Catalysis Letters 23 (1994) 161–168

Transalkylation and disproportionation of toluene and C_9 aromatics over zeolite beta

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Received 14 May 1993; accepted 30 August 1993

Transalkylation and disproportionation (TADP) of toluene and C_9 aromatics from a commercial stream have been studied over a zeolite possessing a three-dimensional, 12-membered ring pore system. The study encompassed the effect of C_9 aromatics content in feed on TADP. Formation of xylenes was maximum with a feed containing 50 : 50 toluene and C_9 aromatics. In order to understand the role of different C_9 aromatics in TADP, experiments using individual C_9 aromatics with and without toluene mixture as feed were carried out. An interesting observation of these experiments was that ethyltoluenes produced xylenes through disproportionation of toluene generated from their deethylation. The total yield of xylenes was much less than that obtained from trimethyl benzenes. A reaction scheme accounting all the reactions taking place during TADP is proposed.

Keywords: Transalkylation; disproportionation; toluene; C_9 aromatics; xylenes; zeolite beta

1. Introduction

Benzene and xylenes are important starting materials for various processes like production of synthetic fibers, plasticizers and resins. The commercial sources for these materials are: (i) naphtha reformate, and (ii) pyrolysis gasoline. In these processes in addition to xylenes substantial quantities of C_7 and C_9 aromatics are produced. Increasing global demand for xylenes and intention to upgrade low value C_7 and C_9 aromatics to valuable C_8 aromatics have led to the development of processes like toluene disproportionation by Mobil Oil Corporation which uses ZSM-5 based catalyst. Another way of enriching xylene production is by mixing toluene with C_9 aromatics and transalkylating over a suitable catalyst [1]. Although toluene disproportionation is well reported in the open literature [2–10], most of the information on transalkylation and disproportionation (TADP) are in the patent form [11–18]. All the TADP processes employ either silica–alumina or mordenite incorporated with noble metal catalysts.

In recent years, a lot of interest is being generated on zeolite beta, the catalytic aspects of this zeolite are not fully explored. Zeolite beta is a high silica, large pore zeolite which possesses a three-dimensional, 12-membered ring pore system [19–21]. Cracking of paraffins, isomerization of meta-xylene and methylation of toluene over zeolite beta are reported [23–25]. Cumene disproportionation on beta zeolite and its stability enhancement by silica deposition and steam pretreatment has been studied by Tsai et al. [26] and Wang et al. [27]. Disproportionation of toluene and 1,2,4- and 1,3,5-trimethylbenzenes and their transalkylations over zeolite beta are also reported [28]. In the present paper our objective was to study systematically the transformation of C_7 and C_9 aromatic feeds obtained from a commercial stream over zeolite beta. In other words, the work was aimed at exploring the potentiality of zeolite beta for transalkylation and disproportionation of C_7 and C_9 aromatic stream.

2. Experimental

Beta zeolite was synthesized hydrothermally from the system $(TEA)_2O$–SiO_2–Al_2O_3–Na_2O–H_2O following the patented procedure [19]. Mordenite and ZSM-5 zeolites used in these studies are commercial samples. It was characterized by XRD for phase purity, SEM for morphology, TPD of ammonia for acidity and the chemical composition was determined by a combination of wet chemical and atomic absorption methods. The XRD pattern matched with that reported earlier. The crystals were of spheroidal shape and size was about 0.4–0.6 μm. Si/Al ratio of the zeolite was estimated to be around 30. In all the catalytic runs the proton form of beta zeolite was employed. The as-synthesized zeolite was calcined at 450°C and then repeatedly ion exchanged with 1 M ammonium nitrate solution. Another calcination again at 450°C converted the ammonium zeolite to its proton form.

