Shape-Selectivity over HZSM-5 Modified by Chemical Vapor Deposition of Silicon Alkoxide

TAKASHI HIBINO, MIKI NIWA, AND YUICHI MURAKAMI

*Department of Synthetic Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku,
Nagoya 464, Japan*

Alkylation of toluene with methanol and toluene disproportionation have been carried out over
HZSM-5 zeolites modified by chemical vapor deposition of silicon alkoxide. As the silica amount
increased, the selectivity to *m*- and *o*-xylenes decreased, whereas that to *p*-xylene increased. The
fraction of the *para* isomer in xylenes increased to more than 98%. From adsorption measurements
and test reactions, it was found that this modification resulted in the narrowing of the pore-opening
size and the inactivation of the external surface. The high *para*-selectivity was caused primarily by
the narrowing of the pore-opening size. © 1991 Academic Press, Inc.

INTRODUCTION

p-Xylene is a valuable aromatic compound because of its demand for production of polyester fibers via terephthalic acid. Selective formation of *p*-xylene is thus a reaction of great industrial interest. In recent years, techniques for producing *p*-xylene selectively over modified HZSM-5 catalysts have been reported (*1–10*). Kaeding and co-workers (*1–3*) have proposed that HZSM-5 catalyst loading with oxides of P, Mg, or B produces *p*-xylene selectively. Yashima and co-workers (*4, 5*) have found that *p*-xylene is produced with high selectivity, when HZSM-5 catalyst is steamed at 1223 K.

We have previously proposed that chemical vapor deposition (CVD) of silicon alkoxide is a useful method for controlling pore-opening size of zeolites. This method was applied to mordenite (*11*) and HZSM-5 (*12*), and their selectivities were effectively improved in cracking and the methanol conversion, respectively. In particular, the HZSM-5 catalyst thus modified (SiHZSM-5) increased the fraction of the *para* isomer in xylene products up to 97% in the methanol conversion. The SiHZSM-5 would thus be a *para*-selective catalyst when used in toluene

alkylation as well as in toluene disproportionation.

Kaeding and co-workers (*1–3*) have proposed that the reduction in pore size is required for the selective formation of *p*-xylene, while Yashima and co-workers (*4, 5*) have suggested that the *para*-selectivity is ascribable mainly to the acidic property on the zeolite. However, since Si(OCH$_3$)$_4$ deposits only on the external surface, the CVD method changes neither the pore size nor the acidic property in the pore. The deposited silica narrows the pore-opening size and simultaneously deactivates the external surface, because the inert silica coats the external surface. Thus, the shape-selectivity over the SiHZSM-5 catalyst would be enhanced either by the narrowing of the pore-opening size or by the inactivation of the external surface.

In this study, we report that the CVD method is a useful and practical modification for producing *p*-xylene selectively in alkylation and disproportionation reactions. Furthermore, we explore whether the selective formation of *p*-xylene over the SiHZSM-5 catalyst is caused by the reduction in pore-opening size or by the inactivation of the external surface.

EXPERIMENTAL METHOD

Catalyst. The as-synthesized ZSM-5 was ion-exchanged in an ammonium nitrate solution three times, and the ammonium form of the zeolite was transformed into the H-form (HZSM-5) by calcining it at 673 K in a flowing mixture of oxygen and nitrogen (1 : 1 molar ratio). The Si/Al atomic ratio of HZSM-5 was 21.0, and the Na/Al atomic ratio was less than 0.008. The average crystal size of HZSM-5 measured with a scanning electron microscope (SEM) was 0.250 μm. The external surface area of HZSM-5 determined by a benzene-filled pore method (*13*) was 11.0 m^2 g^{-1}.

Chemical vapor deposition. The deposition of alkoxide was performed by a method described in a previous paper (*12*). The apparatus consisted of a vacuum system equipped with a conventional quartz spring balance. HZSM-5 was set in a quartz basket hung on the balance and evacuated at 673 K until the decrease of weight was not observed. Then, the alkoxide was deposited at 593 K. For the highly deposited zeolite, the deposition of alkoxide was repeated after the evacuation of the gas phase. After the deposition, the zeolite was calcined in situ in 26.7 KPa of oxygen at 673 K to remove coke formed on the zeolite through the deposition.

