CHAPTER 7

SUMMARY AND CONCLUSIONS

SUMMARY

The contents of the thesis has been divided into six chapters.

Chapter 1 of the thesis deals with the general introduction of ZrO₂ and rare earth oxide systems. Their relevance in catalysis field has been reviewed.

Chapter 2 of the thesis aim at the review of the important surface properties of the oxides namely, electron donor/acceptor properties, acid-base properties and catalytic activity of oxides. The detailed review of each properties have been given with corresponding references at the end of the chapter. In addition to these, the consequences of ZrO₂ and rare earth oxides as catalysts have been also included in this chapter.

Chapter 3 deals with the experimental methods adopted for the thesis works. Experimental part contain the preparation of oxides and characterisation of the oxides by using different techniques. The oxides were prepared by hydroxide method at
constant pH. The experimental details used for the determination of electron donor, acid/base and catalytic properties of the oxides have also been discussed.

Chapter 4 deals with the results of surface electron donor properties of the mixed oxides of ZrO₂ with rare earth oxides. The electron donor properties were studied by the adsorption of different electron acceptors with various electron affinity values ranging from 1.26 to 2.84 eV. The adsorption of electron acceptors were confirmed by the esr studies and electronic spectral studies of the electron acceptor adsorbed on samples. The adsorption of electron acceptors on the surface of the oxides were correspond to the Langmuir adsorption isotherms and verified by the linear form of Langmuir plots. The mixed oxides were found to be possessed by electron donor sites of varying strength and showed variation with activation temperatures.

Chapter 5 deals with the quantitative determination of acid-base properties of metal oxides and mixed metal oxides by titration methods using Hammett indicators. Non aqueous titration method was employed. The colour of the adsorbed indicators can give the measure of acid-base strength of the sites on the surface of the solids. Titration methods provide differentiation of acid -base site of different strength, energy and amount. With this titration methods weak sites can be detected.
Chapter 6 deals with the catalytic activity of oxides for different organic reactions namely, reduction of cyclohexanone in 2-propanol, oxidation of cyclohexanol with benzophenone and esterification of acetic acid with butanol. The oxides were found to be effective for reduction and oxidation, but not for esterification reaction. The former reactions were favoured by the presence of basic sites, especially reduction of cyclohexanone. The three reactions were carried out in liquid phase. The reduction of cyclohexanone was followed by means of UV-visible spectrophotometer and oxidation and esterification reactions were analysed by gas chromatograph. The activity has been reported as the first order rate coefficient of reaction. The mechanisms of the reactions have been discussed. The activity of the oxides parallel with the acid - base properties.

CONCLUSIONS

Results and discussions of the thesis work can be concluded as:

1. The surface of the oxides are associated with electron donor sites of different strength. The electron donor property of oxides depend upon the activation temperature, electron affinity values of the electron acceptors, basicity of the solvent and composition of the oxides. The surface electron donor properties of the oxides depend upon the amount of ZrO₂ phase or rare earth oxide phase present on the surface at a particular activation temperature. The limit of electron transfer is between
1.77 eV and 2.40 eV. That is the surface can act as electron donor sites to the adsorbed electron acceptor molecules with electron affinity value of above 2.40 eV and not below 1.77 eV. The electron donor power of the oxides increases with basic strength of the surface. The electron donor sites of the mixed oxides have the same strength at all temperatures and the number of sites decreases. But the strength of rare earth oxides increases with increase in temperature.

2. Acidity/basicity of oxides determined at different strengths gives an idea of significant distribution of acid-base sites on the surface. No acid-base sites of equal strength has been reported. The maximum number of basic sites is found at $H_0$ value of 3.3. Pretreatment temperature is a factor of importance for the generation of acidic sites. As the temperature is increased, the basicity decreases due to the generation of acidic sites. No acid sites were reported at $H_0$ value of 3.3. $H_{0,max}$ values parallel with the electron donor strength of the oxides, i.e. the order of basic strength parallels with the order of electron donor strength.

3. The mixed oxides obtained by the incorporation of rare earth oxides into zirconia gave good results for the activity towards different reactions. Activity of the oxides for oxidation of cyclohexanol is found high compared to the reduction of cyclohexanone. Both reactions are preferentially favoured by basic sites. Reduction of cyclohexanone is a fully base catalysed reaction while the presence of acid sites are enhancing the activity of oxidation reaction. Oxidation of cyclohexanol can be
considered as a bifunctionally catalysed reaction of strong basic sites and weak acidic sites. Low activity of oxides for esterification of acetic acid with butanol which is a perfectly Bronsted acid catalysed reaction, infers the lack of strong donor sites. The potentiality of the oxides for the base catalysed reactions (reduction and oxidation) indicates that most of the surface sites of the oxides are basic in character.

Thus incorporation of rare earth oxides into zirconia increased the basic character which is reflected in the catalytic activity of oxides.