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NOTE

Transformation of Some Light Mono- and Dialkylbenzenes on H-ZSM-5

The catalytic alkylation of toluene with small olefins is of great industrial importance. Medium pore-size zeolites such as ZSM-5 are active in alkylation and also effect the transformation of alkyl aromatic hydrocarbons, favoring the formation of the *para*-substituted derivatives (1–4). In zeolites, where intracrystalline pore dimensions approach molecular dimensions, the mass transport proceeds in the regime of the so-called "configurational diffusion" (5). In ZSM-5 the diffusivities of aromatic molecules decreases systematically with the increasing effective minimum dimension of the molecules (6). Shape selectivity is governed by the diffusivity of the aromatic molecules inside the zeolite crystals, consequently it decreases with decreasing crystal size and vice versa (4, 7, 8).

In ethylation of toluene on unmodified microcrystalline H-ZSM-5, a complex product mixture containing benzene, xylenes, ethylbenzene, traces of trimethyl- and diethylbenzenes was obtained (1, 2). In this work the expected side reactions of toluene ethylation, as transformations of toluene (T), *p*-ethyltoluene (PET), ethylbenzene (EB), and xylenes (X) were studied on the same H-ZSM-5 under the conditions of ethylation in order to shed some light on the mechanism directing the formation of the product mixture.

In about the first 24 h of the ethylation process of toluene, the yields of aromatics formed via transalkylation decreased rapidly, while the yield of alkylation products increased with the time on stream (TOS) (2). The transient behavior was explained by the partial deactivation of the catalyst due to accumulation of coke deposits. For the same reason, the selectivity also changes with TOS in the reactions of alkylaromatics. This is illustrated by the variation of yields as a function of TOS in the transformation of *p*-ethyltoluene (Fig. 1). It is obvious that the rate of coke formation, and consequently the rate of catalyst deactivation, is different when different reactants are used. In principle, results obtained by extrapolation to zero TOS would be appropriate for the fair comparison of catalyst activities in different reactions. The extrapolation, however, can be carried out with significant error only. In the present work product selectivities were determined from the samples collected in the second hour of the TOS. These data are considered as representative on the inherent catalytic properties in the various reactions.

The Na-ZSM-5 as-synthesized powder was a preparation of the Hungarian Hydrocarbon Institute. The starting material was heated in air at a rate of 50 K/h to 873 K and calcined at this temperature for 4 h. This sample was transformed into the NH_4^+ form by ion exchange with a 1 *N* solution of NH_4 (CH_3CO_2) (60 g zeolite in 1 dm^3 solution for 24 h). After drying at 378 K, the sample was pressed into pellets without binder, crushed, and sieved. Analogously to the procedure used and described in our previous works (1, 2), an aliquot of 0.35–1.50 mm fraction was heated in oxygen flow at a rate of 50 K/h to 973 K and calcined at this temperature for 4 h. X-ray diffraction measurements showed that ZSM-5 was the only crystalline phase present.

The average crystal size determined by electron microscopy was in the range of 1–1.5 μm. The framework Al content calculated from ^{29}Si-MASNMR data was 3.2 $\times 10^{20}$ atom/g (Si/Al = 31). No extralattice Al was found by ^{27}Al-MASNMR. The pore volume of zeolite available for N_2 and *p*-xylene adsorption are 0.17 and 0.1 cm^3/g (2.7×10^{20} molec./g), respectively. Flow gravimetric experiment showed the chemisorption of 1.25×10^{20} molec. pyridine/g at 523 K. IR spectra of pyridine adsorbed at different temperatures (Fig. 2) indicated the presence of both Brønsted (absorption band at 1545 cm^{-1}) and Lewis (absorption band at 1454 cm^{-1}) acid sites. Although no extralattice Al was found by ^{27}Al-NMR, the existence of absorbance band at 1454 cm^{-1} in IR spectra of adsorbed pyridine strongly suggests that some dealumination may have occurred during heat treatment.

