CHAPTER 3

EXPERIMENTAL TECHNIQUES
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Ceria based materials are found to have catalytic activity, structural and electronic promoters of heterogeneous catalytic reactions and oxide ion conducting solid electrolytes in electrochemical cells\(^{52,60}\).

By using co-precipitation procedure, it is possible to achieve a high degree of homogenization together with a small particle size and thereby speed up the reaction rate.

Reactants are dissolved in water, the solutions then being mixed, co-precipitated and the resulting fine powder is a solid solution. The precipitated solids are filtered off and calcined in the usual way, but because of the high degree of homogenization, much lower reaction temperatures are sufficient for reaction to occur.

3.1. Preparation of Cerium and Tin Oxide doped compounds:

The mixed oxide compositions (a) Ce\(_{1-x}\)Sn\(_x\)O\(_2\) (b) Ce\(_{1-x}\)Fe\(_x\)O\(_2\) (c) Ce\(_{1-x}\)Mn\(_x\)O\(_2\) and (d) Sn\(_{1-x}\)Mn\(_x\)O\(_2\) (where x = 0, 0.1, 0.2, 0.3, and 1) were prepared by co-precipitation method, a stepwise process is shown in the flow diagram fig. 3.1. The required amount of metal salt of AR grade was
Fig. 3.1 Flow diagram of Co-precipitation method
dissolved in distilled water and ceric ammonium sulphate was taken in stoichiometric ratio and dissolved in dilute sulphuric acid solution to obtain a clear homogenous solution. Both the solutions were mixed with continuous stirring. 10% sodium hydroxide solution was prepared by dissolving NaOH (AR grade) in distilled water to obtain an approximately equi-molar concentration solution. This was slowly added to the metal solution with constant stirring till the precipitation is complete. The pH of the solution was maintained between 9-10. The resultant precipitate was digested on a water bath for 3 hours. It was then cooled to room temperature and subjected to oxidation by dropwise addition of 30% H₂O₂ with continuous stirring. The precipitate was then filtered, washed and dried at 100°C. The solid was then heated at 400°C for 4 hours. The calcined material was homogenized well in a mortar and then fired in a furnace at 600-800°C for 10-12 hours. The fired material was homogenized well in a mortar and after characterization used as photocatalyst for further study.

3.1.B Phthalocyanine preparation:

Metal phthalocyanines (MPc) (where M = Cu, Ni, Co and Fe) were prepared by method described elsewhere²⁹. Required amount of phthalic anhydride, urea, metal salt and ammonium molybdate were
suspended in nitrobenzene and heated, at 190°C. After 4-5 hours the mixture was filtered hot and then washed with nitrobenzene, followed by methanol. The crude product was boiled 2 hours, first with 1N HCl and then with 1N NaOH, filtered and washed with water each time until the filtrate was neutral. The solid material was then stirred in methanol, suction filtered, and dried at 60°C.

3.2 Characterization

The mixed oxides prepared by co-precipitation method and the phthalocyanines prepared by literature method were characterized by X-ray diffraction technique, vibrational spectroscopy, B.E.T. liquid nitrogen adsorption method and thermal studies.

3.2.1 The X-ray powder diffraction technique

The prepared samples were characterized by recording X-ray powder diffractograms. The diffraction patterns were recorded on ITAL X-ray diffractometer using Cu Kα radiation, filtered through Ni absorber, at a scanning rate of 0.1°/min. The samples were identified by comparing the observed inter planar d-spacings and relative peak intensities, with those reported in the literature (ICDD-PDF data files). The intermediate compositions, which are not reported, were confirmed by comparing with the end compositions.
3.2.2 Vibrational spectroscopy (IR spectroscopy)

The infra red absorption spectra were recorded for all the compositions in the range 4000-400 cm$^{-1}$, on a Shimadzu FTIR instrument, model 8101 A, using KBr as a carrier. The mixture of sample and KBr was pressed into a pellet with thickness of about 1 mm. The spectra were compared with the literature and interpreted.

3.2.3 Atomic absorption spectroscopy

The sodium contamination in the oxides prepared by co-precipitation technique using NaOH, was found out using an atomic absorption spectrometer. Approximately 250 mg of powdered sample was dissolved using 25 ml of pure HCl it was then further diluted to the required concentration. The total amount of sodium was determined by comparing with the standard.

3.2.4 B. E. T. method (Surface area measurement)

Surface areas of the prepared samples under study were measured using BET nitrogen adsorption method on SMARTSORB 91. Specific surface areas of the catalyst were calculated with the help of well-known Brunauer, Emmet and Teller (BET) expression.
\[ \frac{P}{V} (P_0-P) = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \times \frac{P}{P_0} \quad (1) \]

Where 'P' is the equilibrium pressure. 'P_0' is the saturated vapour pressure of the gas at the temperature of the adsorption. 'V' is the volume of the adsorbed gas at S.T.P., 'C' is the constant related to the heat of adsorption and 'V_m' is the volume of the gas at S.T.P. required to form a monolayer. Various quantities from the above equation like P, P_0 and V could be determined experimentally. V_m and C can be obtained by plotting \( \frac{P}{V} (P_0-P) \) versus P/P_0. Plot should give a straight line with slope (S) = C-1/V_m C and intercept (I) = 1/V_m C which proves the validity of the equation (1).

