. Fine Chemicals Ltd
Nickel Nitrate	S. D. Fine Chemicals Ltd
Copper Nitrate	S. D. Fine Chemicals Ltd
Hexadecyl amine	Sigma Aldrich
Methanol	Merck

2.2.2 Methods

A detailed discussion of the experimental procedures used to develop the catalyst systems is given below.

2.2.2.1 Preparation of Cerium oxide [4]

Mesoporous ceria was prepared by surfactant assisted method using the neutral surfactant hexadecyl amine as the template. 0.05M cerium nitrate solution was added to a solution of hexadecyl amine in 1:1 water-ethanol mixture with stirring. A molar ratio of 2 was kept for precursor to the surfactant. The pH of the mixture was maintained above 10. The mixture was stirred for 6 hours and then aged for 3 days at 60°C. The precipitate obtained was washed with ethanol- water mixture several times and then with deionized water and filtered. The dried precipitate is

precalcined at 250°C for 6 hours. The powdered sample is then calcined at 350°C for 4 hrs.

2.2.2.2. Preparation of metal incorporated Cerium oxide

0.5M solution of the corresponding metals [Cr (NO₃)₃.9H₂O, Mn (NO₃)₃, Fe (NO₃)₃, Co (AC) ₂.4H₂O, Ni (NO₃)₂.6H₂O and Cu (NO₃)₂.3H₂O,] containing required amount of metal (2, 4 and 10wt% of metal) was added to the previously prepared mesoporous ceria and was mechanically stirred for 6h, kept overnight and dried at 80°C which was further dried at 110°C. It is powdered and calcined at 350°C to obtain metal incorporated cerium oxide.

2.3 Catalyst Notation

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

Table 2.2 Notations for catalysts prepared

Notation	System
Ce	Pure cerium oxide
CeCr (X %)	Chromium incorporated ceria with x= 2, 4, 10 for 2, 4 & 10 weight % of Cr respectively
CeMn(X %)	Manganese incorporated ceria with x= 2, 4, 10 for 2, 4 & 10 weight% of Mn respectively
CeFe (X %)	Iron incorporated ceria with x= 2, 4, 10 for 2, 4 & 10 weight % of Cr respectively
CeCo (X %)	Cobalt incorporated ceria with x= 2, 4, 10 for 2, 4 & 10 weight % of Co respectively
CeNi (X %)	Nickel incorporated ceria with x= 2, 4, 10 for 2, 4 & 10 weight % of Ni respectively
CeCu (X %)	Copper incorporated ceria with x= 2, 4, 10 for 2, 4 & 10 weight % of Cu respectively

2.4 Characterization Techniques

Catalyst characterization is a highly relevant area in catalysis. Catalytic properties of a surface are determined by its composition and structure on atomic scale. The performance of a catalyst depends on two parameters, physical properties, which influence the lifetime, mass and mass transfer phenomena and active site parameters, which judge the reaction behavior, which is correlated with the number and nature of active sites. The prepared catalyst samples were characterized by adopting a variety of Physico-chemical methods.

2.4.1 Materials

The materials used for catalyst characterization is given in Table 2.3.

Table 2.3 Chemicals used for characterisation

Materials	Suppliers
Liquid Nitrogen	Sterling gases, Ambalamugal
Magnesium oxide	Merck
Con.H ₂ SO ₄	S. D. Fine Chemicals
Sodium Hydroxide	Merck
Oxalic acid	Merck
Cumene	Sigma Aldrich chemicals

2.4.2 Methods

A brief discussion of each method of characterization adopted along with its experimental aspects is presented in the following sections. Before each characterization, the samples were activated at 350 °C for 1 hour.

2.4.2.1 X- ray diffraction studies (XRD)

X-ray diffraction is one of the most important tools in solid state chemistry since it is a powerful and readily available method for the identification and characterization of crystalline solid phases in heterogeneous catalysis. It can provide information about specific component in a system, purity of substance, transition to different phases etc.

The principle of XRD is based on the interaction of X-rays with the periodic structure of a polycrystalline material, which acts as a diffraction grating. A fixed wavelength is chosen for the incident radiation and the diffraction patterns obtained by observing the intensity of the scattered radiation as a function of scattering angle 2θ .

The relationship among the wavelength of X-ray beam, the angle of diffraction and the inter planar distance or d-spacing d , is given by Bragg's equation [5],

$$n \lambda = 2d \sin\theta$$

Where,

- n - Order of diffraction
- θ - Bragg angle
- d - Inter planar spacing
- λ - Wavelength of x-rays

This relation demonstrates that interference effects are observable only when radiation interacts with physical dimensions that are approximately the same size as the wavelength of the radiation. Since the

distances between atoms or ions are of the order of 1\AA , diffraction methods require radiation in the X-ray region of the electromagnetic spectrum, or beams of electrons or neutrons with similar wavelength. So, through X-ray spectra one can identify and analyse any crystalline matter. The degree of crystallinity or order will decide the quality of the obtained result. In order to do this, a diffractometer is needed. Basically, an X-ray diffractometer consists of X-ray generator, sample holder and an X-ray detector, such as photographic film or a movable proportional counter. The most usually employed instrument to generate X-rays is X-ray tubes, which generate X-rays by bombarding a metal target with high energy (10-100 keV) electrons which knock out core electrons. Thus, an electron in an outer shell fills the hole in the inner shell and emits an X-ray photon. Two common targets are Mo and Cu, which have strong $K\alpha$ X-ray emissions at 0.71073 and 1.5418\AA , respectively. Apart from the main line, other accompanying lines appear which have to be eliminated in order to facilitate the interpretation of the spectra. These are partially suppressed by using crystal monochromator. Perhaps the most routine use of diffraction data is for phase identification [6, 7]. Each crystalline powder gives a unique diffraction diagram, which is the basis for a qualitative analysis by X-ray diffraction.

