CHAPTER 3

EXPERIMENTAL TECHNIQUES
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Perovskites have been reported to possess interesting structural, solid state and catalytic properties. Ceramic method is commonly used for the preparation of mixed metal oxides whose textural characteristics are not important for their use. The technique involves the heating of an intimate mixture of the respective binary oxides or their precursors (hydroxides, nitrates, carbonates etc.) in solid state at high temperature. Sol-gel method for the preparation of perovskites is based upon the formation of a sol of the precursors which is destabilized to the formation of a gel. In combustion method, the high temperature required for the formation of the oxides is achieved by the exothermicity of the redox reactions between the decomposition products of metal nitrate (oxidizer) and the fuel during combustion. Perovskites can also be prepared by other methods like dry evaporation, explosion, spray-drying, freeze-drying, crystallization, complexation and co-precipitation.

In wet co-precipitation method, the constituent metal ions are jointly precipitated as a single or two separate precursors like citrates, oxalates, carbonates, cyanides and hydroxides. The derived precursors are normally stable in air.
and ensure better homogeneity. The subsequent decomposition and heating yield fine and higher surface area particles\textsuperscript{188-189}. This old non-conventional technique is extensively used as a powerful method. Bell et. al.\textsuperscript{28} have reported compounds prepared by this method which are found to be most efficient to facilitate oxidation type of reactions.

In the present context, co-precipitation technique has been fully exploited for the preparation of some perovskites and mixed metal oxides for their solid state and catalytic studies. Some other perovskites for similar studies have been prepared by combustion technique.

### 3.1 MATERIAL PREPARATION

Perovskites of the compositions:

- (I) $\text{Zn}_{1-x}\text{Ni}_x\text{MnO}_3$ (where, $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$)
- (II) $\text{AMnO}_3$ (where, $A = \text{Sr, Sm and Nd}$), $\text{BaCeO}_3$ and $\text{ZnSnO}_3$

Supported metal oxides of the compositions:

- (III) $\text{Fe}_2\text{O}_3/\text{ZnO}$ (where, $\text{Fe}_2\text{O}_3 = 0\%, 5\%, 10\%, 20\%$ and $100\%$)
- (IV) $\text{NiO}/\text{ZnO}$ (where, $\text{NiO} = 0\%, 5\%, 10\%, 20\%$ and $100\%$)

were prepared by wet co-precipitation technique\textsuperscript{51,131,175,189}.

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- (I) $\text{Zn}_{1-x}\text{Ni}_x\text{MnO}_3$ (where, $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$)

were prepared by combustion technique\textsuperscript{184}.

The step wise process involved in co-precipitation technique is shown in flow diagram (fig.3.1). Stoichiometric quantities of the respective metal nitrates and
acetates of A.R. grade quality as required in the desired final compositions were weighed and dissolved in about 200 ml of distilled water. The solution was heated at 60-80°C with stirring to get a clear homogeneous solution. 5% sodium hydroxide solution was prepared by dissolving NaOH (A.R. grade) in distilled water to obtain an approximately equimolar concentration solution. This was filled in a burette and was added slowly to the metal ions solution in a beaker on a magnetic stirrer with constant stirring, till the precipitation was complete. The pH of the solution was maintained between 9-10. The precipitate was digested on a hot water bath for about 3 h and then cooled. This was oxidized by drop wise addition of 30% hydrogen peroxide in a burette with continuous stirring of the precipitated mixture on a magnetic stirrer. The precipitate was then washed and filtered using warm distilled water till it was free from nitrate and sodium ions. This was followed by the drying of the precipitate in an oven at 80°C for 10-15 h. The dried precipitate was ground well in a mortar and then heated in a muffle furnace at 700-800°C for 10-12 h to form the required oxides. If X-ray diffraction of the desired perovskites showed any biphasic character, further heating was done for few more hour to obtain monophasic compound. The characterized compositions were finally designated as perovskite and supported metal oxide catalysts.