It can be shown from equation (1) that \( V_m = \frac{1}{S+1} \) and \( C = \frac{S}{1+1} \). Since V_m is the volume of the gas at 0°C and 1 atmospheric pressure necessary to cover the surface with one layer of the gas, it is easy to convert it to the no of molecules involved. Assuming 16.2^0A as the value of the cross sectional area of single nitrogen molecule at liquid temperature Brunauer, Emmet and Teller have shown that,

Surface area = 4.38 \( V_m \) (C.C., S.T.P.) m^2/g \quad (2)

Surface area for various oxide samples were observed in the range of 2.6 to 46 m^2/g.
3.3 Electrical resistivity measurements

The electrical resistivity measurements were carried out to study the conductivity behaviour of the samples and possible relationship with catalysis.

Electrical resistivity measurements were carried out using a two-probe conductivity cell in the temperature range from room temperature to 250°C. For the resistivity measurement, sample was pelletized using an approximately 1-2 g of the sample, under a pressure of 7,500 Kg/cm³. The prepared pellets were subjected to the heat treatment in an electrical furnace at 600-800°C for 10–12 hours. Metal phthalocyanines were pelletized and heated at 200°C for 24 hours. Silver paint was applied on both the surfaces of the pellet. The pellet was tightly held between two polished and cleaned silver electrodes by adjustable type assembly and the resistivity measurements were carried out from room temperature to 250°C, point-by-point measurement. Measurements were recorded while cooling the pellet.

3.4 Magnetic Susceptibility Measurements:

The magnetic susceptibility ‘χΣ’ in air of the samples was determined by Gouy’s method at room temperature. A field of the order of 8,000 Gauss was employed. A sensitive analytical balance of DONA was used to measure the difference in weights. Mercury tetra thiocyanatocobaltate \( \text{Hg[Co(SCN)₄]} \)
was used as the standard material. The sample tube was washed, dried and filled with the standard material up to a certain mark and hanged between the electromagnets of the Gouy balance.

The weight was recorded before and after applying the appropriate magnetic field. The procedure was repeated for the sample whose $\chi_g$ is to be determined. The magnetic susceptibility of the sample was calculated by using the following calculations.

In the first part, tube constant or $\beta$ – constant is calculated, as $\chi_g$ value of the standard material is known. Using the relation,

$$\beta\text{- Constant } = \chi_g \times \frac{W}{\Delta W} \quad (Xg = 16.44 \times 10^{-6} \text{ cgs units for Hg[Co(SCN)₄]})$$

$$W = (W_3 - W_1) = \text{Wt. of standard material taken}$$

$$\Delta W = \Delta W' + \Delta W'' \quad (+ \text{ve for paramagnetic and } -\text{ve for diamagnetic})$$

$$\Delta W' = (W_4 - W_3) \text{ and } \Delta W'' = (W_1 - W_2) \text{ where}$$

$$W_1 = \text{Weight of the empty tube},$$

$$W_2 = \text{Weight of the empty tube with field}$$

$$W_3 = \text{Weight of the tube with standard material and}$$

$$W_4 = \text{Weight of the tube and standard material with field}$$

Hence $\beta$ - constant was calculated. In the second part, to calculate $\chi_g$ of the sample, substitute $\beta$- constant in the above relation, gives the magnetic
susceptibility. Further this data is utilized to calculate unpaired electrons present in the sample as follows.

\[ \chi_m = \chi_g \times \text{molecular weight of the sample} \]

Where \( \chi_m \) = molar susceptibility and

\[ \chi_g = \text{gram susceptibility} \]

The magnetic moment \( \mu \) effective (\( \mu_{\text{eff}} \)) of the sample was calculated by using the equation given below.

\[ \mu_{\text{eff}} = 2.84 \sqrt{\chi_m \times T} \text{ B. M.} \text{ where } T = \text{absolute temperature and} \]

\( \mu_{\text{eff}} \) is the magnetic moment

3.5 Saturation magnetization study

The saturation magnetization is studied with the help of hysteresis loop tracer. These measurements were done on selected magnetic samples, using a high field hysteresis loop tracer and the three major components are electromagnet, pick-up coil and integrating circuits.

The loop tracer consists of an electromagnet working at 50 Hz mains frequency. The alternating magnetic field of about 3600 Oersted is produced in an air gap of about 1 cm, in the instrument and a special balancing coil is used to measure the saturation magnetization of the sample in the air gap. Depending upon the magnetic induction in the sample, pick-up coil produce a
field proportional to the magnetic induction of the sample. A supporting coil produces a signal that is equivalent to the strength of the magnetic field. The signal is displayed as a hysteresis loop on the screen of an oscilloscope. A digital AC Voltmeter, which is connected to the output, displays the peak or RMS value of the signal proportional to the saturation magnetization, in millivolts. The calibration of the vertical scale corresponding to the magnetization value is done using Nickel as a standard substance having magnetization of $5\times10^6$ emu/g. The saturation magnetization values, in emu/g of some selected samples was found out.

