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Ethylation of Toluene and Transformation of *p*-Ethyltoluene on H-ZSM-5 and ZSM-5 Modified with MgO

Shape-selective properties of medium pore size zeolites like ZSM-5 are well known (*1, 2*). For the conversion of alkyl aromatics, the paraselectivity is of great interest. It was found (*3*) that in toluene ethylation on ZSM-5, *p*-ethyltoluene is the primary product. Isomerization to *m*-ethyltoluene and transalkylation and disproportionation of toluene and ethyltoluene may result in a complex reaction mixture. Modification of ZSM-5, e.g., with different phosphorous and magnesium compounds or by coke deposition, leads to the increase in selectivity in the formation of *p*-ethyltoluene (*2, 3*).

Ethylation of toluene and expected side reactions, such as transformation of toluene and *p*-ethyltoluene, were studied in this work on unmodified H-ZSM-5 and ZSM-5 modified by MgO inclusion.

Toluene and ethylene were industrial products of 99.99% and polymerization grade purity, respectively. *p*-Ethyltoluene was distilled from product obtained in our earlier toluene ethylation experiments; it contained 2.8% *m*-ethyltoluene and 0.2% *p*-xylene as impurities. The nitrogen used was high-purity grade.

ZSM-5 as synthesized powder (Si/Al = 40) was heated in air at a rate of 50 K/h to 873 K, calcined at this temperature for 4 h, and then transformed to NH_4^+ form by ion exchange with a 1 *N* aqueous solution of $NH_4(CH_3CO_2)$ (60 g zeolite in 1 dm^3 solution for 24 h). Wet samples were admixed with an amount of $Mg(NO_3)_2 \cdot 6H_2O$ and $Mg(CH_3CO_2)_2 \cdot 4H_2O$ (2 : 1 molar ratio) calculated to give 0, 4, 8, 12% MgO in the final product. After drying at 105°C, samples were pressed into pellets without binder, crushed, sieved, heated in oxygen flow at a rate of 50 K/h to 973 K, and calcined at this temperature for 4 h.

Catalytic experiments were carried out in a fixed-bed downflow reactor made of quartz. Before reaction, the catalyst was flushed with oxygen at 773 K overnight and then cooled to the reaction temperature (673 K) in nitrogen flow. Nitrogen also served as a diluent: toluene or *p*-ethyltoluene was fed continuously by micropump into the stream of nitrogen or in the case of ethylation into a mixture of ethylene and nitrogen. The procedure is described in more detail elsewhere (*3*).

Reaction conditions were usually as follows: 1.5 g of catalyst, atmospheric pressure, reaction temperature 673 K; 1/1 mole ratio of aromatic hydrocarbon/nitrogen, or 5/1/5 mole ratio of toluene/ethylene/nitrogen and WHSV = 2.0 $g_{aromatic}/g_{cat.}$ h. The yield of products is defined as

$$Y(\%) = (\text{moles of product/moles of aromatic fed}) \times 100.$$

After certain catalytic experiments the reactor was purged with nitrogen at 763 K for 2 h. The hot catalyst was poured into vials and closed for further studies. The carbon content of the coke was determined by burning in oxygen and measuring the amount of CO_2.

The yield of products in the ethylation of toluene on catalysts containing 0 and 12% MgO at different times on stream (TOS) can be seen in Table 1. On unmodified H-ZSM-5, the yield of ethyltoluenes increases, but the yield of other aromatics decreases with

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TABLE 1

Yield of Products in Ethylation of Toluene (%, mol/mol T)

TOS (h):	MgO content of catalyst							
	0				12%			
	2	6	30	50	2	6	30	50
B	2.01	1.29	0.55	0.40	0.24	0.08	0.04	0.03
EB	0.39	0.32	0.21	0.16	0.11	0.07	0.03	0.02
PX	0.58	0.44	0.24	0.18	0.19	0.11	0.04	0.02
MX	0.90	0.60	0.25	0.16	0.02	0	0	0
OX	0.37	0.24	0.10	0.06	0	0	0	0
PET	1.96	2.41	3.03	3.22	5.48	5.61	3.78	2.73
MET	3.95	4.53	4.62	4.31	0.13	0.10	0.04	0.02
OET	0.05	0.02	0.01	0	0	0	0	0
TMB	0.05	0.04	0.02	0	0	0	0	0
DEB	0.12	0.12	0.08	0.07	0.06	0.05	0.02	0.02
Carbon content (%/wt/wt)	n.d.	2.9	4.2	4.5	n.d.	1.5	3.6	5.1
ET	5.96	6.96	7.66	7.53	5.61	5.71	3.82	2.75
oA	4.42	3.05	1.46	1.05	0.62	0.31	0.13	0.11

Note. $T_r = 673$ K, $T/C_2H_4/N_2 = 5/1/5$, WHSV = $2.0\, g_T/g_{cat.}$ h. Abbreviations used: B, benzene; T, toluene; X, xylene; EB, ethylbenzene; DEB, diethylbenzene; ET, ethyltoluene; TMB, trimethylbenzene; oA, other aromatics (Σ aromatic products except ethyltoluenes).

