7.1 SUMMARY

The prime intention of the present project was a systematic investigation of the physico-chemical properties and catalytic activity of some transition metal promoted sulphated zirconia systems. The characterisation and catalytic activity results were compared with that of pure ZrO₂ and simple sulphated zirconia systems. Sulphated zirconia samples were prepared by a controlled impregnation technique. In the case of metal incorporated systems, a single step impregnation was carried out using required amounts of sulphuric acid and metal salt solutions. As a preliminary step, optimisation of calcination temperature and sulphate content was achieved. For further studies, the optimised sulphate loading of 10 ml per gram of hydrous zirconium oxide and a calcination temperature of 700°C was employed. Metal incorporation had a positive influence on the physico-chemical properties. Vapour phase cumene conversion served as a test reaction for acidity. Some industrially important reactions like Friedel-Crafts reaction, phenol hydroxylation, nitration, etc. were selected to test the catalytic activity of the prepared systems.

The chapter-wise organisation of the thesis is as follows.

Chapter 1 covers a brief literature review on different sulphated zirconia systems. The effect of sulphate doping on the physico-chemical characteristics and catalytic properties is included in this chapter. The mechanism of acidity generation and nature of acidity in sulphated zirconia systems is discussed in detail. The effect of incorporation of a second metallic species is also reviewed.

Chapter 2 is devoted to a complete description of the materials used in the present work and the experimental techniques employed for the catalyst characterisation. The
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preparation methods adopted are described in detail. The experimental details for the evaluation of catalytic activity are also incorporated in this chapter.

Chapter 3 discusses the physico-chemical characteristics of the catalyst systems. The catalyst systems were characterised by surface area and pore volume measurements, XRD analysis, thermal studies and IR spectroscopy. The elemental composition was revealed by EDX analysis. Selected samples were also analysed by Laser Raman Spectroscopy and Scanning Electron Microscopy. Surface acidic properties were examined by three independent techniques namely ammonia TPD, perylene adsorption and thermodesorption studies using pyridine and 2,6-dimethylpyridine as probe molecules. Cumene conversion reaction served as a test reaction for acidity.

Chapter 4 focuses on the application of the catalytic systems for Friedel-Crafts reactions. Benzoylation of aromatics was achieved using benzoic chloride. Benzyl chloride and benzyl alcohol were employed as reagents for Friedel-Crafts benzylation. Methylation of aniline was accomplished in vapour phase using methanol as alkylation agent. The influence of different reaction parameters on the catalytic activity and selectivity was subjected to investigation. The reusability of the catalytic systems was also checked. Attempt has been made to correlate the catalytic activity with the surface acidic properties of the catalyst systems and plausible mechanisms have been drawn out in each case based on the experimental observations.

Chapter 5 illuminates the application of sulphated zirconia systems as efficient catalysts for the hydroxylation of phenol. Here also, the variation in the catalytic activity and product selectivity with experimental parameters has been taken care of. A possible mechanism has been suggested after a critical analysis of the catalytic performance.

Chapter 6 discusses the nitration reaction of toluene over sulphated zirconia systems under different reaction conditions.

Chapter 7 presents the summary and important conclusions of the present work.
7.2 CONCLUSIONS

The following are the conclusions elucidated from the present study.

- Sulphate loading modifies the physico-chemical properties of pure zirconia. The major outcome includes enhancement of surface area and stabilisation of the catalytically active tetragonal phase. Traces of monoclinic phase appear at high sulphate loading indicating the diminution of the special stabilisation of the tetragonal phase.

- Sulphate doping considerably improves the surface acidic properties, the nature of the surface acidity being a function of the calcination temperature, sulphate loading, etc.

- Incorporation of transition metal promoters enhances the sulphate retention capacity, thermal stability and the surface acidic properties. Among the different metal promoted systems, total acidity remains comparable whereas the acid strength distribution varies considerably.

- An increase in iron loading for a given sulphate loading results in a reduction in surface area, gradual disappearance of the monoclinic phase, enhancement of Lewis acidity and generation of strong acid sites at the expense of weak acid sites.

- Vapour phase cumene conversion reaction works out as a test reaction for acidity. Good correlation was obtained between cumene conversion and the amount of strong acidic sites. Cracking and dehydrogenation product selectivity could be correlated with the Brönsted acidity and Lewis acidity of the systems respectively.

- Transition metal incorporated sulphated zirconia systems exhibited improved catalytic activity for the benzylation of aromatics when compared with pure ZrO₂ and simple sulphated zirconia systems. Iron incorporation was found to be most effective for the reaction. An increase in iron loading enhanced the catalytic activity. In all the cases, para isomer was formed preferentially with around 80-84% selectivity. The reaction seemed to be driven by the Lewis acidic sites.
which was further confirmed by the positive influence of the calcination temperature of the catalyst and the negative influence of moisture on the reaction. The catalyst systems were found to be sufficiently stable for repeated operations.

- Pure and metal promoted sulphated zirconia systems were found to be efficient for the benzylation of benzene, the most efficient being the iron promoted systems. An increased iron loading seems beneficial for the reaction at the expense of selectivity towards monoalkylated product. Investigations on temperature influence showed that high reaction temperature favours dialkylation. Negative influence of moisture and the positive influence of calcination temperature of the catalyst suggest the involvement of the Lewis acid sites in the reaction. Exceptionally high activity in the case of iron and copper promoted samples leads us to propose the operation of a free radical mechanism side-by-side with the involvement of Lewis acid sites.

- Benzyl alcohol seemed a less efficient reagent for benzylation when compared with benzyl chloride. Benzyl ether was a major side product in this case. The catalytic activity seems to be a function of the Brönsted acidity of the systems. The low conversions observed may be a result of the low Brönsted acidity of the sulphated zirconia systems.

- Vapour phase methylation of aniline over sulphated zirconia systems gave predominantly N-alkylated products. Parameters like reaction temperature, molar ratio, feed rate, etc. profoundly influenced the catalytic activity and product selectivity. The strong acidity of the sulphated zirconia systems promotes secondary alkylation resulting in the formation of N,N-dimethyl aniline in high proportions. A balanced action of Brönsted as well as Lewis acid sites seems to be essential for the efficient advancement of the reaction.

- Transition metal promoted sulphated zirconia systems proved to be efficient catalysts for the disposal of phenolic wastes. The reaction was found to be sensitive towards the reaction conditions like reaction temperature, duration of
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run, H\textsubscript{2}O\textsubscript{2} to phenol ratio and catalyst composition. The experimental observations prompt us to suggest a free-radical mechanism for the reaction.

Nitration of toluene proceeded efficiently over metal incorporated sulphated zirconia systems. Brønsted acid sites, especially the medium and strong ones, decided the catalytic activity. The product selectivity seemed to be governed mainly by the statistical factors. The product selectivity remained the same for different catalytic systems while a slight alteration was observed with variation in the reaction conditions.