Shape Selectivity of ZSM-5 Type Zeolite for Alkylation of Ethylbenzene with Ethanol

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The alkylation of ethylbenzene with ethanol on ZSM-5 zeolites was studied at 673 K. The primary product in this alkylation on HZSM-5 catalyst was only *p*-diethylbenzene because of the transition-state selectivity. Therefore, the isomerization of *p*-diethylbenzene has to be restrained for the selective formation of *p*-diethylbenzene. The modified HZSM-5 catalysts with oxide of magnesium, phosphorus or boron showed much higher para-selectivity than the parent HZSM-5. The modification reduced not only the effective pore dimension of HZSM-5 but also the amount of strong acid sites. We claim that the absence of strong acid sites is necessary rather than the narrowness of pores for the suppression of the isomerization of *p*-diethylbenzene produced as a primary product.

The main channel of ZSM-5 type zeolite is cylindrical and its window is composed of a 10-membered oxygen ring, whose dimension is smaller than that of Y type zeolite.[1] In fact, *p*-xylene can be adsorbed selectively in the pores of HZSM-5 in the liquid phase competitive adsorption of the three xylene isomers at a low temperture as 273 K.[2] Therefore, it was expected that *p*-xylene could be selectively produced in the alkylation of toluene with methanol on HZSM-5 type zeolite catalysts. However, Yashima et al.[3] and Kaeding et al.[4] have reported that the equilibrium composition of xylene isomers is obtained in the alkylation of toluene with methanol on HZSM-5 at a high yield of xylene. When oxide of magnesium,[3,4] phosphorus,[4] or boron[4] is incorporated into HZSM-5 catalyst, a dramatic increase in para-selectivity is observed. That is, the fraction of the para-isomer in xylenes produced is above 90%. It has been also reported that in the ethylation of toluene[5] and ethylbenzene[6] on modified ZSM-5 zeolites a high para-selectivity is observed.

Many researchers suggest that the high para-selectivity for the alkylations mentioned above is caused by the shape selectivity of the modified ZSM-5 zeolites.[3–6] Kaeding et al. have proposed that the high para-selectivity of modified ZSM-5 zeolites is due to product selectivity (a kind of shape selectivity), namely the much higher intracrystalline diffusivity of the para-isomer in relation to the other two isomers.[4,6] Wei has presented a theoretical explanation for the experimental data, assuming product selectivity, and has concluded that the enhancement of para-selectivity happens under decreasing in conversion of alkylation and under increasing in catalytic activity for isomerization.[7]

On the other hand, Yashima et al. have reported the results of the alkylation of toluene with methanol on HY and HZSM-5 catalysts.[3] In the case of HY, *o*- and *p*-xylenes are primary products, while on HZSM-5, only *p*-xylene is a primary product. This is because of transition-state selectivity (a kind of shape selectivity) of HZSM-5. Accordingly, the alkylation to form any xylene other than the para-isomer is prevented as the transition state necessary for the alkylation to proceed is not reached due to steric and space restriction. When HZSM-5 is modified with oxide of magnesium, an enhancement in para-selectivity is observed. They suggested that the amount of strong acid sites must be reduced for the suppression of the isomerization of *p*-xylene produced preferentially in order to produce *p*-xylene selectively.

In this paper, we aim to clarify a role of oxide compounds, whose incorporation results in the improvement of para-selectivity of ZSM-5 zeolites. We choose the alkylation of ethylbenzene with ethanol as a para-selective reaction, because the larger alkyl groups in diethylbenzene are expected to provide clearer results compared with the case of the alkylation of toluene with methanol.

Experimental

Materials. ZSM-5 type zeolite was synthesized by a similar method to that described in Mobil's patent[8] using tetrapropylammonium bromide, sodium silicate, aluminium sulfate, sulfuric acid and sodium chloride. The synthesized zeolite was calcined at 773 K for 3 h in air. Its sodium cation was exchanged for a proton by using 1 mol dm^{-3} hydrochloric acid at 333 K. The HZSM-5 (Si/Al=96) modified with magnesium oxide, designated as Mg-HZSM-5, was prepared by impregnation of HZSM-5 with aqueous magnesium acetate solution followed by drying at 373 K and calcined at 823 K for 18 h in an air stream. P-HZSM-5, B-HZSM-5 were prepared by impregnation of HZSM-5 with aqueous phosphoric acid solution and aqueous boric acid solution, respectively, followed by a method similar to that for Mg-HZSM-5. The weighed catalyst was set in a quartz reactor and dehydrated at 823 K for 1 h in a helium stream before use.

