CHAPTER 8

SUMMARY AND CONCLUSIONS

8.1   SUMMARY

Heterogeneous solid acid catalysts for organic reactions are gaining significance, because of the current awareness of clean technology for chemical processes. In the recent years, a large number of solid acid catalysts have been developed to replace conventional homogeneous catalysts such as $AlCl_3$, H_2SO_4, HF, etc for organic reactions. In the present study, clay minerals, supported reagent catalysts, sulphated zirconia, heteropoly acid and zeolites were used to promote four industrially important organic reactions, namely, Friedel-Crafts acylation of anisole with acetic anhydride, decomposition of cumene hydroperoxide, alcoholysis of epichlorohydrin with allyl alcohol and acetolysis of epichlorohydrin with acetic acid, in liquid phase.

8.1.1   Preparation of catalysts

The catalyst samples were prepared by hydrothermal synthesis (NaY and MCM-41), ion-exchange of NaY and montmorillonite K10 by metal ions (Zn^{2+}, Fe^{3+}, Ce^{3+} and La^{3+}), wet impregnation (supported $ZnCl_2$, $FeCl_3$, $LaCl_3$ and $CeCl_3$ and supported DTPA catalysts) and acid activation of montmorillonite K10 and vermiculite clays (activated in 0.3, 0.5, 0.7, 1 and 3 M HCl).

8.1.2   Characterisation

The catalyst samples were subjected to a variety of physico-chemical methods to characterise their surface properties. The chemical composition of the catalyst samples was determined by wet chemical analysis and surface area by BET method. The phase purity and single phase formation in zeolite NaY and MCM-41 were determined by X-ray diffractometry. The XRD of DTPA supported on silica (10 - 60 wt % loading) showed the optimum loading of DTPA to be 40 wt %.

In order to determine the nature, strength and density of acid sites, infra-red spectra and differential scanning calorimetric thermograms of pyridine adsorbed catalyst samples were recorded. IR spectral data have clearly indicated the nature of acid sites. These have been identified as weak acid sites, Lewis acid sites and Bronsted acid sites. The FT-IR spectra of montmorillonite K10 has shown the presence of weak and Bronsted acid sites. On zinc chloride impregnation on montmorillonite K10, Lewis acid sites were found to be created at the expense of Bronsted acid sites. The FT-IR spectra of acid activated montmorillonite K10 (activated in 0.3 M, 0.5 M and 0.7 M HCl), DTPA supported on MCM-41, and zeolites HY and CeY revealed the presence of Bronsted acid sites.

Differential scanning calorimetric studies of a few representative samples of pyridine adsorbed catalysts gave confirmatory evidence for the presence of the weak acid sites, Lewis acid sites and Bronsted acid sites. The relative density and strengths of acid sites were determined from DSC studies. The montmorillonite K10 showed two peaks in the DSC thermogram, exhibiting the presence of weak and Bronsted acid sites. However, $ZnCl_2$ impregnation on montmorillonite K10 has resulted in a new peak corresponding to the Lewis acid sites, in addition to the two peaks. This indicated that upon impregnation of $ZnCl_2$ on montmorillonite K10,

some Bronsted acid sites in the support were destroyed and Lewis acid sites were created.

The DSC thermogram of the acid activated montmorillonite K10 (activated in 0.3 M, 0.5 M and 0.7 M HCl) showed two desorption peaks corresponding to weak acid sites and Bronsted acid sites. Acid activation of montmorillonite K10 enhanced the strength of Bronsted acid site, as indicated by the shift of the pyridine desorption peak, to higher temperature compared to montmorillonite K10. DTPA supported on silica and MCM-41 showed all the three types of (weak, Lewis and Bronsted) acid sites. A comparison of the density of their Bronsted acid sites indicated that, DTPA supported on MCM-41 possessed higher density than DTPA supported on silica. Zeolites NaY, HY and CeY have shown two desorption peaks, corresponding to weak acid sites and Bronsted acid sites. CeY possessed higher density of Bronsted acid sites compared to NaY and HY.

8.1.3 Catalytic activity

The catalytic activity of the catalyst samples was investigated for four organic reactions namely, acylation of anisole with acetic anhydride, decomposition of cumene hydroperoxide, alcoholysis of epichlorohydrin and acetolysis of epichlorohydrin. The reaction products were analysed by GC, GC-MS and ^{1}H NMR studies. The various reaction parameters such as, catalyst activation temperature, active component loading, mole ratio of reactants and catalyst weight were optimised.

