CHAPTER 6
SUMMARY AND CONCLUSIONS
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The Thesis describes the preparation of doped manganese oxides and supported manganese oxides catalysts. These prepared catalysts were characterized by various instrumental techniques. The solid state studies were carried out on doped manganese dioxide catalysts. All these catalysts were tested for carbon monoxide oxidation reaction. Various parameters like effect of partial pressure oxygen, influence of moisture in the feed on the catalytic activity of the catalysts were studied. This chapter will present a brief summary of the work described in the previous chapters and the general conclusions arrived from these chapters.

Chapter 1 gives the brief introduction regarding the CO oxidation catalysts along with the organization of the thesis, aims and objectives.

Chapter 2 briefly describes the literature survey regarding the carbon monoxide, catalysis in general and nanotechnology in catalysis. It gives information on manganese oxides, their crystallographic structures and various method of preparation by different routes. The brief survey of CO oxidation reaction over manganese oxide based catalysts was also presented. In addition, the influence of moisture and excess oxygen in the feed for the CO oxidation reaction over catalyst surface was also shown.

Chapter 3 describes the method of preparation of catalysts, the doped manganese oxides (MnO₂ and Mn₂O₃) were prepared by co-precipitation method and the supported catalysts were prepared by wet impregnation method. These prepared compounds were characterized by various instrumental technique such as XRD, Thermal analysis (TG/DTA), FTIR spectroscopy, SEM, TEM, BET surface area etc. The solid state studies
such as magnetic susceptibility and electrical resistivity were carried out on the doped manganese oxide compounds.

Chapter 4 describes the spectroscopic and solid state studies of all the prepared compounds. X-ray diffraction technique was used to investigate the structure as well as the phase of the synthesized catalyst. The XRD patterns authenticate the formation of MnO$_2$ and Mn$_2$O$_3$ phases, the data obtained from XRD agree well with the reported data (ICDD card and JCPDS card).

Thermal analysis (TG/DTA) was preformed for all the samples. MnO$_2$ decomposes at a temperature above 550 °C with loss of oxygen and there is a conversion of the MnO$_2$ phase to Mn$_2$O$_3$ with corresponding endothermic peak. Further, Mn$_2$O$_3$ converts to give Mn$_3$O$_4$ phase with the loss of oxygen at a temperature above 950 °C. This shows that MnO$_2$ is stable up to a temperature of around 550 °C. Mn$_2$O$_3$ shows the major weight loss above 950 °C with an endothermic peak, this weight loss is due to the loss of oxygen and conversion of the phase from Mn$_2$O$_3$ to Mn$_3$O$_4$.

FTIR spectra gives the characteristic Mn-O vibrations of Mn oxides. The MnO$_2$ shows characteristic broad peaks at ~525 and 630 cm$^{-1}$, which are attributed to the antisymmetric stretching mode of MnO$_6$ octahedra. These peaks are also prominent in doped MnO$_2$ catalysts indicating that the MnO$_2$ phase is stable even after doping. The Mn$_2$O$_3$ gave peak at ~ 665 cm$^{-1}$ which is attributed to Mn–O stretching vibration of Mn$_2$O$_3$ and at ~ 528 cm$^{-1}$ is due to Mn–O bending vibration of Mn$_2$O$_3$. Similar features are also shown by the doped Mn$_2$O$_3$ samples.

The DC Electrical resistivity ($\rho$) of different samples at various temperatures were measured in conductivity unit cell by two probe method in air and in temperature range from room temperature to 400 °C. Initially at lower temperature, all the samples show low
conductivity, but there is a raise in conductivity with increase in temperature. Thus all the samples show decrease in resistivity with increase in temperature indicating that these samples are semiconducting type. In some samples dopants also play a role in the conductivity, an increase in conductivity of MnO₂ is observed after doping.

Magnetic studies show that all these samples are paramagnetic in nature. Magnetic moment value of the doped MnO₂ catalysts is almost above 3 B.M. This confirmed that the Mn⁴⁺ ion in MnO₂ has three unpaired electrons, whereas the magnetic moment value of doped Mn₂O₃ shows values above 4 B.M. indicating that Mn is present in 3+ oxidation state having four unpaired electrons. The pristine MnO₂ and Mn₂O₃ showed higher values of magnetic susceptibility and magnetic moment as compared to the doped samples, with increasing concentration of dopants the magnetic susceptibility and magnetic moment values found to decrease due to the influence of dopants in the lattice structure of MnO₂ and Mn₂O₃.

The diffuse reflectance spectra (DRS) for all the samples were recorded in the range 400 to 800 nm wavelength and the % reflectance was measured against wavelength. The band gap was calculated for all the samples. The band gap calculated was found to be in the semiconducting range.

From the XPS data of pristine MnO₂ it is evident that manganese is present in 4+ oxidation state. The data also shows the presence of two types of oxygen species, one is lattice oxygen and other is the surface oxygen.

Chapter 5 describes the CO oxidation reaction over all the prepared catalysts. Doped MnO₂ samples showed good surface area than the undoped MnO₂. The Mn₂O₃ samples exhibits lower surface area as compared to MnO₂ samples, this may be due to higher calcination temperature. Pd supported MnO₂ and Rh supported MnO₂ catalysts showed
higher surface area among all supported samples. Catalytic activity also depends on the surface area, higher surface area corresponds to more surface available for adsorption of reactant molecules giving better activity.

The surface morphology and particle nature of the prepared catalysts were investigated by SEM. All these samples are nano-sized with spherical morphology, some samples also showed rod-like elongated morphologies. The doped MnO₂ samples showed smaller particle size as compared to doped Mn₂O₃ samples. The TEM images of doped MnO₂ samples show particle size in the range 20-40 nm, whereas those of doped Mn₂O₃ samples are in the range 50-80 nm.

