CHAPTER 5

SUMMARY AND CONCLUSION

Narrow porous materials, particularly the zeolites are found to be the suitable catalyst for industrial applications. These molecular sieves are called as solid acids, and have been exploited for catalytic applications. But there are problems of (a) rapid catalyst deactivation due to the blocking of active sites by coke formation (b) isomerisation of the products (c) more diffusional constraints for the reactants and products (d) less turn over number and (e) impossibility in processing large feed stock molecules. Hence intense researches have been carried out in expanding the pore size from micropore to mesopore region.

Mesoporous molecular sieves suit as best catalysts and occupy an unique position based on the combination of acidity, hydrothermal stability and pore size. Their large surface area enhances the catalytic and sorptive activity. Recently, a new family of mesoporous molecular sieves, designated as M41S has been reported by mobile scientists. It possesses a regular hexagonal array of uniform pore openings with broad spectrum of pore diameters between 20-100 Å. Based on these extensive reports available, in the present investigation, the Al-MCM-41, Fe-MCM-41, Al,Zn-MCM-41 and HPA supported MCM-41 catalysts were synthesised, characterised and their catalytic activities were tested. Diethyl carbonate was used as alkylating agent instead of alcohols.
MCM-41 (Si/Al = 33, 52, 75, 114; 30, 52, 70, 112; Si/M = ∞ (M = metals), Si/Fe = 61, 115; Si/Al+Zn = 104) molecular sieves were synthesised by hydrothermal crystallization procedure. The synthesised materials were converted into H-form by ion-exchange with aqueous 1 M NH₄NO₃ followed by calcination at 550°C for 5 h. The sophisticated instrumental methods used for the characterisation of all synthesised MCM-41 are studied. The experimental set-up of the vapour phase alkylation and liquid phase condensation are also studied in detail.

The physico-chemical characterization presents the details derived from the characterization of mesoporous MCM-41 molecular sieves. In the present investigation MCM-41 (Si/Al = 33, 52, 75, 114; 30, 52, 70, 112; Si/Fe = 61, 115; Si/Al+Zn = 104), HPA, 20 and 30 wt.% HPA over Si-MCM-41) have been synthesised. These materials were then characterised by the XRD, ICP-AES, BET-nitrogen sorption, ²⁹Si-MAS-NMR, ²⁷Al-MAS-NMR, DRS UV-Vis, TPD-NH₃ and FT-IR spectroscopy of pyridine-adsorbed catalysts. The low angle XRD patterns of hydrothermally synthesised catalysts confirm the hexagonal nature of the materials. In all the XRD patterns of the materials, an intense signal around 2.2-2.9 (2θ) is observed. It is assigned to (100) plane of the hexagonal mesophase. The higher aluminium containing catalysts show lower d-spacing values. This may be due to the leaching of aluminium from the framework. The nitrogen adsorption studies confirm the mesoporous nature of the materials. The pore diameter and pore volume were found to decrease with increasing metal incorporation. All the mesoporous materials have high surface area. The SEM images of the substituted materials show the formation of aggregates without regular shape and size. The ²⁷Al-MAS-NMR has revealed the evidence for tetrahedrally co-ordinated aluminium. The presence of octahedral aluminium is also confirmed by the observation of the less intense peak for MCM-41 molecular sieves with Si/Al = 33, 52, 75; 30, 52 and 75, Si/Al+Zn = 104. The
The surface area of the materials is in the range of 800 to 1100 m$^2$/g. The DRS UV-Vis spectra show a band around 250 nm for tetrahedral co-ordinated iron. The acidity measurements of samples by TPD of NH$_3$ and FT-IR spectroscopy of pyridine adsorbed catalysts show that the incorporation of Zn in Al-MCM-41 framework increases the total acidity of catalysts.

The Results and Discussion describes the results obtained from the ethylation of phenol and isopropylbenzene, esterification of phthalic anhydride and tetrahydro phthalic anhydride and synthesis of bisphenol.

