CHAPTER 2

EXPERIMENTAL METHODS

2.1 MATERIALS

Hydrothermal synthesis of mesoporous KIT-6 was carried out using triblock copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, EO_{20}PO_{70}EO_{20}; Aldrich) as the structure-directing agent and n-butanol (Merck) as the co-solute. Aluminium isopropoxide (Merck) and cerium nitrate (Merck) were used as the precursor for aluminium and cerium in the synthesis of Al-KIT-6 and Ce-KIT-6 respectively. Other chemicals such as tetraethylorthosilicate, hydrochloric acid, phenol, acetic acid, isobutylbenzene, acetic anhydride, cyclohexanol, cyclohexane, acetone, methanol and hydrogen peroxide used in the study were purchased from Merck. All the chemicals were used as such without any further purification. Deionised water was used in all the synthesis procedure. The glassware used in all the experiments were either borosil or quartz.

2.2 SYNTHESIS OF MESOPOROUS MATERIALS

2.2.1 Synthesis of Al-KIT-6

Al-KIT-6 materials with different Si/Al ratios were synthesized using triblock copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123) as the structure-directing agent and n-butanol as the co-solute with the following molar gel
composition: (1-0.95) TEOS : (0.006-0.05) Al(OiPr)_3 : 0.053 P123 : (1.84) HCl 35% : 1.3 n-BuOH : 194 H₂O. The typical procedure used for the synthesis of Al-KIT-6 (40) is as follows: Pluronic P123 (4 g) was added to 144 g water and 7.9 g 35% HCl. After stirring for four hours, a clear solution was obtained. n-Butanol (4 g) was then added and the stirring was continued for one hour. Tetraethylorthosilicate (TEOS) (8.4 g) and aluminium isopropoxide (Al(OiPr)_3) (0.2 g) were added to the solution. The resulting mixture was stirred for 24 h at 35 ºC. The synthesis was carried out in a closed polypropylene bottle. Subsequently, the mixture was aged at 100 ºC for 24 h under static hydrothermal condition. The precipitated material was filtered hot without washing and then dried at 100 ºC for 12 h in air. The dried solid material was crushed to obtain fine powder and this was calcined at 540 ºC in air for 24 h to remove the template. The final material was Al-KIT-6 (40). The aluminium incorporated KIT-6 is denoted as Al-KIT-6 (x) where x denotes Si/Al ratio of the gel.

2.2.2 Synthesis of Ce- KIT-6

Cerium containing KIT-6 (Ce-KIT-6) materials were synthesized hydro thermally using the following procedure: Pluronic P123 (4 g) was added to 144 g water and 7.9 g 35% HCl. After stirring for four hours, a clear solution was obtained. n-Butanol (4 g) was then added and the stirring was continued for one hour. Tetraethylorthosilicate (TEOS) (8.4 g) and cerium nitrate (0.352 g) were added to the solution to maintain Si to Ce ratio as 50. The resulting mixture was stirred for 24 h at 35 ºC. The synthesis was carried out in a closed polypropylene bottle. Subsequently, the mixture was aged at 100 ºC for 24 h under static hydrothermal condition. The precipitated material was filtered hot without washing and then dried at 100 ºC for 12 h in air. The dried solid material was crushed to obtain fine powder and this was
calcined at 540 °C in air for 24 h to remove the template. The final material was Ce-KIT-6 (50). The cerium incorporated KIT-6 is denoted as Ce-KIT-6 (x) where x denotes Si/Ce ratio of the gel.

2.3 PHYSICO-CHEMICAL CHARACTERIZATION

It is necessary to characterize the materials to predict their physico-chemical properties for possible catalytic applications. There are number of techniques such as XRD, ICP-AES, TG-DTG, FT-IR, DRIFT-IR, SEM, HR-TEM, UV-DRS, XPS and Nitrogen adsorption studies have been used to correlate the physico-chemical properties of the modified materials and their catalytic activities. The procedure for various characterization techniques are discussed in the following sections.

