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Reactions of ethylbenzene in the presence of toluene over external surface passivated MFI zeolite

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The reactions of ethylbenzene in the presence of toluene were studied over external surface passivated MFI zeolite. With increase in extent of external surface passivation the para selectivity of both transalkylation and disproportionation reactions enhanced. The effects of mole ratio of ethylbenzene to toluene, reaction temperature and WHSV on the performance of the modified zeolite are discussed. It was observed that the high para selectivity feature of the modified zeolite is not influenced by changes in reaction conditions.

Keywords: Ethylbenzene; toluene; external surface passivation; MFI zeolite

1. Introduction

The dialkylbenzenes like para-xylene, para-diethylbenzene, and para-ethyltoluene are important starting materials for various commercial processes. These chemicals can be produced by direct alkylation of monoalkylbenzene with alcohol/olefins or by disproportionation and transalkylation of monoalkylbenzene. The latter method is in commercial practice for producing para-xylene [1,2]. In this context it is of great interest to study the reactions of alkylbenzene in the presence of other alkylbenzenes.

On MFI zeolite of smaller crystal size, the disproportionation and transalkylation of monoalkylbenzene produce dialkylbenzenes of near thermodynamic equilibrium composition. However, using modified MFI zeolite the product distribution can be directed to the selective formation of para-dialkylbenzenes. A proportion of para-xylene rather higher than that of the thermodynamic equilibrium value in the product mixture is reported by treatment of MFI zeolite with different agents by means of several procedures [3–5]. Olson and Hagg [1] proposed the mechanism of toluene disproportionation over modified MFI zeolite. According to them, toluene disproportionation inside the zeolite structure results in ben-

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zene and xylenes as initial products. These products diffuse out of the zeolite channel and simultaneously undergo isomerization giving the primary product. The proportion of para isomer in the primary product is higher than that of the thermodynamic equilibrium composition since the smaller kinetic diameter of paraxylene allows a faster diffusion than that of the other two isomers. The primary product undergoes secondary isomerization by re-entry into the channel network or over the acid sites located on the external surface, resulting in the secondary product observed in the reactor effluent. The zeolite modification prevents the isomerization on the external surface sites due to deposition or linkage of modifying agents and enhances the diffusivity difference between para and other isomers. The catalytic activity of the external surface sites plays a dominant role in deciding the isomer distribution, even though these sites constitute a very small percentage of total number of sites, since the intrinsic rate constant for isomerization is much higher than that for disproportionation.

Among the various modifying agents used for modifying the zeolite external surface, the chemical vapor deposition of tetraethyl orthosilicate has attracted a lot of attention of various researchers [6–8]. This technique involves blocking of nonselective external surface and pore mouth sites without altering the internal structure. In the present work, the reactions of ethylbenzene in the presence of toluene over external surface passivated MFI zeolite are reported. The effects of the extent of modification and reaction conditions on para product selectivity have been considered.

2. Experimental

MFI zeolite with Si/Al ratio = 80 was synthesized by hydrothermal technique under autogeneous pressure [9] using tetrapropyl ammonium bromide as the template. The crystallization was carried out at 443 K for 5 days. The product was filtered, and washed and dried in an oven at 383 K for 6 h. The characterization of the sample is based on XRD for MFI phase purity, FT-IR for pentasil structure, SEM for morphology and crystal size, MAS-NMR for Al incorporation into the framework (fig. 1), TPD of ammonia for acidity and chemical analysis for zeolite composition. The proton form of MFI zeolite was obtained by calcination of as-synthesized material at 813 K in air for 10 h followed by repeated ion-exchange with an aqueous solution of NH_4NO_3 and a further calcination at 773 K in air for 8 h.

Catalytic runs were carried out in a continuous down flow mode with a fixed bed reactor. The quantity of proton form or modified MFI zeolite was in the range of 1–3 g. The product analysis was done in a Varian Visa 6000 gas chromatograph equipped with flame ionization detector and a LB-550 capillary column. Analytical grade of ethylbenzene and toluene were used as feed and hydrogen was employed as a carrier gas.

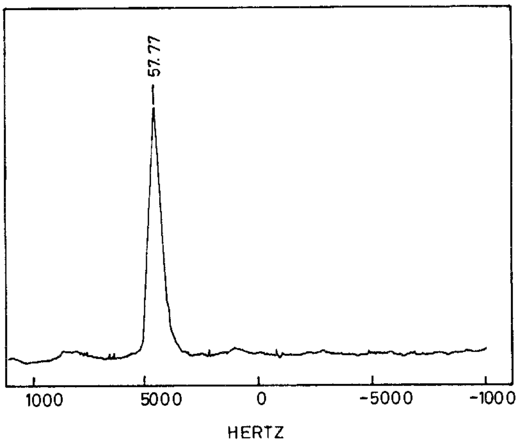

Fig. 1. ^{27}Al MAS-NMR spectrum of MFI zeolite.