Alkylation of toluene and isomerization of o-xylene. The apparatus consisted of a continuous fixed-bed reactor packed with 0.1 g of 24/48 mesh catalyst. The catalyst was dehydrated at 773 K for 1 h in a helium stream, and reactants were fed into the catalyst bed with a microfeeder after the temperature was decreased to 673 K. Contact times defined by W/F were 6.85 and 8.08 g h mol^{-1} in the toluene alkylation and the *o*-xylene isomerization, respectively. Products were analyzed by GC with a column of Bentone 34 operating from 343 K to 393 K.

Disproportionation of toluene and cracking of 1,3,5-triisopropylbenzene. These reactions were performed by a pulse technique. The catalyst was pretreated with helium at 773 K for 1 h. Reactants were
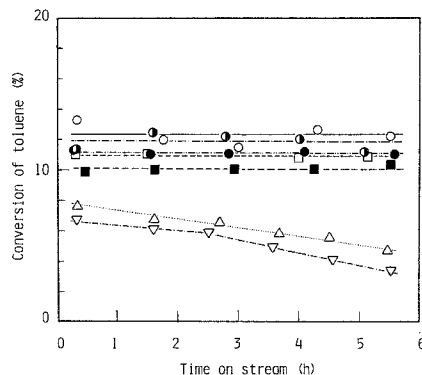

FIG. 1. Changes of toluene conversions with time-on-stream over HZSM-5 (○) and SiHZSM-5 with 1.72 (◑), 4.18 (●), 6.02 (□), 8.44 (■), 11.1 (△), and 13.3 (▽) wt% of silica amount.

injected at 673 and 573 K in the disproportionation of toluene and the cracking of 1,3,5-triisopropylbenzene, respectively.

Sorption experiments. Adsorption rates of *p*- and *o*-xylenes at 393 K were measured with a gravimetric apparatus. 0.1 g of the catalyst was evacuated at 673 K for 2 h and then used for adsorption at 393 K by keeping it in contact with 0.5 KPa of xylene vapor. The rate constant of the adsorption was obtained from the equation

$$V_e \ln\{V_e/(V_e - V)\} - V = kt, \quad (1)$$

where V and V_e are adsorption amounts at time t and at equilibrium, respectively, and k denotes the rate constant of the adsorption.

RESULTS

Alkylation of Toluene

Alkylation of toluene with methanol was carried out over HZSM-5 and SiHZSM-5 catalysts. Changes of toluene conversion with time-on-stream are shown in Fig. 1. Conversions remained unaltered over 5 h of operation over HZSM-5 and SiHZSM-5 with less than 8.44 wt% of silica but decreased gradually with time-on-stream over SiHZSM-5 with more than 11.1 wt% of silica. The deactivation was probably due to the coke deposition on the catalyst, because