Apparatus and Procedure. The reaction was carried out in a fixed bed type apparatus with a continuous flow system at atmospheric pressure. The reactant (ethylbenzene/ethanol=1/1 mol/mol) was fed with a microfeeder. Helium was used as a carrier gas. The conditions of the alkylation of ethylbenzene with ethanol on HZSM-5 were: activation temperature=823 K; reaction temperature=673 K; (carrier gas)/(reactants)=(3 mol)/(2 mol); W/F=7.14 g h mol^{-1}. The effluent gas was cooled with an ice trap, and samples for analysis were collected periodically and were analyzed by gas chromatography.

The measurements of temperature programmed ammonia desorption (NH_3-TPD) from the catalysts were carried out as follows. After the catalyst was evacuated at 823 K for 1 h and exposed 80 Pa of ammonia gas at room temperature for 15 min, the catalyst was evacuated at room temperature for 15 min and then the temperature was brought to 773 K at a constant rate of 10 K min^{-1} under evacuation through the capillary. The relative amount of ammonia desorbed from the catalyst was determined by measuring the pressure in the system.

The competitive adsorption of three cresol isomers was carried out at 313 K using 1,3,5-triisopropylbenzene as solvent the molecular dimension of which was too large to enter the pores of the adsorbents. The competitive adsorption was initiated by adding 2 ml of 2 wt% adsorbate solution to 0.5 g of adsorbent. The amount of each isomer adsorbed was obtained from the change of concentration of each isomer in liquid phase. The concentration was determined by gas chromatographic analysis.

Results and Discussion

In the alkylation of ethylbenzene with ethanol on the HZSM-5 zeolite, *p*- and *m*-diethylbenzenes, benzene, ethylmethylbenzenes, and xylenes were observed as aromatic products and unreacted ethanol was not observed. Figure 1 shows the results of the alkylation. The activity and the selectivity for the catalyst did not change with process time. The conversion of ethylbenzene was 44% and the yield of diethylbenzene was 26%. The main product was diethylbenzene. The fraction of para-isomer in the diethylbenzenes produced was 39% and little *o*-diethylbenzene was produced. Therefore, it seems that HZSM-5 zeolites do not exhibit the para-selectivity.

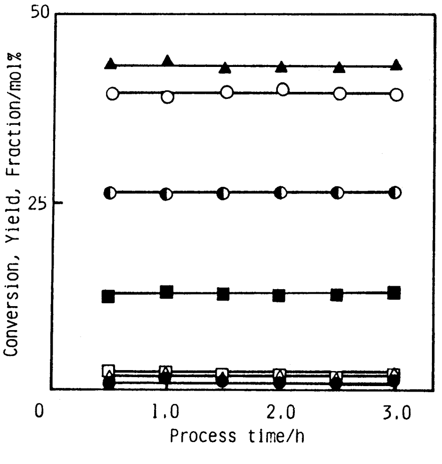

Fig. 1. Alkylation of ethylbenzene with ethanol on HZSM-5 at 673 K and W/F=7.14 g h mol^{-1}. Conversion of ethylbenzene (▲), fraction of para-isomer in diethylbenzene produced (○) and yields of diethylbenzene (◐), benzene (■), ethyltoluene (□), toluene (△), and xylene (●), as a function of process time.

In order to clarify the primary product in the alkylation of ethylbenzene with ethanol on HY or HZSM-5, the change in the distribution of diethylbenzene isomers with decreasing W/F was determined. The results on HY (Toyo Soda Ind. Co., Lot Y-30) at 548 K in the diethylbenzenes yield range of 41 to about 4% are shown in Fig. 2. The fraction of *m*-diethylbenzene decreased but those of *p*- and *o*-diethylbenzenes increased with decreasing W/F. In the case of HY catalyst, the primary product is not clear, but may be *p*- and *o*-diethylbenzenes. HY is not thought to exhibit the shape selectivity for this alkylation and the para/ortho orientation for this alkylation generally predominates.

