Chapter 4

CONCLUSION
4.1 Summary:

This section embodies the summary of the entire research work:

(i) Metal ion–Metal-Salt-metal ion–Montmorillonite as solid acid catalysts for Friedel-Crafts alkylation reaction:

Anhydrous CuCl₂, NiCl₂, ZnCl₂, Cu²⁺-Mont, Ni²⁺-Mont, Zn²⁺-Mont, CuCl₂-Cu²⁺-Mont, NiCl₂-Ni²⁺-Mont and ZnCl₂-Zn²⁺-Mont have been prepared, characterized and evaluated as catalysts (1.5 mmol metal, activated at 120°C) in Friedel-Crafts alkylation reaction, particularly benzylation of benzene to diphenylmethane against time. The results obtained indicate that, in general, the percentage yields in the benzylation of benzene increases with time, irrespective of the nature of catalysts activated at 120°C. Further, it has been observed that the anhydrous metal salt catalysts namely CuCl₂, NiCl₂ and ZnCl₂ show the lowest activity. In case of ZnCl₂, only about 12% conversion occurred even after a period of 48 hrs reaction time, while the activity in the case of other two salts were found to be negligible. However, the conversion in presence of the metal²⁺-Mont catalysts has been found to be higher than that with the anhydrous metal salt catalysts alone. Zn²⁺-Mont (activated at 120°C), among others has been found to show the highest conversion of about 82% within a period of 48 hrs, while Cu²⁺-Mont and Ni²⁺-Mont show only 16 and 14% conversion respectively. Amongst the metal salt-metal²⁺-Mont catalysts, ZnCl₂-Zn²⁺-Mont has shown conversion of 76%, where as CuCl₂-Cu²⁺-Mont and NiCl₂-Ni²⁺-Mont have shown only 48 and 6.4% conversion respectively. The reason for low activity is attributable to poor acidity of the composites. It is observed that during the initial period of reaction,
the catalytic activity of ZnCl$_2$-Zn$^{2+}$-Mont is very low, which increases gradually and near 48 hrs of reaction, the catalytic activity become almost same as that of Zn$^{2+}$-Mont composite. About 95 and 100 $\%$ conversions are found for Zn$^{2+}$-Mont (activated at 150$^0$C) during 24 and 48 hrs of reaction time respectively. It has been found that at 150$^0$C activation temperature, Zn$^{2+}$-Mont and ZnCl$_2$-Zn$^{2+}$-Mont composites show higher catalytic activity than activated at 120$^0$C.

(ii) Alkylation reaction of phenol with 4-hydroxybutan-2-one to produce 4-(4'-hydroxyphenyl)butan-2-one (Raspberry Ketone) in presence of clay catalysts:

The catalysts Fe$^{3+}$-Mont (Swy-2), Fe$^{3+}$-Mont (GMB), loaded Mont K-10 (Ald)-Fe(NO$_3$)$_3$ and Mont-AT(GMB) (AT = acid treated) were prepared and used as solid acid catalysts in the Friedel Crafts alkylation reaction of phenol with 4-hydroxybutan-2-one to produce Raspberry ketone under different conditions. Mont K-10 (Ald) was used as its purified form.

Under refluxing condition for about 48 hrs, the catalyst Fe$^{3+}$-Mont (Swy-2) produces para alkylated (4-(4'-hydroxyphenyl)butan-2-one) product with yield and selectivity 7.01 and 21.82 $\%$ respectively, which enhance correspondingly to 7.59 and 22.12 $\%$ when the reaction was carried out under autoclaving condition (temp. 125 $\pm$ 5$^0$C, Pr. 12 $\pm$ 3 bar, time 12 hrs). On increasing the reaction time to 24 hrs, the yield and selectivity enhanced marginally to 9.13 and 25.12 $\%$ respectively, while the catalyst Fe$^{3+}$-Mont (GMB) under the same reaction conditions for 12 hrs showed the yield and selectivity of the para product as 10.88 and 28.82 $\%$ respectively, which increase correspondingly to 22.30 and
47.54 % for reaction time of 24 hrs. Thus, it reveals that autoclaving conditions are preferred to refluxing conditions for such alkylation reaction.