TABLE 1

Alkylation of Toluene with Methanol over HZSM-5 and SiHZSM-5

Catalyst	HZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5
Amount of silica (wt%)	0.00	1.72	4.18	6.02	8.44	11.1	13.3
Conversion (%)							
methanol	100.00	99.80	100.00	99.85	99.92	97.15	99.83
toluene	13.45	11.43	11.45	11.21	9.89	7.64	6.75
Selectivity of aromatic product (%)							
benzene	2.54	2.59	2.24	2.10	1.99	2.21	2.37
ethylbenzene	0.82	0.92	0.73	0.73	0.78	2.36	1.34
xylene *para*	19.66	24.13	24.88	32.63	42.74	74.94	81.33
meta	38.47	35.76	37.30	32.72	24.45	4.68	1.43
ortho	18.99	16.37	15.52	12.71	8.78	2.09	0.27
ethyltoluene *para*	2.94	3.36	3.03	3.45	5.03	8.84	9.15
meta	3.68	4.03	4.58	4.02	3.31	0.85	0.00
ortho	1.00	0.99	0.79	0.16	0.00	0.00	0.00
1,3,5-TMB	1.12	0.98	0.13	0.00	0.00	0.00	0.00
1,2,4-TMB	5.70	5.22	5.31	6.02	5.79	3.01	1.95
1,2,3-TMB	1.50	1.62	1.79	1.66	2.23	0.98	0.00
1,2,3,5-TTMB	3.50	3.63	3.37	3.47	4.59	0.00	0.00
1,2,4,5-TTMB	0.00	0.35	0.26	0.28	0.23	0.00	0.00
Other aromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yield of xylene (%)							
para	2.65	2.75	2.85	3.65	4.22	5.72	5.49
meta	5.17	4.08	4.27	3.66	2.41	0.35	0.09
ortho	2.55	1.87	1.77	1.42	0.86	0.16	0.01
Fraction of para in xylene isomers (%)							
	25.48	31.60	32.05	41.80	56.34	91.81	98.21

Note. Toluene/methanol molar ratio: 8. W/F: 6.85 g h mol^{-1}. Reaction temperature: 673 K. Reaction pressure: 1 atm.

its color was found to be dark after the experimental run.

Details of the catalytic activity after 20 min of operation are summarized in Table 1. Methanol was completely reacted at any amount of deposited silica. The conversion of toluene, however, decreased with increasing amount of silica. The principal products were xylenes. Small amounts of benzene, ethylbenzene, ethyltoluene, and tri- and tetramethylbenzenes were also formed. The change of xylene distribution with the deposition of silica is shown in Fig. 2. The ratio of xylenes over the HZSM-5 was in good agreement with that predicted from thermodynamics (*p*-xylene 23.5%, *m*-xylene 52.2%, *o*-xylene 23.9% at 673 K). But the deposition of silica drastically changed their distribution. Increasing the silica amount enhanced the yield of *p*-xylene and reduced that of *m*- and *o*-xylenes. Especially, the yield of *p*-xylene over the SiHZSM-5 (13.3 wt%) was approximately twice as much as over the HZSM-5. Similar

trends were observed for ethyltoluenes. *o*-Ethyltoluene was initially suppressed, and *m*-ethyltoluene was then inhibited. At 13.3 wt% silica, the fraction of *p*-ethyltoluene in total ethyltoluenes was 100%. In addition, 1,2,4-trimethylbenzene was formed selectively among A$_9$ aromatics. A$_{10}$ aromatics
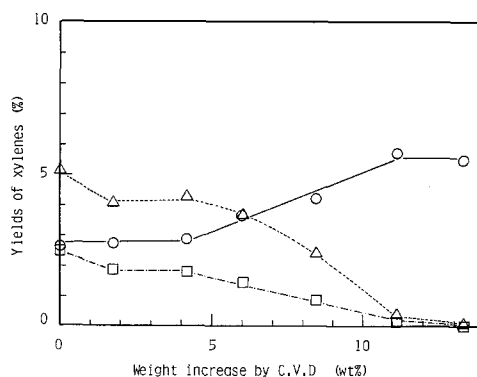

FIG. 2. Change of xylene distribution with increasing silica amount. Yields of *p*- (O), *m*- (△), and *o*-xylene (□).
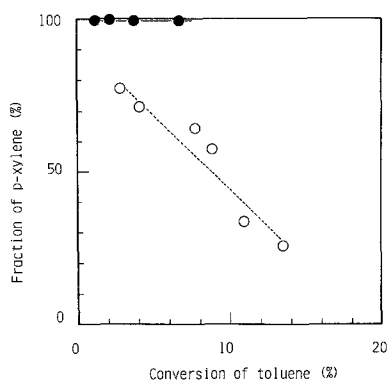
FIG. 3. Plot for fraction of *para* isomer in xylenes against conversion of toluene over HZSM-5 (○) and SiHZSM-5 with 13.3 wt% of silica (●).

over the SiHZSM-5 is not caused by the decrease in the catalytic activity.

