ABSTRACT

In heterogeneous catalysis, use of zeolites as catalysts for organic transformations began in the early 1960’s. They possess the usual advantages over homogeneous systems viz. easy separation, regeneration and easy handling. Though the zeolites are known for its catalytic activity in the chemical transformations like oxidation and alkylation reactions, it poses diffusional constraints for the processing of larger molecules. Hence, in the recent years fundamental and industrial demands have meant that considerable effort has been devoted in expanding the pore size range of well-ordered zeo-type materials in the mesoporous range. The past decade has successfully fabricated porous materials with ordered structures for the application of chemical transformations. A lot of work has been devoted to the understanding catalytic properties of the mesoporous materials through various physico-chemical techniques. Recently, efficient and ecofriendly metal incorporated mesoporous MCM-41 molecular sieve catalysts are put forward as feasible catalysts for a variety of industrially important organic transformations.

A breakthrough for increasing pore sizes to overcome the diffusional constraints into the mesoporous range came in the early 1990’s when truly mesoporous molecular sieves were synthesized by researchers in Mobil Corporation USA. Since then, there has been a global resurgence in the synthesis of mesostructured materials, whose pore channels are in the
mesoporous domain. Such mesostructured materials are of great interest for a number of reasons. They are unique because of

(i) extremely large uniform pores (easily modifiable)

(ii) large surface area > 1000 m$^2$/g

(iii) high thermal stability and

(iv) tunable hydrophobic and hydrophilic nature

With these promising characteristics, MCM-41 has been largely exploited as heterogeneous catalysts for the oxy-functionalization of aromatic hydrocarbons, alkylation of large molecules and various chemical transformations. Incorporation of heteroelements such as Mn, V, Al etc., into the silica matrices introduces a negative charge that could be balanced by a cation. This cation can be a mono- or – divalent metal ion, as well as ammonium or a proton. However, the presence of multivalent metal cations like vanadium, manganese in the framework creates redox centers, which can act as good heterogeneous oxidant catalyst for the chemical tranformations in the presence of air oxidant. The Al-MCM-41 materials with different Si/Al ratios have bridged hydroxyl and Si-OH groups, which have been proved to be good alkylation catalyst.

In the present study, Mesoporous Mn-MCM-41, V-MCM-41, Al-MCM-41 (Si/Metal=25, 50, 75, 100) catalysts were synthesized under hydrothermal conditions. Vanadium impregnated MCM-41 molecular sieves were also synthesized. Phosphotungstic heteropoly acid were supported on
Al-MCM-41 molecular sieve with various weight percentages (10, 20, 30 wt %).

All the above synthesized materials were characterized by XRD, N$_2$- adsorption (BET), FT-IR, TG-DTA, SEM with EDX and TEM techniques. Some of them were characterised by $^{27}$Al-MAS-NMR, $^{31}$P-MAS-NMR, DRS-UV, EPR, ESCA techniques.

The low angle XRD patterns of synthesised catalysts confirm the hexagonal nature of the materials. Nitrogen adsorption studies indicate that high surface area of the materials, whereas pore diameter and pore volume are observed to decrease with increasing metal incorporation. FT-IR techniques represent the presence of T-O-T link in the framework and removal of template in the calcined material. $^{27}$Al-MAS-NMR spectra evidenced the presence of tetrahedral and octahedral aluminium in the framework. ESCA analysis also done to investigate the oxidation state of redox molecular sieves.

To understand the catalytic properties of synthesized catalysts alkylation reactions are carried out. The results indicate that the transformations occur in good conversion with excellent yields. Furthermore, these catalysts can easily be recovered and reused without practically affecting the yields.

The vapour phase alkylation of $p$-hydroxy toluene and $p$-hydroxy anisole with methyl tertiary butyl ether was carried out over Al-MCM-41 (Si/Al = 75,50,25) and HPA loaded Al-MCM-41(10,20,30 wt% HPA) catalysts at 200 to 400°C at the intervals of 50°C. The activity of the
catalyst was found to be in the order Al-MCM-41(50) < Al-MCM-41(25) < 10%HPA-MCM-41 < 30% < 20%. The high activity of 20% HPA loaded is pronounced by bronsted acidity. The optimization studies for experimental parameters indicate that product selectivity and conversion are maximum at 225°C with feed ratio 1:3 (p-hydroxy toluene: MTBE) and WHSV 1.1 h⁻¹. The results also revealed that the bronsted acidity of the HPA loaded catalyst plays a crucial role in catalytic performance. The effect of time on stream was also investigated under optimum conditions and the results are discussed.