The external surface passivation was achieved by chemical vapor deposition of tetraethyl orthosilicate in situ followed by calcination at 813 K for 8 h [7]. The extent of external surface site inactivation was monitored by a standard test reaction [8].

3. Results and discussion

3.1. ACTIVITY/SELECTIVITY OF MFI ZEOLITE

The product pattern of ethylbenzene conversion in the presence of toluene over MFI zeolite at three different WHSV is reported in table 1. An interesting observation when WHSV varied from 2.83 to 17 h^{-1} was that ethylbenzene conversion increased sharply with decrease in WHSV, while toluene conversion increased till 6.8 h^{-1} after that it showed a narrow increase at 2.83 h^{-1}. The formation of ethyltoluenes and xylenes increased with decrease in WHSV. Selectivities for para-dialkylbenzenes enhanced with increase in WHSV. From the product pattern it appears that the main reactions of ethylbenzene conversion in the presence of toluene are ethylbenzene disproportionation, toluene ethylation and toluene disproportionation.

3.2. PERFORMANCE OF EXTERNAL SURFACE PASSIVATED MFI ZEOLITE

The technique chosen for the external surface passivation was chemical vapor deposition of bulky molecule, tetraethyl orthosilicate, at 503 K followed by calcination at 813 K to decompose the alkoxy compound. As the molecular dimension of alkoxy compound is larger than that of MFI zeolite pore opening, on decomposi-

Table 1
Ethylbenzene conversion in presence of toluene over MFI zeolite at different WHSV [a]

Product composition (wt%)	WHSV (h^{-1})		
	2.83	6.8	17
benzene	18.94	11.06	5.56
toluene	38.40	37.25	41.69
ethylbenzene	21.45	35.24	44.33
xylenes	0.95	0.53	0.09
ethyltoluenes	14.05	10.40	4.85
diethylbenzenes	4.86	4.98	3.33
others	1.18	0.45	0.17
Performance			
% toluene conversion	19.21	18.11	8.87
% ethylbenzene conversion	59.04	35.41	18.13
% para-dialkylbenzene selectivity			
para-xylene	24.52	26.91	29.85
para-ethyltoluene	27.83	30.44	33.96
para-diethylbenzene	32.34	34.18	37.05

[a] Temperature = 623 K; ethylbenzene : toluene mole ratio = 1 : 1; $H_2/HC = 2$; others: lighters, cumene, unidentified aromatics.

tion the deposition of silica takes place on the external surface and pore mouth entrance. The initial deposition reaction involves hydroxyl groups located on the zeolite external surface, and of subsequent reaction between gaseous alkoxide and surface residue or between deposit molecules. This can be considered as a sort of polymerization accompanied by hydrolysis. The internal structure remains unaffected while only the pore opening size is reduced [10].

The results of ethylbenzene reaction in the presence of toluene over external surface passivated MFI zeolite is presented in table 2. With modification, the conversion of both ethylbenzene and toluene decreased, while selectivities for para-xylene, para-ethyltoluene and para-diethylbenzene enhanced. Due to space constraints inside the zeolite channel, transalkylation and disproportionation take place only at the para position, while ortho- and meta-alkylated products form only at the pore mouth entrance or on the external surface sites. The pore size regulation by silica deposition passivates the pore mouth and the external surface sites and the extent of formation of ortho and meta isomer is a function of extent of silica deposition. The higher the silica deposition, the lower is the formation of ortho and meta isomer. Hence the primary products of disproportionation and transalkylation are the para-dialkylbenzenes and their further isomerization is suppressed by the external surface passivation. Fig. 2 depicts the enhancement in para selectivity of dialkylbenzenes with progressive silylation of external surface.

It would be interesting to study the effect of mole ratio of the two reactants,

Table 2
Ethylbenzene conversion in presence of toluene over external surface passivated MFI zeolite [a]

Product composition (wt%)	Catalyst external surface passivated MFI zeolite
benzene	11.67
toluene	43.22
ethylbenzene	34.65
xylenes	0.32
ethyltoluenes	6.89
diethylbenzenes	2.95
others	0.32
Performance	
% toluene conversion	9.06
% ethylbenzene conversion	33.84
% para-dialkylbenzene selectivity	
para-xylene	90.12
para-ethyltoluene	98.23
para-diethylbenzene	99.51

[a] Temperature = 623 K; WHSV = 2.83 h^{-1}; H_2/HC = 2; ethylbenzene : toluene mole ratio = 1 : 1.