The results on HZSM-5 at 673 K in the diethylben-

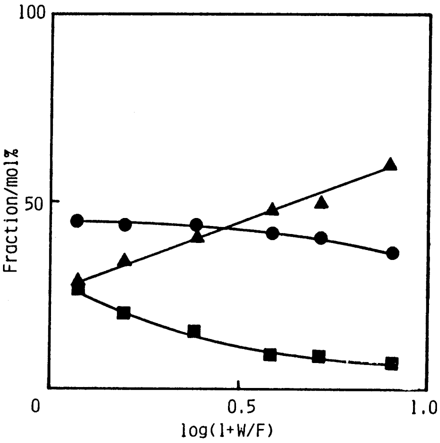

Fig. 2. Change in fraction of each diethylbenzene isomer with W/F in alkylation of ethylbenzene with ethanol on HY at 548 K. Fractions of para-isomer (●), meta-isomer (▲) and ortho-isomer (■) in diethylbenzene produced.

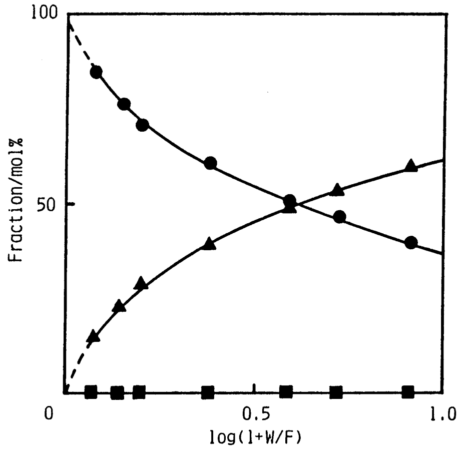

Fig. 3. Change in fraction of each diethylbenzene isomer with W/F in alkylation of ethylbenzene with ethanol on HZSM-5 at 673 K. Fraction of para-isomer (●), meta-isomer (▲), and ortho-isomer (■) in diethylbenzene produced.

zene yield range of 26 to about 3% are shown in Fig. 3. Although the molecular dimension of *o*-diethylbenzene was almost the same as that of *m*-diethylbenzene, little *o*-diethylbenzene was observed in these experiments. This indicates that HZSM-5 catalysts do not exhibit the product selectivity due to configurational diffusion effects. Instead they exhibit transition-state selectivity due to transition state restrictions. The formation of *o*-diethylbenzene through the alkylation of ethylbenzene with ethanol and through the isomerization of diethylbenzene produced is accordingly suppressed. The fraction of *p*-diethylbenzene increased to 100%, and the fraction of *m*-diethylbenzene decreased to 0% with decreasing W/F to 0. These results clearly indicate that the primary product of this alkylation on HZSM-5 catalyst is only *p*-diethylbenzene. The primary product on HZSM-5 is different from that of HY because of the transition-state selectivity of HZSM-5. Therefore, we believe that for the selective formation of *p*-diethylbenzene, the isomerization of *p*-diethylbenzene produced as a primary product must be suppressed.

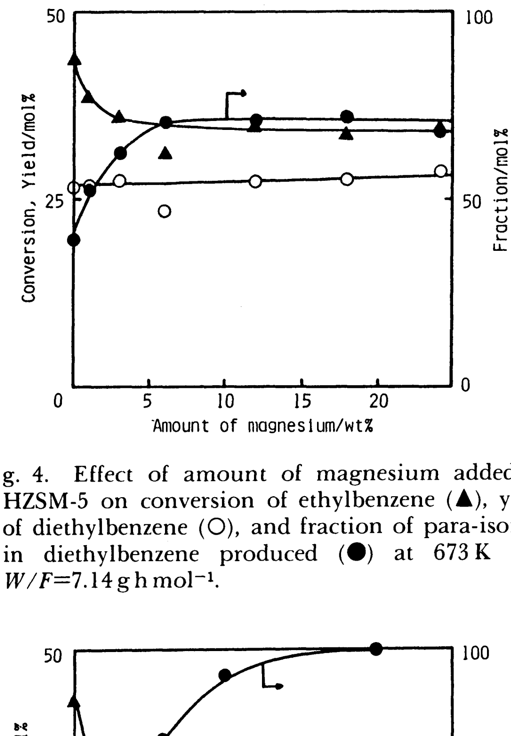

Fig. 4. Effect of amount of magnesium added to HZSM-5 on conversion of ethylbenzene (▲), yield of diethylbenzene (○), and fraction of para-isomer in diethylbenzene produced (●) at 673 K and W/F=7.14 g h mol^{-1}.