Reaction runs were conducted in a continuous fixed bed reactor system. The zeolite powder was pelletized, crushed and sieved to 12–18 mesh particles. 1–2 g of zeolite was used in the catalytic experiments. C_7 and C_9 aromatics feeds were prepared by mixing appropriate quantities of toluene, and commercial C_9 stream obtained from naphtha reformate. The hydrocarbon feed was vaporized in a preheater before it is contacted with the catalyst bed maintained at the desired reaction temperature. Ultra high purity hydrogen gas was used as a carrier gas. The products coming out of the reactor were condensed in a chilled water circulated condenser and analyzed in a Varian Vista 6000 gas chromatograph. The gas chromatograph was equipped with flame ionization detector and 5% Bentone + 5% DIDP on a Chromosorb W column.

3. Results and discussion

Results of transalkylation and disproportionation of toluene and C_9 aromatics (50 : 50 composition) over the three zeolites are shown in fig. 1 in terms of xylenes

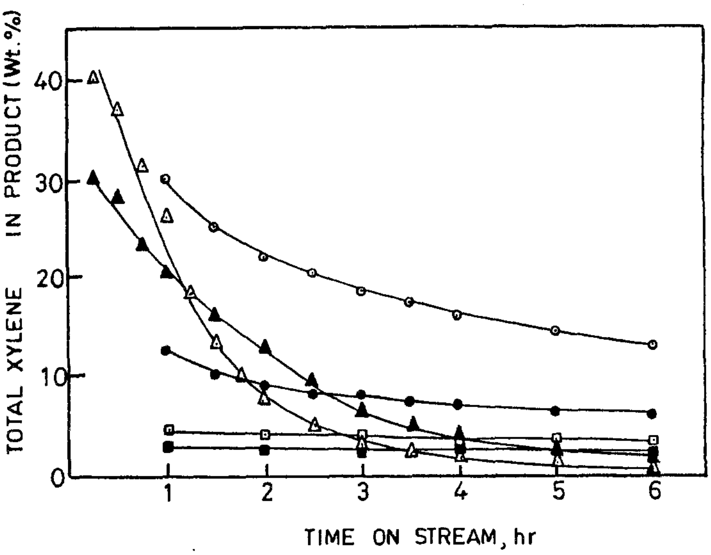

Fig. 1. Time on stream behaviour of beta, mordenite and ZSM-5 for xylene formation. Beta: (●) TDP, (○) TADP; mordenite: (▲) TDP, (△) TADP; ZSM-5: (■) TDP, (□) TADP.

formation versus time on stream plot. The composition of C_9 aromatics used in the study is reported in 9th column of table 2. The xylenes formation using pure toluene as feed is also included in the figure. The profiles are of similar trend for both disproportionation and transalkylation, however there is a quantum jump in xylenes formation with all the three zeolites during transalkylation. Further the extent of xylenes formation on the three zeolites showed the order ZSM-5 < mordenite < beta.

The time on stream behavior of the zeolites ZSM-5, mordenite and beta for toluene disproportionation (TDP) and transalkylation and disproportionation of C_7 and C_9 aromatics as well as extent of xylenes formation can be rationalized on the basis of their Si/Al ratio, channel dimensions and pore structure. The characterization data of the zeolites is summarized in table 1. ZSM-5 has got a three-dimensional 10-ring pore system consisting of two types of channels of dimensions 5.3 × 5.6 Å and 5.1 × 5.5 Å. This system can sorb molecules like toluene, xylenes but not bulkier 1,3,5-trimethylbenzenes. Hence transalkylation of toluene and trimethylbenzenes and disproportionation of trimethylbenzenes do not occur inside

Table 1
Characterization data of zeolites used for transalkylation and disproportionation

Zeolite	Si/Al ratio	Crystallite size (μm)	Morphology	Acidity (meq. NH_3 adsorbed)
ZSM-5	40	0.5–1.0	spheroidal	0.42
mordenite	15	0.3–0.7	spheroidal	0.56
beta	30	0.2–0.5	spheroidal	0.49

the channels and can take place on the external surface sites. Due to this, the amount of xylene formation in case of TADP is only marginally higher than that of TDP on ZSM-5. On the other hand, mordenite possesses 12-ring pore openings with unidimensional channels. The pore dimensions are of the order 6.5 × 7.0 Å which can sorb trimethylbenzenes, hence xylenes formation is more during TADP. However, because of its unidimensional nature it deactivates fast with time on stream. The difference in xylene formation during TADP and TDP was highest on zeolite beta which can be attributed to its three interconnecting 12-ring pore systems. The pore openings in the linear channels are approximately 5.7 × 7.5 Å. The tortuous channel system is formed by the intersections of the two linear channel systems each of approximately 5.6 × 6.5 Å. Due to this advantage further work was carried out on zeolite beta.