3.6 Thermal studies

The thermal technique of Thermogravimetric analysis (TG) and Differential scanning calorimetry (DSC) was carried out using NETZSCH–Geratebau GmbH Thermal Analyzer. TG was used to study the heat effects, associated with the physical and chemical changes of the substances in the temperature range from room temperature to 800°C. Thermal effects, exothermic or endothermic preceding physical and chemical changes were studied by differential method in which the sample temperature is continuously compared against the temperature of thermally inert reference material. TG was recorded to study the behaviour of weight loss of the precursor sample.
The samples, in a powdered form and weighing between 5 to 10 mg, were placed in alumina crucible covered with lid. Sample was continuously weighed as it is heated at a constant linear rate of $10^\circ$C/min.

### 3.7 Electron Spin Resonance (ESR) study

Electron Spin resonance occur when a spinning electron in an externally applied magnetic field absorbs sufficient electromagnetic radiation to cause the inversion of spin state of the electron, which is also known as electron paramagnetic resonance and as electron magnetic resonance.

ESR study was carried out for the sample containing paramagnetic species. In ESR spectroscopy, a magnetic field strength of 3220 gauss (commonly used field strength = 3300 gauss) was employed. The energy level difference due to electron spin was $6.1 \times 10^{-17}$ ergs (or about $1.5 \times 10^{-24}$ calories) and frequency ‘$V$’ is $9.2$ GC (Giga cycles or $10^9$ cycles per sec.), this frequency lies in the microwave region of the electromagnetic radiation spectrum. The ESR spectra were taken at the X-band on a varian E-112 spectrometer at room temperature. The sample was mounted in a quartz tube and TCNE was used as a field calibrant taking its g-value as 2.00277. Spectroscopic spitting factor (g) or gyro magnetic ratio was obtained from the following relation,
\( \mu = -g \beta s \)

Where \( \mu \) is the magnetic moment, and \( \beta \) is the Bohr magneton (ergs/gauss), \( g \) is the gyro magnetic ratio and \( s \) is the spin of electron +1/2 or −1/2

3.8 UV-Visible Spectroscopy

The UV-visible absorption spectra were recorded for phthalocyanines in the range 400-700 nm, on a UV-visible spectrophotometer (spectro119) using pyridine as a solvent. The phthalocyanines were dissolved in pyridine and the solution was scanned from 400 to 700 nm using glass cuvettes, each phthalocyanine showed maximum absorbance at particular wavelength which was compared with the literature.

3.9 UV-Visible diffuse reflectance study

The UV-VIS-DRS spectra were recorded on UV-visible spectrophotometer with BaSO\(_4\) as a reference material. The samples were taken in the form of 2mm thick self supported pellets to measure the reflectance. Samples were scanned from 200 to 700 nm. Band gap energy was calculated at absorption edge shown by each sample in the spectra.
3.10 Photocatalytic Studies

Prepared samples were tested for two model reactions such as photodegradation of textile diazo dye Naphthol Blue Black and basic Yellow Auramine O.

$10^{-3}$ M dye solution was prepared by dissolving the Naphthol Blue Black dye in distilled water and was used as stock solution. From this, $10^{-5}$ M solution was prepared in a standard volumetric flask and used as test solution. 200 mg of the prepared sample was used for the degradation of the dye that was found to be optimum amount for the degradation. The degradation rate was monitored using UV-visible spectrophotometer (spectro 119) by measuring absorbance of the reaction mixture after every hour. Naphthol Blue Black absorbs at 618 nm.

100 ml of the $10^{-5}$ M dye solution was aerated with oxygen for 2-5 minutes and to this 200 mg of prepared photocatalyst was added and stirred well. This reaction mixture was kept in sunlight for irradiation. Small amount of reaction mixture was taken out after every hour, filtered with Whatmann no 41 and absorbance was measured at $\lambda_{\text{max}}$ 618 nm.

The reaction was carried out at various experimental conditions like change in pH, with different amount of photocatalyst and with and without oxygen. The pH of the solution was adjusted by using previously standardized...
1N HCl and 1N NaOH. The pH was measured with pH paper. The degradation product was analyzed by HPLC method and qualitative analysis. The dye Naphthol Blue Black degrades to a colourless solution.

Photocatalytic degradation of another textile dye basic Yellow Auoramine O was studied on selected samples. Test solution was prepared with distilled water and used for degradation. 100 mg of the photocatalyst was used and the absorbance of the reaction mixture was measured at wavelength 432 nm by taking out small amount of the solution after every hour. Absorbance versus time was plotted for every sample. The degradation rate was found to increase with time.