CHAPTER 2

MATERIALS AND METHODS

2.1 NANOPARTICLE CHARACTERIZATION

The structural, physical and chemical characteristics of nanoparticles are essential. Different methods were employed to characterize the synthesized nanoparticles and doped nanoparticles. The following physico-chemical characterization techniques have been adopted in the present study.

2.1.1 X-Ray Diffraction Studies

XRD is a very important experimental technique that has long been used to address all issues related to the crystal structure of solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, preferred orientation of polycrystals, defects, stresses, etc. The conventional X-ray source consists of a target which is bombarded with high energy electrons. Commonly CuKα and MoKα are used as the sources for X-ray. Usually CuKα radiations with energy of 8.04 keV are used. When X-ray photons collide with a material, they can be scattered, reflected, absorbed or transmitted just like normal electromagnetic radiation. In terms of scattering, the process can be elastic or inelastic. Due to its high energy, inelastic scattering causes Compton scattering. Elastic scattering often exist. But if the X-ray photons coincide with the crystal lattice, the elastically scattered X-rays are in some path difference away from the reflected X-rays.
This path difference can be described by the Bragg's law of diffraction (Bragg & Bragg 1949).

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

(2.1)

where \( \lambda \) is the X-ray wavelength, \( d \) is the distance between atomic planes in the crystalline phase and \( \theta \) is the angle of which the X-rays incident onto the crystal planes called as Bragg's angle. \( n \) is an integer, \( n\lambda \) shows the path difference in units of \( \lambda \). This reveals the crystal properties in terms of its d-spacing, \( d \) (Culity and Stock 2001). The intensity of the diffracted X-rays is measured as a function of the diffraction angle \( 2\theta \) and the specimen's orientation.

Crystal structures can be produced several thousand unique reflections, whose special arrangement is referred to as diffraction pattern. Indices \((hkl)\) may be assigned to each reflection, indicating its position within the diffraction pattern. The pattern has a reciprocal Fourier transform relationship to the crystalline lattice and the unit cell in the real space. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties. XRD is nondestructive and does not require elaborate sample preparation, which partly explains the wide usage of XRD method in materials characterization.

Diffraction peak positions are accurately measured with XRD, which makes it the best method for characterizing homogeneous and inhomogeneous strains. Homogeneous or uniform elastic strain shifts the diffraction peak positions. From the shift in peak positions, one can calculate the change in d-spacing, which is the result of the change of lattice constants under a strain. Inhomogeneous strains vary from crystallite to crystallite or within a single crystallite and this cause a broadening of the diffraction peaks.
that increase with \( \sin \theta \). Peak broadening is also caused by the finite size of crystallites, but here the broadening is independent of \( \sin \theta \). When both crystallite size and inhomogeneous strain contribute to the peak width, these can be separately determined by careful analysis of peak shapes. If there is no inhomogeneous strain, the crystallite size, \( D \), can be estimated from the peak width with the Scherrer’s formula (Culity and Stock 2001):

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]  

(2.2)

where \( \lambda \) is the X-ray wavelength, \( \beta \) is the full width of half maximum (FWHM) of a diffraction peak, \( \theta \) is the diffraction angle, and \( K \) is the Scherrer’s constant of the order of unity for usual crystal. However, one should be alerted to the fact that nanoparticles often form twinned structures; therefore, Scherrer’s formula may produce results different from the true particle sizes. In addition, X-ray diffraction only provides the collective information of the particle sizes and usually requires a sizable amount of powder. It should be noted that since the estimation would work only for very small particles, this technique is very useful in characterizing nanoparticles.

The XRD patterns of Nanostructures were recorded in an X-ray diffractometer (BRUKER D2 PHASER) using CuK\( \alpha \) (\( \lambda = 0.15406 \) nm) as the radiation source. The diffractograms were recorded in the \( 2\theta \) range between 10 and 80° with a step size of 0.02° and a count time of 20s at each point.

2.1.2 Fourier Transform-Infrared Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) is a multidisciplinary analytical tool, which yields information pertaining to the structural details of a 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 infrared region of the spectrum which results 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.

It is particularly useful for the nondestructive analysis of solids and thin films. The goal of the basic infrared experiment is to determine changes in the intensity of a beam of infrared radiation as a function of wavelength or frequency after it interacts with the sample. The ratio of the intensity before and after the light interacts with the sample is determined. The plot of this ratio versus frequency is the infrared spectrum. The infrared spectrum originates from the vibrational motion of the molecule. The vibrational frequencies are a kind of fingerprint of the compounds and are used for characterizing of organic, inorganic and biological compounds. The band intensities are proportional to the concentration of the compound and hence qualitative estimations are also possible. The IR spectroscopy is also carried out by using Fourier transform technique. The interference pattern obtained from a two beam interferometer as the path difference between the two beams is altered, when Fourier transformed, gives rise to the spectrum. The transformation of the interferogram into spectrum is carried out mathematically with a dedicated on-line computer.