8.1.3.1 Acylation of anisole

Acylation of anisole with acetic anhydride was carried out on various solid acids such as metal chloride ($ZnCl_2$, $FeCl_3$, $LaCl_3$ and $CeCl_3$) impregnated montmorillonite K10, metal ion (Zn^{2+}, Fe^{3+}, La^{3+} and Ce^{3+}) exchanged montmorillonite K10, $ZnCl_2$ impregnated on various supports

(acid activated montmorillonite K10 and vermiculite, titania, alumina, zirconia, silica and MCM-41), sulphated zirconia, DTPA impregnated on various supports (montmorillonite K10, silica, titania and MCM-41) proton and metal ion (Zn^{2+}, Fe^{3+}, Ce^{3+}, La^{3+} and Nd^{3+}) exchanged zeolite NaY, H-β H-mordenite and HZSM-5. All the catalysts were found to be catalytically active for the acylation of anisole, selectively yielding p-methoxyacetophenone. Montmorillonite K10 and acid activated montmorillonite K10 (activated in 0.5 M HCl) were found to be less active. However, impregnation of $ZnCl_2$ on montmorillonite K10 resulted in a very efficient catalyst for acylation of anisole. The optimum activation temperature of the $ZnCl_2$ impregnated montmorillonite K10 was found to be 120°C. The Lewis acid sites in $ZnCl_2$ montmorillonite K10 favoured acylation of anisole. Among the various supported zinc chloride catalysts investigated for the acylation of anisole, zinc chloride impregnated MCM-41 was found to be the most active catalyst.

Among the metal ion exchanged NaY zeolites, CeY exhibited higher activity towards the acylation of anisole. Comparing all zeolite catalysts, H-β showed maximum activity towards acylation of anisole. Sulphated zirconia was found to be less active.

The supported DTPA catalysts were found to have very high initial activity towards the acylation of anisole. The catalyst got deactivated within a very short period (5 minutes). The catalyst deactivation may be due to the strong adsorption of the product p-methoxyacetophenone. The kinetic analysis for acylation of anisole on $ZnCl_2$ impregnated montmorillonite K10 showed that, the reaction followed first order kinetics with respect to anisole and Langmuir-Hinshelwood adsorption seemed to be the most probable mechanism.

8.1.3.2 Decomposition of cumene hydroperoxide

Decomposition of cumene hydroperoxide carried out in cumene over acid activated montmorillonite K10 (0.3 M, 0.5 M, 0.7 M and 1 M HCl), $ZnCl_2$ and DTPA impregnated on various supports (montmorillonite K10, silica, titania and MCM-41), selectively yielded phenol and acetone. $ZnCl_2$ impregnated on various supports were active for decomposition of cumene hydroperoxide. Among various supports for impregnation of $ZnCl_2$, MCM-41 was highly favourable. Montmorillonite K10 was less active for decomposition of cumene hydroperoxide at 30°C, but the acid activated montmorillonite K10 was very efficient for decomposition of cumene hydroperoxide. Supported DTPA catalysts were also highly effective for decomposition of cumene hydroperoxide. The kinetic study on the decomposition of cumene hydroperoxide catalysed by $ZnCl_2$ impregnated on silica revealed that the reaction followed first order kinetics, with respect to cumene hydroperoxide.

8.1.3.3 Alcoholysis of epichlorohydrin

When alcoholysis of epichlorohydrin with allyl alcohol was carried out in excess of allyl alcohol over acid activated montmorillonite K10 (0.3 M, 0.5 M, 0.7 M and 1 M HCl), $ZnCl_2$ impregnated montmorillonite K10 and supported DTPA catalysts, 1-allyloxy-3-chloro-2-propanol was obtained as an exclusive product. Montmorillonite K10 was less active towards alcoholysis of epichlorohydrin and acid activated montmorillonite K10 was found to be highly active. The effect acid activation of montmorillonite K10 showed that, montmorillonite K10 activated in 0.3 M HCl exhibited higher catalytic activity towards alcoholysis of epichlorohydrin. Supported DTPA catalysts were found to be effective for alcoholysis of epichlorohydrin and the optimum loading of DTPA impregnated on silica was found to be 40%. The DTPA supported on MCM-41 was more active towards alcoholysis of epichlorohydrin. The exclusive formation of 1-allyloxy-3-chloro-2-propanol

confirmed that the alcoholysis of epichlorohydrin proceeded through S_{N2} mechanism. The kinetic analysis for alcoholysis of epichlorohydrin with allyl alcohol on montmorillonite K10 (activated in 0.3 M HCl) showed that, the reaction followed first order kinetics with respect to epichlorohydrin and Langmuir-Hinshelwood adsorption seemed to be the most probable mechanism.

