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The Mechanism of Aromatic Transalkylation in ZSM-5

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The ZSM-5-catalyzed transalkylation of ethylbenzene, which yields benzene and diethylbenzenes, occurs by acid-catalyzed cleavage of the ethyl group followed by addition of the ethyl group to another ethylbenzene. Xylenes transalkylate much more slowly because methyl groups are more difficult to cleave than ethyl groups due to their decreased carbonium ion stability. When a mixture of xylenes and ethylbenzene reacts, diethylbenzenes are produced preferentially to dimethylethylbenzenes if the ZSM-5 crystallites are in a size range that allows the disubstituted benzenes to diffuse out of the zeolite crystallites much faster than the trisubstituted benzenes. The dimethylethylbenzenes (produced by ethyl group addition to the xylenes) diffuse so slowly from the larger crystallites that the added ethyl group is cleaved and xylene exits, apparently unreacted. © 1986 Academic Press, Inc.

INTRODUCTION

The selective transalkylation of ethylbenzene in the presence of xylenes is an important process for the purification of xylenes (*1*). In this process, ethylbenzene, which is difficult to separate from the xylenes by distillation, is converted to benzene and diethylbenzene. After transalkylation, the remaining xylenes can be easily separated from the mixture by distillation. ZSM-5 is used as a catalyst for this process, and this paper describes our study of the reaction mechanism for selective ethylbenzene transalkylation over ZSM-5.

The material covered in this paper covers two aspects of ZSM-5-catalyzed ethylbenzene transalkylation. First, we describe the initial step of the reaction over ZSM-5, the dissociation of ethylbenzene to form benzene and an ethyl moiety. Second, we provide an explanation for the preferential migration of the ethyl group to another ethylbenzene rather than to the equally abundant xylene component. Recently, others have attempted to explain this process (*2*).

EXPERIMENTAL

The catalysts used in the study are described in Table 1. The experimental runs are conducted using a microreactor system consisting of a 9.5-mm diameter, 0.9-m long stainless-steel reactor tube, mounted in a tube furnace, connected to stainless-steel feed lines, and equipped with pressure and flow controllers. The products are analyzed with an on-line gas chromatograph (GC). The reactor tube is packed with 0.2 to 2.0 g of catalyst in the middle and alundum on both ends. The catalyst bed, which is less than 50 mm in length, is separated from the alundum with glass wool plugs. The on-line GC is equipped with an OV 101 capillary column and a flame ionization detector (FID) for hydrocarbon product detection. The hydrocarbons are identified by comparison of GC retention times of authentic samples. The hydrocarbon values are not corrected for the small differences in detector efficiencies.

The runs are conducted as follows. The system is flushed with helium at atmospheric pressure as the reactor is heated to the desired temperature. The helium flow is adjusted to 20 ml/min, and the feed is injected at a continuous rate of 1 ml/hr. GC analyses are made at selected intervals during the run.

The pore probe experiments are conducted as described in a previous paper (*3*).

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TABLE I

Reactor Results of Aromatic Transalkylation Reactions over Various Catalysts[a]

Catalyst	Feed[b]	Reaction products, wt%										Cl[c]
		C_5^-	Benzene	Toluene	Ethylbenzene	Xylenes	Methylethylbenzenes	Trimethylbenzenes	Diethylbenzenes	Dimethylethylbenzenes	Higher aromatics	
H-Y[d]	1	3.5	9.8	21.9	21.7	25.7	8.5	4.2	3.0	1.0	—	
	2	4.5	17.5	5.9	55	—	4.2	—	9.8	—	—	
	3	0.1	3.8	90.8	—	4.9	—	—	—	—	—	0.4
	4	1.0	1.0	17.2	0.1	60.5	0.4	17.5	—	—	1.8	
	1[e]	0.1	1.0	1.7	47.1	46.3	1.1	0.7	1.5	0.5	—	
	6[e]	0.1	1.0	1.4	47.8	46.3	0.46	0.25	1.1	0.65	—	
Amorphous SiAl[f]	1	0.1	3.5	1.9	44.8	46.2	0.7	0.6	1.8	0.4	—	0.4
ELZ-105-6[g] H-ZSM-5	1	1.2	7.5	2.2	34.3	48.3	0.9	0.09	4.1[h]	0.6	—	
	2	1.3	12.2	1.6	73.8	—	0.8	—	8.9	—	—	
	3	—	0.8	98	—	1.1	—	—	—	—	—	5
	4	—	—	1.8	—	97.4	—	0.8	—	—	—	
	5	0.7	11.5	47.7	27.1	0.6	9.3	—	3.3	—	—	
40 μm H-ZSM-5[i]	1	0.8	4.3	0.7	40.0	50.2	0.2	—	3.0[j]	0.03	—	4.5
0.02 μm H-ZSM-5[k]	1	0.8	10.5	0.5	30.2	45.5	0.2	0.07	7.3[l]	4.7	—	4.3