IR spectra of 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 infrared spectra in the range 4000-400 cm\(^{-1}\).

### 2.1.3 Transmission Electron Microscopy

Shortly after the discovery of the particle-wave duality of electrons, people realized that the wave characteristics of electrons could be used to build a microscope that could surpass the resolution limit of optical microscopes. Transmission electron microscopy (TEM) is widely used to observe the size of small nanoparticles through imaging, revealing phase/crystallographic orientation information through a diffraction pattern and discovering chemical composition by means of the energy spectrum.

The TEM usually consists of an electron gun, a set of electromagnetic lenses and apertures, a sample chamber, and a screen. Electrons beams are first generated through either field emission (monochromatic electron beam) or thermionic emission (white electrons) and then accelerated through a bias voltage to achieve high energy. The acceleration voltage determines the energy of the electron beam and thus the wavelength of the electron. A series of electromagnetic lenses then magnifies this transmitted electron beam and focused on the specimen.

After the beam transmits through the specimen, the transmitted electrons pass through another set of electronic optics to finally fall on a fluorescent screen where the image is produced and recorded on a photographic film. Diffracted electrons can be observed in the form of a diffraction pattern beneath the specimen. Transmitted electrons form images from small regions of sample that contain contrast, due to several scattering mechanisms associated with interactions between electrons and the atomic constituents of the sample. The scattering processes experienced by electrons
during their passage through the specimen determine the kind of information obtained. Elastic scattering involves no energy loss and gives rise to diffraction patterns. Inelastic interactions between primary electrons and sample electrons at heterogeneities such as grain boundaries, dislocations, second-phase particles, defects, density variations, etc., cause complex absorption and scattering effects, leading to a spatial variation in the intensity of the transmitted electrons.

The high magnification or resolution of all TEM is a result of the small effective electron wavelengths, \( \lambda \), which is given by the de Broglie relationship:

\[
\lambda = \frac{h}{\sqrt{2mqV}}
\]  

where \( m \) and \( q \) are the electron mass and charge, \( h \) is Planck's constant, and \( V \) is the potential difference through which electrons are accelerated. The higher operating voltage of a TEM instrument, its lateral spatial resolution is greater. The resolution can go down to the nanometer region, making it an excellent tool for nanomaterials characterization. The greatest advantages that TEM offers are the high magnification ranging from 50 to \( 10^6 \) and its ability to provide both image and diffraction information from a single sample. High resolution TEM (HRTEM) can even image lattice points that are in the range of angstroms.

In this study, the TEM observations were carried out on a JOEL-CX300 with an accelerating potential of 300 kV. Bright field images and selected-area electron diffraction patterns were taken to examine the crystal structure and identify the shape and size of the nanostructures.
2.1.4 Scanning Electron Microscopy

Unlike transmission electron microscopes, a scanning electron microscope scans electron beam across the sample surface and collects scattered electrons for imaging. Because the image is formed using backscattered signals instead of forward-transmitted signals, the electron beam energy does not need to be high (40 keV) and the sample also does not require electronic transparency; it has only a conductivity requirement to prevent charging.

Scanning electron microscopy (SEM) is one of the most widely used techniques for the characterization of size and morphology of the particles. SEM provides not only topographical information like optical microscopes but also gives information of chemical composition near the surface. SEM creates magnified images by using electrons instead of light. It gives detailed 3-D images at higher magnification than an optical microscope. The various processes of interaction of primary electron beam with catalysts in an electron microscope are shown in Figure 2.1. In the scanning electron microscope, back scattered electrons and secondary electrons are captured by a detector to form the image.

Secondary electrons arise due to inelastic collision between primary electrons (the beam) and loosely bound electrons of the conduction band or tightly bound valence electrons. The energy transferred is sufficient to overcome the work function which binds them to the solid and they are ejected. The ejected electrons have 5-10 eV energy and they are detected by scintillator / photomultiplier tube. Back scattered electrons arise due to elastic collisions between the incoming electron and the nucleus of the target atom. Higher the atomic number, higher is the number of back scattered electrons. They are detected by semiconductor detectors.
Most of the particles used in the study are low conducting specimens and hence the catalysts were coated with gold by sputtering method. The morphology of the materials 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 they give rise to charging phenomena resulting blurred images.
2.1.5 Energy Dispersive X-ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDAX) is an analytical technique used for the elemental analysis of the sample. A high energy beam of electrons is focused on the sample. The incident beam of electrons excites an electron in the inner shell of an atom thus creating an electron-hole. An electron from an outer higher energy shell then fills the hole. The difference in the energy between higher energy shell and lower energy may be released in the form of an X-ray. The number and energy of X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of X-rays is characteristic of the difference in energy between the two shells and atomic structure of the element from which they are emitted, this allows the elemental composition of the specimen to be measured. The detector converts X-ray energy into voltage signals and the information is sent to the pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis.