The step wise process involved in combustion technique is shown in flow diagram (fig.3.2). Stoichiometric quantities of pure (A.R. grade) Sr/Sm/Nd/Ce/Sn nitrate and Mn/Ba/Zn acetate were separately dissolved in distilled water.
Fig. 3.1 Flow diagram of co-precipitation preparative method
Fig. 3.2 Flow diagram of combustion preparative method
The two aqueous solutions were mixed in an evaporating dish and heated slowly with constant stirring on a sand bath to a pasty mass. Further careful heating involved the exothermic combustion of the substrate leading to the formation of residue. The residue was mixed and ground in a mortar and finally calcined in a muffle furnace at 700-800°C for 10-12 h. The characterization of the compounds were done by employing powder X-ray diffraction technique.

3.2 CHARACTERIZATION

Materials prepared by the above methods were characterized by powder X-ray diffraction (XRD) technique, Infra Red Spectroscopy (FTIR), Atomic Absorption Spectroscopy (AAS), B.E.T. surface area measurement and Thermal studies (TGA/DSC).

3.2.1 Powder X-ray diffraction technique

XRD patterns for the powdered samples were recorded on X-ray diffractometer (Philips PW 3710 / Rigaku), using Cu Kα / Cr Kα radiations, at a scanning rate of 2°/min. These compounds were identified by comparing their d_{hkl} values and the relative peak intensities obtained from diffractogrammes with those reported in JCPDS data files. The intermediate compositions, not reported, were confirmed by comparing with the end compositions.
3.2.2 **Infra Red Spectroscopy**

FTIR absorption spectra for all the samples were recorded on a Shimadzu IR Prestige-2 model spectrometer. The solid sample was finely ground along with pure and dry KBr, in the ratio 1:10. The mixture was pressed in a special die which was mounted on the sample holder in the sample chamber of the spectrometer. The absorption spectra was recorded in the range 300 cm\(^{-1}\) to 1500 cm\(^{-1}\). The spectra were compared with literature and were interpreted accordingly.

3.2.3 **Atomic absorption spectroscopy**

Sodium contamination in the samples prepared by co-precipitation technique was determined by using an atomic absorption spectrometer. About 250 mg of powdered sample was dissolved in 25 ml of pure HCl which was further diluted to the required concentration using deionised water. The total amount of sodium was determined by comparison with the standard. Sodium contamination in these samples was found in the range 0.2 to 0.4% by weight.

3.2.4 **B.E.T. Method (Surface area measurement)**

Surface areas of the samples under study were determined using B.E.T. nitrogen adsorption method, employing SMARTSORB-92/93 model Surface Area Analyzer. Specific surface areas of the catalysts were calculated with the help of well known Brunauer, Emmet and Teller (BET) expression:

\[
\frac{P}{V (P_o-P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \cdot \frac{P}{P_o} \quad \text{-------------------(1)}
\]
Here 'P' is the equilibrium pressure, 'P_o' is the saturated vapor pressure of
the gas at the temperature of adsorption, 'V' is the volume of the adsorbed gas at
S.T.P., 'V_m' is the volume of the gas at S.T.P. required to form a monolayer and 'C'
is the constant related to the heat of adsorption. The quantities P, P_o and V can be
determined experimentally. The plot of P/V (P_o-P) versus P/P_o is a straight line with
slope S = C-1/V_m C and intercept I = 1/V_m C, which proves the validity of equation
(1). V_m and C can be obtained from the above plot.

From equation (1) it can be shown that V_m = 1/S+I and C = S/I+1. Since V_m
is the volume of the gas at 273 K and 1 atm pressure necessary to cover the surface
with single layer it can be converted into the number of molecules involved.
Assuming 16.2 A° as the value of the cross sectional area of single nitrogen molecule
at liquid nitrogen temperature, Brunauer, Emmet and Teller have shown that,

Surface Area = 4.38V_m (c.c., S.T.P.) m^2/g

---------- (2).

3.2.5 Thermal studies (TGA/DSC)

Thermal study of the co-precipitated hydroxide precursors of the perovskites
was carried out employing NETZSCH Geratebau GmbH Thermal Analyzer (STA
409PC). Around 10 to 15 mg of the powdered hydroxide precursor sample weighed
in an alumina crucible covered with lid was mounted on a sample holder of the
analyzer which is then operated in the temperature range 30 to 800°C. Thermal
gravimetric analysis (TGA) and Differential scanning calorimetry (DSC) patterns
during heating were recorded. TGA pattern was used to interpret the heat effects
associated with the physical and chemical changes and the behaviour of weight loss of the precursor sample. The thermal effect, exothermic or endothermic preceding physical and chemical changes were studied using DSC patterns.