The X-ray diffraction pattern of a crystalline phase is a characteristic fingerprint, which enables the determination of phase purity and of the degree of crystallinity. Identification is practically always accompanied by the systematic comparison of the obtained spectrum with a standard one (a pattern), taken from any X-ray powder data file catalogues, published by the American Society for Testing Materials (JCPDS). Structural details of porous materials on a scale covering from approximately 1 to 100 nm may

be determined from measurements of the small angle scattering (SAS) of both X-rays (SAXS) and neutrons (SANS). For mesoporous materials reflexes are observed in X-ray powder patterns at low 2θ angles ($0.5 < 2\theta < 10^\circ$). These reflexes are due to the long-range order induced by the very regular arrangement of the pores. Because d -spacings are rather big for the mesopores, the reflexes appear at low angles. Unit cell parameter (a_0) of cubic lattice can be calculated from,

$$a_0 = d (h^2 + k^2 + l^2)^{1/2}.$$

The unit cell dimension determined by XRD is also used to calculate the frame wall thickness (FWT) of the channels of the mesoporous materials.

A rough estimate of crystallite size can be obtained from the line broadening using the Scherrer's equation [8]

$$d = 0.9\lambda / \beta \cos\theta$$

Where

- β : Full Width half maximum (FWHM) of the strongest peak
- d : Inter planar spacing
- 2θ : Scattering angle

Powder XRD of the prepared samples were taken on a Rigaku *Xpert PRO MPD* model with Ni filtered Cu $K\alpha$ radiation (λ -1.5406 Å) within the 2θ range 0-10° at a speed of 1°/min. The crystalline phases were identified by comparison with standard JCPDS (Joint Committee on Powder Diffraction Standards) data file [9].

2.4.2.2 Adsorption Isotherm

Gas adsorption is a prominent method to obtain a comprehensive characterization of porous materials with respect to the specific surface area, pore size distribution and porosity. This requires, however, a detailed understanding of the fundamental processes associated with the sorption and phase behaviour of fluids in porous materials and their influence on the shape of sorption isotherms, which serves as a basis for surface and pore size analysis. Pore width, pore shape and the effective adsorption potential are the factors that determine the pore filling. In case of so-called micropores (pore width < 2 nm, according to IUPAC classification) the pore filling occurs in a continuous way, whereas in case of mesopores (pore widths in the range from 2-50 nm) pore filling occurs by pore condensation, which reflects a first order gas-liquid phase transition. Nitrogen physisorption is a commonly applied technique to characterize porous and nonporous materials [10, 11, 12]. Properties like surface area pore size pore volume, and pore size distribution can be obtained by careful analysis of the measured data. The amount of adsorbed/desorbed nitrogen is measured as a function of the applied pressure, giving rise to the adsorption/ desorption isotherm. The shape of the isotherm depends on the porous texture of the measured solid. According to the IUPAC classification six types of isotherms can be distinguished as shown in Fig. 2.1

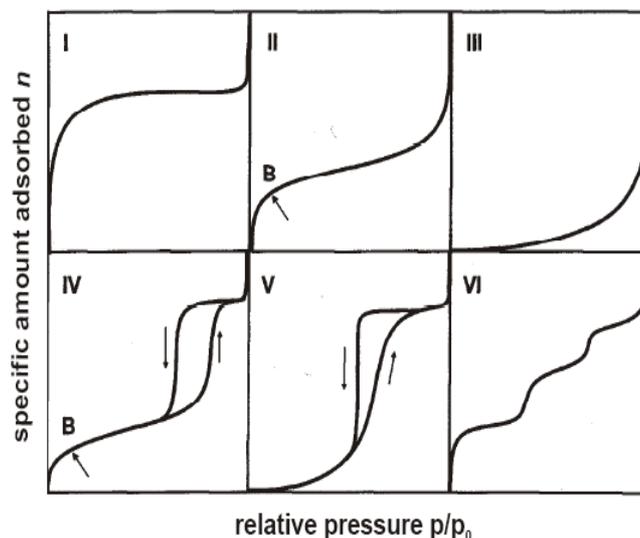


Fig. 2.1 Isotherm types according to IUPAC definition.

- Type I* – microporous material,
Type II – macro- or non-porous material,
Type III – macro- or non-porous material with weak adsorbate-solid interactions,
Type IV – mesoporous material,
Type V – mesoporous material with weak adsorbate – solid interactions,
Type VI – stepwise adsorption at very weak adsorbate- solid interactions.

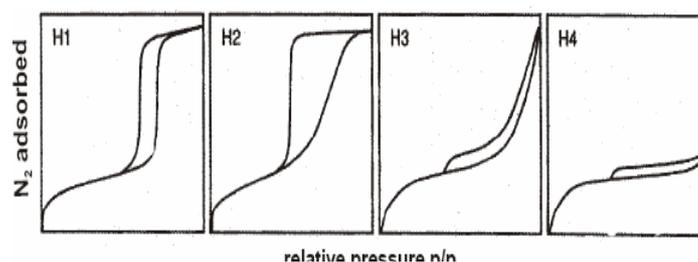


Fig. 2.2 Hysteresis types according to IUPAC definition.