Catalytic reactions were carried out at atmospheric pressure in a fixed-bed down-flow reactor made of quartz. The method was described in more detail elsewhere (2). First the reactor with the catalyst was flushed with oxygen at 773 K overnight, then cooled to the reaction temperature (673 K) in a nitrogen flow. Nitrogen served also as diluent; aromatic hydrocarbons were fed continuously by a micropump into the stream of nitrogen (hydrocarbon/N_2 = 1/1 mol/mol). The effluents were cooled to 290 K. The liquid condensed was collected and

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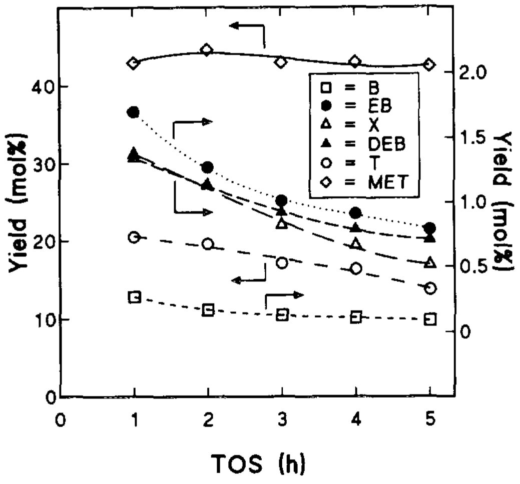


FIG. 1. Yield of products in transformation of *p*-ethyltoluene as a function of TOS; T_r = 673 K and WHSV = 5 $g/g_{cat.} \cdot h$.

analyzed from time to time by gas chromatography. In some cases the gases exiting the condenser were also analyzed.

Reactions of toluene (T), *p*-ethyltoluene (PET), *p*-ethyltoluene/toluene (PET/T), and *p*-ethyltoluene/benzene (PET/B) mixtures (15/85 mol/mol) were studied (Table 1, columns 1–4). The conversion of toluene was significantly lower than the conversion of ethyltoluene. Only disproportionation of toluene was observed; benzene and xylenes formed in equimolar quantities.

In transformation of PET, besides the facile isomerization, toluene formation by deethylation (reserve process for toluene ethylation) was the dominant reaction. Ethylene and about two orders of magnitude less methane were found in the gas phase. In the absence of hydrogen, demethylation could not proceed. Some hydrogen must be generated, for instance, in the process of coke formation (2). Much more ethylbenzene was found in the product than expected on the basis of methane formation, substantiating that routes alternative to demethylation are also operative in the ethylbenzene formation, e.g., transmethylation between ethyltoluene and primary formed toluene.

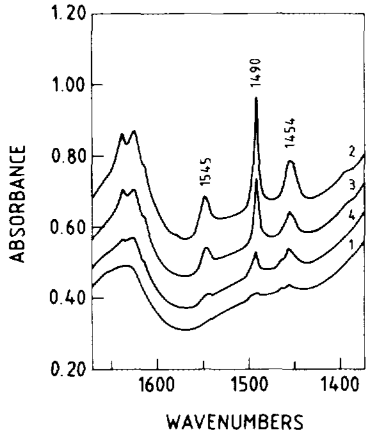


FIG. 2. IR spectra of H-ZSM-5 (1), and pyridine chemisorbed on H-ZSM-5 after adsorption at 300 K followed by evacuation at 573 K (2), 673 K (3), and 773 K (4) for 1 h.

TABLE 1

Composition of Reaction Mixtures in Conversion of Toluene, *p*-Ethyltoluene, and Binary Aromatic Mixtures (mol%)[a]

