Chapter VIII

Summary and Conclusion

The role of metal oxides in materials science is paramount and this is well established in the multitude of applications they find such as structural materials, refractories, adsorbents, insulators, and corrosion resistant materials. Both their electronic and geometric features contribute to many of their properties including metallic, semiconductor or insulator behaviour that are crucial to materials applications. Much focus has now been given on studies on mixed metal oxides since the properties of the metal oxides can be tuned and modulated by judicious mixing with suitable other metal oxides. In principle, the combination of two metals in an oxide matrix can produce materials with novel structural or electronic properties that can lead to superior materials with enhanced properties. Although the importance of this class of materials has been known for many years, it is only in the relatively recent past with the advancement of analytical techniques, studies related to their structure and structure property relationship have attained momentum.

One of the well-known metal oxides is that of Al which is widely used as adsorbents and active catalysts as well as catalyst supports for a number of technological applications. Its advantages are good mechanical properties, high melting point, large surface area and good acid-base properties. It is well established that even trace amount of a dopant including a different metal oxide can bring about substantial change in electronic and materials properties of the parent oxide. Though some the mixed metal oxides of alumina are known no systematic studies have been carried out on
doping the system with transition metal ions and studying the structural evolution of various phases and their surface properties on heat treatment. The present study is thus aimed at looking at this aspect in some detail. The dopants chosen were Cu$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Ce$^{4+}$ and Ti$^{4+}$. The selections of the dopants are based on the fact that the surface properties of oxides have been associated with surface defects such as surface vacancies. Surface vacancies are basic or acidic, depending on which ion is missing. Cation vacancies can be highly basic while anion vacancies are acidic. Doping the alumina matrix with a compound in which the metal ion has a valence other than the metal in the host oxide generally makes defects in solid oxides.

We exploited sol-gel technology as a route to process mixed metal oxides. Sol-gel synthesis of mixed metal oxides provides an approach to control structures at the nano-scale, thus enabling the formation of highly homogeneous new materials, generally having improved or entirely new properties. We have used boehmite, AlOOH, as the starting material for the preparation of the matrix since it remains an important precursor or intermediate for the synthesis of transition aluminas. Boehmite is easily dispersible in water around pH 3-3.5 and hence it can be used for sol-gel processing of alumina which is less expensive compared to the alkoxide method generally employed for the preparation of multi-component oxides.

The thesis “Structural evolution and surface characteristics of metal ion doped and sol-gel derived alumina from boehmite” is presented in VIII chapters. In Chapter I an overview of sol-gel processing, alumina and alumina mixed oxides and the scope and objectives of the present work are discussed. The reagents used and the methods employed for the preparation of various metal ion doped alumina mixed oxides are described in Chapter II.
The principles involved in the analytical methods used for the characterization of the different samples are also discussed in this chapter.

Chapter III describes our experimental results on the structural evolution and surface characteristics of Cu$^{2+}$ ion doped alumina generated at various calcination temperatures and the phase formation characteristics of CuAl$_2$O$_4$ spinel and its influence on the structural evolution of $\alpha$-Al$_2$O$_3$ from boehmite xerogels on calcination. This chapter also includes the study of the effect of the doped Cu$^{2+}$ ion on the surface acidity and surface area of the mixed oxides generated at various calcination temperatures. The results indicated that Cu$^{2+}$ ion doping in sol-gel boehmite could significantly decrease the temperature of phase transformation of $\alpha$-Al$_2$O$_3$ from transition aluminas by about 200°C by nucleation effect of \textit{in situ} generated CuAl$_2$O$_4$ spinel. It was observed that the sol-gel incorporation of Cu$^{2+}$ ions into the alumina matrix results in the increase of the surface acidity of the resulting mixed oxides. The highest surface acidity was observed for 4CuAl6 (see Table 3.1 for details on sample codes used), which shows a 28% increase in surface acidity than the corresponding undoped sample calcined at the same temperature. The surface areas of the Cu$^{2+}$ ion doped alumina mixed oxides generated in the temperature range 500-700°C are higher than the corresponding undoped samples. The increase in surface area is higher for 4CuAl6.

In Chapter IV the influence of the doped Mn$^{2+}$ ion on the structural evolution of alumina from boehmite and the \textit{in situ} formed MnAl$_2$O$_4$ spinel on phase formation temperature of $\alpha$-Al$_2$O$_3$ are discussed. This chapter also discusses the effect of Mn$^{2+}$ ion on the surface properties such as surface acidity and surface area of the mixed oxides formed. Even though there is substantial oxidation of doped Mn$^{2+}$ ion to Mn$^{3+}$, we find that all the calcined
samples are EPR active indicating the presence of Mn$^{2+}$ ion in these samples; even traces of Mn$^{2+}$ in the system, can form MnAl$_2$O$_4$ spinel at comparatively low temperature which nucleates and facilitates the very early formation of $\alpha$-Al$_2$O$_3$ (at 900°C) from the system. While the residual Mn$^{2+}$ ions present get converted to MnAl$_2$O$_4$ spinel at higher calcination temperatures, the oxidized Mn$^{3+}$ ion present in substantial quantity is seen to be existing in highly dispersed and impregnated form without forming any crystalline MnO$_x$ phase. The surface acidity data show that the sol-gel incorporation of Mn$^{2+}$ ions into alumina matrix produces an increase in surface acidity and as the level of doping increases the surface acidity also increases. The surface acidity of the sample containing 8 mol.% Mn$^{2+}$ ions and calcined at 500°C (8MnAl5) is about 55% higher than that of the undoped sample calcined at the same temperature. It was also observed that the incorporation of Mn$^{2+}$ ions into alumina matrix produces an increase in specific surface area at relatively lower calcination temperatures.

