Chapter 3

Summary and conclusions
In this thesis, a detailed study on developing various non-noble catalytic systems, their characterization and evaluation for the industrially important hydroxyalkylation and liquid phase oxidation reactions has been carried out. Section A deals with solid acid catalysts developed for hydroxyalkylation reactions of various phenolic compounds with an aldehyde or a ketone. A variety of solid acid catalysts developed in this work are: (i) phosphotungstic acid (PTA) impregnated on different supports like MCM-41 and montmorillonite for hydroxyalkylation of phenol with phthalic anhydride to give phenolphthalein, (ii) sulphonic acid graphated magnetically separable solid acid catalysts for hydroxyalkylation of guaiacol to give selectively vanillin alcohol and (iii) metal cations exchanged montmorillonite clay for p-Cresol hydroxyalkylation to give 2, 2’-methylenebis (4-methylphenol) [DAM]. Section B of the thesis includes the development of non-noble metal oxide catalysts for liquid phase oxidations of phenolic compounds some of which are considered to be the sub-structures of lignin. The products of these oxidations are valuable intermediates and/or end products used in flavoring or perfumery industries. The major outcome of the thesis was the understanding of structure-activity correlation through detailed catalyst characterization and activity evaluation studies. The main conclusions of this work are summarized below.

- Three different solid acid catalysts developed for hydroxyalkylation reactions were: PTA/MCM-41, SO$_3$H-Fe$_3$O$_4$@MCM-41 and metal cation exchanged montmorillonite catalyst was developed with both Brönsted and Lewis acid sites which mainly contributed to give highest selectivity of 91% to phenolphthalein. The same catalyst was also found to be highly efficient for the hydroxyalkylation reaction of p-cresol and formaldehyde to give DAM. In another attempt, water tolerant magnetically separable solid acid catalyst SO$_3$H-Fe$_3$O$_4$@MCM-41 was developed for guaiacol hydroxyalkylation to give vanillyl alcohol. The acidity of the catalyst was due to –SO$_3$H functionalization confirmed by FT-IR and TGA studies. Third category of solid acid catalysts developed was montmorillonite clay incorporated with metal cations among which Al-mont showed the highest Brönsted acidity. This was due to polarization of interlayer water molecules by
highly charged Al\textsuperscript{3+} cations. Because of highest acidity and delamination, Al-mont gave the highest p-cresol conversion and almost completes selectivity to DAM. The recyclability of this catalyst was also proved up to 8 times.

- Four different catalysts developed for liquid phase oxidations include mono – metallic Co and Mn oxides as well as mixed oxides of both the metals. These were prepared by solvothermal as well as co-precipitation methods between which mixed oxides of Co and Mn prepared by solvothermal method exhibited the highest activity for oxidation of vanillyl alcohol to vanillin. Formation of tetragonal \text{CoMn}_2\text{O}_4 and \text{MnO}_2 spinel phase was established by XRD,XPS and HR-TEM. A very novel catalyst for the oxidation of p-cresol to p-hydroxybenzaldehyde developed was the composite of r-GO and mixed metal oxide (MnCo). The structural characteristics of r-GO provide active sites for p-cresol adsorption through π-π stacking. Also, r-GO caused charge transfer leading to the enhancement in redox potential of MnCo mixed oxide. For veratryl alcohol oxidation to aldehyde, MnOx preapered by solvotheraml method gave higher activity than that of both MnOx and Co\textsubscript{3}O\textsubscript{4} prepared by co-precipitation method.