ABSTRACT

Catalytic technologies have played a vital role in the economic development of chemical industries in the twentieth century. More than 90% of chemical industries involving products such as food, fuels, polymers, textiles, pharma, agrochemicals, etc make use of catalysts. Both homogeneous and heterogeneous catalysts find wide applications in the field of oil refining, petrochemicals and chemicals production. Heterogeneous catalysts generally offer advantages such as easy handling, simplicity and versatility of process engineering, catalyst regeneration, decreasing reactor and plant corrosion problems and environmentally safe disposal. These catalysts can also be designed to give higher activity, selectivity and longer catalyst life. Heterogeneous catalysts not only minimise the production of waste but also exhibit activity and selectivity comparable or superior to the existing homogeneous route. Large number of solid acid catalysts such as zeolites, zeotype molecular sieves, oxides, ion-exchange resins and phosphates are employed for industrial applications. However zeolites are the most exploited heterogeneous catalyst in most of the chemical industries.

Zeolites are a group of hydrated, microporous, crystalline aluminosilicates, made up of $\text{TO}_4$ of $\text{SiO}_4$, partially substituted by units of $\text{AlO}_4^-$ tetrahedra. They possess exchangeable cations that allow introduction of cations with various catalytic properties. Zeolites have framework structure encloses cavities or pores occupied by cations and water molecules permitting ion-exchange and reversible dehydration. They possess highly regular structure of pores and channels that allow some molecules to pass through and cause others to be either excluded or broken down.
ZSM-5 is a type of zeolite built from the pentasil unit. ZSM-5 and silicalite have two types of channels, both of which have ten membered ring openings. One channel system is sinusoidal and has nearly circular cross section and the other channel system has elliptical openings. These are straight and perpendicular to the first system. The cavity at the intersection of the channels is about 9 Å in diameter. It is the only zeolite with high silica to alumina ratio. It is often considered as a prototype shape selective catalyst. The properties of zeolite catalysts have to be fine tuned in order to carry out specific synthesis of high value chemicals such as pharmaceuticals and cosmetics.

Modification of zeolites is important for the synthesis of specialty and fine chemicals. Generally, modification of zeolites can be done by passivating the external acid sites to suppress isomerisation. Whereas narrowing the pore size enhances the selectivity. Since the number and strength of acid sites play a crucial role in controlling the catalytic activities, the properties of catalysts are carefully tuned for the desired catalytic process. The acid-base properties of zeolites depend on the aluminium content in the framework. The adjustment of acidity may be realised by proper Si/Al molar ratio, incorporation of foreign elements in the framework or modification of the zeolites. Dealumination is a well known procedure for stabilising zeolites and creating mesopores that help to overcome diffusional constraints in the zeolite micropores. Silylation passivates the external surface and thus reduces the non-selective surface reactions.

The catalytic properties of ZSM-5 can be enhanced by incorporation of group VA elements especially phosphorus, which provides the catalyst with greater number of acid sites but lesser strength than the parent zeolite in addition to pore size modification. Generally, phosphorus modification is
done by post-synthesis method with various phosphorus agents. Phosphoric acid is the most versatile modifying agent. The impregnation of phosphoric acid in ZSM-5 exerts an effect, which is similar to that obtained by thermal and hydrothermal treatments. The number of Brönsted acid sites decreased but dealumination was not observed. The decrease of Brönsted acidity is due to reversible interaction between orthophosphoric acid and part of the acid bridged hydroxyl groups of zeolite framework. Phosphorus obviously exerts certain influence that protects aluminium in the framework. This modification also results partial blocking of the pore openings and as a result of this enhanced para selectivity is observed.

The present investigation focused on the modification, characterisation and catalytic evaluation of ZSM-5. Modification was done by wet impregnation method using phosphoric acid as the modifier. Further, the modified materials were characterised using physico-chemical techniques such as XRD, TG-DTG, FT-IR, nitrogen sorption studies, TPD of ammonia, $^{27}$Al MAS NMR and $^{31}$P MAS NMR and the results are discussed. The catalytic activity of the modified catalysts has been evaluated in three industrially important reactions.

Vapour phase ethylation of ethylbenzene with diethyl carbonate was carried out over H-ZSM-5, 8% P-ZSM-5(C), 10% P-ZSM-5(C) and 12% P-ZSM-5(C). The products were found to be 1,2-diethylbenzene, 1,3-diethylbenzene and 1,4-diethylbenzene. 10% P-ZSM-5(C) showed higher conversion and selectivity to 1,4-diethylbenzene than all other catalysts at 300 °C. The selectivity to 1,4-diethylbenzene increased up to 3 h after that it remained steady. The selectivity to 1,2-diethylbenzene and 1,3-diethylbenzene isomers also attained a steady value without any significant decrease or increase. This may be due to channel tortuosity, the
important feature of modified catalysts. Further, the catalysts offer much steric hindrance for the formation of coke within the pores. Since the acidity of modified catalysts decreased, multialkylation in these catalysts is prevented. tert-Butylation of ethylbenzene was carried out over H-ZSM-5, 8% P-ZSM-5(C), 10% P-ZSM-5(C) and 12% P-ZSM-5(C) between 200 and 400 °C. The major products were found to be 2-tert-butylethylbenzene and 4-tert-butyl ethylbenzene. The higher selectivity to 4-tert-butylethylbenzene is due to avoidance of steric hindrance and medium pore size of the catalysts. Even though P⁺ site is a Lewis acid site, the catalyst showed much resistance for coke formation. This is the cause for higher conversion over modified catalysts than H-ZSM-5. Isomerisation of 4-tert-butylethylbenzene was not observed over modified catalysts. Disproportionation of ethylbenzene, which occurred on H-ZSM-5, is greatly suppressed in the modified catalysts. The time on stream study showed steady conversion and selectivity to 4-tert-butyl ethylbenzene for 6 h, which revealed the absence of coke formation.

Liquid phase Beckmann rearrangement of cyclohexanone oxime was carried out over H-ZSM-5, 10% P-ZSM-5(AM) and 10% P-ZSM-5(C). The important observation in this study is the high selectivity to caprolactam and less selectivity to side products. All the catalysts exhibited high conversion but selectivity to caprolactam was higher over 10% P-ZSM-5(C) than other catalysts. The P⁺ sites of 10% P-ZSM-5(C) without any Brönsted acid sites play active role in this rearrangement. The catalyst also maintained same activity for three recycles thus illustrating absence of blocking of active site by the reaction products. The P⁺ site catalyses this reaction by Lewis acid-base interaction. Although there is complete absence of strong acid sites in phosphoric acid modified catalyst with respect to H-ZSM-5, it exhibited activity comparable to H-ZSM-5.