- H1* – typical for type IV isotherms,
H2 – characteristic for “ink-bottle” pores,
H3 and H4 – slit pores

2.4.2.3 BET Surface area and pore volume measurements

Surface area determination is an important factor in predicting the catalyst performance. Of the several techniques to estimate the surface area and pore volume of the porous materials, BET method [13] is the widely adopted procedure and this method is based on the extension of the Langmuir theory to multilayer adsorption. This method was established by Brunauer, Emmet and Teller [9]. The model, on which it is based, assumes that the heat of adsorption on the bare surface is different from the heats of adsorption of all successive layers. The BET equation extends the Langmuir isotherm to multilayer adsorption,

The general form of BET equation can be written as

$$P/V(P_0-P) = 1/CV_{\text{mono}} + C-1/CV_{\text{mono}}(P/P_0) \text{-----}(2.1)$$

Where

- P : Adsorption equilibrium pressure
- P₀ : Saturated vapor pressure of the adsorbate
- V : Volume occupied by the molecules adsorbed at equilibrium pressure
- V_m : Volume of the adsorbate required for monolayer coverage
- C : Constant related to the heat of adsorption

The BET plot is linear as long as only multilayer adsorption occurs. Plot of P/V (P₀-P) against P/P₀ is a straight line with slope C-1/CV_m and intercept 1/CV_m. From the slope and intercept V_m can be calculated and the specific surface area of the sample can be calculated using the relation,

$$A = V_m N_o A_m / W \times 22.414 \text{ -----(2.2)}$$

Where

N_o : Avogadro number

A_m : Molecular cross sectional area of the adsorbate (0.162nm² for N₂)

W : Weight of the catalyst sample

In BET method, adsorption of nitrogen is carried out at liquid nitrogen temperature. Previously activated samples were degassed at 200°C under N₂ for 2hrs and then brought to -196°C using liquid N₂ for adsorbing N₂ gas at various pressures. The pore volume is measured by the uptake of nitrogen at a relative pressure of 0.9. When data points in the pressure range of capillary condensation are included in the BET analysis, the plot is not linear. The obtained specific surface areas are too large. To avoid that, data points in the relative pressure range of 0.02 < p/p₀ < 0.2 were used in this work.

In the t-plot method the measured adsorbed volumes are plotted against the statistical layer thickness 't' [14]. The t-plot allows the examination of three properties of an adsorbent (a) to detect the onset of capillary condensation, denoted by deviation from linearity in the higher regions of the plot; (b) to detect the micro porosity from an estimate of the amount of micro pores, from the intercept of the extrapolated plot on the ordinate, (c) to compute the V_m from the multi-layer region of the isotherm. This method of isotherm data analysis was introduced by de Boer. The statistical thickness is specific for the combination of an adsorptive capacity, the temperature, and the surface of a solid material. The specific pore volume is calculated from the intercept of the straight line that is drawn through the second linear

region in the t plot. From the slope of this line a value for the external surface area could be calculated.

Pore diameter distributions were calculated by the BJH method developed by Barret, Joyner and Halenda [14]. In this approach the filled pores are taken as a starting point. The emptying of the filled pores with decreasing relative pressure is incrementally evaluated to obtain a pore diameter distribution. For each increment the pore diameter of pores emptied is calculated according to the Kelvin equation (equation 2.3).

$$P/P_0 = \exp(-2\gamma V^l / r_k RT) \text{-----} (2.3)$$

The Kelvin equation (P/P_0) is the relative vapour pressure over a curved surface, γ is the surface tension, V^l is the molar volume of the liquid, and r_k is the radius of curvature expresses mathematically that adsorption on a curved surface is more favourable than on a flat surface. According to equation (2.3), the vapour pressure over a concave surface is lower than over a flat surface. This causes the filling of the mesopores at relative pressures, which are characteristic for the pore diameter. This process is often called capillary condensation because the environment of the adsorbate in filled mesopores is comparable to a liquid state environment. Since the assumptions of Kelvin equation (2.3) are not completely fulfilled in small mesopores, the real pore diameter may vary a little from the calculated value. But in a relative sense the BJH distributions are correct.

Nitrogen adsorption measurements were performed at liquid nitrogen temperature with a *Micromeritics Tristar 3000* surface area and porosity analyzer. Prior to the measurements the samples were degassed for 1 hour at 90°C followed by 200°C overnight.

2.4.2.4 Energy dispersive X-ray analysis (EDX)

The EDX analysis is a relatively new technique for qualitative and quantitative elemental analysis of solid samples. In this method, the characteristic X-rays are separated on the basis of photon energies rather than on their wavelength. The Si (Li) detector cooled by liquid nitrogen receives the undispersed characteristic X-rays from the specimen. The amplified detector output is then digested and the pulses are accumulated in the channels, which represents a small range of energy. For qualitative analysis the data are transferred into a computer for calculation of elemental concentrations. For quantitative analysis, the data may be displayed in a number of ways such as a series of peaks (intensity Vs energy) on a cathode ray oscillograph. The simultaneous measurement and display of the energy spectrum result in rapid qualitative and quantitative elemental analysis. EDX analysis of the samples was recorded in a JSM-840 EDX analyzer.

The fundamental principle is that, when incident beam bounces through the sample creating secondary electrons, it leaves thousands of sample atoms with vacancies in the electron shells. If these vacancies are in inner shells, the atoms are not in a stable state. To stabilize the atoms, electrons from outer shell will drop into the inner shells, however, because the outer shells are at a higher energy state, to do so the atom will lose some energy. Energy will be lost in the form of X-rays. The X-rays emitted from the sample atoms are characteristic of the element.

2.4.2.5 FT-IR Spectroscopy

Infrared spectroscopy is a very useful technique for characterization of materials, providing information about the structure of molecules [15].

IR spectrum of a compound is the superposition of absorption bands of specific functional groups. The advantages of infrared spectroscopy include wide applicability, nondestructiveness, measurement under ambient atmosphere and the capability of providing detailed structural information. Besides these intrinsic advantages the more recent infrared spectroscopy by Fourier transform (FT-IR) has additional merits such as higher sensitivity, higher precision (improved frequency resolution and reproducibility), quickness of measurement and extensive data processing capability. IR spectra originate in transitions between two vibrational levels of a molecule in the electronic ground state and are usually observed as absorption spectra in the infrared region. For a molecule to present infrared absorption bands it is needed that it has a permanent dipole moment. When a molecule with at least one permanent dipole vibrates, this permanent dipole also vibrates and can interact with the oscillating electric field of incident infrared. Thus, if the vibrational frequency of the molecule, as determined by the force constant and reduced mass, equals the frequency of the electromagnetic radiation, then adsorption can take place. As the frequency of the electric field of the infrared radiation approaches the frequency of the oscillating bond dipole and the two oscillate at the same frequency and phase, the chemical bond can absorb the infrared photon and increase its vibrational quantum number or increase its vibrational state to a higher level. As an approximation, larger the strength of the bond higher will be the frequency of the fundamental vibration. In the same way, the higher the masses of the atoms attached to the bond, the lower will be the wavenumber of the fundamental vibration. As a general guide, the greater the number of groups of a particular type, more polar the bond, the more intense the band. The infrared spectrum can be divided into two regions, one called the functional group region and the other the fingerprint region. The functional group