Feed	T	PET	PET/T[b]	PET/B[b]	EB/T[b]	MX/B[b]
B	0.32	0.33	0.27	76.00	3.67	84.65
T	99.38	25.19	86.66	10.42	81.80	0.45
EB	0	1.21	0.25	8.08	11.27	0.02
PX	0.19	0.87	0.16	0.04	[c]	2.29
MX	0.09	0.44	0.12	0.06	0.07	11.44
OX	0.03	0.18	0.04	0	0	1.15
Σx	0.31	1.49	0.32	0.10	[c]	14.88
PET		45.06	6.06	1.96	1.56	
MET		25.66	6.35	3.06	1.30	
OET		0	0	0	0	
ΣET		70.72	12.41	5.02	2.86	
TMB		0.17	0.02	0.02	0	0
PDEB		0.50	0.04	0.20	0.15	
MDEB		0.35	0.03	0.13	0.10	
ΣDEB		0.85	0.07	0.33	0.25	
ΔT	0.72					
ΔX						0.47
ΔEB					3.74	
ΔET		29.28	2.34	10.32		
PET/ΣET		0.64	0.49	0.39	0.55	
PX/ΣX	0.61	0.58	0.50	0.40		0.15
PDEB/ΣDEB		0.59	0.57	0.61	0.60	

[a] T_r = 673 K, Feed/N_2 = 1/1, WHSV = 10$g/g_{cat.} \cdot h$, values at 2 h on stream. B, benzene; T, toluene; EB, ethylbenzene; PX, MX, and OX: *p*-, *m*-, and *o*-xylene; PET, MET, and OET: *p*-, *m*-, and *o*-ethyltoluene; TMB, trimethylbenzenes; PDEB and MDEB, *p*- and *m*-diethylbenzene

[b] 15/85 mol/mol.

[c] Peaks of PX were partly covered in the chromatograms by broad EB peaks.

The yield of products from ethyltoluene is plotted in Fig. 3 as a function of conversion. The experiments were carried out at different space velocities by keeping the feed rate constant and varying the amount of catalyst. Data suggest that toluene is an unstable primary product and that benzene and trimethylbenzenes are secondary products. Xylenes, ethylbenzene, and diethylbenzenes, however, were formed in the superposition of primary and secondary processes. Side-chain demethylation of ethyltoluene (see later toluene formation in transformation of ethylbenzene) may produce a fraction of xylenes. The secondary formation of xylenes, ethylbenzene, and

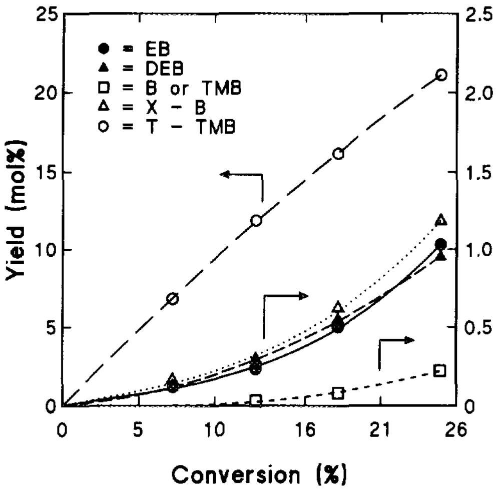
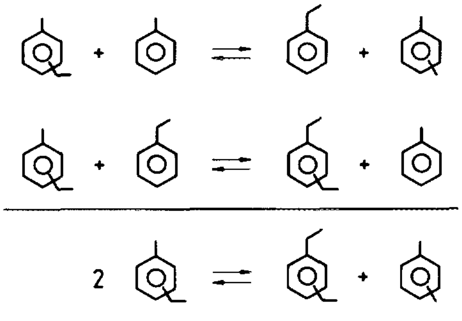


FIG. 3. Yield of products in transformation of *p*-ethyltoluene as a function of conversion; T_r = 673 K.

diethylbenzene can be described by a series of transalkylation reactions:


[1]

[2]

[3]

The conversion of ethyltoluene in the presence of benzene was significantly higher, under identical conditions, than that in the presence of toluene (Table 1, columns 3 and 4), indicating that toluene suppresses deethylation, the reverse process of toluene ethylation. The amount of toluene formed in the presence of benzene was close to the amount of ethyltoluene reacted. Transethylation between ethyltoluene and benzene forming ethylbenzene was the main reaction.