3.3 PHYSICAL AND SPECTROSCOPIC STUDIES

Different physical and spectroscopic studies like electrical resistivity, magnetic susceptibility, saturation magnetization, electron spin resonance, diffuse reflectance spectroscopy and scanning electron microscopy were performed on the prepared samples using suitable techniques.

3.3.1 Electrical resistivity measurements

Electrical resistivity measurements of all the samples were carried out to study the conductivity behaviour of the samples and to establish the possible relationship with the catalytic activity.

The dc electrical resistivities of the samples were measured in air using a two probe method during cooling cycles in the temperature range 400-30°C. Pellets of the powdered samples with 10 mm diameter and 2 to 3 mm thickness under a pressure of 5000 kg/cm² were made. The pellets were heated at 800°C for 18-20 h. These were silver pasted on either side. The pellets were fitted between the polished electrodes of a two-probe conductivity cell suspended within a furnace. The constant voltage of 3 V was supplied to the cell and the varying current at different temperatures was noted on KEITHLEY make multimeter. Electrical resistivities at different temperatures were calculated during the cooling cycle.
3.3.2 Magnetic susceptibility measurements

The magnetic susceptibility $\chi_g$ measurements of the samples in air at room temperature were done using Gouy method. During the measurements, magnetic field of the order of 8000 gauss was used. Mercury tetra(thiocyanato)cobaltate $\{\text{Hg}[\text{Co (SCN)}_4]\}$ as a standard material with the known magnetic susceptibility $\chi_g$ ($16.44 \times 10^{-6}$) and sensitive analytical balance of DONA make were employed. The sample tube was washed, dried and hanged between the electromagnets of the Gouy balance. The weight of the tube was recorded before and after applying the magnetic field. The sample tube was filled with the standard material up to a certain mark and was weighed on Gouy balance before and after applying the field. The procedure was repeated with the sample whose $\chi_g$ was to be determined. The magnetic susceptibility of the sample was found out by using the following calculations:

In the first part, tube constant or $\beta$ - constant was calculated with the known $\chi_g$ value of the standard material, using the relation,

$$\beta - \text{Constant} = \chi_g \cdot \frac{W}{\Delta W} \quad (\chi_g = 16.44 \times 10^{-6}).$$

$W = (W_3-W_1)$ = Weight of the standard material taken and $\Delta W = \Delta W' \pm \Delta W''$

$\Delta W' = (W_4-W_3)$ and $\Delta W'' = (W_1-W_2)$

$W_1$ = weight of empty tube,

$W_2$ = weight of the empty tube with field,

$W_3$ = weight of the tube with standard substance and

$W_4$ = weight of the tube and standard substance with field.
In the second part, substituting $\beta$ - constant value in the above relation, \( \chi_g \) of the sample under study was calculated. Molar susceptibility\( (\chi_m) \) of the samples were calculated using the relation:

\[
\chi_m = \chi_g . \text{Molecular weight of the sample}
\]

The magnetic moment \( (\mu_{\text{eff}}) \) of the samples was found out using the formula:

\[
\mu_{\text{eff}} = 2.84 \sqrt[4]{\chi_m . T} \text{B.M., where } T = \text{absolute temperature. With these values, the}
\]

number of unpaired electrons in the samples were calculated.

### 3.3.3 Saturation magnetization study

Saturation magnetization study was done on selected magnetic samples, using high field hysteresis loop tracer described by Likhite et. al. The three major components of the loop tracer are electromagnet, pick-up coil and balancing with integrating circuits.

The electromagnet works 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. A special balancing coil is used to measure the saturation magnetization of the sample in the air gap. Pick-up coil produces a field proportional to the magnetic induction in the sample. The 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 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 53.34 emu/g. The saturation magnetization values, as in emu/g of the magnetic samples were found out.