region is generally considered to range from 4000 to 1500 cm^{-1} and all frequencies below 1500 cm^{-1} are considered characteristic of the fingerprint region. The fingerprint region involves molecular vibrations, usually bending motions that are characteristic of the entire molecule or large fragments of the molecule and these are used for identification. The functional group region tends to include motions, generally stretching vibrations, which are more localized and characteristic of the typical functional groups, found in organic molecules. While these bands are not very useful in confirming identity, they do provide some very useful information about the nature of the components that make up the molecule. FT-IR spectroscopy is one of the most widely used analytical techniques used for material analysis. This characterization technique has a decisive role in identifying the surface species of supported ceria catalysts. Dispersion of metal species and their structure, support-metal interaction, metal-metal interaction, surface acidity of catalysts, bulk catalyst structure etc. are some of the valuable informations that can be attained from FT-IR spectroscopy. The intensities of FT-IR absorption bands depend on the effects induced by the acid-base interactions in the spectral features of the absorbed probe molecules. FT-IR spectra of the prepared samples were measured by the KBr pellet procedure over the range of 4000-500 cm^{-1} region using *JASCO FTIR* spectrometer. The entire frequency range of the electromagnetic waves transmitted through the sample was recorded simultaneously and the output was fed to a computer, which reinforces the spectrum using Fourier transform.

2.4.2.6 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope capable of producing high-resolution images of a sample surface by analyzing electrons emitted from a specimen. Scanning Electron

Microscopy 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 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. This makes 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 particularly because of its high spatial resolution [16]. In SEM analysis finely powdered sample was applied on to a double sided carbon tape placed on a metal stub. The stub was then inverted in such a manner that the free side of the carbon tapes gently picked up a small amount of the sample, thereby creating a thin coating. It was then sputtered with a thin layer of gold to obtain better contrast and provide improved cohesion [17]. During SEM inspection, a beam of electrons is focused on a spot volume of the specimen, resulting in the transfer of energy to the spot. These bombarding electrons, also referred to as primary electrons, dislodge electrons from the specimen itself. The dislodged electrons, also known as secondary electrons, are attracted and collected by a positively biased grid or detector, and then translated into a signal. To produce the SEM image, the electron beam is swept across the area being inspected, producing many such signals. These signals are then amplified, analysed, and translated into images of the topography being inspected. Finally, the image is shown on a cathode ray tube. SEM analysis of the samples was done using *JEOL JSM-840 A* (Oxford make) model 16211 scanning electron microscope analyzer with a resolution of 13eV. The sample was dusted on alumina and coated with a thin film of gold to prevent surface

charging and to protect the material from thermal damage by electron beam. A uniform film thickness of about 0.1 mm was maintained for all samples.

2.4.2.7 Transmission electron microscopy

Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is transmitted through a specimen, then an image is formed, magnified and directed to appear either on a fluorescent screen or layer of photographic film or to be detected by a sensor such as a CCD camera (charge couple device) [18]. The transmission electron microscope is based on the fact that electrons can be ascribed a wavelength but at the same time interact with magnetic fields as a point charge. A beam of electrons is applied instead of light, and the glass lenses are replaced by magnetic lenses. The lateral resolution of the best microscopes is down to atomic resolution. Like SEM, TEM uses an electron gun to produce the primary beam of electrons that will be focused by lenses and apertures into a very thin, coherent beam. This beam is then controlled to strike the specimen. A portion of this beam gets transmitted to the other side of the specimen, is collected, and processed to form the image. The HR-TEM of the samples was carried out in ultrahigh resolution analytical electron microscope JEOL 3010. This gives a lattice resolution of 0.14 nm and a point to point resolution of 0.12 nm. Bulk materials have to be thinned to make them electron transparent. The typical column vacuum in the machine is $< 1 \times 10^{-5}$ pa.

2.4.2.8 Thermo gravimetric analysis (TGA)

Thermo gravimetry (TG) in which the catalyst sample is subjected to a controlled heating to higher temperatures at a specified heating rate is a well-established technique in heterogeneous catalysis. It finds widest applications in the determination of drying range, calcinations temperature,

phase composition, percentage weight loss and stability limits of the catalyst. Thermo gravimetric analysis (TGA) is an analytical technique used to determine thermal stability of a solid and its fraction of volatile components by monitoring the weight change that occurs as the specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve (DTG) can be used to tell the point at which weight loss is most apparent. A sample of material (ranging from 1 to 100 mg) is placed on an arm of a recording microbalance, also called thermo balance where that arm and the sample are placed in a furnace. The furnace temperature is controlled in a pre-programmed temperature/time profile (most commonly), or in the rate controlled mode, where the pre-programmed value of the weight changes imposes the temperature change in the way necessary to achieve and maintain the desired weight-change rate. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans: (Differential thermal analysis or DTA) or the heat flow into the specimen pan compared to that of the reference pan (differential scanning calorimetry or DSC). The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process. Any transition that the sample undergoes results in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. A plot of the differential temperature (ΔT) versus the programmed temperature T indicates the transition temperatures and whether the transition is exothermic or endothermic. When an endothermic change occurs, the sample temperature lags behind the reference temperature because of the heat in the sample.

Exothermic behaviour is associated with the decrease in enthalpy of a phase or a chemical system. DTA and thermo gravimetric analyses are often run simultaneously on a single sample [19].