The favored formation of *para*-isomers and the absence of *o*-ethyltoluene and *o*-diethylbenzene in the product indicate that shape-selective reactions were effected.

Experiments with ethylbenzene/toluene (EB/T) and *m*-xylene/benzene (MX/B) (15/85 mol/mol) were carried out (Table 1, columns 5 and 6) in order to obtain more information about transalkylation. The conversion, under identical conditions, decreases in the sequence of PET (in benzene) > EB (in toluene) > MX (in benzene). Transethylation between both EB alone (diethylbenzene formation) and EB–T (formation of benzene and ethyltoluene) were recognized. Transmethylation of MX (formation of trimethylbenzene and toluene) was not detected, but transmethylation between MX and B (formation of toluene) was observed. Within the ZSM-5 pores, the formation of trisubstituted benzene derivatives was less favored than the formation of dialkylbenzenes.

According to Santilli (8) the ZSM-5 catalyzed transalkylation of alkyl aromatics proceeds via subsequent dealkylation and alkylation steps. The alkyl group is released first as a carbenium ion and is added then to another aromatic molecule. Xylenes transalkylate much more slowly than ethylbenzene since less stable carbenium ions are formed from methyl groups than from ethyl groups.

As observed in the experiments with ethylbenzene and xylene (see above), the rate of transethylation between ethyltoluene–benzene and transmethylation between ethyltoluene–toluene was also different. The transethylation (formation of ethylbenzene and diethylbenzenes in PET/B mixture; Table 1, column 4) is much faster than transmethylation (in PET/T mixture, the greater fraction of xylene must be formed in the transmethylation—disproportionation—of toluene; Table 1, column 3).

Experiments with ethylbenzene/toluene (EB/T) (Fig. 4) and ethylbenzene/*m*-xylene (EB/MX) (Fig. 5) mixtures of different concentration were carried out. In toluene, a linear correlation was found between the conversion (ΔEB) and the initial concentration of ethylbenzene. The toluene is competing with the ethylbenzene for accepting the ethyl group, therefore the yield of ethyltoluene and the conversion of toluene (ΔT) passes through maximum at about 50% as a function of concentration. The transalkylation between two ethylbenzene molecules (yield of diethylbenzene) increases with EB concentration continuously. The difference between the conversion of toluene and the yield of ethyltoluene indicates that a small amount of toluene was consumed in transmethylation (disproportionation).

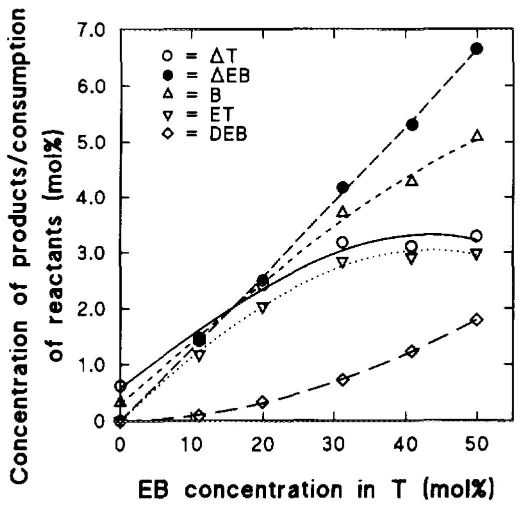


FIG. 4. Concentration of products and conversion of reactants (ΔT, ΔEB) in the reaction of toluene/ethylbenzene mixtures of different concentrations; T_r = 673 K.