[a] Unless otherwise indicated, conditions are 1 ml/hr feed, 20 ml/min helium, 1 atm pressure, 343°C. The catalysts deactivate over time. For single-component runs (Footnote *b*, Numbers 2–4) which are used to compare activities, the various feeds were run alternatively several times to make sure the activity changes between the runs were negligible. This precaution was not taken for the runs which used two reactants.

[b] The feeds indicated are as follows: 1, 50/50 ethylbenzene/xylenes (equilibrium mixture); 2, ethylbenzene; 3, toluene; 4, xylenes; 5, ethylbenzene/toluene; 6, ethylene/ethylbenzene/xylene (ca. 1 ml ethylene is injected over 15 s into the carrier gas which contains a 1:1 mix of ethylbenzene and xylene).

[c] The constraint indices were measured for the different crystallite size ZSM-5 samples. This was measured by running a 50/50 mixture of *n*-hexane and 3-methylpentane at 1 ml/hr over the catalyst in 20 ml/min of helium at 371°C. The CI is defined as log(fraction of nC_6 remaining)/log(fraction 3MP remaining). The CI values have a standard deviation of ca. 1 for 10 experiments. It has been shown that the CI is a measure of pore size for ZSM-5 which is independent of crystal size (*3*, *6*). The fact that the CI's for the different crystallite size ZSM-5 samples are almost the same shows that, as expected, the pores are the same size for all the samples.

[d] This material is low Na diuturnal Y zeolite from Linde; 0.2 g was used.

[e] These runs were conducted at ca. 280°C so that normal transalkylation reactions are held to a minimum. This makes it easier to see where the ethyl group formed from ethylene is adding. In the ethylene run, the ethylene peak is not counted in the C_5 product, but ethylene probably forms some benzene and toluene; so absolute product weight percentages are not exact. The ethylene also decreases conversion somewhat because of decreased contact time. Assuming that the ratio of methylethylbenzenes and trimethylbenzenes to diethylbenzenes and dimethylethylbenzenes from transalkylation reactions remains constant in these two runs, one calculates that 0.6 and 0.2 wt% of diethylbenzene and dimethylethylbenzene, respectively, in the ethylene run are from transalkylation reactions. Therefore, $1.1 - 0.6 = 0.5$ wt% of the diethylbenzene is from ethyl group addition to ethylbenzene, and $0.65 - 0.2 = 0.45$ wt% of the dimethylethylbenzene is from ethyl group addition to xylene.

[f] This sample is a commercial amorphous silica–alumina cracking catalyst. The pore volume is ca. 0.3 ml/g, and the pores range in size from 50 to 200 Å, 2.0 g of catalyst was used.

[g] This sample is Linde ELZ-105-6 ZSM-5. The bulk silica–alumina ratio (SiO_2/Al_2O_3) is 40, and the SiO_2/Al_2O_3 according to X-ray photoelectron spectroscopy (XPS) is 50 ± 5. Scanning electron micrographs (SEM's) show that the crystallites are 1–2 μm in size; 0.2 g of catalyst was used.

[h] The ortho/meta/para ratio (*o*/*m*/*p*) for this product (diethylbenzene) equals 0/1.4/1. [Equilibrium values (from Y zeolite) = 0.2/2.1/1.0.]

[i] This sample of ZSM-5 was prepared by S. I. Zones of Chevron Research. SEM's show the crystallites to be 40–50 μm in size. The bulk $SiO_2/Al_2O_3 = 80$, and surface SiO_2/Al_2O_3 (XPS) = 70 ± 7; 0.2 g of this catalyst was used.

[j] *o*/*m*/*p* diethylbenzene = 0/1/10. This ratio changes during the run. The value given here is after 100 min on stream. Coking probably restricts diffusion so that at 15 min into the run, *m*/*p* = 1/4; while after 210 min, *m*/*p* = 1/15.