In TG, the weight loss of a sample is being continuously recorded over a period of time under controlled heating rate. Changes in weight are due to the rupture and /or formation of various physical and chemical bonds at elevated temperatures, which lead to the evolution of volatile products or the formation of heavier reaction products. From the thermo gram, where we plot weight against temperature, information about dehydration, decomposition and various forms or products at various temperatures can be obtained. 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.

Perkin Elmer TG analyzer instrument was used for carrying out thermo gravimetric studies. About 20mg of the sample was used at a heating rate of 20 °C per min in nitrogen atmosphere. The TG data were computer processed to get thermogram. 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.

2.4.2.9 Diffuse Reflectance UV-VIS Spectroscopy (UV-Vis DRS)

UV-Vis spectrophotometer measures the intensity (I), of light passing through a sample and compares it to the intensity of light (I₀) before it passes through the sample. The ratio I / I₀ is called the transmittance, and is usually expressed as a percentage (%T). The absorbance A is based on the transmittance:

$$A = - \log (\%T)$$

A spectrophotometer can be either single beam or double beam. In a single beam instrument, all of the light passes through the sample cell. I_0 must be measured by removing the sample. In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference, the other beam passes through the sample. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam.

Diffuse reflectance UV-Visible spectroscopy allows the study of electronic transitions between orbital or bands in the case of atoms, ions and molecules in gaseous, liquid or solid state. In catalysis, the information given by DRS mainly includes the active phase-supports interaction, the chemical changes during a modification procedure leading to the active phase and the nature of the co-ordination sphere of the active surface species.

Electronic transitions of transition elements are two types, metal centred transitions (d-d) or [(n-1)d-ns] and charge-transfer (CT) transitions. (d-d) transitions give information about the oxidation state and co-ordination 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 sensitive to the nature of donor and acceptor atoms [20]. In DR measurements, the light emitted by the sample and the integration sphere collects the reference material and detector of the double beam spectrometer gives the apparent absorbance. Diffuse reflectance UV-Vis. spectroscopy is widely used in the surface characterization of supported ceria catalysts.

Diffuse reflectance UV-Vis. spectra of the samples were recorded using a conventional spectrophotometer (Ocean Optics 2000) with CCD detector. Magnesium oxide (MgO) was used as the reference material.

2.4.2.10 Elemental Analysis-Inductively Coupled Plasma-Atomic Emission Spectroscopy

Inductively Coupled Plasma-Atomic Emission Spectroscopy is used for the elemental analysis of prepared samples. Most of the elements in the periodic table can be analyzed by this technique. The main advantages of the technique are that some elements can be analyzed with greater sensitivity or can be analyzed simultaneously. The elemental composition is carried out by analyzing the atomic spectrum emitted by a sample. The wave length at which emission occurs identifies the element, and the intensity of radiation emitted can be used to find out the amount of the element present.

High temperature non-flame atomic emission spectroscopy has more advantages because of the greater concentration of emitting atoms. Main high temperature non-flame sources are usually plasmas and can operate at temperature in the range of 7000-15000K. Thus the plasma source produces a greater number of excited emitted atoms, especially in the UV region. Plasma is a cloud of highly ionized gases, composed of ions, electrons and neutral particles. In plasma emission spectroscopy the gas, usually Argon is ionized by the influence of a strong electrical field either by direct current or by radio frequency. Both types of discharge produce plasma, the direct current plasma (DCP) or the inductively coupled plasma (ICP).

The Plasma source produces a greater number of excited atoms, especially in the UV region. The plasma source is able to produce atomization. ICP source comprises three concentric silica quartz tubes;

each is open at the top. The Ar stream that carries the sample in the form of an aerosol passes through the central tube. The excitation is provided by two or three turns of a metal induction tube through which flows a radio frequency current (frequency $\approx 27\text{MHz}$). The second gas flow of Ar at a rate between 10 and 15 min^{-1} maintains the plasma. It is this gas stream that is excited by the radio frequency power. The plasma gas flows in a helical pattern which provides stability and helps to isolate thermally the outside quartz tube. The plasma is initiated a spark from a Tesla coil probe and thereafter self-sustaining. ICP-AES were done on Thermo electron IRIS INTERPID II XSP DUO model. The application of this instrument is in elemental level analysis of environmental samples, pharmaceuticals, research samples, soil etc. The sample is used to introduce by solution nebulization which converts the sample into a form more amenable to rapid atomization.

2.4.2.11 Temperature Programmed Reduction - Hydrogen (TPR-H₂)

Temperature programmed reduction (TPR) is unique to study the temperature dependence reduction behaviour of ceria based materials [19a]. The reduction of high surface area ceria takes place essentially in two temperature regions. The first region is 573-873 with T_{max} around 790K and the second region is 973-1273K with T_{max} around 1100K. These two reduction regions are characteristics of ceria and are attributed to the surface oxygen ions and bulk oxygen ions respectively, while the sintered ceria shows only one reduction feature at higher temperature due to bulk reduction. The higher mobility of the surface oxygen ions helps in the removal of lattice oxygen during reduction process. The co-ordinately unsaturated surface capping oxygen ions can be easily removed in the low temperature region. However, bulk oxygen requires to be transported to the

surface before their reduction. Consequently, the bulk reduction takes place at higher temperature compared to the surface reduction. The extent of reduction in the low temperature region depends on the surface area of the sample. Oxygen storage measurements consist in the determination of the amount of a reducing gas (H_2 , CO) which is oxidized after passing through an oxygen pre saturated catalyst.

Temperature-programmed reduction (TPR) was carried out in a Micromeritics Instrument: Chemi Soft TPx V1 TPR system and 0.1725 mg sample was used for each measurement. Prior to the reduction, the sample was pretreated in an air stream at room temperature for 30 min. After that, H_2 - N_2 mixture (5% H_2 by volume) was switched on and the temperature was increased linearly at a rate of $10^\circ C \text{ min}^{-1}$. A thermal conductivity cell detected the consumption of H_2 in the reactant stream.

