Chapter 6
Summary and conclusions

6.1 Summary of the work

Spinels attracted the attention of physicists and chemists due to their interesting structural, electrical and magnetic properties. These properties depend on the nature of ions, their charge and their distribution among tetrahedral and octahedral sites. Spinels are found to be very efficient catalysts for a number of industrially important reactions. Individual metal oxides lose their catalytic activity rapidly due to ageing and coke formation whereas spinel lattice imparts extra stability to the catalysts under various reaction conditions so that these systems have sustained activity for longer periods. Spinels used for studying many industrially important reactions were prepared by co-precipitation method. The spinels used for the present study viz. chromium and gadolinium incorporated nickel ferrites, nickel cobaltites and copper cobalities were prepared by co-precipitation method using NaOH as the precipitant. Ferrites were prepared by low temperature method whereas cobaltites were prepared by high temperature method. The prepared spinels were characterized by various physico-chemical methods. The catalytic activities of these spinels were investigated for liquid phase oxidation of hydrocarbons such as cyclohexane, styrene and benzyl alcohol, and vapour phase alkylation of aromatics such as phenol, m-cresol and aniline.

Chapter 1 contains introduction and literature survey on catalysis. A brief description about the spinel structure, preparation of spinels and catalysis by spinels is presented. A detailed description regarding the acid-base properties is also included in this chapter.

Cochin University of Science and Technology
252
Summary and conclusions

Chapter 2 presents a description about the various experimental techniques—both physical and chemical—employed for characterization and principles behind them.

Chapter 3 contains the characterization results of the prepared systems. The spinel phase formation was identified by analyzing the XRD pattern. Crystallite sizes were calculated from the XRD data and all the systems were found to exist in the nanometer range. Crystallite size was found to be varying with substitution and variation in concentration of ions. Existence of spinel phase was again confirmed from DRIFT spectra, which will usually give bands characteristics of spinel phase. Bands at around 500 cm\(^{-1}\) and 700 cm\(^{-1}\) confirmed the formation of spinel phase. The stoichiometries of the prepared systems were checked by EDAX analysis and the observed results were in good agreement with theoretical values. Surface area of the prepared systems was found to be varying considerably with substitution and variation in concentration of ions. Morphology of the systems was studied by SEM analysis. Replacement of iron by chromium and gadolinium has different effects on the morphology of nickel ferrite. SEM analysis also revealed that copper cobaltite particles are larger in size than nickel cobaltite. Mössbauer spectra were taken for iron containing systems. Systems having chromium lost the magnetic hyperfine splitting where as for gadolinium containing systems, only one site is showing magnetic hyperfine splitting. Acid-base properties of the prepared systems were studied thoroughly. Total acidity was determined by NH\(_3\)-TPD studies. Perylene adsorption studies were employed to find out Lewis acidity. IR studies of pyridine adsorbed samples gave a qualitative idea about acidity. For all the prepared systems, contribution towards total acidity
Chapter 6

comes mainly from Lewis type sites. Adsorption studies using electron acceptors such as TCNQ, chloranil and \( p \)-dinitrobenzene has been used to study electron donating property of the systems. Acid-base properties are varying considerably with substitution and variation in concentration of ions. Two test reactions- cumene cracking and cyclohexanol decomposition- were employed to obtain a qualitative idea about acid-base properties. Ratio of products obtained from cumene cracking reaction gave a qualitative idea about Lewis and Brönsted acid sites. Results obtained from cumene cracking reaction supports pyridine IR results. Results of cyclohexanol decomposition reaction correlates well with the results obtained from \( \text{NH}_3 \)-TPD studies. Since dehydration is an acid catalyzed reaction, the dehydration activities of the systems leading to cyclohexene has been taken as measure of their acid strength.

Chapter 4 contains the results of activity studies towards various alkylation reactions. Effect of change in catalyst composition on activity has been discussed after optimizing the reaction parameters. The parameters were optimized such as to obtain better conversion and product selectivity. Reaction parameters such as flow rate, reactant molar ratio, temperature etc. were optimized. The prepared systems were found to be highly active towards the alkylation reactions. The variation in acid-base properties of the systems with change in composition is found to be influencing their catalytic activity.