viz. ethylbenzene and toluene, on the observed product pattern over external surface passivated MFI zeolites. Table 3 summarizes the results of the runs in which ethylbenzene to toluene mole ratio was varied. In the absence of toluene, the

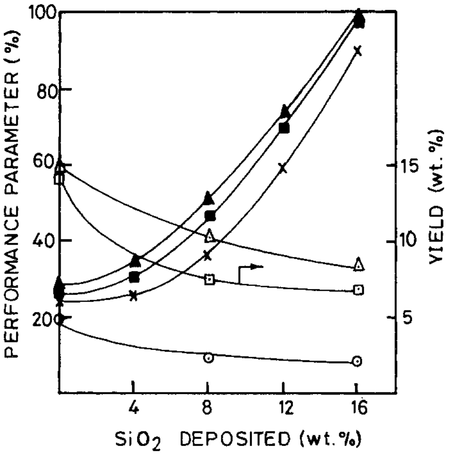

Fig. 2. Enhancement of para selectivity with progressive external surface passivation. Temperature = 623 K, WHSV = 2.87 h^{-1}, H_2/HC = 2, (○) toluene conversion, (△) ethylbenzene conversion, (×) para-xylene selectivity, (■) para-ethyltoluene selectivity, (▲) para-diethylbenzene selectivity, (□) ethyltoluene yield.

Table 3

Ethylbenzene conversion in presence of toluene in different molar composition over external surface passivated MFI zeolite[a]

Product composition (wt%)	Ethylbenzene : toluene molar ratio				
	1 : 0	1 : 1	1 : 4	1 : 8	0 : 1
benzene	15.15	11.67	6.91	4.85	0.75
toluene	1.71	43.22	74.14	83.29	97.51
ethylbenzene	71.52	34.65	11.65	6.03	0.03
xylenes	0.18	0.32	1.38	1.50	1.08
ethyltoluenes	0.08	6.89	5.27	4.02	0.56
diethylbenzenes	9.33	2.95	0.51	0.17	–
others	2.04	0.32	0.11	0.14	–
Performance					
% toluene conversion	–	9.06	6.34	6.14	2.49
% ethylbenzene conversion	28.48	33.84	44.09	46.45	–
% para-dialkylbenzene selectivity					
para-xylene	–	90.12	90.96	91.98	92.80
para-ethyltoluene	–	98.23	98.16	98.06	–
para-diethylbenzene	99.20	99.51	99.43	99.50	–

[a] Temperature = 623 K; WHSV = 2.83 h^{-1}; $H_2/HC = 2$.

observed main products are benzene and para-diethylbenzene. The selectivity of para-diethylbenzene was as high as 99%. While in the absence of ethylbenzene, the main products are benzene and xylenes. The selectivity of para-xylene was of the order of 93%. However, in the presence of both ethylbenzene and toluene in the feed the major product formed para-ethyltoluene. The other products formed in appreciable quantities were benzene, diethylbenzene and xylenes. As the mole ratio of ethylbenzene to toluene was varied from 1 : 1 to 1 : 8 in the feed, formation of benzene, ethyltoluene and diethylbenzene decreased and percentage of xylenes in the product went up. The various reactions occurring are presented in fig. 3.

The influence of temperature variation on the reactant conversion as well as product selectivities are shown in fig. 4. With raise in temperature from 573 to 648 K, ethylbenzene conversion increased while toluene conversion went through a maximum. It is important to note here that with increase in reaction temperature, ethyltoluene and diethylbenzene formation went through a maximum. This type of product distribution clearly revealed that toluene mainly goes for ethyltoluene formation and transalkylation of the ethyl group from ethylbenzene to toluene takes place through dealkylation and realkylation [11]. The extent of dealkylation proportionately increased with rise in temperature, while the extent of toluene or ethylbenzene realkylation decreased. However, high para selectivity was maintained at all the temperatures studied.

The results of WHSV variation on conversion and selectivities are depicted in fig. 5. With change in WHSV from 1.78 to 6.5 h^{-1}, the contact time between the cat-