2.5 Surface Acidity Measurements

Quantification and characterization of surface acid sites forms an important aspect of characterization of catalysts [21]. The concentration and strength of acid sites in solids cannot readily be measured using the types of basic molecular indicators used in the study of acid solutions because the sites in solids may be inaccessible to these molecules. Consequently, alternative techniques have been developed that are more applicable to solids and that enable their acidity to be compared with that of liquid acids. These include the thermal desorption of basic probe molecules (such as pyridine) coupled with IR spectroscopy. An estimate of the number of acid sites, their types, and their strength can be made in this way. Catalytic test reactions, such as alkane cracking, are also widely used to estimate acidity, because the rate and product distribution is indicative of

the type and strength of active sites. Several quantitative and quantitative methods have been employed to study surface sites. Here we used adsorption technique Temperature Programmed Desorption (TPD) of ammonia for the measurement of acid amount. Cumene cracking was used as the test reaction for determining the ratio of the amount of Lewis to Brønsted acid sites.

2.5.1 Materials

The materials used for surface acidity measurements are given below.

Table 2.4 Materials used for acidity measurements

Materials	Suppliers
Ammonia	Qualigens
Sulfuric acid	Merck
NaOH	CDH
Liquid Nitrogen	Sterling gases, Ambalamugal
cumene	Aldrich

2.5.2 Adsorption Techniques

The chemisorption of bases such as pyridine, ammonia, and aliphatic amines is frequently used to characterize solid acid catalysts and to correlate their catalytic activity with the concentration of a particular type of acid site. Pyridine and ammonia, because of their capability of interacting with both Brønsted and Lewis sites are widely used to get total acid amount of the systems. Temperature programmed desorption of ammonia, thermo desorption of 2, 6-dimethyl pyridine and test reactions like cumene cracking and decomposition of cyclohexanol can be used to obtain acidity of the samples.

2.5.3 Temperature Programmed Desorption (TPD) of Ammonia

Temperature programmed desorption (TPD) is one of the basic experimental tool in surface science for identifying the desorbing species and hence can obtain their adsorption kinetics. TPD analysis helps us to identify the strength, the number and active sites that are available on the catalyst surface. Determining the quantity and strength of the acid sites on catalyst is crucial to understand and predict performance. The technique consists of adsorption of a reactive gas previously chemisorbed on the surface by a linear temperature rate increases. Three types of probe molecules are used for TPD studies: NH_3 , non- reactive vapour and reactive vapours.

The probe molecules generally used are ammonia, pyridine and methylamine to identify acid sites and CO_2 or NO to identify the basic sites. As a probe molecule ammonia has its advantages:

- Its molecular size facilitates access into all pores in a solid.
- It is highly basic, hence titrates even weak acid sites. Strongly polar adsorbed NH_3 also capable of adsorbing additional NH_3 from gas phase. The rate of adsorption is achieved either by detecting the desorbing species or by monitoring the remaining coverage on the surface.
- When chemisorbed on a surface possessing acid properties, ammonia can interact with the acidic protons, electron acceptor sites and hydrogen from neutral or weakly acidic hydroxyls and thus can detect most of the different type of acid sites [22].
- An ammonia molecule can be retained on the surface of oxides in different modes [23].

- Hydrogen bonding via one of its hydrogen atoms to surface oxygen or to the oxygen of surface hydroxyl group.
- Transfer of proton from surface hydroxyl to the adsorbate.
- Co-ordination to an electron deficient metal atom. It is the strongest mode of interaction.

Thus a fairly reliable interpretation of the TPD pattern of Ammonia from solid acids can be attributed to ammonia chemisorbed on weak, medium and strong acid sites respectively, being not possible to discriminate between Brønsted and Lewis acid sites.

In this technique a definite weight of pelletalised activated sample is placed in a specially designed reactor that is heated at linear rate. The sample is preheated at 300°C for 30 minutes under nitrogen flow. After that, the sample is cooled to room temperature. A definite amount of (20ml) ammonia was injected into the system and was allowed to attain equilibrium. Then excess physisorbed ammonia is flushed out of the reactor by a current of nitrogen. The temperature is gradually increased and ammonia desorbed at an interval of 100°C is scrubbed into dilute sulphuric acid. The ammonia desorbed at each stage is determined by titrating the unreacted sulphuric acid against standard sodium hydroxide using phenolphthalein indicator. The amount of desorbed ammonia was calculated using the equation,

$$\text{Ammonia desorbed in mmol /g} = (N_{\text{NaOH}} \times V \times 5)/W$$

Where

V : The difference in titre value between the blank and the scrubbed acid with desorbed NH₃ at different temperatures

W : Weight of the sample in gram

N : Normality.

Finally by knowing the correct stoichiometry of the gas/solid reaction, it is possible to quantify the total number of active acid sites that is available on the catalyst surface. The adsorption temperatures indicate the strength of the active sites of the catalyst. The ammonia desorbed in temperature ranges 100-200, 201-400, 401-600°C is considered to represent the surface sites of physisorbed or weakly chemisorbed, medium and strong acid sites respectively.

2.5.4 Test reaction for acidity

Catalytic cumene cracking reaction was performed as test reaction for acidity.

2.5.4.1 Vapour phase cumene cracking reaction.

Vapour phase cumene cracking reaction is a model reaction for identifying the Lewis/Brønsted acid ratio of a catalyst. The major reactions taking place during the cracking of cumene are dealkylation to give benzene and propene over BAS and dehydrogenation to give α -methyl styrene over LAS. A comparison of the amount of benzene and α -methyl styrene gives an idea about the BAS and LAS possessed by the catalyst.