Phenol methylation mainly gave two industrially important chemicals- \( o \)-cresol and 2,6-xylenol. In the NiCr ferrite series, the system having the composition NiCr\(_{1.2}\)Fe\(_{8}\)O\(_9\) (which is having maximum acidity in that series) gave a phenol conversion of 94 % and 2,6-xylenol selectivity of 86.3 %. For

Cochin University of Science and Technology
254
Summary and conclusions

all the systems, acidity is the determining factor for the catalytic activity. Nickel gadolinite gave a phenol conversion of 93.5 %. NiGd ferrite series gave o-cresol as the main product, with 100 % selectivity for NiGd$_{1.8}$Fe$_{4}$O$_{4}$ and NiGd$_{2}$O$_{4}$. In the case of cobaltites, copper cobaltites are more active and are giving better selectivity for 2,6-xylenol.

For phenol tert butylation, NCrF3 and NG are giving maximum phenol conversion. In the ferrite series, up to NCrF2 and NGF3, 2- tert butyl phenol is the preferred product and only after that the selectivity for 4- tert butyl phenol increases. All the cobaltite spinels gave 4- tert butyl phenol as the preferred product. Copper cobaltite having more copper content gave more selectivity for 4-tert butyl phenol. 2-tert butyl phenol is the preferred product at shorter contact time. The selectivity for 2,4-ditertiary butyl phenol decreases as temperature increases and this may be due to the dealkylation reaction. Copper cobaltite gave the highest selectivity for 4-tert butyl phenol (~ 70 %).

For thymol synthesis, gadolinium containing ferrites are more active than chromium containing ferrites. Both m-cresol conversion and thymol selectivity are better for gadolinium containing systems. NiGd$_{2}$O$_{4}$ gave a maximum m-cresol conversion of 88 % with a thymol selectivity of 92 %. All the cobaltite systems gave a thymol selectivity of greater than 80 %.

Ferrites are found to be highly active for the methylation of aniline as compared to cobaltite series. Of these, chromium containing ferrites showed better activity than gadolinium containing series with NiFe$_{2}$O$_{4}$ showing maximum aniline conversion. N-methyl aniline is the major product formed. Considerable amount of the C-methylated product, p-toluidine is formed only in the case of cobaltites. Catalysts having high acidity are found to be forming
Chapter 6

benzene and toluene. In the cobaltite series, nickel cobaltites show greater activity than copper cobaltites. Variation in activity of the systems was found to be controlled by the basicity of the systems.

Catalyst stability was studied by running the reactions continuously for long periods. The systems maintained their activity for long periods showing their excellent catalytic stability.

Chapter 5 presents the results of activity studies towards oxidation reactions. Hydrogen peroxide was used as oxidant for all the reactions. The oxidation reactions under study were styrene oxidation, benzyl alcohol oxidation and cyclohexane oxidation. The prepared spinels oxidized styrene and benzyl alcohol to benzaldehyde, where as in the case of benzyl alcohol, little benzoic acid is also formed. The catalysts showed good activity towards cyclohexane oxidation. Cyclohexane oxidation mainly yielded three products-cyclohexene, cyclohexanone and cyclohexanol with greater selectivity towards cyclohexanol. Both ferrites and cobaltites showed almost same selectivity towards cyclohexanol but cobaltites are more active in terms of cyclohexane conversion, which gave a maximum conversion of 73.4%.

Among the spinels studied for styrene oxidation reaction, cobaltites were found to be more active than ferrites, of which, NC1.5 was found to be more active. Benzaldehyde was the only product obtained in all the cases under optimized conditions. Of the various solvents used for the reaction, aprotic solvents such as acetonitrile and acetone exclusively yielded benzaldehyde where as with solvents such as IPA and methanol, the selectivity for benzaldehyde decreased.
Summary and conclusions

Unlike in the case of styrene oxidation reaction, benzyl alcohol oxidation yielded little benzoic acid. All the catalysts showed high activity for this reaction. Except in the case of copper cobaltites, all the other systems gave a benzaldehyde selectivity of greater than 90% whereas copper cobaltite systems gave exclusively benzaldehyde. Here acetone was found to be good solvent than acetonitrile.