The HZSM-5 loaded with oxide of magnesium, phosphorus or boron showed much higher selectivity for *p*-diethylbenzene formation than the parent HZSM-5 catalyst as observed in the alkylation of toluene with methanol.[3,4] Figures 4, 5, and 6 show the effect of the amount of magnesium, phosphorus or boron added to HZSM-5 zeolite on the fraction of *p*-diethylbenzene in diethylbenzenes produced, on the conversion of ethylbenzene and on the yield of diethylbenzenes. On the Mg-HZSM-5 (Fig. 4), the fraction of *p*-diethylbenzene increased and the conversion of ethylbenzene decreased with increasing amounts of magnesium added. It reached a maximum around 6 wt% of magnesium. In this case, the fraction of para-isomer in diethylbenzenes produced was 73%, and the conversion of ethylbenzene was 34%. The yield of diethylbenzene increased slightly with increasing amounts of magnesium (26—28%).

On the P-HZSM-5 (Fig. 5), the fraction of *p*-diethylbenzene increased to 100% with increasing amounts of phosphorus up to 10 wt%. However, the conversion of ethylbenzene and the yield of diethylbenzene decreased notably with increasing amounts of phosphorus, suggesting that the zeolite channels were rigorously blocked with phosphorus oxide and/or that the acid sites on the zeolite disappeared on the addition of phosphorus oxide.

On the B-HZSM-5 (Fig. 6), the fraction of *p*-diethylbenzene increased with increasing amounts of boron added, as well as magnesium and phosphorus. However, on B(10)HZSM-5 (Number in parentheses indicates the amount of boron added in wt%) the fraction of *p*-diethylbenzene was 100% at a conversion of ethylbenzene and a yield of diethylbenzene of 17, 14%,

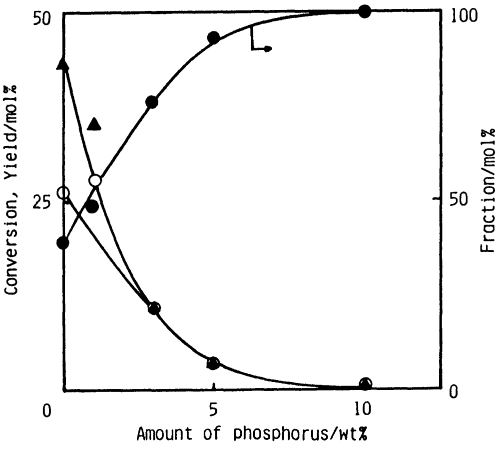

Fig. 5. Effect of amount of phosphorus added to HZSM-5 on conversion of ethylbenzene (▲), yield of diethylbenzene (○), and fraction of para-isomer in diethylbenzene produced (●) at 673 K and W/F=7.14 g h mol^{-1}.

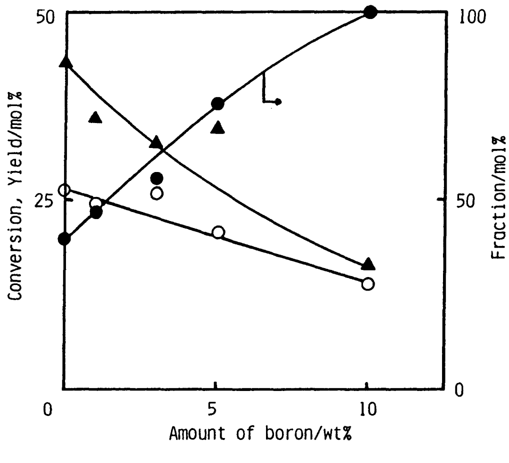

Fig. 6. Effect of amount of boron added to HZSM-5 on conversion of ethylbenzene (▲), yield of diethylbenzene (○), and fraction of para-isomer in diethylbenzene produced (●) at 673 K and W/F=7.14 g h mol^{-1}.