The Mont K-10 (Ald) shows the yield and selectivity of the \textit{para} alkylated product as 35.16 and 63.42 % while and Mont-AT (GMB) exhibits 19.91 and 62.20 % respectively for 24 hrs reaction time, which are much higher than those exhibited by the metal exchanged Mont catalysts. Supported Mont K-10 (Ald)-Fe(NO$_3$)$_3$ shows the highest selectivity i.e. 67.26 % but the yield was only 25.39 %.

Surface area of the acid treated Mont catalysts is always higher than those of the non-acid treated ones. It was observed that the enhancement of surface area of the catalysts, the yield and particularly the selectivity also increase in general. The metal salt support on such acid activated Mont also enhances the selectivity but the yield was found to decrease. Thus, the supported Mont K-10 (Ald)-Fe(NO$_3$)$_3$ having surface area 195.10 m$^2$/g less than the catalyst Mont K-10 (Ald)(surface area 208.89 m$^2$/g) shows the highest selectivity i.e. 67.26 % but with lower yield i.e. 25.39 %. Therefore, in addition to surface area of the catalysts, other factors like nature of support and active sites, microporosity of the siliceous matrix, cation exchange capacity etc. also contribute to the yield and selectivity of the \textit{para} product of the alkylation reaction.

(iii) Effect of different anion on intersalation reaction:

The intersalation reactions carried out between [Ni(Phen)$_3$]Cl$_2$, [Ni(Phen)$_3$]SO$_4$, [Ni(Phen)$_3$](CH$_3$COO)$_2$, [Ni(Phen)$_3$]$_2$[Fe(CN)$_6$] and [Ni(Phen)$_3$]$_3$[Fe(CN)$_6$]$_2$ with Na-Mont (Swy-2) under ordinary stirring and ultrasonic conditions reveal that the latter reaction condition is more efficient and the
reaction was completed within about 30 min. The basal spacings of the intersalated products treated at different temperatures, starting from room temperature to 600°C were determined by XRD. The highest (30.04 Å) and the lowest (28.61 Å) basal spacings are shown by [Ni(Phen)3]SO4, and [Ni(Phen)3](CH3COO)2-Mont product obtained, respectively at room temperature when treated with about 4 times CEC equivalent with metal complexes of the clay. The influence of the different anions of the metal complex [Ni(Phen)3]2+ on the intersalation reaction with Na-Mont particularly in respect of basal spacings enhancement follows the order SO4²⁻ > [Fe(CN)6]³⁻ > [Fe(CN)6]⁴⁻ > Cl⁻ > CH3COO⁻. These basal spacing of the intersalated products indicate the formation of bilayer and pseudo-trilayer metal complexes in the interlamellar spacing. Thermal stability indicates that the bilayered metal complexes-Na-Mont (Swy-2) composites are stable upto 250-300°C while the monolayered composites are stable upto 500°C for complexes [Ni(Phen)3]X₂ / X' only and on further increasing the temperature above 600°C, unidentifiable multiple reflections were observed indicating collapsing of the complexes.

(iv) Evaluation of clay surface characteristics by cationic dye molecules (Probes) adsorption:

The adsorption of cationic dyes PY and R6G on Montmorillonite takes place largely by cation exchange mechanism. Upon adsorption of such dyes on three different forms of clay – (i) Na-Mont; (ii) H⁺-Mont and (iii) Mont K-10, visible spectra show red and blue shift of the parent monomeric dye band; the former shift is due to the surface polarity and the latter is because of
metachromasy caused by π-interaction between the dye molecule and surface oxygen of the silicate layers of the clay or dye-adsorbed-dye interaction etc. In respect of polarity, the order Mont K-10 > H⁺-Mont > Na-Mont is observed while a reverse trend i.e. Na-Mont ≥ H⁺-Mont > Mont K-10 is noticed in case of metachromasy. R6G is less prone to cause metachromasy compared to PY, which may be due to structural hindrance of the molecule. The XRD values of PY and R6G adsorbed Na-Mont and H⁺-Mont suggest that in the interlamellar spacing, monolayer of dye formation is possible and the observed metachromasy is attributed to π-interaction of the aromatic moiety of the dyes with the surface of the silicate layers. Besides adsorption by interaction, the dye molecules may aggregate with other dye molecules on the external surface of the clay at higher dye concentration, may cause metachromasy. The IR spectral bands of pure PY and R6G are found to shift after adsorption on clays. These spectral changes indicate that a monomeric PY or R6G exists in lower concentration of dye treatment, while for higher concentration of the dye, in addition to monomeric species, existence of external surface adsorbed dye – dye aggregation may be possible. From the IR study of adsorbed PY and R6G on Na-Mont, H⁺-Mont and Mont K-10, it reveals that, the clay – dye interactions are of similar in nature for Na-Mont and H⁺-Mont while that with Mont K-10 system is different. From the thermal data it is observed that the weight loss in the first temperature region (30 – 300°C) for all the clay – dye systems, is contributed mainly by the clay mineral, due to dehydration and evolution of interlayer water. In the 2 nd (300 – 700°C) and 3 rd temperature zone, (700 – 800°C), the major contribution for the weight loss comes mainly from the dye and that too from oxidation of residual carbon. In
higher concentration of dye treatment, the weight loss is also higher, because at higher concentration, the dye molecules not only intercalate into the clay interlayer spacing but also absorb on the external clay surface and aggregate due to \(\pi-\pi\) interaction between the dye molecule and the absorbed dye molecules. In case of Mont K-10-PY, the highest weight loss in the 1st temperature zone is due to non-existence of layered structure where the retention capacity of the dye molecules is minimum. On the other hand, the Mont K-10-R6G shows the lowest weight loss among the three clay R6G composites and it may be due to the different structural feature of R6G. From the thermal study, it reveals that Na-Mont and H\(^+\)-Mont behave in a similar way while Mont K-10 exhibit different feature due to different surface characteristics. From the surface area data, it indicates that upon treatment of different clays with different dyes, the surface area are invariably reduced, indicating interlamelluer spacing as well as pores (for Mont K-10) are occupied with the dye molecules.

(v) XRD evaluation of enantiomeric and racemic metal complex-Mont composites:

The metal complexes \(d\left\lbrack\text{Ni(Phen)}_3\right\rbrack\text{(ClO}_4)\rbrack_2\cdot3\text{H}_2\text{O},\) and enantiomers \(d\)- and \(l\)- \([\text{Ni(Phen)}_3\]([\text{ClO}_4]_2\cdot3\text{H}_2\text{O}\) were prepared and studied for their adsorption behaviour on Montmorillonite clay under different reaction conditions and the products were characterized by XRD analysis. It reveals that the enantiomers \(d\)- or \(l\)\[\text{Ni(Phen)}_3\]\(^{2+}\) behaves differently from their racemic \(d\left\lbrack\text{Ni(Phen)}_3\right\rbrack^{2+}\) complex in respect of adsorption amount irrespective of reaction conditions and treatment amounts (lower or higher than CEC). The adsorbed amounts in the
products obtained from $d$- or $l$-[$Ni(Phen)_3]^{2+}$ compared to that of the racemic complex $dl$-$[Ni(Phen)_3]^{2+}$ are lower. Upto CEC of the clay, the enantiomer $l$-[$Ni(Phen)_3]^{2+}$ adsorbed under 1 hr stirring condition, shows about 17.34 Å indicating formation of monolayer metal complex in the interlayer, which under 4 hrs stirring exhibits two values 26.56 and 17.98 Å indicating bilayer and monolayer metal complexes respectively. The enantiomer $l$-$[Ni(Phen)_3]^{2+}$ shows intersalated (adsorption higher than CEC) reactions and could form pseudo-trilayer, bilayer along with monolayer metal complex when treated with higher amount like 200 or 400 meq / 100 g clay and stirring under 1 or 4 hrs.

4.2 Future scope:

(i) Development of clay-base solid acid catalysts:

Modification of layered clay minerals like Montmorillonite clay through metal ion exchange, enhancing surface area by acid leaching, supporting with active metal catalysts etc. are likely to generate useful catalysts for organic synthesis.

(ii) Development of antiracemization column for enantiomeric separation:

Layered clay minerals may be modified by adsorbing optically active metal complexes exhibiting adsorption of opposite enantiomers from racemic mixer of molecules, thus may pave ways for development of enantiomeric separation systems.
(iii) Modification of layered clay for abatement of Environmental pollution:

Layered clay may be modified by enhancing surface area through acid leaching and supporting with suitable metal ion exchange for arresting pollution gases or ions in solution through coordination / complex salt formation.

(iv) Development of simple technique for probing clay surface:

Different activities of clay occur on its surface and require detail evaluation of surface characteristics which involve different sophisticated tools. Therefore, there is a big scope for developing simple laboratory technique through standardizing / optimizing devices involving different types of inorganic / organic probing molecules.