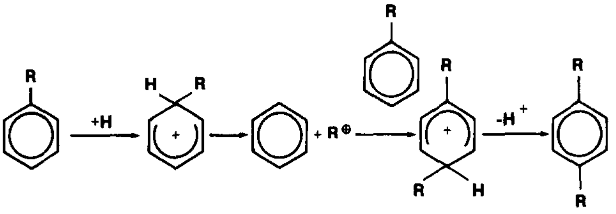
[k] This sample of ZSM-5 was prepared by R. A. Van Nordstrand and Lun-Teh Yuen of Chevron Research. XRD line broadening analysis show these crystals to be ca. 0.02 μm in size. This was confirmed by transmission electron microscopy. Bulk $SiO_2/Al_2O_3 = 105$ and surface SiO_2/Al_2O_3(XPS) = 125 ± 13; 1.5 g of this catalyst was used.

[l] *o*/*m*/*p* dimethylbenzene = 0.2/2.2/1.

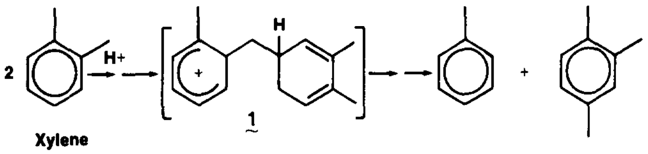
RESULTS AND DISCUSSION

The Dissociation Step

Two mechanisms have been proposed for the transalkylation reaction (*4*). In one mechanism, the alkyl group (R) on the benzene ring cleaves by acid catalysis. Then R^+ adds to another benzene ring (Eq. (1)). In the second mechanism, a dimeric intermediate is formed in which the aromatic rings are bridged by an R group. Subsequent cleavage effects R group transfer from one ring to the other (Eq. (2)).



(1)

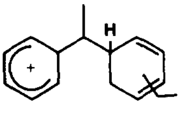


(2)

If R is a simple alkyl group, Equation 2 would appear to be the lower energy process due to resonance stabilization of the carbonium ion intermediate. However, an intermediate such as **1** is large relative to the reactants, and its formation may be hindered in small catalyst pores such as the 5- to 6-Å pores in ZSM-5 (*4*).[1] In Y zeolite with 12-Å supercages or in amorphous silica alumina with >50-Å pores, the steric restraints to the formation of intermediate **1** would be minimal. Therefore, over these catalysts, the reaction can proceed via Eq. (2) (*4*). The rates of formation of **1–4** (the transalkylation intermediates from a mixture of xylene and ethylbenzene) are expected to be similar for a variety of reasons, and thus the rates of xylene and ethylbenzene transalkylation over Y zeolite and amorphous silica alumina are expected to be similar.

When an equimolar mixture of ethylbenzene and xylenes is reacted over H-Y zeolite or an amorphous silica alumina cracking catalyst, the rate of ethylbenzene disappearance is about equal to the rate of xylene disappearance (Table 1).

Over Linde H-ZSM-5 (ELZ-105-6), ethylbenzene disappears 10 times faster than the xylenes.



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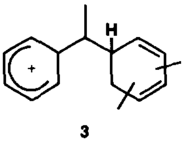

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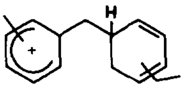

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Although **1** may be larger than **2**, it is not likely that the selective transalkylation of ethylbenzene by ZSM-5 is due to the greater steric hindrance in forming **1** rela-

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[1] This type of transition state steric hinderance by zeolite pores was originally discussed by Csicery (*5*).

tive to **2**. We concluded this after comparing toluene and ethylbenzene transalkylation rates over ZSM-5 and H-Y and finding that the rate of toluene transalkylation/the rate of ethylbenzene transalkylation over ZSM-5 $\cong$ 0.07, which is one-third of the corresponding ratio of rates for H-Y (Table 1). Since the dimeric intermediate for toluene transalkylation is smaller than **1** or **2**, one would not expect toluene to react so slowly in ZSM-5 if Eq. (2) described the mechanism. Therefore, we concluded that the mechanism shown in Eq. (2) does not occur in ZSM-5.

If the transalkylation reaction in ZSM-5 proceeds via Eq. (1), then the rate of reaction will be dependent on the stability of the carbonium ion, R^+. For toluene and the xylenes, R^+ is CH_3^+; while for ethylbenzene, R^+ is $CH_3CH_2^+$, which is ca. 5 kcal/mole more stable than the methyl carbonium ion (7). For this reason, ethylbenzene is predicted to dissociate much faster than xylene or toluene in ZSM-5.

