ABSTRACT

Inorganic solid acids are a prosperous class of catalysts for the development of environmentally friendly chemical processes. The use of such catalysts can eliminate or minimise the serious pollution problems associated with the conventional catalytic materials. The immense potential of these catalysts has been highlighted in the present study to promote a few chosen organic reactions.

Different catalysts such as zeolite NaY, proton and metal exchanged zeolite-NaY, MCM-41, acid activated montmorillonite K10 and vermiculite clays, transition and inner transition metal chloride impregnated/exchanged montmorillonite K10, zinc chloride impregnated on various oxide supports, dodeca - tungstophosphoric acid impregnated on various oxide supports and sulphated zirconia were prepared by hydrothermal synthesis, wet impregnation and ion exchange methods.

The catalyst samples have been characterised for their composition, surface area, structure, acidity and catalytic activity. The composition and surface area were determined by wet chemical analysis and BET method respectively. The nature of acid sites has been analysed through the use of pyridine as a probe molecule by FT-IR and DSC studies. The catalytic activity of the prepared catalysts has been evaluated towards 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. The reaction products were analysed by GC, GC-MS and ^{1}HNMR studies. The various reaction parameters such as, catalyst activation temperature, active component loading, catalyst weight, reaction temperature and mole ratio of reactants were optimised and a detailed kinetic study was carried out. The catalytic activity has been correlated to surface acidity.

$ZnCl_2$ impregnated on montmorillonite K10 turned out to be a very efficient catalyst for acylation of anisole. $ZnCl_2$ impregnated montmorillonite K10 was a better catalyst compared to zinc ion exchanged montmorillonite K10, due to stronger Lewis acidity and the easier accessibility of the Lewis acid sites in the former.

The supported DTPA catalysts showed very high initial activity towards acylation of anisole, but the catalyst got deactivated due to the strong adsorption of product. Sulphated zirconia was found to be less active for the acylation of anisole. The supported $ZnCl_2$ catalysts, CeY, H-β, HZSM-5 and H-mordenite were found to be efficient catalysts for the acylation of anisole. Both Lewis and Bronsted acid sites favoured the acylation of anisole.

The decomposition of cumene hydroperoxide over these solid acid catalysts selectively produced phenol and acetone. Supported $ZnCl_2$ catalysts, acid activated montmorillonite K10 and supported DTPA catalysts were found to be highly active for the decomposition of cumene

hydroperoxide. Both Lewis and Bronsted acid sites favoured cumene hydroperoxide decomposition.

In the alcoholysis of epichlorohydrin over modified clay and supported DTPA catalysts, 1-allyloxy-3-chloro-2-propanol was formed. Acid activated montmorillonite K10 and supported DTPA catalysts were effective towards alcoholysis of epichlorohydrin. Supported $ZnCl_2$ catalyst was found to be inactive for alcoholysis of epichlorohydrin. The exclusive formation of 1-allyloxy-3-chloro-2-propanol confirmed that the alcoholysis of epichlorohydrin with allyl alcohol proceeded through $S_{N}2$ mechanism.

The acetolysis of epichlorohydrin over modified clay and supported DTPA catalysts yielded 1-acetoxy-3-chloro-2-propanol. The acid activated montmorillonite K10 and supported DTPA catalysts were highly active, towards acetolysis of epichlorohydrin. The exclusive formation of 1-acetoxy-3-chloro-2-propanol, confirmed that the acetolysis of epichlorohydrin with acetic acid proceeded through $S_{N}2$ mechanism.

All the reactions were found to follow first order kinetics and Langmuir-Hinshelwood mechanism was applicable to acylation of anisole, alcoholysis and acetolysis of epichlorohydrin.

The present study has indicated that solid acids have immense potential application as catalysts in the development of eco-friendly processes.