Summary And Conclusions

6.1 Summary of the work

Spinels of simple \((\text{AFe}_2\text{O}_4)\) type and mixed \((\text{A}_{1-x}\text{B}_x\text{Fe}_2\text{O}_4)\) type ferrites are known. These special group of inorganic compounds attracted the attention of physicists, technologists and chemists due to their peculiar cation distribution, thermal and mechanical stability and interesting electrical and magnetic properties. Also, they are found to be effective catalysts for various reactions due to the following reasons. (a) The ease with which iron can change its oxidation state between 2 and 3, (b) the reduction of \(\text{Fe}^{3+}\) to \(\text{Fe}^{2+}\) takes place without altering the lattice configurations so that upon reoxidation the original state can be regained and (c) individual metal oxides lose their catalytic activity rapidly owing to ageing and formation of the coke over the catalyst surface whereas the spinel lattice imparts extra stability to the catalysts under various reaction conditions so that these systems have sustained activity for longer periods. For studying the catalytic properties, the low temperature co-precipitation method is preferred over the usual ceramic method as the former method yields homogeneous, and fine ferrite particles. The present study, accordingly, employed low temperature co-precipitation method for the preparation of \(\text{Mn}_{(1-x)}\text{B}_x\text{Fe}_2\text{O}_4\) specimens, where B is a metal cation such as Cr, Co, Ni, Cu and Zn. The prepared ferrite samples were characterized by adopting various physico-chemical techniques. The catalytic activities of the systems were investigated for liquid-phase benzoylation of aromatic compounds and phenol hydroxylation and for vapour-phase reactions such as aniline alkylation, phenol methylation and ODH of ethylbenzene. The description of the work is presented in six chapters.

Chapter 1 presents an introduction to heterogeneous catalysis and a literature survey on catalysis by transition metal oxides and spinel ferrites. A detailed description on various methods of preparation of ferrites, spinel structure, electrical and acid-base properties of ferrites and catalytic effectiveness for various reactions are also given in this chapter.
Chapter 2 deals with various experimental procedures and principles of characterization methods employed for the present work.

Chapter 3 reports the results and discussion of the catalyst characterization procedure. The spinel phase formation at the calcination temperature of 500°C has been ascertained by the XRD data. The unit cell parameters of the pure manganese ferrite were found to be increasing by the incorporation of various metal cations. The crystallite size characterized from the XRD broadening is in the range 21-58 nm. The SEM analysis for MnFe₂O₄ at three different calcination temperatures is in concordance with the XRD data. The stoichiometries of the compositions checked by the ICP analysis were found to be in good agreement with the theoretical values. The spinel phase formation is further confirmed by the appearance of two strong infrared bands $\nu_1$ and $\nu_2$ around 700 cm⁻¹ and 500 cm⁻¹, respectively. The spinel ferrites prepared by low temperature co-precipitation method possess sufficiently large surface area. The transport studies revealed that the different series of manganese ferrites are semiconductors and possess holes as the major charge carriers except for MnFe₂O₄ where electrons are the major charge carriers. Activation energy or energy gap determination by the DC conductivity studies showed that incorporation of Cr, Ni and Zn cations increased the energy gap whereas the incorporation of the other metal cations decreased the same. The Mössbauer spectra revealed the presence of Fe²⁺ and Fe³⁺ ions in MnFe₂O₄. Also, the inherent magnetic behaviour of the sample is proved by the Mössbauer hyperfine splitting. NH₃-TPD studies revealed that the weak plus medium acidity is increased by the incorporation of Cr, Ni, Co and Cu ions whereas the strong acidity is increased by the progressive substitution of Zn ion. The thermodesorption studies of pyridine adsorbed samples well supported the NH₃-TPD results. The thermodesorption studies of 2,6-dimethylpyridine adsorbed samples showed that incorporation of metal cations decreased the Bronsted acidity of pure manganese ferrites. The electron donating property studies revealed that the limiting amount of the electron acceptors adsorbed on the catalyst surface is enhanced with metal ion incorporation in manganese ferrite and is more pronounced in Cr-substituted manganese ferrites. Cyclohexanol decomposition reactions were performed to evaluate the acidity of the
systems. 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 is divided into three sections. The first section gives the detailed discussion of the liquid-phase benzoylation of the aromatic compounds using benzoyl chloride as the benzoylating reagent over different manganese ferrite catalysts and also the effect of various reaction parameters on product distribution of toluene benzoylation. The decisive properties in the catalytic activity for activated and deactivated benzenes are observed to be different. It is evident that in the case of activated benzenes like toluene, xylenes and anisole, the aromatic ring is highly activated and therefore less acidity of the samples is sufficient to bring about such reactions and activation energy of the catalysts is seemed to be more involved than the acidity. But in the case of benzene and halobenzenes, the aromatic ring is not activated or deactivated respectively, the adsorption of the aromatic substrate over the catalyst surface is difficult and hence the acidity of the catalysts plays the decisive role. It was observed that various reaction parameters such as amount of catalyst, reaction temperature, catalyst composition, presence of moisture in the reaction mixture as well as in the catalyst and aromatic substrate /BOC molar ratio have crucial roles in determining the catalytic performance. The second section deals with a thorough investigation of alkylation of aniline using methanol over the prepared systems. The detailed discussion regarding the influence of factors such as reaction temperature, molar ratio, time-on-stream and contact time are also presented in this section. The weak plus medium acidity of the catalyst was involved in determining the catalytic activity towards aniline alkylation and Cr-substituted manganese ferrites are found as good options for this reaction. The alkylation of phenol using methanol over all the catalyst systems and effects of various reaction parameters are depicted in the third section. It is seen that manganese ferrospinels produce ortho-alkylated products (formation of o-cresol and 2,6-xylenol, but not meta- or para-cresols and xylenol isomers) and the total ortho-selectivity always exceeded 97%, whereas the individual selectivities depend greatly on reaction parameters. The manganese ferrites in which Zn progressively substitutes Mn are particularly selective and active for ortho methylation of phenol. Zn_{0.8}Mn_{0.2}Fe_{2}O_{4} is found to be the most active and selective catalyst for this reaction.
Chapter 5 is divided into two sections. The first section depicts the liquid-phase phenol hydroxylation using hydrogen peroxide as the oxidant over different manganese ferrospinels and the effects of various reaction parameters on the product distribution. The enhanced amount of holes or cation vacancies and their appreciable mobility in the systems are the decisive factors determining the improved catalytic activity in phenol hydroxylation of different series of manganese ferrites. A heterogeneous-homogeneous free-radical reaction mechanism is proposed for phenol hydroxylation over different manganese ferrites. The second section focuses on the vapour-phase oxidative dehydrogenation of ethylbenzene and effect of various reaction parameters for styrene conversion. The acidity in the medium-strong region was found to determine the catalytic activity of different manganese ferrite series in the oxidative dehydrogenation reaction.