3.3.4 Electron spin resonance (ESR) study

Electron spin resonance occurs when a spinning electron in an externally applied magnetic field absorbs sufficient electromagnetic radiation to cause the inversion of spin state of the electron. This phenomenon is exhibited by a paramagnetic species and is also referred as electron paramagnetic resonance and as electron magnetic resonance.

ESR study of the samples was carried out at room temperature at X-band using a Varian E-112 X-band spectrometer to get an insight of the catalytically active and paramagnetic species. During the measurements, the magnetic field of the strength 3000 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 ‘ν’ was 9.2 GC (Giga cycles or $10^9$ cycles per sec). This frequency lies in the microwave region of the electromagnetic radiation spectrum. The sample was mounted in a quartz tube and TCNE was used as a field calibrant, taking its g-value as 2.00277. Spectroscopic splitting factor (g) or gyromagnetic ratio was obtained from the following relation:

$$\mu = g \beta s$$

where ‘μ’ is the magnetic moment, ‘β’ is the Bohr magneton (ergs/gauss) and ‘s’ is the spin of electron $+1/2$ or $-1/2$. 
3.3.5 Scanning Electron Microscopy

Scanning Electron Micrographs of powdered materials of some samples were taken on microscope (JEOL make, model JSM 5800 LV). Interpretation of the surface morphology and the calculation of the average particle size of the compounds were done with the help of the micrographs.

3.3.6 Diffuse Reflectance Spectroscopy (DRS)

Diffuse reflectance spectra of the samples were recorded in the wavelength range 300 to 700 nm, using UV-visible spectrometer (SHIMADZU model no. 2450). Powdered reference sample of BaSO4 and the sample under consideration were fitted into the sample holders which were mounted on a stand in sample chamber and the spectra were recorded. The spectra were used to calculate the band gap energy possessed by the samples. On the basis of the band gap energy, the conducting behaviour and the catalytic activity of the samples were visualized.

3.4 CATALYTIC STUDIES

Perovskites and the supported metal oxides were tested for a model CO oxidation reaction with oxygen using AMIL-NUCON series gas chromatograph (GC) on line for the analysis of the reactants and the products. Experimental set up for online analysis is shown in fig. 3.3. Hydrogen was used as a carrier gas with a constant flow rate of 30 ml/min. Porapak Q as a reference column and molecular sieve 13x as a column for CO oxidation analysis of the reactants and the products were used. Injector and detector were operated at a temperature of 60°C and oven at
50°C. Throughout the reaction studies, constant current flow of 150 mA was supplied to the thermal conductivity detector (TCD). GC used is equipped with eight port valve to inject the gaseous samples for the online analysis. The analyzed data were recorded on Omniscribe recorder at an appropriate chart speed to obtain qualitative and quantitative information of the reaction under study.

CO gas used for the catalytic reaction was prepared in the laboratory by dropwise addition of formic acid (A.R. grade) to the warm sulphuric acid in a specially designed glass reactor. The evolved gas was bubbled through 20% NaOH solution, also through molecular sieve and finally dried over calcium chloride. Prepared CO gas was found to be highly pure as confirmed by GC. Pure oxygen, nitrogen and hydrogen gases were used from commercial cylinders.

Reaction studies were carried out in a continuous flow fixed bed glass reactor in which around 1 g of powdered catalyst was supported in between glass wool plugs and glass beads on either side. The catalyst activity was determined using gas feed composition of 5% CO, 5% O₂ and 90% N₂. The individual gas flow rates were controlled using flow meters and precision needle valves. CO oxidation was checked at various catalyst temperatures point by point measurement from room temperature to 400°C. The total flow rate used was 5000 ml/h. By using a three way valve the provision was made to pass the reactants to GC, without passing through the catalyst. At regular intervals the products were injected into the GC which were analyzed by molecular sieve 13x and detected by the TCD.
Fig. 3.3. Schematic diagram of the experimental reaction set up.
The analysis of the reaction products at different temperatures was used to evaluate the temperature dependent CO oxidation efficiency of the catalysts and kinetics of CO oxidation over the catalysts. The reactions were also used to study CO oxidation cycles over the catalysts and to study the life of these catalysts.