TOS. There is a rapid coke deposition in the first few hours of the process, and then the coke formation slows down.

On catalyst containing 12% MgO, the yield of other aromatics is very low, even initially, and decreases further with TOS. Coke deposition increases continuously with TOS. The yield of ethyltoluenes remains constant in the first 6 h and then, like other aromatics, decreases with TOS.

The correlation between the increase in the coke content of the catalysts and the decrease in the yield of other aromatics is quite obvious. All reactions, leading to the given product mixture, proceed on Brønsted acid sites (*3*). In the course of reaction, these sites are partially poisoned or blocked by coke. It is not clear, however, why the yield of ethyltoluenes increases with increasing coke content on unmodified catalyst. In order to shed some light on this question, experiments with different amounts of catalyst, consequently containing different numbers of active sites, were carried out. The product distribution obtained at 6 h on stream is plotted in Fig. 1. At low "space times" (reciprocal space velocity) *p*- and *m*-ethyltoluene are the sole products. With increasing space time, the yields of *p*- and *m*-ethyltoluene go through maxima. The maximum yield of ethyltoluenes is approximately 17%. If only the ethylation–deethylation is considered, the calculated "partial" thermodynamic equilibrium concentration of ethyltoluene is 18.8% (*4*). At approximately 0.3–0.4 h $g_{cat.}/g_T$ space time the yield of ethyltoluenes reached the thermodynamically possible maximum.

The yields of other aromatics, which are represented in Fig. 1b by the yields of benzene and xylenes, increase continuously with increasing space time. For comparison, the yields of benzene and xylenes formed from toluene alone, under otherwise identical conditions, are also shown. Yields of toluene disproportionation products are lower than the yields of benzene and xylenes in the toluene ethylation mixture. This shows that during toluene ethylation, toluene is not the only source of benzene and xylenes.

Norval and Phillips (*5*) reported a calculated "final" equilibrium product distribution of the toluene–ethylene system. At 700 K, atmospheric pressure, and toluene/ethylene/inert gas mole ratio of 5/1/5, the equilibrium yield of ethyltoluenes (including *o*-isomer) is only 3.8%, while the yields of benzene and xylenes are 17.6 and 28.6%, respectively. It follows that in the range of higher space times, the system proceeds from the partial equilibrium condition reached for toluene ethylation to the final equilibrium condition: the yield of ethyltoluene decreases and the yields of other aromatics increase.

This hypothesis is supported by the results collected in Table 2. The reaction of PET/T mixture was carried out on unmodified H-ZSM-5 under conditions identical to those of the reaction of C_2H_4/T. The close resemblance of the results obtained in the two reactions at relatively high space time is fascinating. For comparison, the thermo-

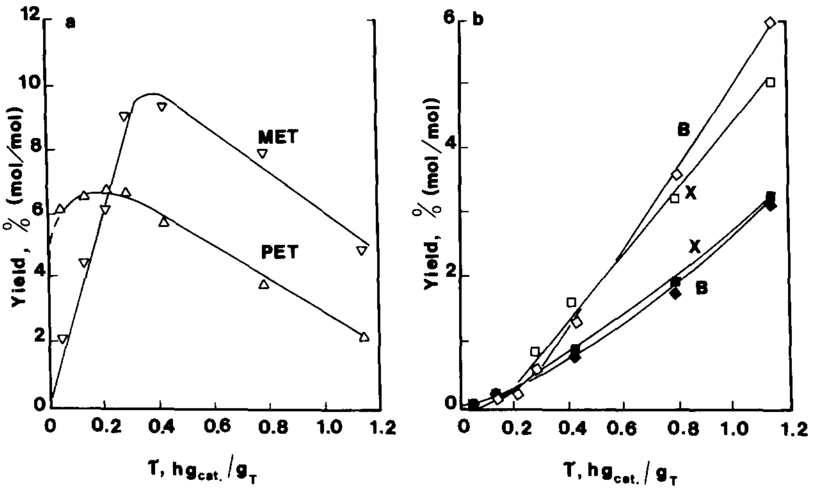

FIG. 1. (a) Yield of *p*- and *m*-ethyltoluene in toluene ethylation. (b) Yield of benzene (◇ ◆) and xylenes (□ ■) in toluene ethylation (◇ □) and in toluene disproportion (◆ ■) as a function of space time; catalyst with 0% MgO. T_r = 673 K, T/C_2H_4/N_2 = 5/1/5, or T/N = 1/1, time on stream, 6 h.

dynamic equilibrium composition of the ethylene–toluene system, calculated for identical conditions by Norval and Phillips (*5*), is shown in Table 2.