6.2 Conclusions

- Manganese ferrospinels prepared by the low temperature co-precipitation technique provides homogeneous, fine and reproducible ferrite powders with high surface areas.

- All the peaks in the XRD pattern matched well with the characteristic reflections of the ferrites. Close resemblance of the ‘d’ values with the standard values indicated the formation of spinel phase at the calcination temperature of 500°C. The spinel phase formation is again confirmed by the appearance of two strong infrared bands below 1000 cm⁻¹.

- The successive incorporation of metal cations such as Cr, Co, Ni, Cu and Zn decreased the total acidity of MnFe₂O₄ as evident from the NH₃-TPD studies. The weak plus medium acidity is improved by the progressive addition of Cr, Co, Ni and Cu whereas the strong acidity is enhanced with Zn ion substitution.

- The thermodesorption data of pyridine adsorbed samples is in concordance with the NH₃-TPD results.

- The general observation that dehydration is favoured by acid sites and dehydrogenation is favoured by both acidic and basic sites is confirmed by the
cyclohexanol decomposition reaction carried over different series of manganese ferrites.

- Liquid-phase benzoylation of various aromatic compounds proceeded efficiently over different series of manganese ferrites. It is observed that for activated benzenes, activation energy of the systems play the decisive role in determining the conversion of BOC. But in the case of benzene and activated benzenes, increase in strong acidity of the systems has the key role in the conversion of BOC.

- Among the various systems studied, Cr0.8Mn0.2Fe2O4 exhibits excellent selectivity and high yield for N-methylaniline even at comparatively low temperatures and methanol to aniline molar ratios. Only a minimum acidity is required for the reaction and surplus acidity does not favour the reaction.

- The manganese ferrites in which Zn progressively substitutes Mn are particularly selective and active for ortho-methylation of phenol leading to o-cresol and 2,6-xylenol. Zn0.8Mn0.2Fe2O4 is found to be the most active and selective catalyst for this reaction. Under the optimized reaction conditions the ortho-selectivity (o-cresol and 2,6-xylenol) exceeded 97% whereas the individual selectivities depended on the reaction parameters.

- Optimization process for hydroxylation of phenol revealed that the reaction parameters such as amount of catalyst, reaction temperature, H2O2/phenol volume ratio, solvent and pH have critical influence on the reaction. CuFe2O4 is found to be most efficient for the hydroxylation of phenol since both giving maximum conversion of phenol and selectivity for diphenol.

- Catalytic studies of oxidative dehydrogenation of ethylbenzene pointed out that sufficient number of both acidic and basic sites is needed for the conversion of ethylbenzene and selective formation of styrene. Co0.8Mn0.2Fe2O4 is found to be most efficient for this reaction. Increase in temperature and decrease of flow rate enhance the conversion of ethylbenzene. However, increase of temperature above 500°C reduces styrene selectivity.
6.3 Further scope of the work

The different series of manganese ferrites are proved to be excellent catalysts for various industrially important reactions such as Friedel-Crafts benzoylation of aromatic compounds, methylation of aniline and phenol, hydroxylation of phenol and oxidative dehydrogenation of ethylbenzene. These catalysts were found to be active not only for benzoylation of activated benzenes but also for deactivated benzenes. Thus, the work can be extended to the development of environmentally friendly ferrite catalysts for the acylation/benzoylation of various aromatic compounds using different acylating agents. Interestingly, it is observed that Cr-Mn series of ferrites are very good catalysts for the active and selective formation of N-methylamine. Thus, this series of ferrites can be further modified for the alkylation of substituted aniline using various alkylating agents. Again, the different series of manganese ferrites yield ortho-alkylated products and total ortho-selectivity always exceeded 97% for phenol methylation. The activity and selectivity can be further improved by incorporating suitable metal cations into the pure manganese ferrite and can be used for the alkylation of substituted phenols. Various manganese ferrites, especially copper substituted ones, are found to be potential catalysts for the production of diphenols under mild reaction conditions and prolonged reaction resulted in the complete conversion of phenol to C-oxides and tar. Due to the tightening of the environmental regulations, production of diphenols from phenol hydroxylation and reduction of phenolic pollutants in waste waters using these catalysts can be a promising approach because it demands only simple techniques and produce little environmental pollution.