Chapter V discusses the phase formation characteristics of Al based spinels MAI$_2$O$_4$ (M= Co$^{2+}$ and Ni$^{2+}$) from Co$^{2+}$/Ni$^{2+}$ doped boehmite xerogels on calcination and also the effect of these in situ formed spinels on the surface characteristics of the mixed oxides. The CoAl$_2$O$_4$ spinel formation in cobalt doped alumina system is favoured when the cobalt content is low and the calcination temperature is high. However, high content of cobalt and low calcination temperatures favour the formation of Co$_3$O$_4$. In the case of Ni$^{2+}$ doped system, the formation NiAl$_2$O$_4$ spinel was observed in all the calcined samples with various amount of Ni$^{2+}$. For the Co$^{2+}$ doped system the surface area and surface acidity are higher for samples which contain dispersed CoO$_x$ than CoAl$_2$O$_4$ spinel. However, in the case of Ni$^{2+}$
doped system the surface area and surface acidities of all the samples are less than the corresponding undoped samples.

The various types of ceria entities present in the ceria-doped alumina mixed oxides generated at different calcination temperatures and the effect of these phases on the surface properties such as surface acidity and surface area of the mixed oxides are discussed in Chapter VI. The results indicate that the phase separation of crystalline CeO$_2$ is dependent on the ceria loading and the calcination temperature of the xerogels. The 1% samples at all calcination temperatures and the 2% samples up to a calcination temperature of 700ºC are solid solutions, which contain Ce$^{4+}$ in a highly dispersed state. The 2% samples at the calcination temperatures 800, 900 and 1000ºC and the 4 and 8% samples at all calcination temperatures contain crystalline CeO$_2$ phase and transition aluminas. At low calcination temperatures (400-600ºC), the alumina ceria mixed oxides containing 1 and 2 mol.% ceria show surface acidity values higher than that of the corresponding undoped samples while that containing 4 and 8 mol.% ceria show values lower than that of the undoped samples. However, at higher calcination temperatures (800, 900 and 1000ºC) all the mixed oxides containing various levels of ceria show higher surface acidity than the corresponding undoped samples. It is observed that the incorporation of Ce$^{4+}$ ions into alumina matrix did not produce any effect on the surface area at low calcination temperatures. However, at high calcination temperatures the samples that contain 2mol.% ceria produce maximum increase in surface area. Thus it should be noted that the sol-gel incorporation of 2 mol.% Ce$^{4+}$ ions into alumina matrix produces significant modification in surface properties such as specific surface area and surface acidity for the samples calcined at 800, 900 and 1000ºC. This is of great interest as a potential high temperature catalyst material since catalysts are often exposed to both
oxidation and reduction environments at high temperatures, resulting in loss of surface properties.

Chapter VII discusses the concentration and temperature dependent structural and surface characteristics of sol-gel derived titania doped alumina solid solutions. It was found that the single-phase composition was retained even at a calcination temperature of 1000°C for samples with up to 4 mol.% titania. However, in the case of sample with 8 mol.% titania, α-Al₂O₃ phase separation takes pace at the calcination temperature of 1000°C. The surface acidity is the highest for the sample with 8 mol.% titania calcined at 600°C. Thus this study has shown that single-phase alumina-titania mixed oxide with 8 % titania generated by sol-gel technique at the calcination temperature of 600°C has good specific surface area and pore size distributions and also has very high surface acidity than the corresponding undoped sample and so it has the potential for use as a more effective solid acid catalyst.