2.3.1 X-ray Diffraction

X-ray diffraction (XRD) is one of the important and most powerful methods for the identification and characterization of crystalline solid phases in heterogeneous catalysts. Yet it is extensively used for the determination of unit cell parameters, analysis of structural imperfections, crystallite size determination and recently in the refinement of the structures. This method is based on the scattering of X-rays by the electrons of atoms. The wavelengths of X-rays are similar to interatomic distances and so the X-rays scattered by different atoms will interfere destructively or constructively, in the latter case giving rise to diffracted beams. In case of crystalline samples, sharp diffraction patterns result. XRD patterns of mesoporous phases exhibit peaks in the low angle region, the most intense peak being the (100) reflection. X-ray diffraction patterns of as-synthesized and calcined catalysts were recorded using a Rigaku diffractometer with Cu Kα (λ = 0.154 nm) as the radiation source. The diffractograms were recorded in the low angle 20 range 0.8°-10° and high angle 20 range 10°-80° with 20 step size of 0.01° and a step
time of 10 s. The peaks were identified with reference to compilation of simulated XRD powdered patterns. The d-spacing values were calculated by using the Bragg’s equation \( n\lambda = 2d\sin\theta \), where \( n \) represents the order of reflection, \( \lambda \) represents the wavelength of the incident X-ray beam and \( d \) represents the spacing between reflecting crystal planes.

### 2.3.2 Inductively Coupled Plasma - Atomic Emission Spectroscopy

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) is an analytical technique used to determine the concentration of a wide range of elements in solution. ICP-AES is a fast multi-element technique with a dynamic linear range and moderate-low detection limits (~0.2-100 ppb). ICP-AES makes use of the fact that the atoms of elements are excited by the energy from inductively coupled plasma and fall back to their ground state emitting their characteristic wavelength. The identification of this radiation permits the qualitative analysis of a sample. Their quantitative determination involves measurement of the emitted radiation intensity and use of their calibration chart. Aluminium and cerium content in mesoporous KIT-6 was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Labtum Plasma 8440 instrument.

### 2.3.3 Nitrogen Adsorption Studies

Surface area measurement of solid materials is an important parameter in catalyst characterization. Specific surface area and pore volume of the materials were determined by nitrogen adsorption at 77 K using a sorption analyzer (Belsorb mini II). Before nitrogen adsorption-desorption measurements, the samples were outgassed for 3 h at 573 K under vacuum (p<10^{-5} mbar) in the degas port of the adsorption analyzer. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) equation. Surface area of mesoporous materials was calculated by
measuring the adsorption of nitrogen at liquid nitrogen temperature. The surface area was computed using the BET equation (2.1).

\[
\frac{p}{V(p_o - p)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C^{\frac{1}{2}}} \frac{p}{p_o^{\frac{1}{2}}}
\]  

(2.1)

where \( V_m \) is the volume of the gas forming the monolayer on the adsorbent at STP, \( p \) is the pressure at which the volume \( V \) of the gas is adsorbed, \( p_o \) is the saturated vapour pressure of the gas and \( C \) is a constant.

The plot of \( \frac{p}{V(p_o - p)} \) versus \( \frac{p}{p_o} \) gave a straight line with the slope = \( \frac{C}{V_m C} \). From the slope and intercept, \( V_m \) was derived. Then, the number of molecules of nitrogen adsorbed was calculated using the equation (2.2).

Number of molecules of nitrogen adsorbed = \( \frac{V_m}{6.023 \times 10^{23}} \frac{10^{23}}{0.0224} \)  

(2.2)

The specific surface area (\( S \)) was obtained by multiplying the same with cross-sectional area of nitrogen molecule, which was taken as 16.2 \( 10^{-20} \) m\(^2\), as shown in equation (2.3).