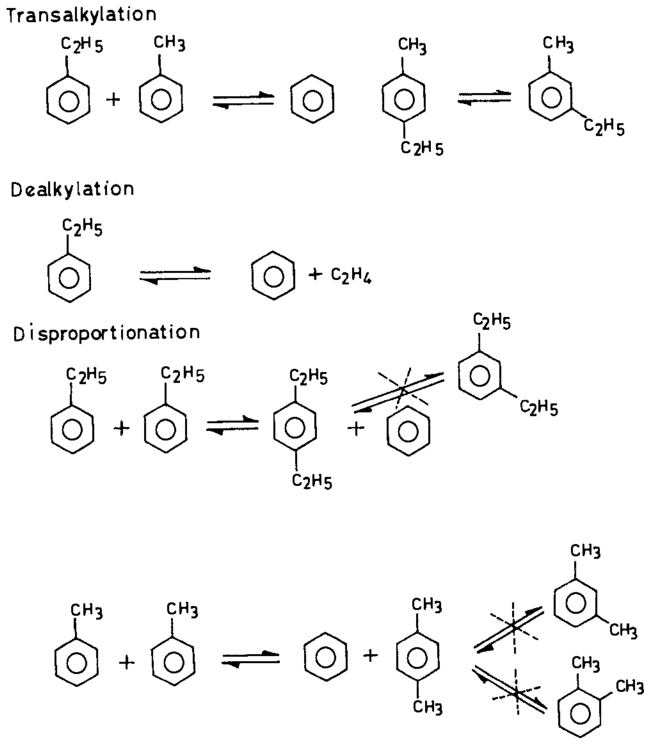

Fig. 3. Reactions of ethylbenzene in presence of toluene over external surface passivated MFI zeolite.

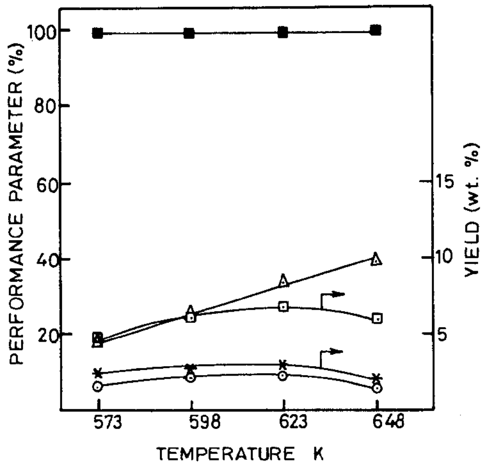

Fig. 4. The influence of reaction temperature on the performance of external surface passivated MFI zeolite for ethylbenzene conversion in presence of toluene. WHSV = 2.87 h^{-1}, $H_2/HC = 2$, (○) toluene conversion, (△) ethylbenzene conversion, (■) para-ethyltoluene selectivity, (□) ethyltoluene yield, (✻) diethylbenzene yield.

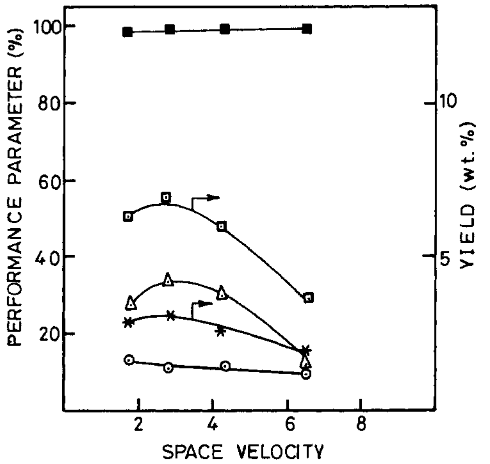

Fig. 5. The effects of WHSV variation on ethylbenzene conversion in the presence of toluene over external surface passivated MFI zeolite. Temperature = 623 K, H_2/HC = 2, (○) toluene conversion, (△) ethylbenzene conversion, (■) para-ethyltoluene selectivity, (□) ethyltoluene yield, (✳) diethylbenzene yield.

alyst and the reactants decreased. More than the conversion of toluene, ethylbenzene conversion got affected by WHSV variation. With decrease in WHSV from 6.5 to 1.78 h^{-1}, ethylbenzene conversion increased upto about 2.8 h^{-1}; after that it decreased. This may be attributed to dealkylation of both diethylbenzene and ethyltoluene at higher contact time which was reflected by the decreased formation of ethyltoluene and diethylbenzene. There was no effect of contact time on the high para selectivity feature of modified MFI zeolite.

4. Conclusions

The reactions of ethylbenzene in the presence of toluene over MFI zeolite are mainly transalkylation, disproportionation and dealkylation. The external surface passivation by silica deposition enhances the para selectivity in both transalkylation and disproportionation reactions. As the mole ratio of ethylbenzene to toluene in the feed changes from 1 : 1 to 1 : 8, the formation of benzene, diethylbenzene and ethyltoluene decreases and the percentage of xylenes in the product goes up. With enhancement in reaction temperature from 573 to 648 K the extent of dealkylation proportionately increases, while the extent of realkylation to either ethylbenzene or toluene decreases. However, a high para selectivity is maintained at all the temperatures. With decrease in WHSV from 6.5 to 1.78 h^{-1} ethylbenzene conversion increased upto about 2.8 h^{-1}, after that at 1.78 h^{-1} it decreased. This may be attributed to dealkylation of both ethyltoluene and diethylbenzene at higher contact time. There is no effect of contact time on high para selectivity feature of modified MFI zeolite.

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