Considering the above sequence of ideas, we can now explain the increase in ethyltoluene yield with increasing coke content on unmodified catalyst. Over fresh catalyst, the toluene–ethylene system is presumably in the range between partial and final equi-

TABLE 2

Composition of Reaction Mixtures at 4 h on Stream in Conversion of T/C_2H_4/N_2 = 5/1/5 and T/PET/N_2 = 5/1/5 on Unmodified H-ZSM-5 (%, mol)

Feed	T/C_2H_4/N_2	T/PET/N_2[a]	Thermodynamic equilibrium[b]
B	2.69	2.60	17.6
T	81.49	84.97	39.8
EB	0.94	0.71	2.6
PX	0.76	0.72	6.7
MX	1.28	1.30	14.9
OX	0.57	0.55	7.0
PET	3.66	2.56	1.2
MET	7.72	5.92	1.9
OET	0.30	0.32	0.7
TMB	0.13	0.13	7.6
DEB	0.44	0.22	n.c.

Note. T_r = 673 K, WHSV = 1.0 $g_{aromatic}/g_{cat.}$ h.

[a] Feed contains 2.8% MET and 0.2% PX.

[b] From Ref. (*5*) at 700 K, atmospheric pressure, T/C_2H_4/inert gas = 5/1/5.

TABLE 3

Composition of Reaction Mixtures at 4 h on Stream in Conversion *p*-ethyltoluene on Catalysts with Different MgO Content[a] (%, mol)

	MgO content of catalyst			
	0	4%	8%	12%
B	0.14	0.04	0	0
T	18.04	14.80	6.16	5.59
EB	0.74	0.22	0.12	0.12
PX	0.51	0.34	0.22	0.20
MX	0.23	0.06	0.02	0.02
OX	0.09	0.03	0	0
PET	54.51	67.84	88.40	90.27
MET	24.95	16.26	4.74	3.42
OET	0	0	0	0
TMB	0.15	0.08	0.06	0.04
DEB	0.61	0.33	0.18	0.15

Note. T_r = 673K, PET/N_2 = 1/1, WHSV = 2.0 $g_{PET}/g_{cat.}$ h.

[a] Feed contains 2.8% MET and 0.2% PX.

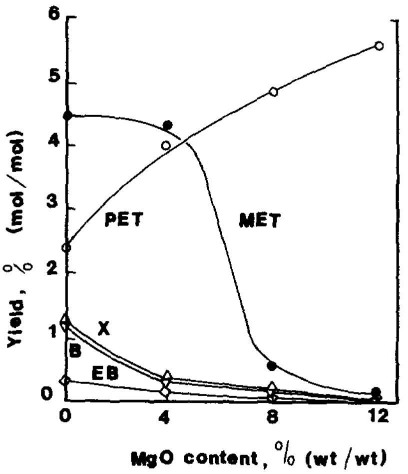

FIG. 2. Yield of products in toluene ethylation at 6 h on stream as a function of the MgO content of the catalyst. T_r = 673 K, T/C_2H_4/N_2 = 5/1/5, WHSV = 2.0 $g_T/g_{cat.}$ h.

librium. Owing to coke deposition, the number of available active sites, and hence the *effective* space time (if unpoisoned, unblocked active sites are considered only), decreases; the system moves toward partial equilibrium (Fig. 1), which involves a decrease in other aromatics and an increase in ethyltoluene yields.

On catalyst containing 12% MgO, the ethylene–toluene system, under the given experimental conditions, is presumably in the range before partial equilibrium. Therefore, according to Fig. 1, with decreasing available active sites (due to deposition of coke) the yields of both ethyltoluenes and other aromatics decrease.

Transformation of *p*-ethyltoluene on catalysts with different MgO content was carried out (Table 3). The dominant products are *m*-ethyltoluene and toluene, i.e., products of isomerization and deethylation. Isomerization decreases continuously with increasing MgO content and it is sufficiently low on catalysts with 8 and 12% MgO. Deethylation of *p*-ethyltoluene decreases also with increasing MgO content, but remains significant even over catalysts with higher MgO content.

Results obtained at 6 h on flow in ethylation of toluene over catalysts with different MgO content are plotted in Fig. 2. The yield of *p*-ethyltoluene, like that due to increasing coke deposition on the catalyst, increases with increasing MgO content. Even 4% MgO significantly suppresses the formation of other aromatics. Paraselectivity, however, is high enough on those catalysts only when isomerization activity is low.

A low concentration of MgO in ZSM-5 results in a deceleration of disproportionation and consequently in an increase in ethylation selectivity; a higher concentration of MgO suppresses isomerization as well, thereby increasing the paraselectivity.

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