

Selectivity Enhancement in Xylene Isomerization over NiHZSM5

Para- and *ortho*-xylenes are obtained from C₈ aromatic streams (from naphtha reformate or pyrolysis gasoline) containing a mixture of ethylbenzene and the three xylene isomers by isomerization (of *meta*-xylene) and hydroisomerization (of ethylbenzene) reactions. Bifunctional catalysts containing hydrogenation (metals like Pt and Ni) and acidic (SiO₂-Al₂O₃, mordenite, HZSM5) functions are commonly used (1). In addition to the main desirable reactions (isomerization and hydroisomerization) certain, undesirable, side reactions also occur which lower the selectivity of the catalyst to yield *para*- and *ortho*-xylenes. These are dealkylation (of ethylbenzene and xylenes to yield benzene and toluene, respectively) and disproportionation (of ethylbenzene and xylenes). The net result of these two side reactions is that C₈ aromatics (ethylbenzene and xylenes) are converted into C₆, C₇, C₉, and C₁₀ aromatics. It is the purpose of this paper to demonstrate the feasibility of suppressing the loss of C₈ aromatics and enhancing the yield of *para*- and *ortho*-xylenes by selectively poisoning (with NH₃) the acid sites responsible for the dealkylation and disproportionation reactions.

A NiHZSM5 catalyst (0.3 wt% Ni, SiO₂/Al₂O₃ = 35), prepared as described earlier (2), was used. The composition of the feedstock containing the C₈ aromatic hydrocarbons is shown in Table 1. The reactions were carried out in a "Catatest" reactor (Model B, Geomecanique, France). Pure, dry, H₂ (IOL, Bombay) and anhydrous NH₃ (RCF, Bombay) were used. The catalyst

(30 g, 1.6 mm extrudates) was first activated in dry air at 723 K for 4 hr and then reduced in H₂ at 723 K for 8 hr prior to the reaction. The products were analyzed by gas chromatography (Hewlett-Packard Model 5840 A) using bentone-34-diisodecyl phthalate column (2 m). The reproducibility of the data was about ±0.3%. Material balance checks indicated values better than 98-99% (wt). Anhydrous NH₃ (1 ml (NTP)/g catalyst) was injected into the H₂ stream after the catalyst had been operating continuously for more than 100 hr yielding the product pattern shown in Table 1 (columns A). After the injection of NH₃, the system attained a steady state within a couple of hours and remained steady thereafter for about 50 hr. The steady-state product pattern after the injection of NH₃ is shown under columns B in Table 1.

As may be seen from Table 1, NH₃ injection reduces the loss of C₈ aromatics from 7.8 to 4.6% (wt) under the usual operating conditions (633 K, 16 bars, WHSV = 3, and H₂/hydrocarbon = 6). A similar effect is also observed at atmospheric pressure and 685 K. At a pressure of 16 bar, the concentrations of *para*- and *ortho*-xylenes in the catalysate are not significantly affected by poisoning with NH₃, while that of *meta*-xylene and ethylbenzene are increased. On the other hand, *m*-xylene is not increased even after NH₃ injection at 685 K and atmospheric pressure. Whereas at high pressure the C₈ aromatics loss is due to both the dealkylation and disproportionation reactions, the latter reaction is not significant at atmospheric pressure. The dealkylation of

TABLE I
Influence of Ammonia on Selectivity in Xylene
Isomerization

	Temperature, K	633	685		
	Pressure, bar	16	1		
	H ₂ /HC	6	6		
	WHSV	3	3		
Product composition, wt%	Feed	A ^a	B ^a	A	B
C ₈ aliphatics	6.1	4.1	4.6	3.2	3.5
Benzene	1.4	5.3	3.9	6.6	5.7
Toluene	1.6	4.2	2.8	3.5	2.7
Ethylbenzene	19.3	10.4	12.8	5.8	7.5
<i>para</i> -Xylene	12.9	17.4	17.6	18.7	18.8
<i>meta</i> -Xylene	54.4	38.8	39.5	43.7	43.4
<i>ortho</i> -Xylene	4.3	16.5	16.4	17.5	17.5
C ₉ + C ₁₀ aromatics		3.3	2.4	1.0	0.9
C ₈ aromatic loss		7.8	4.6	5.2	3.7

^a A and B refer to the product distribution before and after ammonia injection, respectively.