The Addition Step

If the predominant mechanism for transalkylation in ZSM-5 is as depicted in Eq. (1), there still remains the important question concerning why the ethyl carbonium ion preferentially adds to ethylbenzene to give diethylbenzenes rather than to the equally abundant xylenes to give dimethylethylbenzenes. The importance of this selectivity can be appreciated by noting that during transalkylation of a 50/50 mix of xylenes and ethylbenzene over Linde ELZ-105-6 H-ZSM-5, the ratio diethylbenzene/dimethylethylbenzene = 7. Were it not for this selectivity, substantial amounts of xylene would be consumed and the economic value of the process would be significantly less.

We have considered four possible reasons for the selective addition of the ethyl group to ethylbenzene in the presence of xylene in ZSM-5. First, even in an environment free of steric constraints, an ethyl group may prefer to add to ethylbenzene rather than to xylene. This would mean that the ZSM-5 pores are only important in that they discriminate in favor of the dissociative transalkylation reaction (Eq. (1)). Second, the steady-state concentration of ethylbenzene may be higher than that of xylene in the ZSM-5 pores, Third, the restrictive pores of ZSM-5 may hinder the formation of trisubstituted benzene products (formed by ethyl group addition to xylene) relative to the formation of disubstituted benzene products. Fourth, the diffusion of trisubstituted benzene products may be hindered relative to diffusion of disubstituted benzenes to such an extent that even if the dimethylethylbenzenes are initially formed, they would remain in the ZSM-5 crystallite long enough to revert to xylene plus the ethyl group. Then, the ethyl group could escape from the zeolite by adding to ethylbenzene to form the less hindered diethylbenzenes. (The ethyl group could also add to benzene to form ethylbenzene, but this is equivalent to no reaction occurring.)

Experiments described below show that the ZSM-5 pores are indeed important in the selective addition of an ethyl group to ethylbenzene in the presence of xylene. In one experiment, ethylene is reacted with a 50/50 mixture of ethylbenzene and xylene over H-Y zeolite (Table 1). The H-Y can convert the ethylene to the ethyl carbonium ion which can add to either ethylbenzene or xylene. The observed ratio of diethylbenzenes to dimethylethylbenzenes from ethylene addition is 1.1 (Table 1, Footnote *e*). Thus, in large pores (12 Å) the ethyl group does not discriminate significantly between ethylbenzene or xylene during addition. In the second experiment, a 50/50 mixture of toluene and ethylbenzene is reacted over ZSM-5 (Table 1). In this case, toluene is competitive with ethylbenzene in accepting the ethyl group to form methylethylbenzene. Very little xylene forms, and we conclude that only the ethyl group is moving. This experiment shows that a methyl-substituted benzene can be competitive with ethylbenzene for accepting an ethyl group in ZSM-5.

Since the ethyl group would add preferentially to ethylbenzene if the steady-state concentration of ethylbenzene were higher than that of xylene in the ZSM-5 pores, we did experiments to measure the amount of ethylbenzene and xylenes in the pores near reaction conditions. We have established that there can be preferential adsorption of certain compounds in ZSM-5 pores at elevated temperatures (*3*). By using the pore probe technique which measures the steady-state concentration of hydrocarbons in pores, we have found that if a mixture of *n*-hexane and 3-methylpentane in helium is flowed over ZSM-5, the *n*-hexane is concentrated in the pores relative to 3-methylpentane by a factor of 20 at room temperature and by a factor of about 2 at 240°C (*3*). To determine whether ethylbenzene is adsorbed preferentially to xylene, we did the pore probe experiment described in Table 2. At 240°C, an equimolar mixture of ethylbenzene and xylenes was passed over ZSM-5. In the ZSM-5 pores at steady state, there were equal amounts of ethylbenzene and xylenes present. Therefore, even though the diffusivities of these compounds differ, there is no concentrating of ethylbenzene relative to xylene by the ZSM-5 pores.