A silicon semiconductor is used with high impedance zone which is radiation sensitive. Each absorbed X-ray quantum is converted into a cloud which consists of pairs of charge carriers i.e. electrons and holes. Hence, the energy of the X-ray photons can be calculated. Due to high voltage, which is between both ends of the sensitive area of the detector, the charge carriers are moved and collected at the ends of the sensitive zone. With a charge sensitive preamplifier, the charge quantity is finally converted into a voltage pulse. The pulse is amplified and shaped in a spectroscopic amplifier. The elemental analysis of modified catalysts was recorded using TEM coupled with EDAX instrument (HITACHI (Japan) H-7650-80KV).
2.1.6 UV-Visible Absorption Spectroscopy

Optical spectroscopy has been widely used for the characterization of nanomaterials and the techniques can be generally categorized into two groups: absorption and emission spectroscopy and vibrational spectroscopy. The former determines the electronic structures of atoms, ions, molecules or crystals through exciting electrons from the ground to excited states (absorption) and relaxing from the excited to ground states (emission). The optical absorption is a result of interaction between the material and light. When a frequency of light is in resonance with the energy difference between states the transition allowed or partly allowed by selection rules, a photon is absorbed by the material. By measuring the absorption of the sample as a function of the frequency of light, a characteristic absorption spectrum of the material can be obtained.

The characteristic lines observed in the absorption spectra of nearly isolated atoms and ions due to transitions between quantum levels are extremely sharp. As a result, their wavelengths or photon energies can be determined with great accuracy. The lines are characteristic of a particular atom or ion and can be used for identification purposes. Molecular spectra, are usually less sharp than atomic spectra, and are also relatively sharp. Positions of spectral lines can be determined with sufficient accuracy to verify the electronic structure of molecules. In solids, the large degeneracy of the atomic levels is split by interactions into quasi-continuous bands (valence and conduction bands) and makes their optical spectra rather broad.

The energy difference between the highest lying valence (the highest occupied molecular orbital, HOMO) and the lowest lying conduction (the lowest unoccupied molecular orbital, LUMO) bands is designated as the fundamental gap. Penetration depths of electromagnetic radiation are on the
order of 50 nm through most of the optical spectrum (visible light). Such small penetration depths limit the applications of optical absorption spectroscopy for the characterization of bulk solids; however, this technique is readily applicable for the characterization of nanostructures and nanomaterials.

In present study, a SHIMADZU UV-2450 spectrophotometer is used for recording the absorption spectra in the range of 200-800 nm at room temperature. This contains double beam and double pass monochromator system with good resolving power and photometric efficiency in the UV and visible regions. The light beam from Deuterium lamp passing through the filter is focused onto the grating by a concave mirror. The beam is again reflected by grating and is directed to the partial reflecting mirror which in turn splits the pulsating beam into two paths, one through the sample under investigation and the other through the reference sample. These two beams of light are directed onto a detector. The photograph of SHIMADZU UV-2450 Spectrophotometer

2.1.7 Diffuse Reflectance Ultraviolet - Visible Spectroscopy

Diffuse reflectance Ultraviolet - visible 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 metal containing molecular sieves and in doped semiconductors. It deals with the study of electronic transitions between orbitals or bands of atoms, ions or molecules in gaseous, liquid and solid state. This technique is 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 sample can be studied using DRS-UV-vis spectra. The spectra were recorded using UV-visible spectrophotometer
(Shimadzu model 2450). BaSO$_4$ was used as an internal standard for measurements in the scan range of 200-800 nm. The thickness of the quartz optical cell was about 5 mm. The scattered radiation emanating from the sample is collected in an integration sphere and detected. The most popular continuum theory describing the diffuse reflectance effect is Schuster - Kubelka - Munk (SKM) theory. The diffuse reflectance of the sample ($R_d$) is related to an apparent absorption ($K$) and apparent scattering coefficient ($S$) by the SKM Equation (2.4)

$$F(R_d) = (1-R_d)^2/2R_d$$

(2.4)

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

2.1.8 Photoluminescent Spectroscopy

In luminescence one measures physical and chemical properties of materials by using photons to induce excited electronic states in the material's system and analyzing the optical emission as these states relax. Typically, light is directed onto the sample for excitation and the emitted luminescence is collected by a lens and passed through an optical spectrometer onto a photodetector.