Disproportionation of Toluene

The parent HZSM-5 and SiHZSM-5 catalysts were also used for the disproportionation of toluene. Results are summarized in Table 2. Toluene was mainly converted to benzene and xylenes. A small amount of ethylbenzene was observed as a byproduct. The deposition of silica did not change selectivities to benzene and xylenes but drastically altered the distribution of xylenes. As the silica amount increased, yields of *m*- and *o*-xylenes decreased, but that of *p*-xylene increased. In particular, the yield of *p*-xylene over the SiHZSM-5 (13.3 wt%) was approximately double that over the HZSM-5. SiHZSM-5 is, hence, a *para*-selective catalyst in toluene disproportionation also.

Figure 4 shows the relationship between the toluene conversion and the fraction of *para* isomer (in total xylenes) over HZSM-5 and SiHZSM-5 (13.3 wt%). The selectivity to *p*-xylene over the SiHZSM-5 was much higher than that over the HZSM-5 in the conversion range of 0.17 to 1.97%.

were not formed. Hence, SiHZSM-5 containing 13.3 wt% silica selectively produces the isomer with the smallest dimensions in each class of alkylaromatics.

Figure 3 shows the change of the fraction of *para* isomer (in total xylenes) with decreasing toluene conversion. In this case, the conversion was controlled by changing W/F. The selectivity over the SiHZSM-5 (13.3 wt%) was much higher than that over the parent HZSM-5 at any conversion level. Hence, the selective formation of *p*-xylene

TABLE 2

Disproportionation of Toluene over HZSM-5 and SiHZSM-5

Catalyst	HZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5
Amount of silica (wt%)	0.00	1.72	4.18	6.02	8.44	11.1	13.3
Conversion of toluene (%)							
	1.97	1.89	1.63	1.27	1.38	0.82	1.08
Selectivity of aromatic product (%)							
benzene	53.44	54.81	55.22	55.00	57.25	57.77	54.15
ethylbenzene	0.00	0.42	0.00	0.00	0.00	2.33	1.40
xylene *para*	12.28	12.55	14.04	14.61	22.29	37.44	38.47
meta	24.32	23.07	22.46	22.32	15.62	1.95	0.54
ortho	9.94	9.13	8.27	8.04	4.81	0.48	0.16
Other aromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yield of xylene (%)							
para	0.24	0.23	0.22	0.18	0.30	0.31	0.42
meta	0.48	0.43	0.36	0.28	0.21	0.01	0.00
ortho	0.19	0.17	0.13	0.10	0.06	0.00	0.00
Fraction of para in xylene isomers (%)							
	26.37	27.71	30.98	32.14	52.63	94.18	98.57

Note. W/F: 4.72 mg min ml^{-1}. Reaction temperature: 673 K. Reaction pressure: 1 atm.
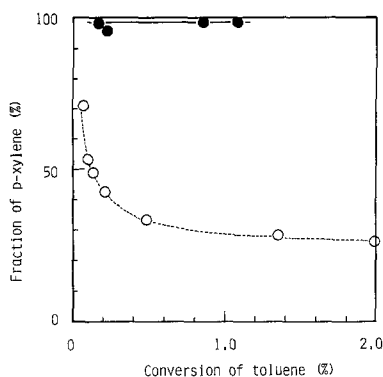
FIG. 4. Plot for fraction of *para* isomer in xylenes against conversion of toluene over HZSM-5 (○) and SiHZSM-5 with 13.3 wt% of silica (●).

Isomerization of o-Xylene

In order to clarify the mechanism for shifting the product distribution into smaller molecules in the above reactions, isomerization of o-xylene was performed over the parent HZSM-5 and SiHZSM-5 catalysts. Results after 20 min of operation are summarized in Table 3. In this case, the conversion of o-xylene was drastically decreased by the deposition of silica. p- and m-xylenes were main products. Benzene, ethyltoluene, and trimethylbenzenes were also obtained. As the silica content in-

creased from 0 to 13.3 wt%, the fraction of *para* isomer (in p- and m-xylenes) increased from the equilibrium value (31.0% at 673 K) to 98.68%. In addition, selectivities to benzene, toluene, and ethylbenzene increased with silica amount. The formation of large trimethylbenzenes was completely suppressed.

