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Fe-MFI zeolite catalyzed C_3 alkylation of benzene

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Benzene alkylation with isopropanol has been carried out over ZSM-5 and Fe-MFI zeolites. It was observed that Fe-MFI zeolite showed a better selectivity for cumene (isopropylbenzene) and $i/(i+n)$ propylbenzene ratio. This can be attributed to the acidity characteristic of the zeolite. The effects of variation in reaction conditions such as temperature, mole ratio of benzene/isopropanol and WHSV on the activity and selectivity of Fe-MFI are discussed.

Keywords: Fe-MFI; ZSM-5; C_3 alkylation; cumene; benzene

1. Introduction

Cumene is invariably used for the production of phenol, an important starting chemical for various processes. Conventionally, cumene is manufactured by using hazardous, harmful catalysts like $AlCl_3$, supported phosphoric acid, etc. Of late, cumene synthesis over zeolite catalysts has drawn the attention of researchers due to environmental restrictions. Very recently, Mobil alongwith Badger introduced a cumene technology based on a new zeolite that rivals the zeolite routes developed by Dow Chemical–Kellog [1]. The Mobil process uses a modified ZSM-5 zeolite, while the Dow process employs mordenite zeolite. The zeolite based process is eco-friendly, poses no problem of disposing off the spent catalyst, no acidic material contamination of the product, and no corrosion of the reactor and downstream units.

There have been many studies reported earlier dealing with the use of zeolites such as mordenite, Y, beta and ZSM-5 for cumene synthesis [2–6]. It was observed that on ZSM-5 in addition to cumene, undesirable *n*-propylbenzene is formed in non-negligible amount. Variation in acidity of the zeolite by changing its Si/Al ratio altered the proportion of *n*-propylbenzene in the product [3]. In other words, the product distribution depends on the acidity of the zeolite. The lower the acidity, the lesser is the extent of *n*-propylbenzene formation. It is a well known fact that

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MFI zeolite acidity can be altered by isomorphous substitution of Al with trivalent elements such as Ga, Fe and B. Hence, the present work was aimed at studying C_3 alkylation of benzene over a MFI zeolite of lower acidity, ferrisilicate. The influence of various reaction conditions on the distribution of cumene and *n*-propylbenzene in the product mixture is discussed.

2. Experimental

ZSM-5 and Fe-MFI zeolites used in the present study were synthesized in accordance with the reported literature [7]. The zeolites were characterized by XRD for phase purity, SEM for crystallite size and morphology, ESCA for elemental composition and TPD of ammonia for acidity. The ratio of SiO_2 to M_2O_3 was obtained by a combination of wet chemical analysis and atomic absorption spectrophotometry. The zeolite was converted to the active proton form by calcination, ion-exchange followed by another calcination. The catalytic runs were carried out in a fixed bed, down flow, glass reactor at atmospheric pressure. The mixture of reactants, benzene and isopropanol, was fed to a preheater, vaporized and contacted with the catalyst bed. Products of the reaction were condensed and collected at the reactor outlet and analysed in a Varian Vista 6000 gas chromatograph equipped with flame ionization detector and LB-550 capillary column.

3. Results and discussion

The characterization data obtained from different techniques are presented in table 1. It is quite indicative from this table that the two zeolites were of nearly equal SiO_2/M_2O_3 ratio, approximately the same size and morphology but of different acidity. The acidity pattern as obtained from TPD of ammonia is depicted in fig. 1. The TPD profile consists of a high and a low temperature peak corresponding to strong and weak acid sites. Both strong and weak acid sites are less in case of Fe-MFI zeolite.