Catalyst reusability study was conducted by running the reactions using the same catalyst after separating from the reaction medium. The activity was found to be decreasing in the third cycle.

6.2 Conclusions

- The spinels were prepared by co-precipitation method using NaOH. Ferrites were prepared at low temperature whereas cobaltites were prepared by high temperature method.

- Electronic and surface properties of ferrites were modified by replacing Fe by Cr and Gd whereas for cobaltites the properties were modified by changing the stoichiometry of Ni, Co and Cu.

- Spinel phase formation was identified by XRD analysis. Existence of spinel phase was again confirmed by taking DRIFT spectra.

- Modification of spinels increased the acidic character. Incorporation of chromium up to 60% into nickel ferrite increased the acidity and then decreased whereas replacement of Fe by Gd resulted in gradual
increase of acidity. For cobaltites, increase in percentage of Ni and Cu was found to increasing the acidity.

- Total acidity was determined by NH$_3$-TPD studies. IR studies of pyridine adsorbed samples showed that the contribution towards total acidity comes mainly from Lewis sites. The strength of Lewis acid sites was determined by conducting adsorption studies using perylene. The variation in Lewis acidity follows the same trend as the total acidity.

- Basic properties were studied by adsorption studies using various electron acceptors. Modification of ferrite by Cr and Gd was found to decreasing the basic character. Increasing the concentration of Ni and Cu in cobaltites also decreased the basic character.

- Test reactions conducted for studying the acid-base properties were cumene cracking and cyclohexanol decomposition reactions. Good correlation has been obtained between the results obtained from these reactions and the results obtained from NH$_3$-TPD and perylene adsorption studies.

- The prepared catalysts were found to be highly active towards many alkylation and oxidation reactions, especially phenol methylation, thymol synthesis, oxidation reactions of styrene, cyclohexane etc.
Summary and conclusions

- For alkylation reactions, catalytic activity was found to be controlled by the variation in acid-base properties of the systems. For oxidation reactions, activity varies in accordance with the reducibility of the systems.

- Although all the prepared spinels are highly active towards phenol methylation, gadolinium containing ferrite series gave o-cresol as the major product and with 100 % o-cresol selectivity by NiGd$_{1.6}$Fe$_{4.0}$O$_4$ and NiGd$_2$O$_4$.

- The prepared catalysts can be conveniently used for the production of benvaldehyde, which is a fine industrial chemical, by the oxidation of styrene and benzyl alcohol. Also, under optimized conditions, all the systems were found to form exclusively benzaldehyde by the oxidation of styrene.

- Deactivation studies were conducted for vapour phase reactions by running the reactions for a long period. Some of the systems were found to maintain their activity during the time period studied showing their excellent catalytic stability.

- Recycling studies were conducted for liquid phase reactions. The catalysts were recycled up to three cycles. Some of the systems were found to be maintaining the selectivity even in the third cycle.
6.3 Further scope of the work

Chromium and gadolinium containing ferrites and different nickel and copper cobaltites were proved to be excellent catalysts for a number of alkylation and oxidation reactions which are industrially important. The prepared systems were found to be highly active towards alkylation of phenol and substituted phenol such as \( m \)-cresol. These observations show that the prepared systems can be conveniently tried as catalysts for alkylation of other substituted phenols such as \( o \) and \( p \)-cresols; the products of these reactions are important in fine chemical industries. Also it is observed that the studied systems were selectively forming N-methyl aniline by the methylation of aniline. The study can be further extended for the alkylation of substituted anilines. Also, the alkylation can be carried out using different alkylating agents. We can modify the properties such as cation distribution, acid-base properties etc. by changing the nature and concentration of ions in the spinel matrix. Since the variation in these properties is found to be very much affecting the catalytic property, we can improve the catalytic activity considerably by incorporating many divalent and trivalent ions. It was observed that the reducibility could be varied considerably by changing the composition of systems. Since reducibility is found to be affecting the oxidation behaviour, we can improve the activity towards oxidation reactions by improving the reducibility by the incorporation of other ions. The excellent catalytic activity towards oxidation reactions shows that the systems can be used for environmentally important reactions such as hydroxylation of phenol, removal of carbon monoxide by oxidation etc.