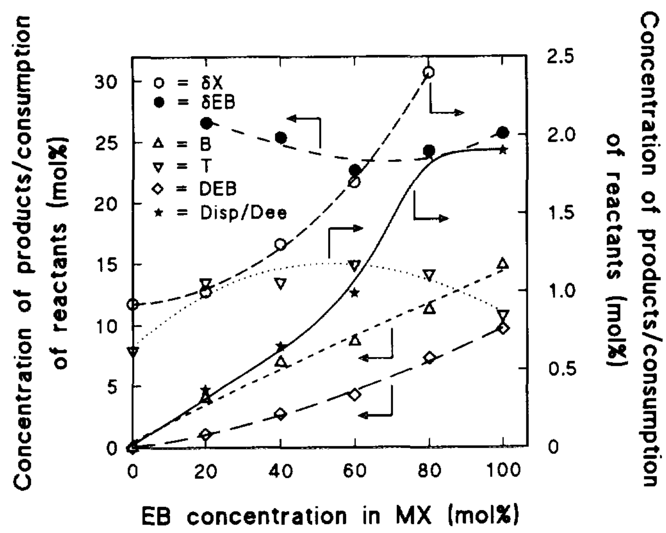


FIG. 5. Concentration of products and relative conversion (δX, δEB) of reactants (see text) in the reaction of *m*-xylene/ethylbenzene mixtures of different concentrations; T_r = 673 K.

In pure ethylbenzene, deethylation (the formation of benzene in excess to diethylbenzene) and side-chain demethylation (the formation of toluene) was observed besides transethylation (the formation of diethylbenzene) (Fig. 5, 100% EB). In *m*-xylene, a linear correlation was established between the yield of benzene and the initial concentration of EB, and an almost linear correlation between the yield of diethylbenzene and the EB concentration. Relative conversions (δX, δEB) were calculated as the ratio of the observed conversions (ΔX, ΔEB) to the initial concentrations of MX and EB, respectively. The rate of ethylbenzene conversion is much higher than the rate of xylene conversion. The relative conversion of EB is almost independent of the concentration, while the relative conversion of MX increased continuously with increasing EB concentration. From this, it follows that the rate of reaction between xylene and ethylbenzene is higher than that between two xylene molecules.

In transalkylation between ethylbenzene and *m*-xylene, dimethylethylbenzene and much less ethyltoluene (besides benzene and toluene) were the expected primary products, but this was not found. Santilli (8) described a similar experiment. A 50/50 mixture of ethylbenzene/xylene mixture was reacted on ZSM-5. The ratio of diethylbenzene to dimethylethylbenzene was found to be a function of crystallite size. It varied from 1.5 to about 100, while crystallite size changed in the 0.02–40 μm range. This phenomenon can be explained as follows.

In the *m*-xylene/ethylbenzene mixture the ethyl group detached from an EB molecule can be added either to another EB or to a X molecule. The dimethylethylbenzene is held in the ZSM-5 pores significantly longer than diethylbenzene due to diffusional differences. This allows to dimethylethylbenzene to undergo secondary transalkylation reactions resulting in disubstituted aromatic products. The larger the crystallite is, the longer the diffusion path, and a larger fraction of the initially formed dimethylethylbenzene may be consumed. Adopting these ideas for the reaction of ethyltoluene, the extremely low concentration of the expected diethyltoluene and dimethylethylbenzene primary products and the appearance of the diethylbenzene and xylene secondary products can be explained.

Turning our attention back to Fig. 5, the curve disproportionation/deethylation (Disp/Dee) requires some explanation. It was stated above that transethylation of EB (Disp) is accompanied by deethylation. The (Disp/Dee) ratio was calculated by relating the yield of diethylbenzene to the yield of benzene found in excess to diethylbenzene. Because the former is a bimolecular and the second is a monomolecular reaction, this ratio increased continuously with increasing EB concentration. Toluene was formed in demethylation of xylene and side-chain demethylation of ethylbenzene. As can be seen in the figure, the rate of the two processes is almost identical (yield of T at 0 and 100% EB). The toluene concentration in the product mixture is the highest at an equimolar EB/MX reactant composition.

From the results above it follows that during alkylation of toluene with ethylene on unmodified microcrystalline (1–1.5 μm) H-ZSM-5, the initially formed ethyltoluene may undergo a series of transalkylation reactions, especially at higher contact times. The low concentration of trisubstituted and *ortho*-disubstituted benzenes in the product compared to the *para*- and *meta*-disubstituted benzenes suggests that transalkylation proceeds predominantly within the zeolite channels and not on the external surface of crystallites.

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