Table 2 compares the results of the catalytic activity of ZSM-5 and Fe-MFI zeolite at the same reaction temperature and benzene/isopropanol mole ratio. To achieve nearly equal conversions of benzene, WHSV required is lower with Fe-

Table 1
Characterization data of ZSM-5 and Fe-MFI zeolites

Zeolite	Crystal size (μm)	Morphology	SiO_2/M_2O_3	Acidity (meq. ammonia/g)
ZSM-5	0.5–1.0	spheroidal	60	0.47
Fe-MFI	0.5–1.0	spheroidal	63	0.22

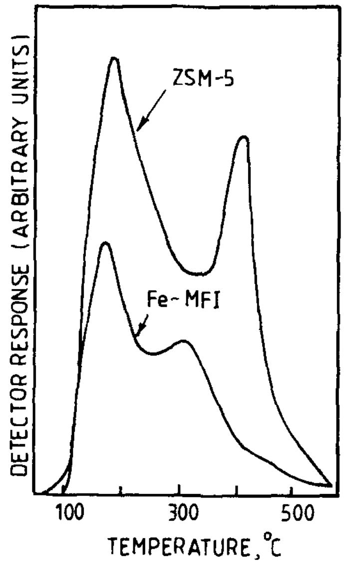

Fig. 1. Ammonia TPD of Fe-MFI and ZSM-5 zeolites.

MFI zeolite, which can be attributed to its lower acidity. Cumene (*i*-propylbenzene) selectivity and $i/(i+n)$ propylbenzene ratio were lower with ZSM-5 zeolite. In other words, *n*-propylbenzene, an isomer of cumene, is formed in lesser concentration on Fe-MFI.

The reactions of benzene isopropylation over zeolite catalyst are presented in

Table 2
Comparison of catalytic activity of ZSM-5 and Fe-MFI zeolites for benzene isopropylation[a]

Products (wt%)	Zeolite	
	ZSM-5[b]	Fe-MFI[c]
aliphatics	0.25	0.12
benzene	83.13	83.59
toluene + C_8 aromatics	1.32	0.80
cumene	13.24	14.81
n-propylbenzene	1.13	0.19
C_{10} aromatics	0.44	0.36
diisopropyl benzenes	0.49	0.13
performance (%)		
C_3 conversion	100.00	99.78
benzene conversion	16.53	16.09
cumene selectivity	80.05	92.05
$i/(i+n)$ propylbenzene ratio	92.13	98.73

[a] Temperature = 220°C, benzene/isopropanol mole ratio = 8.
[b] WHSV = $5.2\ h^{-1}$.
[c] WHSV = $2.6\ h^{-1}$.

fig. 2. The mechanism of *n*-propylbenzene formation on a MFI zeolite can be explained on a similar basis as *n*-propyltoluene formation during toluene isopropylation over ZSM-5 zeolite. The latter aspect has been covered by Wicherlova et al. [8] in their recent paper. They have proposed a mechanism in which *n*-propyltoluene is formed by a bimolecular reaction between toluene and isopropyltoluene. This is most likely caused by the geometrical arrangement of the channel intersections, enabling isopropyltoluene and toluene molecules to approach each other in the most convenient way for the transition complex. This phenomenon can be termed as structure directed transition state selectivity. Further *n*-propyltoluene formation is enhanced by the acid activity of the zeolites, controlled by the number and strength of acid sites. This is clearly reflected by the higher extent of *n*-propylbenzene formation on ZSM-5 of lower Si/Al ratio.