8.1.3.4 Acetolysis of epichlorohydrin

Acetolysis of epichlorohydrin with acetic acid over montmorillonite K10 (activated in 0.3 M, 0.5 M and 0.7 M HCl) and supported DTPA catalysts exclusively yielded 1-acetoxy-3-chloro-2-propanol. Montmorillonite K10 activated in 0.3 M HCl was highly active towards acetolysis of epichlorohydrin. Supported DTPA catalysts were also highly active at 30°C giving 100% conversion within a short reaction time of 5 minutes. The high activity may be attributed to the stabilisation of oxonium ion by heteropoly anion. The exclusive formation of 1-acetoxy-3-chloro-2-propanol confirmed that the reaction proceeded through S_{N2} mechanism.

8.2 CONCLUSIONS

The following are the conclusions derived from the present study on heterogeneous solid acid catalysts for organic synthesis :

i)   Impregnation of zinc chloride on montmorillonite K10 destroyed the Bronsted acid sites in the support and created Lewis acids sites. The strength of Bronsted acidity in montmorillonite K10 increased on acid activation. Supported DTPA and CeY possessed strong Bronsted acid sites.

ii) Acylation of anisole with acetic anhydride over various solid acid catalysts has indicated that supported zinc chloride

catalysts, CeY, H-mordenite, H-β and HZSM-5 were efficient catalysts. The initial activity of supported DTPA catalysts were high, but they got deactivated within a very short reaction time during acylation. Sulphated zirconia was less active towards acylation anisole. Both Bronsted and Lewis acid sites helped acylation of anisole with acetic anhydride.

iii) The catalysts used in the decomposition of cumene hydroperoxide were effective, selectively giving phenol and acetone. Zinc chloride supported catalyst were active towards decomposition of cumene hydroperoxide. Acid activated montmorillonite K10 and supported DTPA catalysts were equally active towards decompostion of cumene hydroperoxide. Both Bronsted and Lewis acid sites favoured decompostion of cumene hydroperoxide.

iv) Alcoholysis of epichlorohydrin with allyl alcohol over acid activated montmorillonite K10 and supported DTPA catalysts yielded 1-allyloxy-3-chloro-2-propanol. This reaction proceeded through $S_{N}2$ mechanism. Supported zinc chloride catalyst failed to catalyse this reaction.

v) Acetolysis of epichlorohydrin with acetic acid was carried out over acid activated montmorillonite K10 and supported DTPA. These catalysts were active towards acetolysis of epichlorohydrin giving 1-acetoxy-3-chloro-2-propanol. This reaction proceeded through $S_{N}2$ mechanism.

vi) The kinetic analysis of all the reactions showed that, the reaction followed first order kinetics and Langmuir-Hinshelwood adsorption seemed to be the most probable

mechanism for acylation of anisole, alcoholysis and acetolysis of epichlorohydrin.

vii) It is possible to tune the surface properties of the catalytic materials by appropriate chemical treatments, so as to obtain tailor-made catalysts for specific reactions. For example, zinc chloride impregnation on montmorillonite K10 created Lewis acid sites of maximum density which favoured the acylation of anisole whereas activation of montmorillonite K10 in 0.3 M HCl increased the strength of Bronsted acid sites on its surface that was responsible for the promotion of cumene hydroperoxide decomposition.

vii) About 50 different catalysts have been investigated for the acylation of anisole, decomposition of cumene hydroperoxide, alcoholysis of epichlorohydrin and acetolysis of epichlorohydrin and most of them have been found to possess excellent catalytic activity. Based on the results of this study, it can be concluded that these solid acid catalysts can be proposed as potential substitutes for the conventional homogeneous catalysts in promoting synthetic organic reactions at industrial level.