The vapour phase cumene cracking reaction was carried out in a fixed bed, down flow vertical glass reactor inside a double zone furnace. 0.25g of the catalyst activated at 350°C for 1hr was immobilized inside the reactor using glass wool. The catalyst was loaded in the middle of the reactor and packed with glass beads. The temperature was measured by a thermocouple placed in the middle of the catalyst bed. Cumene was fed into the reactor at a flow rate of 4mL/h. The temperature of the reaction bed was kept at 400°C. The product analysis was achieved by gas

chromatography (Chemito GC1000) by comparison with authentic samples. The analytical conditions are given in the Table 2.6.

2.6 Catalytic Activity Measurements

In recent years, organic reactions on solid support such as zeolites or mesoporous molecular sieves have attracted much attention because of advantages such as mild acidic properties, shape-selectivity, environment-friendly nature of catalysts, the easy work-up, the high purity of the products and the recycling of catalysts [24, 25, 26]. In 1995, the preparation of a new type of hexagonal mesoporous molecular sieves (HMS) by neutral assembly pathways was reported by Tanev and Pinnavaia [4]. This HMS was reported to possess physical and catalytic properties different from those of MCM-41 prepared by electrostatic assembly pathways [27]. Even though HMS can be prepared much more easily than MCM-41 or other zeolites and has certain advantages such as thicker framework walls, superior thermal stability and a smaller crystalline size, HMS itself has not yet been fully exploited as a new catalyst [28, 29].

Therefore we undertook a study aimed at discovering reactions that can be catalyzed by mesoporous ceria prepared using a neutral assembly pathway as proposed by Tanev and Pinnavaia et al. [4] modified by transition metals. The catalytic activities of the prepared catalysts are studied for the industrially important liquid phase reactions: oxidation of ethyl benzene, Friedel-Crafts benzylation, acetalization and deacetalization of cyclohexanone and Friedel-Crafts methylation of phenol using methanol in vapour phase.

2.6.1 Materials

The materials used for the catalytic activity measurements are given below,

Table.2.5 Materials used for activity studies

Materials	Suppliers
Ethyl benzene	CDH
Acetonitrile	Qualigens
Tert-butyl hydro peroxide (70%)	Aldrich
o-Xylene	Merck
Toluene	S.D. Fine
Anisole	Merck
Benzene	Qualigens
Cyclohexanone	Rankem
Benzyl chloride	Spectrochem
Methanol	Spectrochem

2.6.2 Liquid phase Reactions

All the liquid phase reactions were carried out batch wise in a 50mL double necked glass round bottom flask fitted with a condenser. In a typical run, a known optimized weight of catalyst was dispersed in the substrate with/without solvent. The mixture was refluxed at an optimized temperature with thorough stirring in an oil bath. At the end of the reaction the products were filtered off and identified by GC-MS. Conversion and product selectivity were analysed using GC with FID detector. The analytical conditions are given in the Table 2.6.

2.6.2.1 Oxidation of ethyl benzene

The catalytic selective oxidation is the main route to obtain monomers and intermediates for organic synthesis. The catalysts used are solids, most often mixed oxides with elements with different oxidation states which present redox properties. Selective oxidation reactions of relatively inert C–H bond of hydrocarbons using air or oxygen is one of the

most desirable and challenging reactions since the obtained products are themselves important or act as valuable intermediates for industrial organic chemicals [30, 31]. Metal containing molecular sieves have attracted great interest and applications in heterogeneous catalysis due to their size, shape selective and recyclable properties [32, 26].

The experimental procedure adopted for the catalytic activity measurement is described below. The liquid phase oxidation of ethyl benzene [33] was carried out in a 50 ml R.B. flask fitted with a condenser. The temperature was maintained using an oil bath. In a typical run, 0.05 g of the catalyst was added to ethyl benzene in acetonitrile solvent. The reaction mixture was magnetically stirred. After attaining reaction temperature tert-butyl hydroperoxide was added drop wise. The aromatic compound being taken less, the yields were calculated based on the amount of the ethyl benzene. The selectivity for a product was expressed as the amount of the particular product divided by the total amount of the products multiplied by 100. The products were analyzed by gas chromatography (Chemito 1000 Gas Chromatograph equipped with a flame ionization detector and SE-30 Column-(2m length). Column temperature was adjusted between 60-200°C at a heating rate of 10°C/ min. (injector temp. 250°C, detector temp. 250°C). The major product obtained was acetophenone. The reaction conditions were optimized for the molar ratio of the substrate, oxidizing agent, catalyst weight, temperature, duration of the run, volume of the solvent and type of solvent. The present work also attempted to study the metal leaching to understand the molecular aspects of the reaction and reusability of the system thereby confirming the true heterogeneity of the process.

2.6.2.2 Friedel-Crafts benzylation reaction

Friedel-Crafts alkylation enables the introduction of alkyl chains to aromatic rings. Alkyl chlorides, alcohols and alkenes are the commonly employed alkylating agents [34]. A wide range of homogeneous catalysts like FeCl_3 , AlCl_3 , BF_3 and protonic acids like HF and H_2SO_4 have been found to be well suited for this reaction [35, 36]. The environmental concern and the drive towards a 'clean technology' urge the replacement of the liquid acids by eco-friendly solid acid catalysts. Benzylation of o-xylene with benzyl chloride, which is a typical example of Friedel-Crafts alkylation, is generally known to proceed over a homogeneous Lewis acid catalyst AlCl_3 [37]. Catalytic behaviour of rare earth oxides has been explored for many reactions and a wide variety of catalytic properties have been known [38]. These oxides can be used in Friedel-Crafts reactions too [39].

The liquid phase catalytic runs were carried out batch wise in a mechanically stirred, closed 50 mL glass reactor fitted with a reflux condenser, a thermometer and a septum for withdrawing the product samples. The temperature of the reaction vessel (353 K) was maintained using an oil bath. In a typical run, appropriate amounts of substrate and benzyl chloride (5:1 molar ratio) were charged in the reactor along with 0.05 g catalyst. Samples were withdrawn periodically and analyzed with a gas chromatograph (Chemito GC 1000) fitted with a flame ionization detector and a capillary column (SE-30). Some selected runs were analyzed by GS-MS for product identification. The composition of the reaction mixture was also determined by comparing their gas chromatograms with those of authentic samples. The reactions were done for the benzylation of toluene, o-xylene and anisole.

