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The effect of cyclic dealumination on the catalytic activity of beta zeolite

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The acidity of zeolite beta is decreased by dealumination with $(NH_4)_2SiF_6$ The effect of change in zeolite acidity on catalytic activity for benzene isopropylation has been studied. The reasons for change in the product pattern over zeolite beta dealuminated cyclically have been discussed. The cyclic dealumination of zeolite beta can be effectively used to achieve a predesired product pattern of benzene isopropylation.

At present there is a considerable interest in the catalytic aspect of beta zeolite. It is a high silica large pore zeolite. The framework and the pore structure of the zeolite have several unique features. It is the only large pore zeolite to have chiral pore intersections[1].

Isomerization of *meta*-xylene, alkanes cracking and toluene methylation over beta zeolite have been investigated[2,3]. Tsai *et al.*[4,5] have dealt with stability enhancement during cumene disproportionation by silica deposition and steam pretreatment of beta zeolite. Synthesis of di-isopropylbenzene over dealuminated zeolite beta was studied by Parikh *et al.*[6]. Use of zeolite beta for transalkylation and disproportionation of C_7 and C_9 aromatic streams was attempted by Das *et al.*[7]. Other studies reported on beta zeolite are alkylation of aniline with methanol[8], selective formation of cymenes[9], selective hydrogenation of cinnamaldehyde controlled by host/guest interactions[10], isobutane/1-butene alkylation[11], transalkylation of *meta*-diethylbenzene and selective formation of cymene during isopropylation of toluene[12].

Unlike other catalysts in zeolites the active site is well defined and the catalyst activity directly related to number of acid sites or aluminium atoms in the framework. Total acidity and acid strength distribution of active sites are controlled by Si/Al ratio of the zeolites. This ratio can be altered during synthesis by changing gel composition or by post synthesis modification. One of the latter techniques is dealumination by $(NH_4)_2SiF_6$ treatment. The dealumination decreases acid site density of the zeolite. The present work is aimed at understanding the effect of cyclic dealumination on the catalytic activity of zeolite beta for alkylation of benzene with isopropanol.

Experimental

Zeolite preparation

Following the patented information a gel of composition 2.8 $(TEA)_2O$-56.4 SiO_2-Al_2O_3-0.9 Na_2O-1660 H_2O was prepared and beta zeolite was crystallized out from it under hydrothermal conditions[13]. The zeolite was characterized by XRD for phase purity, SEM for crystal morphology and size, TPD of ammonia for acidity and a combination of wet chemical analysis and AAS methods for Si/Al ratio.

Catalytic reaction

The catalytic reaction runs were carried out in a fixed bed tubular reactor at atmospheric pressure. Beta zeolite in proton form was loaded into the reactor. The details of the experimental set up and analysis procedure are reported elsewhere[7].

Zeolite dealumination

The proton form zeolite was dealuminated by treating with 0.5 *M* $(NH_4)_2SiF_6$ First the zeolite was soaked in aqueous $(NH_4)_2SiF_6$. and refluxed at 368 K for 3 h. For each gram of zeolite 15 ml of silicate solution was used. After reflux the zeolite was repeatedly washed with hot distilled water to remove unreacted $(NH_4)_2SiF_6$. Further it was calcined at 773 K in the presence of air for 8 h.

Results and discussion

The characterization data on samples of zeolite beta with and without dealumination is presented in Table 1. There is a drastic change in the properties of dealuminated samples. After dealumination total acidity and XRD crystallinity have gone down and Si/Al ratio has increased.

The results of benzene isopropylation on beta zeolite dealuminated to different extents are reported in Table 2. With increase in number of dealumination cycles benzene conversion to cumene (*i*-propylbenzene) decreased, while selectivity to $i/(i+n)$ propylbenzene reached 100%. Further, an interesting observation was made on the ratio of *p/m* in diisopropylbenzenes. This ratio was

Table 1—Characterization data of parent and dealuminated beta zeolite

	Parent zeolite	Dealuminated Once	Twice	Thrice
SiO_2/Al_2O_3	60	193	217	245
Acidity mmol/gr cat.	0.470	0.093	0.075	0.066
XRD crystallinity	100	65	50	39

Table 2—Performance comparison of dealuminated beta zeolite with parent zeolite
[Temp = 498 K, WHSV = 2.6 h^{-1}, Benzene/isopropanol mol ratio = 8]