Sorption of p- and o-Xylenes

Adsorption measurements of p- and o-xylenes were carried out on the parent HZSM-5 and SiHZSM-5. Linear plots of Eq. (1) are shown in Fig. 5. Rate constants of adsorption are summarized in Table 4. As the silica content increased from 0 to 13.3 wt%, the rate constant for p-xylene (k_p) decreased from 1.49 to 0.63 mmol min^{-1} g^{-1}, while that for o-xylene (k_o) decreased by three orders of magnitude. Thus, the ratio of k_p to k_o became significantly larger as the silica amount increased (Fig. 6). On the other hand, adsorption amounts of p- and o-xylenes at equilibrium changed little due to the deposition of silica.

Cracking of 1,3,5-Triisopropylbenzene

Amounts of acid sites on the external surfaces of HZSM-5 and SiHZSM-5 were measured by the cracking of 1,3,5-TIPB. The kinetic diameter of 1,3,5-TIPB (0.85 nm) is

TABLE 3

Isomerization of o-Xylene over HZSM-5 and SiHZSM-5

Catalyst	HZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5
Amount of silica (wt%)	0.00	1.72	4.18	6.02	8.44	11.1	13.3
Conversion of o-xylene (%)							
	58.34	54.12	42.61	28.39	8.02	1.42	0.88
Selectivity of aromatic product (%)							
benzene	0.37	0.40	0.47	0.63	1.71	6.65	7.65
toluene	1.18	0.97	0.75	0.76	0.96	2.41	3.01
ethylbenzene	0.08	0.10	0.13	0.20	0.67	2.36	2.81
xylene *para*	31.31	33.60	36.22	41.06	56.09	78.68	84.70
meta	65.68	64.25	61.91	56.95	40.36	9.82	1.75
1,3,5-TMB	0.12	0.01	0.00	0.00	0.01	0.00	0.00
1,2,4-TMB	1.11	0.67	0.48	0.35	0.17	0.06	0.00
1,2,3-TMB	0.10	0.00	0.00	0.00	0.00	0.00	0.00
other aromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fraction of *para* in p- and m-xylene isomers (%)							
	32.28	34.34	36.90	41.87	58.21	90.24	98.68

Note. W/F: 8.08 g h mol^{-1}. Reaction temperature: 673 K. Reaction pressure: 1 atm.
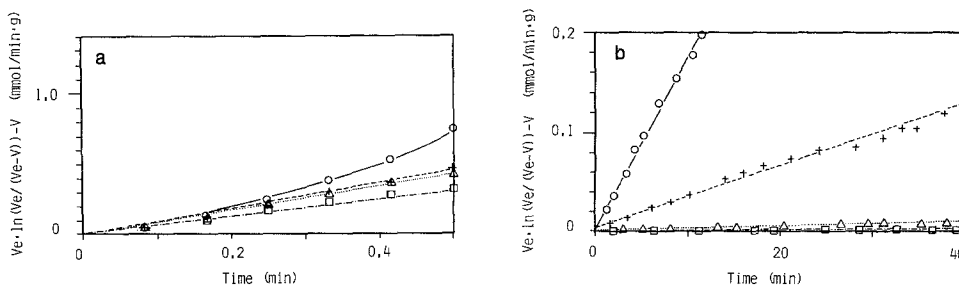
HIBINO, NIWA, AND MURAKAMI

FIG. 5. Plot for adsorption rate of (a) *p*-xylene and (b) *o*-xylene derived from Eq. 1 over HZSM-5 (○) and SiHZSM-5 with 4.18 (+), 8.44 (△) and 13.3 wt% (□) of silica amount.

larger than the pore size of ZSM-5 zeolite (0.54–0.56 nm). The cracking of this molecule takes place only on the external surface, and the conversion of 1,3,5-TIPB corresponds to the relative amount of acid sites on the external surface (*14*). As the silica content increased, the conversion decreased gradually and reached a near-zero value over the SiHZSM-5 with 13.3 wt% of silica (Fig. 6).