TABLE 2

Pore Probe Results for Determining the Amounts of Xylenes and Ethylbenzene in ZSM-5 Pores[a]

	Steady-state amount in ZSM-5 pores (mg hydrocarbon/g ZSM-5)
Ethylbenzene	9.6
m + *p*-Xylene	9.0
o-Xylene	0.7

[a] The pore probe was run at 240°C using 0.7 g of Linde ELZ-105-6 ZSM-5. The feed is ethylbenzene/*m*-xylene + *p*-xylene/*o*-xylene/hexamethylethane (wt ratios = 39.8/31.0/8.2/21). The feed was run at 1.2 ml/hr in 35 ml/min of helium. The hexamethylethane does not enter the pores and is used to measure dead space (3). Approximately 1% transalkylation of ethylbenzene occurs under these conditions.

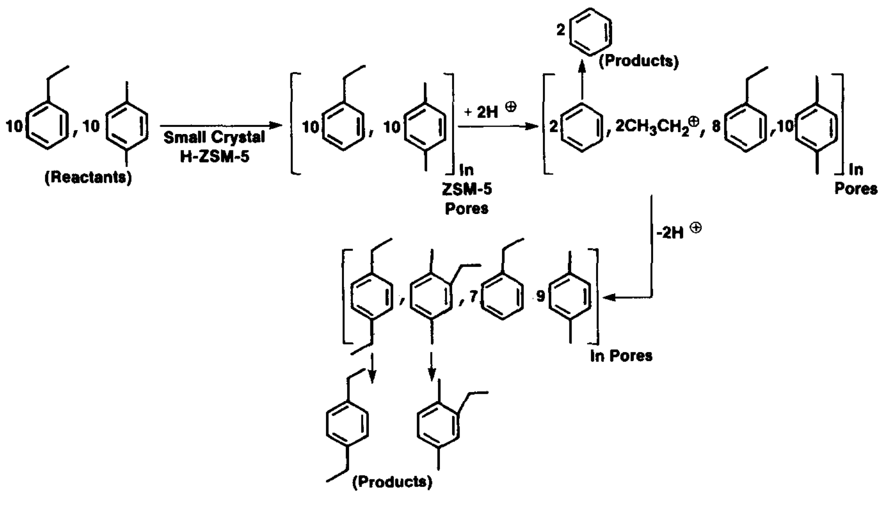
This leaves the third and fourth alternatives to be considered. In ZSM-5 pores, production of the trisubstituted benzene products is less favored than production of the disubstituted products either due to transition state steric hindrance by the pores during dimethylethylbenzene formation or due to diffusional restrictions which would cause the initially formed dimethylethylbenzene products to revert to xylene before the products could exit the zeolite crystallites. (The diffusivities of trisubstituted benzenes are similar to or lower than those of *o*-disbustituted benzenes which are many times lower than the diffusivities of *m*- and *p*-xylenes in ZSM-5.) In order to estimate the relative importance of these two alternatives, ZSM-5 crystallites of different sizes were used as catalysts and dimethylethylbenzene/diethylbenzene was measured. Larger crystallites should yield more diethylbenzene relative to dimethylethylbenzene if diffusional differences are important in determining the relative yields of these products, while smaller crystallites should yield a diethylbenzene/dimethylethylbenzene ratio closer to the ratio initially produced in the pores since the initially formed products can escape the zeolite crystallite before secondary reactions occur.

When a 50/50 mixture of ethylbenzene and xylenes was reacted over Linde ELZ-105-6, ZSM-5 consisting of ca. 1- to 2-μm crystallites, diethylbenzene/dimethylethylbenzene = 7. Over ZSM-5 consisting of 40-μm crystallites, diethylbenzene/dimethylethylbenzene = 100. Over ZSM-5 consisting of 0.02-μm crystallites, diethylbenzene/dimethylethylbenzene = 1.5 (see Table 1). From these results, it can be seen that very large crystallites increase the yield of diethylbenzene over dimethylethylbenzene. The diffusion of the trisubstituted product is apparently hindered, leaving it to revert to xylene and an ethyl group. Even the disubstituted products show selectivity to the smaller para isomer over the bulkier ortho isomer after transalkylation over large crystallites (*8*). Furthermore, the initial formation of trisubstituted benzenes is not hindered by ZSM-5 pores. This is evident because the small crystallites, which allow fast escape of the initially formed products, are not very selective.[2] The large crystallite ZSM-5 is an excellent catalyst for the selective transalkylation of ethylbenzene in the presence of xylenes.