The ethylation reaction of phenol (PhOH) was carried out with diethyl carbonate (DEC) in the presence of Al-MCM-41 (Si/Al = 33, 52, 75 and 114). All the catalysts showed increased conversion rates when the temperature increases from 200 to 300$^\circ$C. Further increases in the temperature show decreases in conversion rate. With the increase in temperature, the selectivity of $p$- and $o$-isomers decreases, whereas the thermodynamically favorable $m$-isomer increases with increase in temperature and the isomerisation of $o$- to $m$-is is also favoured by the increase in temperature. In all the cases, $p$-ethyl phenol was obtained as the major product along with small amounts of $o$- and $m$-ethyl phenols. The selectivities to mono ethylated products increase with increase in flow rate. Also the reactant feed ratio (PhOH: DEC) was observed to play a key role in deciding phenol conversion and $p$-ethyl phenol selectivity. Lower reactant mole ratios were beneficial to higher phenol conversion. Lower space velocity was found to be preferred in enhancing the phenol conversion, but higher space velocity enhances the $para$ product selectivity. The time-on-stream study shows that the conversion of phenol gradually decreases with increase in stream, due to the blocking of active sites by the polyethylene oligomers and/or coke and also 1.87% of coke and 36.34% of olefins.
Alkylation of isopropyl benzene (IPB) with diethyl carbonate (DEC) was carried out in the presence of Al-MCM-41 (Si/Al = 33, 52, 75 and 114). The higher conversion rate seen in Al-MCM-41 (33) was due to the presence of some variety in acid strengths of the Brönsted acid sites, high surface area and also the ease of formation of carbonium ion at the Brönsted acid sites. All the catalysts showed increased conversion rates with an increase in temperature from 200 to 300°C. Further increases in temperature show decreases in conversion rate. The observation from the mass balance calculations showed that 4.93% of coke at the end of 1 h on-stream. The conversion of Al-MCM-41 (114) was lower than the conversion of Al-MCM-41 (33). But lower acidic Al-MCM-41 (114) shows 1.52 times greater value of conversion than the expected value. These results were explained by the hydrophobic property of reactant and catalyst. Catalyst with lower Si/Al ratio shows multi-alkylation, thereby the selectivity of mono-alkylation decreases. The selectivity to 4-ethyl isopropylbenzene is higher in the feed ratio of 2:1 (IPB: DEC) at 200°C. In this reaction, the p-isomer shows higher selectivity than the other isomers, due to the lower impedance offered by the ethyl group in para position. Selectivity to mono-alkylated products increases with increase in the time-on-stream. The blocking of active sites also prevents the cracking of mono-alkylated isopropylbenzene.

Esterification of phthalic anhydride was studied over Al, Fe and Zn containing MCM-41 (Si/Al = 30, 52, 70 and 112; Si/Fe = 61, 115; Si/Al+Zn = 104). The activity of these catalysts is in the order of: Al-MCM-41 (112) > Fe-MCM-41 (115) > Al-MCM-41 (70) > Al-MCM-41 (52) > Fe-MCM-41 (61) > Al,Zn-MCM-41 (104) > Al-MCM-41 (30). The order of the catalyst clearly indicates that the conversion is inversely proportional to the acidity of the catalyst. From this reaction, it can be concluded that MCM-41 containing lower percentage of aluminium shows
better activity. Iron and zinc containing MCM-41 shows less activity due to higher acidity. The activity of the Brönsted acid sites is confirmed by a test reaction over Si-MCM-41 and amorphous silica, which shows that the formation of mono-ester is favoured by the temperature, and the formation of diester is favoured by the Brönsted acid sites. These results confirm that the reaction mainly occurs in the pore than on the external surface. The higher % of alcohol also decreases the conversion and the higher amount of catalyst blocks the reactant. The results show that the selectivity of diester, being facilitated by the hydrophobic nature of the material, shifts the reaction yield towards the right hand side. The influences of hydrophilic and hydrophobic nature of the catalyst are confirmed by the test reaction with water. The higher the content of alcohol in the feed, the selectivity of the diester gradually increases. Maximum conversion and products selectivity are attained at the end of 10 h at 150ºC, which can be achieved only by the specific nature of the solid acid catalyst.

Bisphenol is synthesized over HPA and supported HPA (20%HPA/Si-MCM-41 and 30%HPA/Si-MCM-41). The bisphenols are synthesized by the condensation of two moles of phenolic compound with one mole of aldehyde. The formation of bisphenol was facilitated by the Brönsted acid catalyzing reaction, which needs strong acid sites. The activity of these catalysts is in the order of: HPA > 30%HPA/Si-MCM-41 > 20%HPA/Si-MCM-41. When benzene is used as a solvent, the reaction shows lower yield than when toluene was used as solvent. This may be due to the lower reaction temperature and lower capability of the water separation from the reaction medium. The yield of the reaction is also affected by the hindrance of the group, which is nearer in the reaction center. The reaction with phenol shows better yield than that of the reaction with m-cresol, because in the m-cresol, the –CH₃ group is nearer to the reaction center, which affects the reaction. The mole ratio of the reaction also shows much influence on the
yield of the product. The higher mole ratio of the phenolic compound shows
good yield than the lower mole ratio on the bisphenol formation. Higher mole
ratio of phenolic compound in the feed favours the condensation reaction.
HPA polyhedra with one-fourth aldehyde shows higher TON than the
one-third of aldehyde in the reaction.

Based on the experiment results, it is concluded that the metal
incorporated MCM-41 could be considered as convenient and ecofriendly,
alternative to commercial mineral acid catalysts for alkylation and
condensation reactions. Hence DEC can have a far-reaching impact on
ethylation reaction in the future. In the case of esterification reactions the
hydrophobic materials show much impact on the synthesis of commercially
important esters. The HPA and supported HPA can be considered as the best
alternatives for hazardous mineral acids for synthesis the fine chemicals.