DISCUSSION

The fractions of *para* isomer in xylenes produced in the alkylation and disproportionation of toluene, the isomerization of *o*-xylene, and the conversion of methanol are summarized in Fig. 7. All fractions increased similarly with increasing silica content, indicating that the CVD method leads

to the selective formation of *p*-xylene without influence of the type of the reaction.

The alkylation of toluene on HZSM-5 has been extensively studied. Kaeding and co-workers have proposed that an equilibrium mixture of xylenes is formed as the primary product in the pore of the HZSM-5 (*1–3*). Hence, the narrowing of the pore size is required for the improvement in *para*-selectivity. On the other hand, Yashima and co-workers have reported that only *p*-xylene is formed as the primary product in the pores of HZSM-5 and then isomerized into xylenes with the equilibrium distribution on strong acid sites in the pores (*4, 5*). Accordingly, the reduction of strong acid sites in the pores causes the high *para*-selectivity. Furthermore, Paparatto *et al.* have suggested that *p*-xylene is selectively produced

TABLE 4

Adsorption Measurements of *p*- and *o*-Xylenes over HZSM-5 and SiHZSM-5

Catalyst	HZSM-5	SiHZSM-5	SiHZSM-5	SiHZSM-5
Silica amount (wt%)	0.00	4.18	8.44	13.3
Adsorption amount at equilibrium (mmol g^{-1})				
$\quad$*p*-xylene	0.45	0.45	0.36	0.42
$\quad$*o*-xylene	0.43	0.42	0.42	0.41
Adsorption rate (mmol min g^{-1})				
$\quad$*p*-xylene (k_p)	1.49	0.87	0.89	0.63
$\quad$*o*-xylene (k_o) × 10^5	1770	381	21.4	2.82
Ratio of k_p to k_o (−)				
k_p/k_o	84	228	4158	22340

Note. Temperature = 393 K. Vapor pressures of *p*- and *o*-xylenes = 1.73 and 1.25 Torr, respectively.
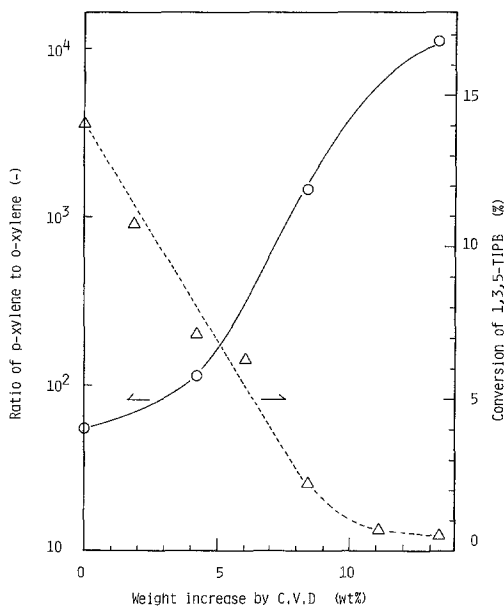
FIG. 6. Plot of k_p/k_o ratio or 1,3,5-triisopropylbenzene conversion with increase of silica amount.

in pores of HZSM-5, and the secondary isomerization of p-xylene proceeds only on the external surface (9). This means that the high $para$-selectivity results from the inactivation of the external surface. We hereinafter discuss how the CVD method improves the $para$-selectivity.

