ABSTRACT

Zeolites are extremely successful as catalysts for oil refining, petrochemistry, and organic synthesis involving production of fine and specialty chemicals. They have been synthesised hydrothermally from highly viscous mixtures of colloidal silica, sodium aluminate, sodium hydroxide, water and a structure directing template. The template free synthesis of zeolites is also well known. In the synthesis under alkaline condition hydroxide ions mineralise silica and regulate its supply during crystallisation.

An additional synthetic route that has attracted much attention is synthesis of zeolites in fluoride medium. Fluoride mediated synthesis has been applied at neutral and acidic regions. Growth of zeolite crystals with large dimensions and high crystallinity and avoidance of ion-exchange to get H-form after synthesis are some of the advantages of this technique. The reduced entry of aluminium into the framework during crystallisation is its drawback. This is attributed to fluoride complexation of aluminium. The present study attempted to suppress fluoride ion complexation of aluminium using a co-complexant, phosphate.

HZSM-5(Si/Al = 25) was synthesised in fluoride medium initially in different F/Si ratio using the gel composition 0.07C₁₂H₂₈NBr : 1.0SiO₂ : 0.006Al₂O₃ : xNH₄F : 80H₂O. The optimum range of F/Si ratio for high crystallinity was 1.0 to 1.6. HZSM-5(25) was then synthesised with the optimum F/Si ratio in the presence of phosphate. The Si/Al ratio of the synthesised HZSM-5(25) was 22, thus confirming good transport of
aluminium from the gel to the framework. In order to prove that this transport was aided by complexation of aluminium with phosphate, potentiometric titrations of phosphoric acid versus KOH, and phosphoric acid, and Al$^{3+}$ versus KOH were conducted. In line with our expectation a decrease in pK$_a$1, pK$_a$2 and pK$_a$3 of phosphoric acid and aluminium mixture compared to phosphoric acid alone was observed in the plots of volume of alkali added versus pH.

Different sources of silica viz., sodium silicate, LUDOX-sodium stabilised silica (HS silica), LUDOX-ammonium stabilised colloidal silica (AS silica), fumed silica and tetraethylorthosilicate were tested as the sources of silica in the synthesis of HZSM-5(25) at pH between 4 and 6 in the presence of phosphoric acid. Among them tetraethylorthosilicate gave higher crystallinity than others. Tetraethylorthosilicate was used as the silica source to synthesise HZSM-5(Si/Al = 25, 50 and 75) in fluoride medium in the presence of phosphate. All the materials were crystalline with high surface area. The SEM analysis illustrated large crystal size with smooth surface. TPD (ammonia) showed presence of weak and medium acid sites. $^{27}$Al MAS-NMR of HZSM-5(25) showed exclusive presence of tetrahedral aluminium. $^{29}$Si MAS-NMR of HZSM-5 (25) showed silicon sites surrounded with four other silicons and also sites with three silicon and one aluminium.

tert-Butylation of ethylbenzene was carried out over HZSM-5 (Si/Al = 25, 50 and 75) at 200, 250, 300, 350 and 400°C. Both tert-butylation of ethylbenzene and isomerisation of 4-tert-butyl ethylbenzene (4-t-BEB) to 3-tert-butyl ethylbenzene (3-t-BEB) occurred. The conversion of
ethylbenzene increased from 200 to 300 °C but decreased at higher temperatures. Isomerisation of 4-t-BEB to 3-t-BEB increased with the increase in temperature, but the increase was not significant due to absence of strong acid sites. Among the catalysts synthesised in fluoride medium HZSM-5(25) was more active than others due to more density of acid sites, but it is less active than commercial HZSM-5(25). Only 4-t-BEB and 3-t-BEB with high selectivity to the former compared to the latter was obtained. Time on stream study was carried out for 5 h to compare the activity of the catalysts. The conversion decreased slowly illustrating resistance to coke formation. Medium pore size and absence of strong acid sites were suggested to be the cause for the slow coke formation.

Ethylation of ethylbenzene was carried out over HZSM-5 (Si/Al = 25, 50 and 75) at 200, 250, 300, 350 and 400 °C. Disproportionation of ethylbenzene, ethylation of ethylbenzene and isomerisation of 1,4-diethylbenzene (1,4-DEB) and 1,2-diethylbenzene (1,2-DEB) to 1,3-diethylbenzene (1,3-DEB) occurred. The conversion increased from 200 to 300 °C and then decreased. Commercial HZSM-5(25) showed higher conversion than the catalysts synthesised in fluoride medium. Among the synthesised catalysts HZSM-5(25) was more active than others. The selectivity of 1,4-DEB was higher than other products. The study of time on stream showed steady ethylbenzene conversion and high selectivity to 1,4-DEB.

Cracking of naphtha to light olefins over HZSM-5(Si/Al = 25, 50 and 75) at 675 °C in helium atmosphere was studied. The commercial catalyst was also tested for the same reaction for comparison. The results indicated
nearly same yield of light olefins over all the catalysts. Though the commercial catalyst carried high density of acid sites compared to the present system of catalysts, similar level of conversion was due to its high hydrogen transfer activity. HZSM-5(50) showed higher yield of olefins than HZSM-5(25), as the former might have less hydrogen transfer activity than the latter. Moderate density of weak and medium acid sites could be sufficient for naphtha cracking. This study concluded that synthesis of HZSM-5 in fluoride medium with phosphate as co-complexant could be more advantageous than those synthesised in alkaline medium for selective alkylation of alkylaromatics and cracking of naphtha to high yield of olefins.

The raise in the use of fossil fuels has significantly contributed to increase in CO$_2$ level of atmosphere. Hence researchers have focused to develop different solid sorbents for CO$_2$ capture. CO$_2$ adsorption on oxides and mixed oxides, high surface area porous materials including zeolites, metal-organic frameworks, amine dendrimers and amine functionalised mesoporous silicas was attempted. In the present study CeO$_2$ (3, 5, 7, 11 and 19 wt%) impregnated NaZSM-5 synthesised using rice husk ash was used for CO$_2$ adsorption. CeO$_2$(5%/NaZSM-5 showed higher CO$_2$ adsorption capacity than others. Dipole-dipole interaction between CeO$_2$ and CO$_2$ was suggested as the cause for CO$_2$ adsorption. Hence, it was established that rice husk ash could be a better source of silica for the synthesis of NaZSM-5 in alkaline medium, and NaZSM-5 could be a convenient support for fine dispersion of transition and rare earth metal oxide for CO$_2$ adsorption.