ethylbenzene to benzene is the main cause of the loss of C₈ aromatics at atmospheric pressure. This is also supported by the higher concentration of benzene in the catalysate in atmospheric pressure runs. By suppressing the dealkylation of ethylbenzene NH₃ injection increases the concentration of ethylbenzene in the catalysate but hardly affects that of the xylenes. There is also a simultaneous decrease in the concentration of benzene, toluene, and (C₉ + C₁₀) aromatics indicating the selective poisoning of the dealkylation and disproportionation reactions by adsorbed NH₃. The C₉ aromatics in the product consisted mainly of ethyltoluenes and trimethylbenzenes while diethylbenzene constituted the C₁₀ aromatic fraction. An additional feature of Table I is that while the C₈ aromatic loss in the atmospheric pressure run is due mainly to dealkylation of ethylbenzene to benzene (685 K, pressure = 1 bar), significant amounts of C₉ and C₁₀ aromatics are formed via disproportionation reactions at higher pressures. Ad-

sorption of NH₃ poisons both disproportionation and dealkylation reactions (columns B, Table I).

Figure 1 illustrates the selectivity of HZSM5, NiHZSM5, and Pt/NiHZSM5 for the disproportionation reaction. Pt/NiHZSM5 was prepared from NiHZSM5 by impregnation with aqueous chloroplatinic acid. At any given isomerization level, the concentrations of the disproportionation products differ on the various catalysts (Fig. 1). This behavior is similar to that observed in the case of mordenite catalysts (6), where it was shown that different acid sites are required for the isomerization and disproportionation reactions, respectively. It is possible that a similar phenomenon prevails in the present case also. While steric, shape-selective effects undoubtedly play a major role in the observed higher selectivity for isomerization vs disproportionation reactions of *o*-xylene over ZSM5 zeolites, the role of acid sites in such phenomena should also be recognized. The selective poisoning of the dealkylation reaction by NH₃ without any modifications in xylene conversion levels further supports the above picture especially since NH₃ is not expected to change the shape selectivity of the zeolite.

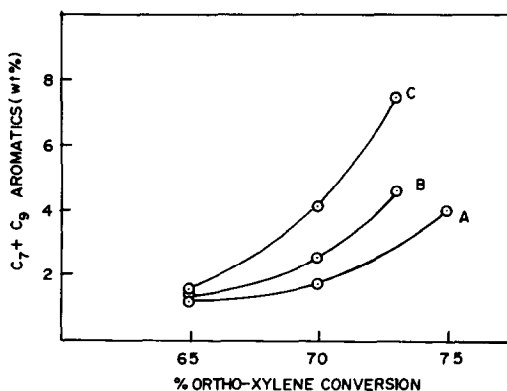


FIG. 1. Selectivity to disproportionation as a function of *o*-xylene conversion. Catalysts A, B, and C refer to HZSM5, NiHZSM5, and Pt/NiHZSM5, respectively. WHSV = 10.0, H₂/*o*-xylene = 2, pressure = atmospheric, and temperature = 623–823 K.

Earlier studies (3, 4) of the surface acidity of these ZSM5 zeolites using temperature-programmed desorption (TPD) of NH_3 had revealed that NH_3 can be held in, at least, four different chemisorption states, which show desorption maxima at 400–450, 500–550, 600–610, and 750–800 K. Topsoe *et al.* (4), using both TPD and ir spectroscopy, had postulated that the acidic sites responsible for the TPD peak at 750–800 K are strong Brønsted acid sites (ir band at 3600 cm^{-1}) and are probably located at channel intersections in the pore system of the ZSM5 zeolites. In the present study, poisoning by NH_3 has been carried out at 630–685 K (Table 1). At these temperatures, only those acid sites responsible for the TPD maxima at 750–800 K will still retain NH_3 . Now, on mordenite-based catalysts, the disproportionation of xylene occurs only on relatively strong acid sites (5). Since, in the present case, the presence of adsorbed NH_3 selectively suppresses the disproportionation reaction, it is probable that the same strong acid sites which retain adsorbed NH_3 up to 800 K are active for xylene disproportionation over NiZSM5 also. Since the bimolecular disproportionation reactions, due to steric restrictions, is more likely to occur at the channel intersections, than in the channels themselves, the selective poisoning (with NH_3) of the strong acid sites located at channel intersections

suppresses the formation of C_7 and C_9 aromatics by disproportionation reactions and hence prevent the loss of C_8 aromatics. The net yield of *para*- and *ortho*-xylenes after ultimate recycle of unreacted C_8 aromatics, will, hence, be increased.

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