NH₃-TPD (temperature programmed desorption) was performed to explore the adsorption sites over these catalysts. Basically, presence of acidic sites is needed on the surface of the catalysts for adsorption of CO molecules. NH₃-TPD was employed to monitor the acidity of the surface.

Catalytic oxidation of CO was performed on all the catalysts. The catalytic activity was determined using a feed gas composition of 5% CO and 5% O₂ in nitrogen. The mixture of gases was then allowed to pass over the catalyst at a rate of 5000 ml h⁻¹. The feed gases and the products were analyzed employing an online Gas Chromatograph with molecular sieve 13X and Porapak Q columns. H₂ was used as a carrier gas. The doped catalyst showed higher activity for CO oxidation and complete conversion was achieved at a much lower temperature as compared to undoped MnO₂ and Mn₂O₃ catalyst. Doped MnO₂ catalysts gave total CO oxidation at a much lower temperature as compared to doped Mn₂O₃ catalysts and showed conversion even at room temperature. Whereas the Ni and Ce doped MnO₂ showed poor activity, incorporation of Ni and Ce did not improve the catalytic activity of MnO₂ for CO oxidation reaction. Doping of Ni in MnO₂ may decrease
the adsorption capability of MnO₂ resulting in lower activity. Supported catalysts also showed good activity at lower temperature and activity was seen even at room temperature.

The stability of the catalyst for CO oxidation reaction was verified by performing time on stream experiments, by maintaining the catalyst at a constant temperature. No decline in activity for CO oxidation was accounted during this period signifying good stability of these catalysts. Influence of excess oxygen on activity of catalysts was carried out by increasing O₂ partial pressure in the feed gas compositions. Under the influence of excess oxygen catalysts are stable and show good activity. Further, time on stream analysis was performed to check the influence of moisture on activity of the catalyst for CO oxidation with low and high moisture contents. All the catalysts showed good activity in presence of moisture. In some cases increase in activity was observed in presence of moisture which indicates that moisture may participate in the catalytic CO oxidation process giving higher activity. Water may furthermore increase the acidic sites on the surface of the catalyst enhancing CO adsorption thus leading to higher activity. Also the effect of excess acidity and basicity was studied for CO oxidation by treating catalyst with dilute acid and base. From this study it may be concluded that both acidic as well as basic sites are important for CO and O₂ adsorption.

Conclusions

Finally it is concluded that, the co-precipitation method was employed to prepare the nano-sized doped MnO₂ and Mn₂O₃ catalysts. This method is a green process wherein no toxic by-products are evolved. Supported catalysts have been prepared by wet impregnation method. XRD substantiates the formation of MnO₂ and Mn₂O₃ phase. XRD also reveals that these catalysts are highly nano-sized particles. Thermal analysis gives the
significant evidence of phase change of MnO₂ to Mn₂O₃ above 550 °C and Mn₂O₃ to Mn₃O₄ phase above 950 °C. The FTIR spectra of manganese oxides showed some characteristic vibrations in 700-400 cm⁻¹. These vibrations are also seen in doped samples indicating that the phase is stable even after doping. DC electrical resistivity measurements for all doped samples reveal the semiconducting nature of these oxides. Magnetic susceptibility measurements showed that these samples are paramagnetic in nature. The pristine MnO₂ and Mn₂O₃ showed higher values of magnetic susceptibility and magnetic moment as compared to the doped samples. Band gap calculated from DRS was found to be in semiconducting range. The XPS data of pure MnO₂ shows that Mn is present in 4+ oxidation state. SEM/TEM images confirmed that these catalysts are nanosized, most of the samples showed spherical morphology and are agglomerated in appearance. The doped MnO₂ samples showed smaller particle size as compared to doped Mn₂O₃ samples. The supported catalysts show higher agglomeration as compared to doped samples. NH₃-TPD data indicates the presence of acidic sites on catalyst surface which are important for CO adsorption.

The doped MnO₂ catalysts showed better activity than pristine MnO₂ catalysts. In case of Pd, Ag and Rh doped MnO₂ catalysts complete conversion was obtained at a much lower temperature. These catalysts even showed room temperature conversion. Drastic decrease in the total conversion temperature was observed due to the synergistic effect. The doping of Ni and Ce in MnO₂ does not improve the catalytic activity of MnO₂. Doped Mn₂O₃ catalysts shows better activity than pristine Mn₂O₃, but as compared to doped MnO₂ catalysts they showed lower activity. Among all doped Mn₂O₃, Pd doped Mn₂O₃ showed interesting results, total CO conversion was seen at a much lower temperature as compared to undoped Mn₂O₃. Supported catalysts also showed good activity for CO oxidation reaction. Pd/MnO₂ showed activity even at room temperature and total CO
conversion was obtained at much lower temperature. Pd/Mn$_2$O$_3$ catalysts also showed good activity for CO conversion. The stability test for the catalysts at fixed temperature showed that activity remains constant with time for longer period, and some catalysts even showed increased in percentage conversion with time. No change in catalytic activity for CO conversion was observed under the influence of excess oxygen. Higher oxygen in feed gas does not affect the CO oxidation activity of the catalysts, however it showed good activity. From time on stream experiments for moisture study, it is clear that the catalysts are highly stable for CO oxidation for longer period in presence of moisture in feed gas. Some of the catalysts showed higher activity for CO conversion in presence of moisture, indicating that moisture facilitates CO oxidation reaction on the catalyst surface. Both acidic as well as basic sites are needed for CO and O$_2$ adsorption for better CO oxidation reaction.