respectively. Although the B(10)HZSM-5 catalyst exhibited a relatively high activity, it showed an extremely high para-selectivity compared with P-HZSM-5 and Mg-HZSM-5 catalysts. The activity and the para-selectivity of Mg-HZSM-5 or P-HZSM-5 catalyst did not change with process time. However, in the case of B-HZSM-5, the conversion of ethylbenzene and the yield of diethylbenzene increased with process time, while the fraction of para-isomer in the diethylbenzene produced slightly decreased. This suggests that boron emerged from the catalyst system during the process time. The modified HZSM-5 type catalysts showed much higher selectivity for *p*-diethylbenzene formation than the parent HZSM-5.

As suggested before, modified HZSM-5 zeolites with the higher para-selectivity must exhibit the lower catalytic activity for the isomerization of *p*-diethylbenzene. In order to clarify the isomerization activity of the modified HZSM-5 catalysts, the reaction of *p*-diethylbenzene on HZSM-5, Mg(18)HZSM-5, P(5)HZSM-5, and B(10)HZSM-5 was carried out at 673 K. The results are shown in Table 1. In the reaction of *p*-diethylbenzene, the isomerization of *p*-diethylbenzene occurred simultaneously with the dealkylation, which was the reverse reaction of the alkylation. In the isomerization of *p*-diethylbenzene, *m*-diethylbenzene was produced, but *o*-diethylbenzene was not. This indicates the transition-state selectivity of HZSM-5. The order of the activities of the various catalysts examined here for the dealkylation of *p*-diethylbenzene agrees with that for the alkylation of ethylbenzene with ethanol. Namely, the order is HZSM-5 > Mg(18)-HZSM-5 > P(5)HZSM-5 > B(10)HZSM-5.

The order of the activities for isomerization of *p*-diethylbenzene is HZSM-5 > Mg(18)HZSM-5 > P(5)-HZSM-5 > B(10)HZSM-5. This order is exactly in reverse order of para-selectivities. From these results, it is concluded that the isomerization of *p*-diethylbenzene, which is the primary product in the alkylation of ethylbenzene with ethanol on the HZSM-5 catalyst, has to be suppressed for the selective formation of *p*-diethylbenzene.

In order to clarify that the modified catalyst, which shows the higher para-selectivity, exhibits the lower activity for *p*-diethylbenzene isomerization than the parent HZSM-5, the competitive adsorption of three cresol isomers and NH_3-TPD were examined. The results of the competitive adsorption and of NH_3-TPD give us the informations on the effective pore dimension of ZSM-5 zeolites[2] and on the acidic properties of the catalysts, respectively. The results of competitive adsorption of three cresol isomers are summarized in Table 2. The adsorption equilibrium was attained within 24 h. Therefore, the total amount of cresol isomers adsorbed and the para-selectivity were determined from the results at 24 h of adsorption time. The total amount of cresol isomers adsorbed decreased by the modification, suggesting that the oxide of magnesium, phosphorus or boron added reduces the effective pore dimension of HZSM-5 and/or blocks the zeolite channels. On the other hand, the para-selectivity for the competitive adsorption (see fraction of *p*-isomer in Table 2.) increased by the modification. This indicates that the effective pore dimension is reduced by the modification. The order of para-selectivities for the competitive adsorption of three cresol isomers are B(10)HZSM-5 > Mg(18)HZSM-5 > P(5)HZSM-5 > HZSM-5. This order is thought to correspond to that of the effective pore dimensions.[2] However it disagrees with that of para-selectivity for the alkylation of ethylbenzene with ethanol, that is, B(10)HZSM-5 > P(5)HZSM-5 > Mg(18)HZSM-5 > HZSM-5. This disagreement may suggest that the narrowness of the effective pore dimension is not so important to improve the para-selectivity in this alkylation on ZSM-5 zeolites.

