CHAPTER 1

INTRODUCTION
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For the last several decades, the field of transition metal oxides (TMO) and mixed metal oxides has served as a source of interesting and challenging research problems to technologists, chemists and material scientists. Transition metal oxides constitute the most fascinating class of materials, exhibiting a variety of structures and properties. TMO have become an area of active research for catalytic studies and efforts are being made to replace the conventional noble metal catalysts by oxide catalysts which are equally efficient, thermally stable and economical.

Most of the environmental pollution is caused due to the combustion of fossil fuels giving out toxic gases causing serious global problems. Automobiles, factories and industrial exhausts contain harmful gases such as carbon monoxide (CO), low weight hydrocarbons, nitrogen oxides (NOx) etc. It is essential to catalyze their conversions into non toxic products. CO oxidation study has a long history. This reaction is essential in terms of practical importance and as a model reaction. It is associated with the reduction of atmospheric pollution.

There is a growing demand for pollution control catalysts which should be viable, more effective, stable and economical. Complex oxides containing two or
more cations have attracted the attention in recent times because of their growing demands in variety of technological and scientific fields. These are used in many heterogeneous oxidation catalysis reactions and found to be active in oxidation-reduction reactions without poisoning. There is an appearance of new phase of ternary oxides identified as perovskites and spinels above certain critical concentrations of the active metal ions. The study of catalytic activity of these perovskites and spinel phases showed that they are better catalysts in regards of their activity and stability as compared with individual oxides.

The perovskite type mixed oxides (ABO₃) occupy a prominent place under all the known ternary systems. These materials have well defined bulk structures, and the compositions of cations at both A and B sites can be variously changed. Therefore these mixed oxides are suitable materials for the study of structure-property relationship.

An important feature of rare earth perovskites is the possibility of varying the dimensions of unit cell by changing the A-site or B-site ions by different metal ions, which make them to behave as chemical chameleons with a wide variety of solid state and catalytic properties. The rare earth and transition metal oxidic perovskites are found to be good catalysts for several oxidation reactions. Some perovskite compositions with rare earth and first row transition series metals show a high catalytic activity for total oxidation of CO. Moreover their activities are not significantly affected by poisons like Pb and S present in automotive exhaust gases, thus making these materials as promising anti contamination catalysts.
Following Wolkenstein's theory of catalysis\textsuperscript{19}, there is a growing awareness of the role of solid state properties in the catalytic phenomena. Since then many correlations of catalytic activity with defects in solids, electrical and magnetic properties have appeared in literature\textsuperscript{20-24}. The knowledge of the relation between the catalytic and solid state properties of catalysts is crucial for systematic design of efficient preparations.

Ternary oxides chosen in the present investigation are series of perovskite systems. The stable structure of the perovskites has attracted the attention in the study of structure and electronic factors in catalysis. The structures of these oxides are flexible and many metal ions with variable valency can be incorporated in them. Many perovskites find potential applications such as thermoelectric, ceramic, magnetic material, electrode for fuel cells, host for laser systems and gas sensor in addition to being good catalysts\textsuperscript{2, 25-29}. Therefore a great concern through research is devoted to these properties to understand and extrapolate the obtained data to design new materials to suit the specific purposes. The perovskite oxides have distinct structural features which play vital role in determining their magnetic, electrical as well as catalytic properties. The study of these systems is much useful in understanding the technological and fundamental aspects to provide a rational basis for catalyst selection.

A series of perovskite compounds containing first row transition metals and supported transition metal oxides discussed in this investigations are prepared by co-precipitation technique in order to achieve homogeneity and low temperature
formation with more surface areas, unlike ceramic method which require high
temperature for their formation leading to the loss of surface area. A series of
perovskites with rare earths is also prepared by combustion method for the
comparative account of properties and catalytic activity. In the present investigations
attempts are made to study the catalytic CO oxidation on these compositions with
respect to activity, selectivity, catalyst life, stability, kinetics and solid state
properties.

The present investigation includes:

1. Preparation of series of perovskites and supported metal oxides such as
   (i) $Zn_{1-x}Ni_xMnO_3$, (Where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$)
   (ii) (a) $SrMnO_3$ (b) $SmMnO_3$ (c) $NdMnO_3$ (d) $BaCeO_3$ and (e) $ZnSnO_3$,
   (iii) $Fe_2O_3/ZnO$ (Where $Fe_2O_3 = 0\%, 5\%, 10\%, 20\%$ and $100\%$) and
   (iv) $NiO/ZnO$ (Where $NiO = 0\%, 5\%, 10\%, 20\%$ and $100\%$).

2. Characterization of the compositions by different techniques such as X-ray
   powder diffraction (XRD), Vibrational spectroscopy (FTIR), Atomic
   absorption spectroscopy (AAS), B.E.T. Surface area measurement and
   Thermal analysis (TGA/DSC) were done.

3. Studies of solid state and spectroscopic properties such as Electrical
   resistivity, Magnetic susceptibility, Electron spin resonance (ESR), Scanning
   electron microscopy (SEM) and Diffuse reflectance spectroscopy (DRS)
   were recorded.
4. Study of temperature dependent CO conversion efficiency and kinetic parameters over the catalysts were undertaken.

5. Study of CO oxidation cycles and catalyst life of the prepared compositions.

6. Identification of the various factors such as valency of cations, oxygen non-stoichiometry, binding energy, tolerance factor, surface area, structure and solid state properties contributing to the observed catalytic activity of the different compounds were attempted.