SUMMARY AND CONCLUSIONS

The theme of the present investigation is mainly centered around the synthesis, characterization and catalytic studies on zeolite encapsulated transition metal complexes and metal oxide catalysts. Characterization data of zeolite complexes point out the encapsulation of complexes and their composition, structure and thermal stability. The catalytic behaviour of these complexes with respect to oxidation activity, recycling ability and poison resistance has been investigated. Studies carried out on Cu-Cr/Al₂O₃ catalyst to recognize the role of the active metal atoms and investigate the effect of additives like CeO₂ or TiO₂ on CO oxidation activity and stability are also reported in this thesis.

Chapter I of the thesis reviews the role of some important proven catalysts. The recent trends in the development of catalyst-technology and the scope of using heterogenized catalysts, especially zeolite encapsulated complexes, for achieving the desired targets are described. This chapter provides a brief account of various methodologies used for the synthesis and characterization of zeolite complexes. The catalytic studies conducted on this system are described.

Chapter II gives a brief account of various reagents and materials used in the present study. The techniques employed for the synthesis, characterization and catalytic studies of zeolite complexes and metal oxide catalysts are described. These techniques include: chemical analysis, CHN analysis, atomic absorption spectrophotometer, XRD, SEM, BET surface area and pore volume, mercury porosimetry, magnetic moment by Gouy method, reflectance spectra, FTIR spectra, EPR, TG analysis, chemisorption studies using microcatalytic reactor and gas chromatograph.

Chapter III reports on studies on the synthesis and characterization of Y zeolite encapsulated Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of dimethylglyoxime. The zeolite NaY used for supporting the complexes was found to posses a unit cell.
formula of Na$_{56}$ [(AlO$_2$)$_{56}$ (SiO$_2$)$_{136}$ ] xH$_2$O. The unit cell formulae of metal exchanged zeolites were also derived from the analytical data. The Si/Al ratio of metal exchanged zeolites is the same as that of the parent zeolite indicating that the collapse of zeolite framework by dealumination during ion exchange could be prevented in the present study by using very dilute metal salt solutions. Surface area, pore volume, XRD and FTIR data of metal exchanged zeolites also reveal the retention of zeolite framework.

The empirical formulae of encapsulated dmg complexes were calculated from the analytical results. Minute traces of uncomplexed metal ions were found to remain in the lattice of zeolite complexes which are unlikely to interfere in the behaviour of encapsulated complexes. SE micrographs of encapsulated Co(II) complex before and after soxhlet extraction indicate that the surface complexes are completely removed. XRD patterns and Si/Al ratio indicate the retention of zeolite framework on encapsulation. The lower surface area and pore volume of zeolite complexes as compared to those of corresponding metal exchanged zeolites is attributed to the encapsulation of complexes in zeolite pores.

The geometries of Mn(II) and Fe(III) complexes could not be inferred from the magnetic moment and electronic spectral data. However, a tentative assignment of an octahedral, distorted square planar and tetrahedrally distorted square planar symmetry for encapsulated Co(II), Ni(II) and Cu(II) complexes respectively has been proposed. The EPR data also support the distorted square planar structure of Cu(II) complex and provide evidence for ionic environment around the metal ion. Furthermore, $g_{II}/A_{II}$ ratio hints at the degree of distortion of the complexes. The formation of the complexes in the zeolite pores was also confirmed from the IR data. The thermal degradation patterns have not provided confirmable results due to the interferences from the deaquation of the sample and the lack of appreciable weight losses for the decomposition of encapsulated complexes which are present only in low amounts in the zeolite. However, approximate stability could be ascertained in most of the cases. The encapsulation of the
complexes accounts for the difference in the TG patterns of metal exchanged zeolites and zeolite complexes.

**Chapter IV** deals with the encapsulation of transition metal complexes of 3-formyl salicylic acid. The complexes were characterized as described previously. The composition hints at a binuclear structure for the encapsulated complexes. Furthermore, magnetic moment and reflectance data are close to those reported for their simple binuclear complexes. Surface area, pore volume and XRD data are presented as an evidence for the encapsulation of complexes without the destruction of zeolite crystallinity. On the basis of magnetic moment, electronic and EPR spectral data, the encapsulated Co(II), Ni(II) and Cu(II) complexes are expected to possess tetrahedral, octahedral and tetrahedrally distorted square planar symmetry respectively. IR spectra confirm the formation of complexes in the cavities and explain the coordination in them. TG patterns also indicate the encapsulation of complexes.