2.6.2.3 Acetalization and deacetalization reactions

Acetalization is one of the most widely used synthetic method for protecting aldehydes and ketones in the course of preparation of a variety of multifunctional complex organic molecules since dimethyl acetals display higher stability towards strong bases, Grignard reagent, lithium aluminium hydride, strong oxidants and esterification reagents than their parent carbonyl compounds [40]. The acetalization reaction is a process that is widely used in organic synthesis to protect the carbonyl group of aldehydes and ketones [41]. Besides, acetals became important reactants for the synthesis of enantiomerically pure compounds which were widely used as steroids, pharmaceuticals, and fragrances [42]. Previously, the catalysts used in the acetalization reactions were generally proton acids, Lewis acids, and a number of transition metal complexes including Rh, Pd and Pt [43]. Although good results were obtained, the separation of the products from the catalyst system after the reaction was still difficult to overcome and the noble metal catalysts used were quite expensive and usually unstable [44]. Therefore, to design and synthesize a catalytic system that may be stable, easily separable and reusable has long been pursued [45].

The nature of the pores of the solid acid catalysts determines acetalization efficiency of a particular catalyst. Dimethyl acetals of ketones: cyclohexanone, acetophenone, and benzophenone have been prepared by reacting ketones with methanol under mild reaction conditions.

Acetalization is a reversible reaction catalyzed by an acid environment and is usually performed in the liquid phase, which leads to the elimination

of water as a byproduct thereby requiring azeotropic distillation to remove the water formed during the reaction, or else leading to the deactivation of the catalyst.

Acetalization reactions of cyclohexanone with methanol were carried out under batch reaction conditions. Cyclohexanone purchased from Aldrich Chemical Company, USA and commercial-grade methanol (available from S.D. Fine Chemicals, India) were used as received. One-pot acetalization reactions of carbonyl compounds were carried out in a 50 mL glass batch reactor equipped with a magnetic stirrer, thermometer, water condenser and temperature controller. In a typical run, cyclohexanone and methanol in a specific ratio was added to 0.05gm of catalyst in to the R.B. flask and magnetically stirred. The products were withdrawn at the end of the reaction and were analyzed with a Chemito GC1000 gas chromatograph equipped with a SE-30 capillary column under the analysis conditions specified in the Table 2.6. The products were further analyzed by GC-MS.

Hydrolysis of dimethyl acetal was done using 1:20 mixture of water and acetone as solvent. Here also the analysis was done by Chemito 1000 gas chromatograph with a capillary SE-30 column.

To have an optimum conversion of cyclohexanone, reaction conditions such as temperature of the reaction, cyclohexanone to methanol molar ratio, duration of reaction and the amount of the catalyst were studied to optimize the reaction parameters. To study heterogeneous nature of the reaction metal leaching studies also carried out.

2.6.3 Vapour phase reaction-methylation of phenol

Alkylation of aromatic substrates catalyzed by solid acids such as zeolites and metal oxides constitutes a class of reactions important both academically and industrially. Among alkylation reactions, methylation of phenol has attracted considerable attention due to industrial importance of methyl phenols as chemical intermediates in the manufacture of pharmaceuticals, agrochemicals, resins, various additives, polymerization inhibitors, antioxidants and various other chemicals [46]. Selective C-methylation of phenol to o-cresol and 2, 6-xylenol in high yields has been carried out with methanol over various solid acid catalysts. In particular, ortho-alkylated phenols such as o-cresol, 2, 6-xylenol and trialkyl substituted phenols are more important alkyl phenols. After suitable processing o-cresol is used in the synthesis of herbicides as well as in sealing material for integrated circuits, whereas 2, 6-xylenol is used in manufacture of disinfectant and in high impact resistant resins [47]. The alkylation of phenol with methanol being an acid–base catalyzed reaction, the product selectivity depends upon the acidity as well as basicity of the catalyst. Phenol alkylations using various acid and base catalysts have been reported. Phenol conversion as well as product selectivity is found to depend on the acid–base properties of the catalyst, temperature [48] and residence time [49]. Methylation was carried out in a vertical down flow glass reactor. All the reactions are carried out using 0.25gm of the catalyst. Prior to the reaction the catalysts were activated for 1hr at 300°C. The catalyst was packed in between quartz wool pack and sandwiched between silica beads. The reactor was placed inside a temperature controlled furnace with a thermocouple to measure the reaction temperature. In a typical reaction, a mixture of phenol and

methanol in an optimized ratio was fed into the reactor at a specific flow rate using a syringe pump at a preset reaction temperature. The products were condensed and collected in an ice trap and analyzed by a Chemito 8610 GC with an FID detector and an OV-17 column. The products are confirmed by GC-MS analysis. The conversion was expressed in terms of phenol reacted and the product selectivity was expressed as the ratio of amount of particular product to 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

Reaction	GC	Temperature(°C)		Programme of analysis
		Injector	Detector	
Cumene cracking	GC1000, SE-30 Capillary column, FID detector	230	230	70°C-2min-10°C/min- 250°C-2min
Ethylbenzene oxidation	GC1000, SE-30 Capillary column, FID detector	250	250	60°C-2min-10°C/min- 125°C-2min-2°C/min- 140 °C-1min-150°C- 200°C -1min
Benzylation	GC1000, SE-30 Capillary column, FID detector	250	250	60°C-4min-10°C/min- 110-4min-10°C/min- 170-1min
Acetalization- deacetalization	GC1000, SE-30 Capillary column, FID detector	100	100	75°C-1min-5°C/min- 125°C-1min- 10°C/min-200°C-1min
Phenol methylation	Chemito8610 GC OV-17Column, FID detector	250	250	60°C-1min-20°C/min- 140-1min-10°C/min- 170-2min

2.7 References

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