ABSTRACT

Traditionally most of the organic reactions have been catalysed by homogeneous mineral acids such as HCl, H$_2$SO$_4$ and HF and by soluble Lewis acids such as AlCl$_3$ and BF$_3$. These acids have many important advantages they are cheap, readily available and very active. Unfortunately, they suffer from some serious disadvantages, they are difficult to separate from the organic products and their use leads to large volumes of hazardous waste. In this context, worldwide efforts have been made for replacing homogeneous catalysts by reusable, easily separable heterogeneous solid catalysts for the synthesis of fine chemicals. A number of new, more environmentally friendly acids for liquid phase organic reactions, notably solid acids have been developed. These include zeolites, clays and other mixed metal oxides, inorganic–organic composite materials, functionalised polymers and supported reagents as well as lanthanide triflates. Zeolites, zeotypes and mesoporous materials are the novel materials, which meet the challenges of industrial applications abiding by the economic and environmental concerns. The discovery of these materials with their enormous practical utility led to synthesis, characterisation and practical applications of these materials playing a crucial role in chemistry, more prominently in catalysis.

The discovery of a novel family of mesoporous materials called M41S has opened new opportunities in catalytic applications in this background. The M41S family has been generally classified into three different categories: MCM-41 (hexagonal), MCM-48 (cubic) and MCM-50 (lamellar). These mesoporous materials have larger surface areas (> 700 m$^2$/g) and well-defined pore sizes (20–100 Å) and tenability to change the pore sizes has made them the most sought after materials of the last decade. The synthesis of these materials has expanded the applications of solid catalysts for developing
new processes for fine and bulk chemicals. Another possible new application is supporting HPA and transition metal oxides on mesoporous materials and exploiting their acidity towards acid catalysed reactions. In the present investigation, various solid acids such as mesoporous Al-MCM-41 with various Si/Al ratios, heteropoly acid supported MCM-41 and various percentage of binary metal oxide loaded MCM-41 were synthesised and characterised by various physico-chemical techniques. The catalytic activity of the synthesised materials tested over the synthesis of esters, acetals, quinoxalines and DATPM derivatives.

The Si-MCM-41 and Al-MCM-41 mesoporous materials with Si/Al ratios 29, 52, 74, 110 and 36, 57, 81, 108 were synthesised by hydrothermal method. The supported catalysts such as HPW (10, 20 and 30wt.%) and various percentage of binary metal oxides ZrO₂/MₓOᵧ (where M = Al, Ga, In and La) were loaded on Si-MCM-41 by wet impregnation method. The synthesised materials were characterised by powder X-ray diffraction (XRD), nitrogen adsorption-desorption measurements (BET), ICP-AES, ²⁹Si-MAS-NMR, ²⁷Al-MAS-NMR, ³¹P MAS-NMR, DRIFT, NH₃-TPD, SEM, TEM and TGA-DTA techniques. The XRD studies indicated the existence of ordered hexagonal structure of mesoporous materials. The XRD patterns of supported materials retained the long-range ordering of the hexagonal mesostructure after the optimum loading of HPW and metal oxides. BET measurements showed the specific surface area, pore volume, and pore size distribution of the samples were comparable to mesoporous molecular sieves. The decrease in pore volume and pore diameter was observed for HPW/MCM-41 and metal oxide loaded catalysts compared with the support. ²⁹Si and ²⁷Al MAS-NMR spectra revealed the co-ordination environment of silicon and aluminium present in the framework of MCM-41. ³¹PMAS-NMR spectra of the supported catalyst show a peak around -15.2 ppm indicating that the Keggin
structure of the heteropoly acid is well retained after loaded on Si-MCM-41. Pyridine FT-IR and NH\textsubscript{3}-TPD experiments indicated the strength of acid sites in the synthesised materials. TEM analysis of Si-MCM-41 and Al-MCM-41 showed that the honey comb like regular arrangement of hexagonal pores present on the molecular sieves. TEM results of the supported materials showed the uniform dispersion of HPW and metal oxides on the support.

The catalytic activity of Al-MCM-41 (Si/Al = 29, 52, 74 and 110) was tested over the esterification of acetic acid (AA) with 1-hexanol (HeOH), 2-ethyl-1-hexanol (2E-1HOH), isoamyl alcohol (IAOH), and propionic acid (PA) with isoamyl alcohol under autogenous conditions. The effects of temperature from 75 to 175 °C, molar feed ratios, (acid : alcohol), 1:1, 1:2, 2:1, 3:2 and 5:2, amount of catalyst and the reaction time were also investigated. Under the experimental conditions, Al-MCM-41 (110) a hydrophobic material showed higher alcohol conversion than the other catalysts. The hydrophobic properties of the catalysts were suggested to play important role in the esterification reaction.

The reaction of benzaldehyde with aliphatic glycols was performed over Al-MCM-41 (Si/Al = 36, 57, 81 and 108) in the temperature range of 50–150 °C. The effects of various parameters like temperature, mole ratio, reaction time and catalyst amount on the formation of acetals were optimised. The activity of the catalysts showed the following order Al-MCM-41 (108) > Al-MCM-41 (81) > Al-MCM-41 (57) > Al-MCM-41 (36). The increase in the chain length of glycol increases the nucleophilicity and hydrophobicity of the glycols; this shows much influence on the conversion of benzaldehyde. The reusability study showed that Al-MCM-41 could be reused at least five times without lowering the catalytic activity. It can be depicted that Al-MCM-41
catalyst could be the convenient eco-friendly alternative to the conventional hazardous mineral acid catalyst for acetalisation reactions.

The catalytic activity of MCM-41 supported HPW catalyst was tested over the condensation reaction of aniline with various aromatic aldehydes at refluxing temperature under liquid phase condition, which yields highly commercial product namely Diamino triphenyl methanes (DATPMs). The product thus obtained were analysed by proton NMR, $^{13}$C NMR and FT-IR techniques. The effects of various parameters like catalyst, mole ratio, solvents and substituent effect on the formation of DATPMs were optimised. The 20wt%HPW is the optimum loading on support for the synthesis of DATPM. The catalytic activity of the catalysts showed the following order: $\text{H}_3\text{PW}_{12}\text{O}_{40}.n\text{H}_2\text{O} > \text{H}_3\text{PMo}_{12}\text{O}_{40}.n\text{H}_2\text{O} > \text{H}_4\text{SiW}_{12}\text{O}_{40}.n\text{H}_2\text{O} > 20$ wt.% HPW/MCM-41 > 30 wt.% HPW/MCM-41 > HM (12) > Hf(8) > HY (4) > HZSM-5 (15) > Al-MCM-41 (25).

The liquid phase condensation reaction of various aromatic diamines with 2,3-diketones were carried out over ZrO$_2$/M$_x$O$_y$/MCM-41 (M = Al, Ga, In, and La) at room temperature. Effect of various solvents, reaction time and substituent effect were optimised for the better formation of product. The purified products were analysed by $^1$HNMR, $^{13}$C NMR and FT-IR techniques. 17%ZrO$_2$/4%Ga$_2$O$_3$/MCM-41 was found to be more active than the other catalysts. The used catalyst was very well recycled and reused without lowering the catalytic activity. The preparative method we adopted for the synthesis of esters, acetals, DATPM derivatives and Quinoxaline derivatives have the many advantages; they are inexpensive, stable, green and reusable catalyst. Therefore, the methods having the above advantages could be the best preparative method for the synthesis of fine chemicals.