**Chapter V** provides details regarding the encapsulation of complexes of the substituted salen like ligand, N, N'-ethylene(7-methylsalicylideneamine). The analytical, XRD, surface area and pore volume data are presented to explain the composition and encapsulation of these complexes. Magnetic moment and electronic spectral data could assign geometries only in the case of Ni(II) and Cu(II) complexes. The encapsulated Ni(II) complex exhibits an octahedral geometry whereas a tetrahedrally distorted square planar symmetry is observed for the Cu(II) complex. The higher $g_{II}/A_{II}$ ratio of Cu(II) complex indicate a high degree of distortion in this case, probably due to the steric effects of methyl groups of the ligand. IR spectral and TG data indicate the formation of complexes in zeolites.

**Chapter VI** deals with the encapsulation of complexes of another bulkier substituted salen like ligand, N,N'-ethylene(5,6-benzosalicylideneamine). Our attempts to synthesize encapsulated Co(II) complex was unsuccessful. Characterization data indicate the formation of monomeric complexes in Y zeolite. An octahedral and
tetrahedrally distorted square planar structure are assigned for the encapsulated Ni(II) and Cu(II) complexes respectively. IR and TG data also suggest the encapsulation of the complexes.

Chapter VII discusses the catalytic properties of zeolite encapsulated complexes. Zeolite complexes were found to be active for the decomposition of hydrogen peroxide and the oxidation of benzyl alcohol or ethylbenzene. These systems can also catalyse the aerobic oxidation of organic compounds. The ability for the partial oxidation of organic compounds is the main attraction of catalysis of zeolite complexes. Encapsulated Cu(II) complexes, especially that with 3-formylsalicylic acid were found to be more active than others. The recycling ability of zeolite complexes was tested in the case of the most promising catalyst, which showed only little deactivation on reusing. Poison resistance of bulkier encapsulated complexes is higher than that of others even though they posses only a lower activity. The substitution in salen ligand reduces activity but enhances poison resistance as compared to zeolite salen complex. The geometry of various zeolite complexes accounts for the variation in the catalytic activity. The expected steric effects in bulkier zeolite complexes reduce the mobility of molecules leading to reduced activity and increased poison resistance.

Chapter VIII describes the preparation of Cu or Cu-Cr catalysts on Al₂O₃, Al₂O₃-CeO₂ and Al₂O₃-TiO₂ supports. The catalytic activity of these catalysts for the oxidation of carbon monoxide was determined. Cu based catalysts are more active than Cu-Cr catalysts, probably because of the enhanced metal dispersion in them. However, the addition of Cr improves the stability of the catalyst by forming stable CuCr₂O₄ phases in the catalyst lattice. The additives, CeO₂ and TiO₂, also enhance the activity and stability of the catalyst to perform effectively in hostile thermal and hydrothermal conditions. However, CeO₂ is much superior to TiO₂ as a dopant with respect to the ability to enhance activity and stability. The promoting action of these dopants is explained in terms of the increased metal dispersion, the redox properties and the metal-dopant interactions which are most likely in modified catalysts.
The general conclusions drawn from our studies are:

1. Well defined encapsulation of transition metal complexes in Y zeolite is possible by carefully synthesizing the metal exchanged zeolite and zeolite complex at optimised conditions.

2. The use of zeolite encapsulated complexes as catalysts avoids the practical difficulties associated with homogeneous catalysis. The encapsulated complexes exhibit the ability to be recycled in reactions by retarding the deactivation processes.

3. Zeolite encapsulated complexes are suitable as catalysts for the partial oxidation organic compounds with hydrogen peroxide and molecular oxygen. Cu(II) complexes, especially binuclear complex of 3-formylsalicylic acid, are more active catalysts than the complexes of other metal ions.

4. The geometry of the encapsulated complexes plays a vital role in regulating the functioning of the catalyst by providing vacant reaction sites. Encapsulated complexes interact with the zeolite framework to slightly distort the geometry which might lead to a modified catalytic activity. Therefore, the activity and poison resistance can be optimised by varying the stereochemistry of the encapsulated complexes by using bulkier ligands.

5. The CO oxidation activity of Cu-Cr/Al₂O₃ catalysts is dependent on the dispersion of Cu sites indicating the structure sensitive nature of this reaction on metal oxide systems.

6. The dopants, CeO₂ or TiO₂, enhance the activity and stability of the catalyst. CeO₂ possess excellent features as an additive, which could be exploited in oxidation reactions.