Specific surface area (\( S \)) = \( \frac{6.023 \times 10^{23} V_m}{0.0224} \frac{10}{16.2 \times 10^{20}} \)  

(2.3)

The total surface area (\( S_t \)) of the sample was obtained using the following equations (2.4 - 2.6).

\[ S_t = n_m A_{cs} N \]  

(2.4)
\[
n_m = \frac{W_m}{N} \quad (2.5)
\]
\[
S_t = \frac{W_m N A_{cs}}{M} \quad (2.6)
\]

where \( N \) is the Avogadro number \((6.023 \times 10^{23} \text{ molecules mol}^{-1})\), \( M \) is the molecular weight of the adsorbate, \( W_m \) is the weight of the adsorbate constituting a monolayer surface coverage, \( n_m \) is the amount adsorbed constituting a monolayer surface coverage and \( A_{cs} \) is the molecular cross-sectional area of the adsorbate molecule. The specific surface area \((S)\) of the solid was calculated from the total surface area \((S_t)\) and the degassed sample weight \((m)\) using the equation (2.7).

\[
S = \frac{S_t}{m} \quad (2.7)
\]

The total pore volume was calculated by converting the volume of nitrogen adsorbed \((V_{ads})\) into volume of liquid nitrogen \((V_{liq})\) using the equation (2.8).

\[
V_{liq} = \frac{P V_{ads} V_m}{RT} \quad (2.8)
\]

where \( P \) and \( T \) are the ambient pressure and temperature respectively.

Specific pore volume \((V_p)\) was calculated from the equation (2.9)

\[
V_p = \frac{V_{liq}}{m} \quad (2.9)
\]

where \( m \) is the weight of adsorbent after degassing.
2.3.4 Thermal Analysis

Thermo analytical technique, the change in the sample weight is measured while the sample is heated at a constant rate, under air or nitrogen atmosphere. This technique is effective for quantitative analysis of thermal reactions that are accompanied by mass changes such as evaporation, decomposition, gas adsorption, desorption and dehydration. Thermogravimetric analysis (TGA) is widely used to study the structural stability of molecular sieves. It provides information about the temperature range required for the expulsion of adsorbed water, decomposition of occluded organic cations, structural modification and phase changes in the pores of molecular sieves. The sample and reference material are simultaneously heated or cooled at a constant rate. Reaction or transition temperatures are then measured as a function of temperature difference between the sample and the reference. It provides vital information of the materials regarding their endothermic and exothermic behaviour at high temperatures. TGA of the materials was performed (Perkin Elmer Diamond series) with 15 mg of the sample under N\(_2\) atmosphere at a heating rate of 10 °C min\(^{-1}\) in the temperature range 50-800 °C.

2.3.5 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is one of the most widely used to study the surface morphology of solid materials on a scale down to about 10 nm. The technique works on the principle that an electron beam is focused onto the sample surface kept in a vacuum by electro magnetic lenses. The beam is then rastered or scanned over the surface of the sample. The scattered electron from the sample is then fed into the detector and then to a cathode ray tube through an amplifier, where the images are formed, which gives the information on the surface of the sample. The morphology of mesoporous molecular sieves were recorded using a scanning electron microscope.
(HITACHI COM-S-4200) operated at an accelerating voltage of 16 kV. The samples were suspended in methanol and the specimen stub was dipped into the liquid and removed. The sample powder deposited onto the surface of the stub evenly when methanol was evaporated. This specimen was coated with gold for two minutes. The beam is scanned over the specimen surface in synchronism with the beam of a cathode ray tube (CRT) display screen. Materials can be studied properly only when they are electrically conducting, otherwise give rise to charging phenomena resulting in blurred images.