The effect of feed compositions (C_7 to C_9 aromatics stream ratio) for TADP on zeolite beta is presented in table 2. With addition of C_9 aromatics to toluene in the feed both xylenes formation and toluene conversion showed a maximum around 50 : 50 toluene and C_9 aromatics composition. C_9 aromatics conversion decreased continuously which indicates that disproportionation of trimethylbenzenes becomes the dominant reaction at higher C_9 aromatic content in the feed, transalkylation of toluene and trimethylbenzenes takes place to a maximum extent at nearly the same proportion of C_7 and C_9 aromatics in the feed, while at higher toluene concentration in the feed mainly its disproportionation occurs. Stoichio-

Table 2
Effect of feed composition on TADP over zeolite beta. (Temperature = 400°C, WHSV = 3.6 h^{-1}, $H_2/HC = 4$)

Components (wt%)	Feed	Prod.	Feed	Prod.	Feed	Prod.	Feed	Prod.	Feed	Prod.
benzene		4.43	–	2.16	–	1.30	–	1.00	–	0.76
toluene	100	87.11	74.40	64.31	50.27	40.81	24.33	23.08	–	4.76
EB		0.16	0.09	1.65	0.08	2.55	0.03	2.85	–	2.83
xylenes		7.82		16.94		18.49		14.33		10.75
cumene		–	0.50	0.07	0.95	0.21	1.47	0.21	0.04	0.35
p-ET		0.03	1.50	1.15	2.90	2.47	4.58	3.15	2.00	3.86
m-ET		0.09	2.89	2.40	5.65	4.98	8.98	6.92	6.10	8.62
o-ET		0.04	1.74	0.62	3.39	1.28	5.38	1.82	11.89	2.30
1,3,5-TMB		0.11	2.65	2.61	5.24	6.67	7.97	10.22	7.06	14.16
1,2,4-TMB		0.21	12.05	6.31	23.62	14.96	35.30	23.90	10.73	33.22
1,2,3-TMB		–	3.69	1.10	7.01	2.81	10.57	4.87	46.03	7.58
C_{10} A		–	0.41	0.62	0.79	4.06	1.33	7.77	14.28	10.67
% tol. conv.		12.89		13.56		18.82		5.14		–
%C_9 A conv.		–		43.01		32.36		31.10		28.54
xylene comp.										
p-X		24.55		24.56		24.77		24.77		21.95
m-X		53.07		52.48		51.81		51.29		49.30
o-X		22.39		22.96		23.42		23.94		28.75

metrically one molecule of toluene reacts with one molecule of trimethylbenzene during transalkylation to give two molecules of xylene, whereas in disproportionation two molecules of either C_7 or C_9 react to yield only one molecule of xylene. Due to this, maximum xylenes are produced with a feed containing nearly same proportions of toluene.

Another interesting observation was that the composition of xylenes formed during TADP changed with the feed composition. When the feed constituted 100% C_9 aromatics, the xylenes fraction in the product contained a higher amount of ortho-xylene than that of the thermodynamic equilibrium value (table 1). Hence we turned to study the behavior of individual C_9 aromatic compounds over zeolite beta under identical reaction conditions. The results of such experiments using three trimethylbenzene isomers and three ethyltoluene isomers are presented in table 3. It is quite clear from this table that in addition to disproportionation, isomerization of C_9 aromatics take place. All the three trimethylbenzenes produced xylenes through disproportionation and the xylene fraction contained ortho-xylene higher than the thermodynamic equilibrium composition. The composition of ortho-xylene in xylenes was very high at lower conversion and lower temperature for all the trimethylbenzenes. This leads to the conclusion that ortho-xylene is the primary product of disproportionation of trimethylbenzenes.