Figure 7 shows the profiles of NH_3-TPD for HZSM-5 and modified HZSM-5 catalyts. The desorbed gas was only ammonia through the run. The HZSM-5 catalyst exhibited two peaks. One at 373 K corresponds to weak acid sites and the other at 603 K corresponds to strong acid sites. The amount of strong acid sites was remarkably reduced by the modification of HZSM-5 with oxide of magnesium, phosphorus or boron. The Mg(18)HZSM-5 catalyst still has a small amount of strong acid sites, while the P(5)HZSM-5 and B(10)HZSM-5 catalysts have few strong acid sites. The order of the amounts of the strong acid sites are HZSM-5 > Mg(18)HZSM-5 > P(5)HZSM-5 > B(10)HZSM-5. This order exactly coincides not only with the order of para-selectivities but also with that of activities for *p*-diethylbenzene isomerization shown in Table 1. These

Table 1. Reaction of *p*-Diethylbenzene on HZSM-5 and Modified HZSM-5 Catalysts at 673 K and W/F=7.14 g h mol^{-1}

	Conversion for isomerization	Conversion for dealkylation
	mol%	mol%
HZSM-5	19	54
Mg(18)HZSM-5	8.2	49
P(5)HZSM-5	0.29	1.6
B(10)HZSM-5	0.27	32

Table 2. Competitive Adsorption of Three Cresol Isomers on HZSM-5 and Modified HZSM-5 Zeolites at 313 K

	Fraction of each cresol isomer adsorbed/%			Total amount adsorbed /mg g^{-1}
	o-	*m*-	*p*-	
HZSM-5	25.7	43.2	31.1	114.3
Mg(18)HZSM-5	22.2	38.5	39.3	104.5
P(5)HZSM-5	25.1	39.6	35.5	78.0
B(10)HZSM-5	21.8	36.8	41.4	89.5

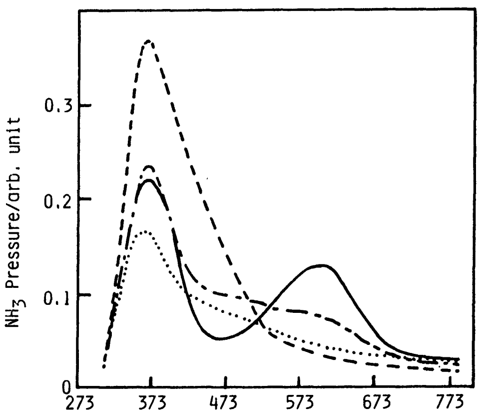

Fig. 7. Profiles of NH$_3$-TPD for HZSM-5 (——), Mg(18)HZSM-5 (-·-·-), P(5)HZSM-5 (······), and B(10)HZSM-5 (----).

facts suggest that the isomerization of *p*-diethylbenzene is more accelerated by the strong acid sites than the alkylation. Moreover, the intrinsic alkylation activities of the catalyst examined here except P-HZSM-5 are high enough, because ethanol is completely converted under our reaction conditions. Therefore, it is concluded that the strong acid sites on the catalyst have to be reduced for the selective formation of *p*-diethylbenzene by the alkylation of ethylbenzene with ethanol.

There is a large difference in yield of ethylbenzene in the alkylation of ethylbenzene with ethanol between P(5)HZSM-5 and B(10)HZSM-5. The difference in the acid properties between P(5)HZSM-5 and B(10)HZSM-5 is in the amount and strength of the weak acid sites. The B(10)HZSM-5 catalyst has more weak acid sites and exhibits a wider distribution in the weak acid site region (up to about 523 K in NH$_3$-TPD profile) compared with the P(5)HZSM-5 catalyst. Therefore, it is suggested that the activity for the alkylation of ethylbenzene with ethanol is related not only to the strong acid sites but also to the weak acid sites. However, the activity for the isomerization of diethylbenzene is related solely to the strong acid sites.

From these results, we conclude as follows. The isomerization of *p*-diethylbenzene, which is the primary poduct in the alkylation of ethylbenzene with ethanol on the HZSM-5 catalyst, has to be suppressed for the selective formation of *p*-diethylbenzene. The suppression of the isomerization of *p*-diethylbenzene is achieved by reducing the amount of strong acid sites rather than by reducing the effective pore dimension of the HZSM-5 zeolites.

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