2.3.6 High Resolution - Transmission Electron Microscopy

High resolution - transmission electron microscopy (HR-TEM) is typically used for high resolution imaging of solid sample for nanostructural and compositional analysis. The ultimate technique to obtain direct structural information at nanometer scale resolution for porous materials is transmission electron microscopy. In SEM the detectors are mounted on the same side of the sample as the impinging beam in order to detect the scattered secondary electrons. In TEM the detectors are mounted behind the sample to detect the electrons transmitted through a thin section (preferably less than 100 nm) of the material. In this technique, a beam of high-energy electrons (typically 100-400 keV) is collimated by magnetic lenses and allowed to pass through a specimen under high vacuum. The transmitted beam and a number of diffracted beams can form a resultant diffraction pattern, which is imaged on a fluorescent screen kept below the specimen. The size and morphology of mesoporous materials were recorded with HR-TEM using an electron microscope (JEOL JEM-4000EX) operated at 400 kV with a field emission gun. Initially, the samples were dissolved in methanol and the solution was subjected to ultrasonification. Then the sample was placed as droplets on a polymer micro grid supported on a Cu grid to record the HR-TEM image.
2.3.7 Fourier Transform - Infra Red Spectroscopy

Fourier transform infra red spectroscopy (FT-IR) is a multidisciplinary analytical tool, which yields information pertaining to the structural details of a siliceous inorganic material. In addition, it can be used to confirm surface characteristics such as acidity and isomorphous substitution by other elements in the material. FT-IR involves the absorption of electromagnetic radiation in the infra red region of the spectrum which results in changes in the vibrational energy of a molecule. It is a valuable and formidable tool in identifying organic compounds which have polar chemical bonds (such as OH, NH, CH, etc.) with good charge separation. Since every functional group has unique vibrational energy, the IR spectra can be seen as their fingerprints. Infra red spectra of all as-synthesized and calcined samples were recorded on a FT-IR spectrometer (Nicolet Avatar 360) using KBr pellet technique. About 10 mg of the sample was ground with about 70 mg of spectral grade KBr to form a mixture, which was then made into a pellet using a hydraulic press. This pellet was scanned 50 times at 4 cm\(^{-1}\) resolution and it was used to record the infra red spectra in the range of 4000-400 cm\(^{-1}\).

2.3.8 Diffuse Reflectance UV-Vis Spectroscopy

Diffuse reflectance UV-vis spectroscopy (DRS-UV-vis) is known to be a very sensitive and useful technique for the identification and characterization of metal ion coordination and its existence in the framework or extra-framework position of a metal containing molecular sieves. Diffuse reflectance UV-vis is a spectroscopic technique based on the reflection of light in the ultraviolet (UV) and visible (Vis) region by a powdered sample. In principle, bulk and surface properties of a catalyst can be studied using DRS. In the present investigation it was used to confirm the presence of Ce in the framework of KIT-6 catalysts. DRS-UV-vis spectra were recorded using UV-Visible spectrophotometer (Shimadzu model 2450). BaSO\(_4\) was used as
the standard for measurements in the scan range 200 - 800 nm. The thickness
of the quartz optical cell was 5 mm. The absorption intensity was expressed as
the Schuster-Kubelka-Munk (remission) function,

\[ F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} \]  \hspace{1cm} (2.10)

where \( R_\infty \) is the diffuse reflectance (DR) of a semi-infinite layer and \( F(R_\infty) \) is
proportional to the absorption coefficient.