Ethyltoluenes, on the other hand, produced xylenes through disproportionation of toluene generated from their deethylation. This is evident from (i) formation of a substantial quantity of toluene (from deethylation of ethylbenzene) and (ii) pres-

Table 3
Transformations of individual C_9 aromatics over zeolite beta. (Temperature = 400°C, WHSV = 3.6 h^{-1}, $H_2/HC = 4$)

Products (wt%)	Feed					
	o-ET	*m*-ET	*p*-ET	1,3,5-TMB	1,2,4-TMB	1,2,3-TMB
benzene	0.20	0.32	0.27	0.03	0.04	0.20
toluene	10.86	13.40	13.78	1.85	1.49	1.41
EB	2.89	3.79	4.04	0.0	0.01	0.16
xylenes	1.74	3.02	2.83	18.39	17.79	3.01
p-ET	17.03	18.08	18.56	0.01	0.12	0.06
m-ET	39.97	36.60	37.70	0.04	0.37	0.05
o-ET	15.83	10.41	9.60	0.01	0.12	0.06
1,3,5-TMB	0.08	0.09	0.08	14.10	14.79	14.44
1,2,4-TMB	0.16	0.26	0.20	32.26	34.55	56.20
1,2,3-TMB	0.92	1.36	1.32	4.90	5.25	17.26
C_{10} A	10.24	12.67	11.53	28.35	25.45	7.15
%C_9 A conv.	84.17	63.40	81.44	85.90	65.45	82.74
xylene comp.						
p-X	26.44	26.12	26.50	23.22	21.58	20.60
m-X	47.70	49.01	48.76	52.20	48.85	46.84
o-X	25.86	24.83	24.74	24.58	29.57	32.56

ence of ethylbenzene in the product stream which can be formed by ethylation of ethyl group or ethylene (from deethylation of ethyltoluene) with benzene. As a result the total yield of xylenes was much less than that obtained from trimethylbenzenes. The other reaction of ethyltoluene was isomerization to other isomers.

In order to understand the mechanism of transformation of C_7 and C_9 aromatics over zeolite beta, transalkylations of toluene with individual trimethylbenzene and ethyltoluene isomers were carried out. The results of experimental runs with nearly equal proportions of toluene and C_9 aromatic compound are summarized in table 4. In each case of toluene–trimethylbenzene an increased amount of xylenes were obtained compared to that with either pure toluene or trimethylbenzene. Toluene–ethyltoluene mixture also produced greater quantity of xylenes than pure ethyltoluene. The maximum yield of xylenes was obtained from toluene–1,3,5-trimethylbenzene and yield was least with toluene–ethyltoluenes.

Based on the above observations a reaction scheme for the transalkylation and disproportionation of C_7 and C_9 aromatics over zeolite beta is proposed as shown in fig. 2.

4. Conclusion

Among the three zeolites studied for transalkylation and disproportionation of C_7 and C_9 aromatics zeolite beta gave highest yield of xylenes at steady state condi-

Table 4
TADP of nearly equal proportion toluene and C_9 aromatics over zeolite beta. (Temperature = 400°C, WHSV = 3.6 h^{-1}, $H_2/HC = 4$)

Components (wt%)	Feed	Prod.	Feed	Prod.	Feed	Prod.	Feed	Prod.
benzene		1.12	–	0.84	–	0.51	–	0.79
toluene	48.49	33.36	49.55	32.27	60.24	55.88	49.27	46.95
EB		0.06		0.05		0.16		3.47
xylenes		30.57		27.33		6.15		4.61
p-ET		0.03		0.04		0.13		7.99
m-ET		0.11		0.08		0.22		17.45
o-ET		0.14		0.05		0.18	50.73	5.25
1,3,5-TMB	51.51	7.93		7.52		8.42		0.68
1,2,4-TMB		18.33	50.45	17.79		21.39		1.64
1,2,3-TMB		3.24		3.22	39.76	3.69		0.70
C_{10} A		5.11		10.81		3.27		10.47
%tol. conv.		31.20		34.87		7.24		4.71
%C_9 conv.		87.36		64.74		90.72		89.65
xylene comp.								
p-X		24.96		25.06		27.32		27.11
m-X		51.62		51.56		48.62		50.33
o-X		23.42		23.38		24.06		22.56