In studying this transalkylation process, we have chosen not to address certain important details of the reaction. For example, toluene, methylethylbenzenes, and excess benzene are formed during ethylbenzene transalkylation over ZSM-5. The toluene and benzene probably form from the oligomerization of C_5^- olefins which form from the cracked ethyl group of ethylbenzene (*4*). Ethyl group addition to toluene gives the methylethylbenzenes. We also have not discussed the nature of the active site in ZSM-5 and the nature of the dissociated ethyl group (*4*, *9*).

CONCLUSION

We believe we have demonstrated that ethylbenzene transalkylates over ZSM-5 by the dissociative mechanism shown in Eq. (1). Due to carbonium ion stability differences, methyl-substituted benzenes dissociated much more slowly. The dissociated ethyl group can add to either ethylbenzene or xylene in ZSM-5, but in large crystallites dimethylethylbenzene is held in the pores significantly longer than diethylbenzene due to diffusional differences. This allows the dimethylethylbenzene to undergo secondary transalkylation reactions resulting in aromatic products that are disubstituted (Eqs. (3) and (4)).



(3)

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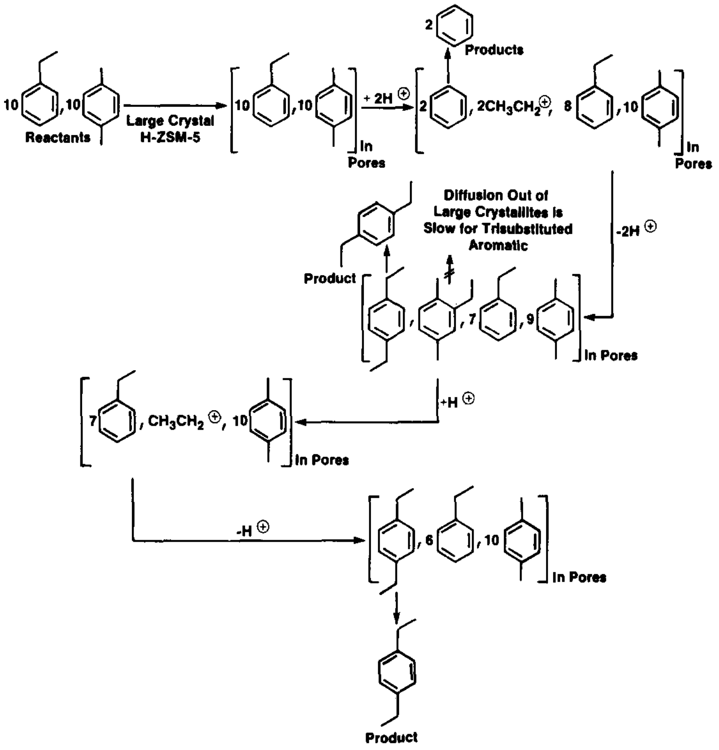
[2] Part of the reason that the dimethylethylbenzene products escape from the small (200 Å) crystallites before reverting to xylene and an ethyl group is the slightly lower alumina content of this sample (SiO_2/Al_2O_3 = 105 for the 200 Å crystallites compared to SiO_2/Al_2O_3 = 80 for the 40-μm crystallites). This results in a lower acid site concentration in the small crystallites. However, it is clear that the crystal size effect is important because even though the 40-μm crystallites have a higher SiO_2/Al_2O_3 ratio (80) than the 1- to 2-μm crystallites (SiO_2/Al_2O_3 = 40), the secondary reactions (reversion of dimethylethylbenzene products to xylene and an ethyl group) occur to a greater extent in the 40-μm crystallites.

Surface sites did not contribute to the activity of these catalysts. This is evidenced by the negligible amount of trimethylbenzene formation during transalkylation reactions involving xylene. One might have argued that the formation of the diethylmethylbenzenes over the small crystallites of ZSM-5 occurs by transalkylation of the product diethylbenzenes and xylene on the zeolite surface since smaller crystallites have more external surface area. However, this is not so. Transalkylation of a xylene/diethylbenzene mixture over an acidic amorphous silica–alumina catalyst under conditions described in Table 1 produces nearly equal amounts of trimethylbenzenes and diethylmethylbenzenes. Therefore, since only 0.07 wt% of trimethylbenzenes were produced during ethylbenzene/xylene transalkylation over the small crystal ZSM-5 (and since there is more xylene present than diethylbenzene), <1.5% of the diethylmethylbenzene products are the result of surface reactions. Furthermore, XPS analysis showed no surface enrichment of alumina (Table 1); and the constraint indexes for all of the samples were the same (Table 1).



(4)

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