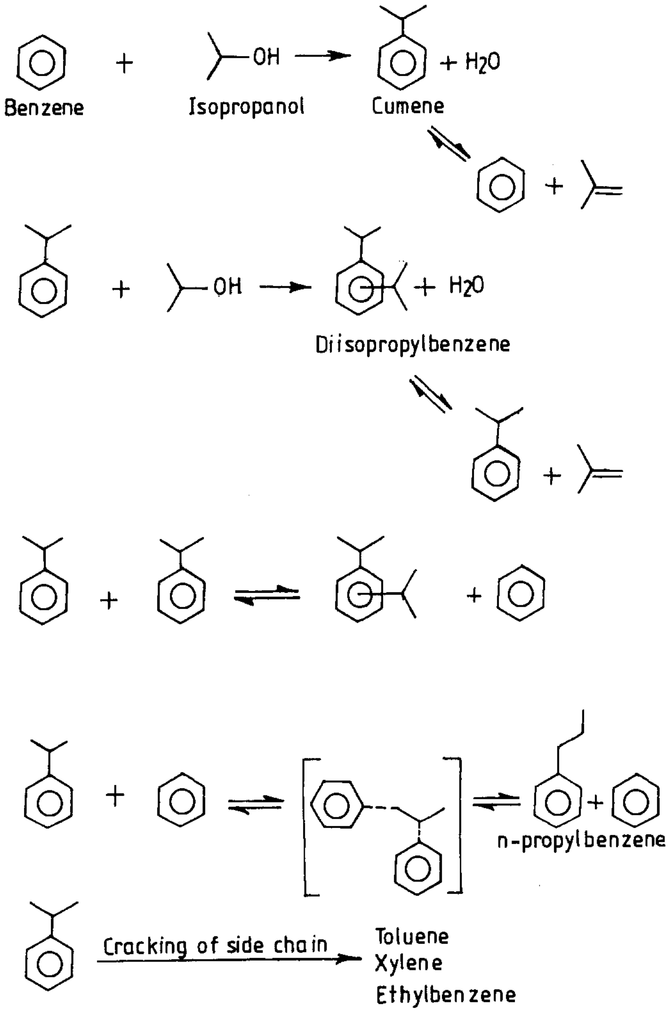

Fig. 2. Reactions of benzene isopropylation over a zeolite catalyst.

As cumene selectivity, as well as $i/(i+n)$ propylbenzene ratio, is higher with Fe-MFI zeolite, it will be interesting to see the effect of different reaction conditions on these performance parameters. The effects of variation in reaction temperature, benzene/isopropanol mole ratio and WHSV are summarized in the following paragraphs.

The effect of change in reaction temperature on the catalytic activity of Fe-MFI zeolite is presented in fig. 3. With increase in temperature from 180 to 240°C, cumene selectivity showed a maximum around 220°C, while the $i/(i+n)$ propylbenzene ratio decreased slightly at elevated temperature. This may be due to the fact that at elevated temperature cumene goes for dealkylation, cracking of side chain and formation of *n*-propylbenzene. Benzene conversion also exhibited a maximum around 220°C. The explanation for this is that at lower temperature alkylation activity increases with enhancement in reaction temperature, while at higher temperature benzene itself is formed from the dealkylation of the primary product of alkylation, cumene.

Fig. 4 reports the influence of the benzene/isopropanol mole ratio on the cumene selectivity and benzene conversion during alkylation. There is no significant effect of mole ratio variation on the $i/(i+n)$ propylbenzene ratio, while the cumene selectivity got enhanced with an increase in mole ratio from 4 to 12. This can be attributed to the fact that at higher mole ratio, isopropanol mostly goes for mono-alkylation, whereas at lower ratio it may go for di-alkylation as well as the formation of olefins. The benzene conversion goes through a maximum around mole ratio 8; this again can be ascribed to a considerable amount of propanol going to secondary reactions at lower mole ratios.

With change in WHSV from 1.75 to 8.6 h^{-1} there is an almost negligible change in $i/(i+n)$ propylbenzene ratio. However, both cumene selectivity as well as ben-

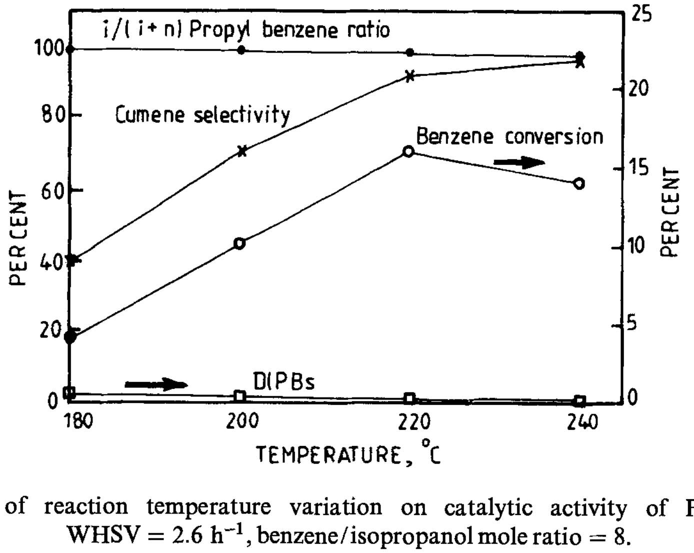

Fig. 3. Effect of reaction temperature variation on catalytic activity of Fe-MFI zeolite. WHSV = 2.6 h^{-1}, benzene/isopropanol mole ratio = 8.