Luminescence spectroscopy is an extremely useful tool for obtaining information about the electronic, optic and photo-electric properties of materials, since it depends on electronic excitations and therefore is an important complement to spectrosopes that depends on lattice excitations (e.g. Raman).
Luminescence refers to the emission of light by a material through any process other than blackbody radiation. The emission of light can result from a variety of stimulations. In photo luminescence (PL) the physical and chemical properties of materials are measured by using photons to induce excited electronic states in the material system and analyzing the optical emission as these states relax. Typically, light is directed onto the sample for excitation and the emitted luminescence is collected by a lens and passed through an optical spectrometer onto a photon detector.

The spectral distribution and time dependence of the emission are related to electronic transition probabilities within the sample and can be used to provide qualitative and, sometimes, quantitative information about chemical composition, structure, impurities, kinetic process and energy transfer. Sensitivity is one of the strengths of the PL technique, allowing very small quantities (nanograms) or low concentrations (parts-per-trillion) of material to be analyzed. Precise quantitative concentration determinations are difficult unless conditions can be carefully controlled and many applications of PL are primarily qualitative.

In PL, a material gains energy by absorbing photon at some wavelength by promoting an electron from a low to a higher energy level. This may be described as making a transition from the ground state to an excited state of an atom or molecule, or from the valence band to the conduction band of a semiconductor crystal or polymer (electron-hole creation). The system then undergoes a non-radiative internal relaxation involving interaction with crystalline or molecular vibrational and rotational modes and the excited electron moves to a more stable excited level, such as the bottom of the conduction band or the lowest vibrational molecular state. After a characteristic lifetime in the excited state, electron will return to the ground state. In the luminescent materials some or all of the energy released
during this final transition is in the form of light, in which case the relaxation is called radiative. The wavelength of the emitted light is longer than that of the incident light. It should be noted that depending on the characteristic lifetime of emission, fast PL with lifetime of sub microsecond is also called "fluorescence", whereas slow ones, $10^{-4}$ to $10^{-1}$ s, are referred to as "phosphorescence". Optical absorption and photoluminescence spectra are commonly used in the characterization of the size of nanocrystals of semiconductor.

In this study, the Fluorescence spectra were obtained on a (JOBIN YVON) equipped with a 30 mW HeCd UV laser (325.09 nm) over the range 330-649 nm. The iris was set at 500 μm with 100% light pass.

2.1.9 Thermogravimetric Analysis

In thermoanalytical technique, the change in 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 due to 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 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
endothric and exothermic behaviour at high temperatures. TGA of the materials was performed (Perkin Elmer Diamond series) with 10 mg of the sample under N₂ atmosphere at a heating rate of 10°C min⁻¹ in the temperature range 50-1000°C.

2.2 MAGNETIC CHARACTERIZATION

The observation of magnetic properties of the nanostructures samples were characterized through the physical property measurement system (PPMS—vibrating sample magnetometer).

2.2.1 Physical Property Measurement System (PPMS)

The physical property measurement system (PPMS) is a multipurpose system (Figure 2.10), used to determine the thermodynamic properties of materials. PPMS are capable of measuring physical properties of samples including electrical resistivity, magnetization, Hall Effect, heat capacity, thermal conductivity and thermal transport. These can be determined to as high degree of accuracy as a function of temperature and/or magnetic field. The lowest temperature which can be achieved is about 0.35 K and the maximum limit is about 400 K. This system is comprised of a large superconducting magnet, cooled by liquid helium which in turn surrounded by a jacket of liquid nitrogen. The superconducting magnet (NbTi/Nb₂Sn hybrid) (Kiyoshi and Wada 2003) is used to generate magnetic fields up to 16 Tesla. It is possible to ramp up the field while measuring certain physical properties of the samples, which makes the system even more versatile.

In this study the PPMS system was used to measure the magnetization of samples as function of both field and temperature. The Quantum design PPMS—VSM linear motor transport uses a uniquely
designed motor to vibrate the sample, and is designed to operate at 40 Hz, with rapid slewing possible over about 6.5 cm of travel. The large range of motion enables the PPMS–VSM system to perform rapid, completely automated centering operations. The characteristics of any magnetic material, whether it is hard, soft, or intermediate, are best described in terms of their hysteresis loop. The most common measurement method employed for hysteresis loop determinations at ambient temperature is the vibrating sample magnetometer (VSM). They are ideally suited for research and development, production testing, quality and process control. Powders, solids, liquids, single crystals, and thin films are all readily accommodated in a VSM.