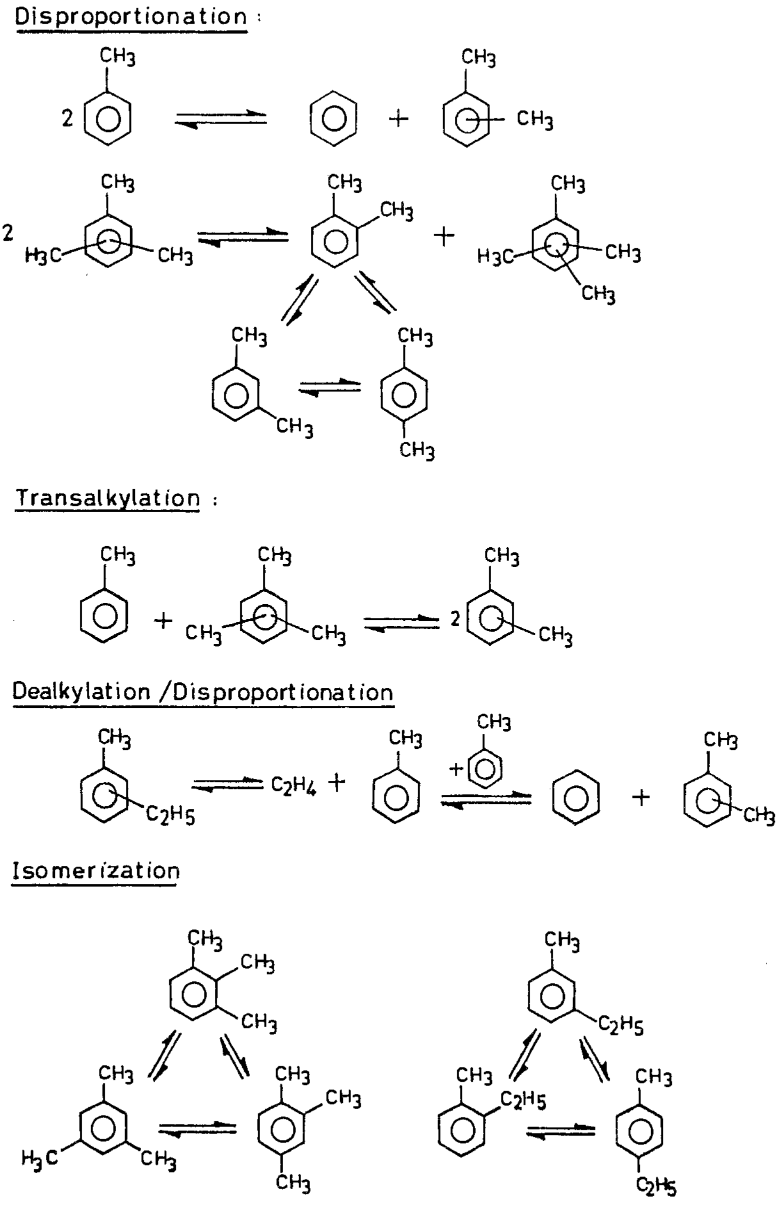

Fig. 2. Reaction scheme.

tions. On this zeolite xylene formation showed a maximum around 50 : 50 toluene and C_9 composition. When the feed constituted 100% C_9 aromatics, the xylenes fraction in the product contained a higher amount of ortho-xylene than the thermodynamic equilibrium composition. Ethyltoluenes produced xylenes through disproportionation of toluene generated from their deethylation. As a result the total yield of xylenes was much less than that obtained from trimethylbenzenes. Among C_9 aromatics 1,3,5-trimethylbenzene in combination with toluene produced highest xylenes.

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