2.3.9 Diffuse Reflectance Fourier Transform Infra Red Spectroscopy

The acidity of Al-KIT-6 samples were measured by DRIFT-IR
spectrometer using pyridine as the probe molecule. DRIFT spectra of the
samples were recorded on a FT-IR spectrometer (Bruker Tensor 27 series)
equipped with a high temperature vacuum chamber. Approximately 30 mg of
the sample was taken in the sample holder and preheated at 723 K for 1 h
under vacuum (10^{-5} mbar). Then the temperature of the sample was brought
down to 298 K and the spectrum was recorded. Then pyridine was adsorbed at
room temperature. The physically adsorbed pyridine was removed by heating
the sample at 150 °C under vacuum (10^{-5} mbar) for 30 minutes, cooled to
room temperature and then the spectrum was recorded. The same sample was
used to record the infra red spectrum in the range 1700-1400 cm^{-1} (pyridine
adsorption region). The samples were subjected to thermal treatment at 373,
423, 473, 523 and 573 K and the spectra were recorded in situ. The number of
Brønsted and Lewis acid sites was calculated by measuring the integrated
absorbance of bands representing pyridinium ion formation and
 coordinatively bonded pyridine.
2.3.10 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is mainly used for surface analysis especially in the qualitative identification of elements in a sample. Based on the chemical shifts, the chemical environment around the atoms can also be estimated. This measurement is useful in determining the valence states of the atoms present in various moieties in a sample. X-ray photoelectron spectroscopic analysis was carried out by high performance XPS spectrometer (Thermo Electron Corporation Instrument Theta 300) equipped with ultra-high vacum chamber. Mg K-alpha X-rays (100 W) was used as the source at a takeoff angle of 5-75° and vacum pressure of $10^{-6} - 10^{-7}$ Torr. The powder samples were fixed on a steel holder with double-face adhesive tape and analyzed as received. An electron flood gun was used to reduce charge effects. The high-resolution spectra were obtained with analyzer pass energy of 100 eV. The binding energies were referenced to an adventitious carbon 1s line set at 284.8 eV. Gaussian line shapes were used to fit the curves for C 1s, O 1s and N 1s, and a mixed Gaussian/ Lorentzian function was employed for Cu 2p, Ti 2p and Ce 3d. The quantitative analysis of elements was carried out using spectral intensities and suitable sensitivity factor. In order to remove the peak corresponds to surface adsorbed hydrocarbon (284.5 eV), cycles of XPS measurements with subsequent Ar$^+$ sputtering (3 KeV, I= 3μA/cm$^2$) were carried out for 20 s with the etching rate of 0.05 nm/s. The elemental compositions were estimated from the relative area intensities of N (1s), Ti (2p) and O (1s) peaks.

2.4 CATALYTIC STUDIES

2.4.1 Vapor Phase Reactions

Vapor phase reactions were carried out in a fixed bed, downward vertical-flow type glass reactor (40 cm 2 cm). The reactor was heated to the
requisite temperature inside a tubular furnace controlled by a digital temperature controller cum indicator. Chromel-alumel thermocouple was used to measure the temperature of the catalyst bed. Appropriate amount of the catalyst was placed in the middle of the reactor and supported on either side with a thin layer of quartz wool and ceramic beads in order to maintain a constant flow of reactants into the catalyst bed. Reactants were fed into the reactor using a syringe infusion pump that could be operated at different flow rates. The bottom of the reactor was connected to a coiled condenser and a receiver to collect the products. The products obtained in the first 10 minutes were discarded to ensure the attainment of steady state. The products then collected for a time interval of 1 h and analysed. The schematic diagram of the reactor set-up is depicted in Figure 2.1.

2.4.2 Liquid Phase Reactions

The reaction was carried out in the liquid phase in a batch reactor consisting of a double-necked round bottom flask fitted with a condenser. The flask with its content was heated at a constant temperature by keeping the flask in an oil bath with simultaneous magnetic stirring. The progress of the reaction was monitored by withdrawing aliquots of the hot mixture at regular intervals. The samples were centrifuged and analyzed. The schematic diagram of the reactor set-up is depicted in Figure 2.2.

2.4.3 Product Analysis

Quantitative analysis of the liquid products of the reactions was carried out using a gas chromatograph (Shimadzu GC-17A) with DB-5 capillary column (30 m 0.25 mm 0.25 m) equipped with a flame ionisation detector (FID). Nitrogen was used as the carrier gas.
Figure 2.1 Schematic model of catalytic reactor set-up for vapor phase reaction
The products were also confirmed using a gas chromatograph (Perkin-Elmer Auto System XL with elite series PE-5 capillary column, 30 m 0.25 mm 1 m) coupled with a mass spectrometer (Turbo) (EI, 70 eV). Helium was used as the carrier gas at a flow rate of 1 ml min\(^{-1}\). Each component of the product mixture was identified from its characteristic m/e value and the fragmentation pattern.