	Parent zeolite	Dealuminated Once	Twice	Thrice
Benzene conversion (%)	17.22	14.57	10.63	4.12
Isopropanol conversion	100	100	100	100
Cumene selectivity	92.7	89.4	85.6	82.1
DIPB selectivity	3.9	5.6	3.3	1.1
$i/(i+n)$ Propylbenzene	98.16	99.7	99.9	100
m/p DIPB	2.25	1.36	1.04	0.64

Table 3—Catalytic performance of parent and dealuminated beta zeolite at comparable conversions
[Temp = 498 K, Benzene/isopropanol mol ratio = 8]

	Parent zeolite	Dealuminated Once	Twice	Thrice
WHSV (h^{-1})	7.5	6.3	4.5	2.6
Benzene conversion (%)	5.26	4.78	4.65	4.12
Isopropanol conversion	100	100	100	100
Cumene selectivity	93.7	90.2	87.4	82.1
DIPB selectivity	2.6	3.9	2.3	1.1
$i/(i+n)$ Propylbenzene	98.5	99.9	100	100
m/p DIPB	1.78	0.95	0.84	0.64

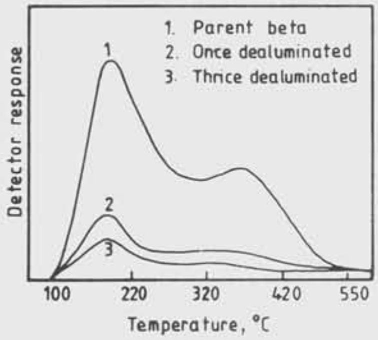

Fig. 1—Ammonia TPD profiles of parent and dealuminated beta zeolites

2.25 over parent beta zeolite, while it was 0.64 over thrice dealuminated beta zeolite. The comparison of performance at nearly same conversion level is given in Table 3. These results confirm the performance trends indicated in Table 2.

The dealumination decreases the acid site density of the zeolite, which is reflected by the ammonia TPD results (Fig. 1). With the result the conversion of benzene decreased as the catalytic activity is proportional to the number of acidic sites. The mechanism of *n*-propylbenzene formation along with cumene can be explained on a similar line to *n*-propyltoluene/cymene formation during toluene alkylation with isopropanol over HZSM-5 and HY zeolites. *n*-Propyltoluenes do not result from the monomolecular isomerization of individual isopropyltoluenes, but they are formed due to the bimolecular transalkylation reaction between cymenes and toluene. This aspect has been dealt in detail by Wichterlova *et al.*[14]. According to them a high acidity of the zeolite is not a sufficient condition for *n*-propyltoluene formation. Eventhough, H-mordenite is sufficiently acidic, it did not give any *n*-propyltoluene. Formation of *n*-propyltoluene occurs only within zeolites possessing three dimensional structural channels like HZSM-5 and HY. The geometrical arrangements of the channel arrangements in these zeolites, enable isopropyltoluene and toluene molecules to approach each other in the most convenient way for the formation of transition complex of bimolecular reaction. Since zeolite beta also possesses three dimensional structural channels like HZSM-5 and HY, *n*-propylbenzene can be formed during benzene isopropylation by structure-directed transition state selectivity between cumene and benzene.

The interesting observation is that on three times dealuminated zeolite there is no trace of *n*-propylbenzene formation. This can be attributed to decrease in number of acid sites and part of the structure collapse as evinced by decrease in relative XRD crystallinity and TPD of NH_3. The diisopropylbenzenes are formed due to the alkylation of cumene with isopropanol or disproportionation of cumene. The isopropyl group on the benzene ring activates only *para* and *ortho* positions for alkylation. However, the steric hindrance at the *ortho* position favours the formation of mostly *para*- diisopropylbenzene. The *meta* isomer is formed by the isomerization of *para* isomer. The change in *p/m* ratio of diisopropylbenzene over dealuminated beta zeolite can be attributed to the acidity of the zeolite. The isomerization of primarily formed *para* to *meta* isomer takes place to a lesser extent on lower acidic dealuminated zeolites.

Based on the above observations it can be concluded that with increase in cyclic dealumination of zeolite beta, benzene conversion to cumene decreased, while selectivity $i/(i+n)$ of propylbenzene reached 100%. The dealumination decreased the acid site density of the zeolite which was reflected by NH_3 TPD. XRD pattern indicated the loss of crystallinity on dealumination. The dealumination of zeolite beta can be used effectively to achieve a predesired product pattern of benzene alkylation with isopropanol.

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