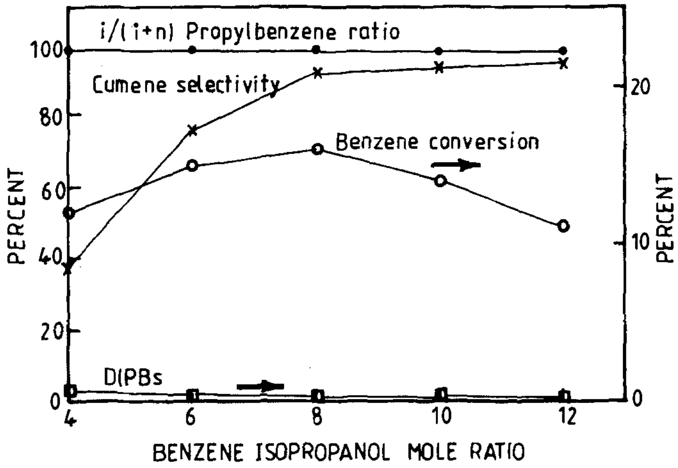

Fig. 4. Influence of benzene/isopropanol mole ratio on activity and selectivity of Fe-MFI zeolite. WHSV = 2.6 h^{-1}, temperature = 220°C.

zene conversion decreased due to lower contact time between catalyst and reactants at higher WHSV. The time on stream behaviour of the zeolite during alkylation is presented in fig. 5. There was a steady, stable and non-deactivating performance of the catalyst throughout the tested period of 19 h.

4. Conclusions

As compared to ZSM-5, Fe-MFI zeolite required a lower WHSV to achieve a similar benzene and isopropanol conversion at the same reaction temperature and

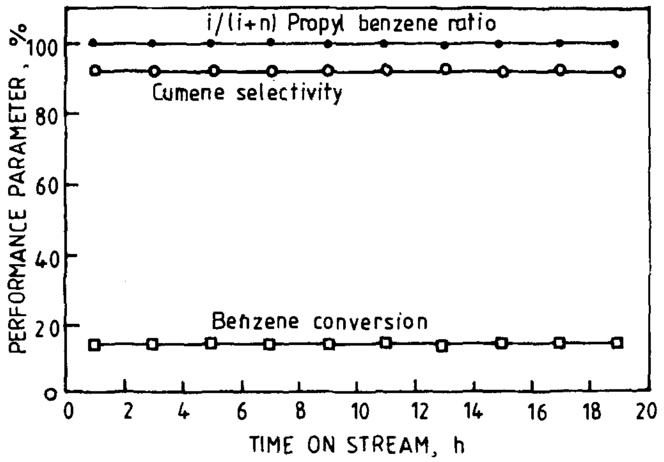

Fig. 5. Time on stream behaviour of the Fe-MFI during benzene alkylation with isopropanol. Temperature = 220°C, WHSV = 2.6 h^{-1}, benzene/isopropanol mole ratio = 8.

benzene/isopropanol mole ratio. Both the cumene selectivity and the $i/(i+n)$ propylbenzene ratio are higher with Fe-MFI zeolite. In other words undesired *n*-propylbenzene formation is lower on Fe-MFI. The selectivity for cumene showed a maximum around 220°C and $i/(i+n)$ propylbenzene ratio decreased slightly at temperatures above 220°C. There was no significant effect of mole ratio on $i/(i+n)$ propylbenzene ratio in the range 4–12, while cumene selectivity was highest at a mole ratio 12. The change in WHSV from 1.75 to 8.6 h^{-1} resulted in decrease in cumene selectivity and benzene conversion due to the decrease in contact time between the catalyst and the reactants. The alkylation activity of the Fe-MFI was steady stable, non-deactivating throughout the tested period of 19 h.

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