In summary, we have studied the concentration and temperature dependent structural evolution and surface characteristics of Cu²⁺, Mn²⁺, Co²⁺, Ni²⁺, Ce⁴⁺ and Ti⁴⁺ ion doped and sol-gel derived alumina from boehmite. It was earlier reported that in boehmite, formation of α-Al₂O₃ from θ-Al₂O₃ requires a reconstruction of the oxygen sub lattice from cubic to hexagonal, which occurs with a large energy difference around 1200°C. However, our studies show that the in situ formed MnAl₂O₄ and CuAl₂O₄ spinel around 900 and 1000°C respectively act as seeds, which provide low energy sites for nucleation and thus reduce the energy barrier required for nucleation of α-Al₂O₃. Facilitation for the conversion to α-Al₂O₃ by these spinels happen essentially due to their formation at a temperature relatively close to the normal α-Al₂O₃ phase formation temperature. In the case of Co²⁺/Ni²⁺ doped systems, even though CoAl₂O₄/ NiAl₂O₄ spinel get formed
in the system no such seeding effect or facilitation was observed for the formation \(\alpha-\text{Al}_2\text{O}_3\). This is presumably due to the very early (low temperature) formation of the spinel which is much lower to the normal initiation temperature (1200ºC) of \(\alpha-\text{Al}_2\text{O}_3\). Thus it is evident that the *in situ* formation of \(\text{MAI}_2\text{O}_4\) spinel alone is not responsible for the early formation of \(\alpha-\text{Al}_2\text{O}_3\) but the temperature of formation of the spinel is also decisive in the phase formation. Thus among the various doping ions studied, \(\text{Mn}^{2+}\) is seen to act as the best facilitator for the formation of \(\alpha-\text{Al}_2\text{O}_3\) followed by \(\text{Cu}^{2+}\). Both \(\text{Co}^{2+}\) and \(\text{Ni}^{2+}\) ions are passive as far as the phase formation is concerned. For copper and manganese doped systems the *in situ* spinel formation shows a direct relation with the amount of doped cations, while in cobalt doped system it shows an inverse relation with the amount of cobalt doped. However, nickel-doped system did not show any such relationship with the concentration of doped nickel. We have also calculated the particle size of the \(\alpha-\text{Al}_2\text{O}_3\) formed on calcination of the \(\text{Cu}^{2+}\) and \(\text{Mn}^{2+}\) ions doped samples at 1000ºC using Scherrer equation and it was observed that the particle size were in the range 23-24 nm for Cu system and 29-30nm for Mn system. This shows that the doped metal ion has influence on the particle size of the \(\alpha-\text{Al}_2\text{O}_3\) formed from metal ion doped boehmite on calcination.

The *in situ* formed Al based spinels \(\text{MAI}_2\text{O}_4\) (\(\text{M} = \text{Cu}^{2+}, \text{Mn}^{2+}\text{Co}^{2+}\) and \(\text{Ni}^{2+}\)) have interesting colours and are important as ceramic pigments because of the d-d transitions within the \(\text{M}^{2+}\) ion. Thus the present study is an innovative approach for the synthesis of nano-sized, thermodynamically stable and structurally compact materials (\(\alpha-\text{Al}_2\text{O}_3\) and \(\text{MAI}_2\text{O}_4\) spinel) with interesting colours from commercial boehmite at relatively low temperatures.

In \(\text{Cu}^{2+}\) and \(\text{Mn}^{2+}\) ion doped alumina systems the doped metal ion form solid solution with the alumina matrix in samples generated at
relatively lower temperatures, which result in an increase in surface acidity and surface area at these temperatures. In cobalt-doped system at low doping levels the spinel formation was observed at 400°C and hence no cobalt is seen to exist in the dispersed state. However, at high doping levels and relatively low calcination temperatures the doped cobalt exists in the dispersed state (solid solution), which increases the surface acidity and surface area. Compared to this in Ni$^{2+}$ doped system for all doping levels studied the spinel formation takes place at around 400°C and resulting in a decrease in the surface acidity and surface area than the undoped sample.

In the case of sol-gel derived ceria doped alumina, the crystallization of CeO$_2$ phase depends on the concentration of Ce$^{4+}$ and calcination temperature of the xerogel. However, in titania doped alumina the doped alumina form solid solution with the alumina matrix at all concentrations and calcination temperatures studied. In the titania doped (8%) system, $\alpha$-Al$_2$O$_3$ phase formation gets initiated at 1000°C for (8TiAl10) sample, but in the ceria alumina system there was no evidence for the formation of $\alpha$-Al$_2$O$_3$ in any of the samples till 1000°C. In both systems the change in surface properties such as surface acidity and surface area were observed for samples, which contain maximum concentration of the dispersed cation. In ceria-doped system, the samples calcined at relatively high calcination temperatures show maximum change in surface properties and for samples calcined at lower temperatures the effect of ceria is seen to be not significant. However, in alumina-titania system the maximum change in surface properties was observed for samples calcined at lower temperatures. At higher calcination temperatures the surface properties such as surface area and surface acidity are less than that of the undoped sample indicating that the doped titania facilitate the sintering and coarsening of alumina matrix.
In conclusion, we have studied the structural evolution and surface characteristics of various transition metal ion doped alumina derived from boehmite through sol-gel route. The concentration and temperature dependent phase characteristics of various mixed oxides and their structure surface property correlations are explained. The formation characteristics of stoichiometric compounds between dopant and matrix component and its influence on the structural evolution and surface features of these mixed metal oxide systems are also explained. We could also identify some of the metal ion doped alumina systems that have enhanced surface properties brought about by the dopant by varying the extent of dopants and the calcination temperatures. These properties are of great relevance in catalysis and we expect that some of the systems that have been developed in our study can be used as very effective catalysts. Another noteworthy observation we have made is with regard to the surface property enhancement at high temperatures that can be achieved by selective doping. We have noticed that the thermal deterioration generally seen in alumina at high temperatures can be completely curbed and the surface properties can even be enhanced significantly by doping with a low percentage of Ce$^{4+}$ ions.