From sorption measurements, the deposition of silica was found to suppress the adsorption of o-xylene more remarkably than that of p-xylene (Fig. 5). Assuming that the cation site density of HZSM-5 is 8.9 nm^{-2} and the deposition site is the same as the cation site, the number of silica layers corresponding to the 13.3 wt% silica would be 13.6 (15). Since the monolayer thickness is ca. 0.3 nm, the average crystal size would increase from 0.250 to 0.258 μm by 13.3 wt% silica. However, the subsequent investigation indicates that a significant amount of alumina exists as a contaminant on the external surface of the parent HZSM-5 (16). Most of the deposited silica appears to be spent in covering the alumina surface. Thus, the average crystal size would be practically less than 0.258 μm. Olson and Haag have

shown that when the average crystal size increases from 0.05 to 0.7 μm, the diffusivity of o-xylene at 393 K does not change remarkably (6). Thus, the increase in the crystal size by the silica is not enough to explain the decrease in the adsorption rate of o-xylene by a factor of 1000. However, 13.6 silica layers is a sufficient number for narrowing the pore opening. Based on the above considerations, the decrease in the adsorption rate of o-xylene is caused by the reduction in the pore-opening size.

On the other hand, the cracking of 1,3,5-triisopropylbenzene testified that acid sites on the external surface of the HZSM-5 were deactivated by the deposited silica (Fig. 6). Therefore, the high $para$-selectivity is caused either by the narrowing of the pore-opening size or by the inactivation of the external surface.

The para-selectivity increase slightly at less than 4.18 wt% (Fig. 7). In this range, the pore-opening size was scarcely narrowed (Fig. 6), but the amount of acid sites on the external surface was reduced to half its initial value (Fig. 6). The $para$-selectivity increased largely with increasing silica amount from 4.18 to 8.44 wt%. In this range, the pore-opening size was largely narrowed, but the number of acid sites on the external surface was not much remarkably reduced.
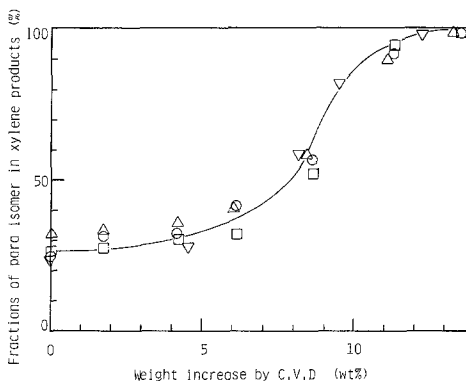

FIG. 7. Changes of fractions of $para$ isomer in xylene products with increasing silica amount in toluene alkylation (○), toluene disproportionation (□), and o-xylene isomerization (△).

Therefore, the *para*-selectivity results mainly from the narrowing of the pore-opening size until the silica amount is 8.44 wt%. The *para*-selectivity was more than 98% at 13.3 wt%. At this silica amount, the pore-opening size was further narrowed, so that only *p*-xylene could escape from the pore. Large aromatics were isomerized or dealkylated into small *p*-xylene, benzene, toluene, and ethylbenzene in the pore. In addition, the external surface was completely deactivated, so that the *p*-xylene product was not further isomerized. Based on the above findings, we conclude that the selective formation of *para* isomer over the SiHZSM-5 is caused primarily by the narrowing of the pore-opening size. Yashima *et al.* have reported that a high *para*-selectivity is not achieved only by poisoning selectively the external surface with 2,4-dimethylquinoline (*4*). This finding supports our conclusion in the present study.

The narrowing of the pore-opening size changes the activity for the disproportionation relative to the isomerization also (Table 2,3). Over the parent HZSM-5, the activity for the disproportionation was lower than that for the isomerization. This is due to the restricted transition state selectivity (*6*). However, over the SiHZSM-5 (13.3 wt%), the disproportionation occurred with the higher activity than the isomerization. The passage of *o*-xylene through the narrowed pore-opening is restricted more remarkably than that of toluene. That is, hence, due to the reactant selectivity.

CONCLUSION

When the alkylation of toluene with methanol or the disproportionation of toluene was carried out over the SiHZSM-5, more than 98% *para* isomer in xylene products was obtained. The CVD method is an effec-

tive and practical modification for the selective formation of *p*-xylene. The deposited silica reduced the pore-opening size and deactivated acid sites on the external surface. The high *para*-selectivity results primarily from the narrowing of the pore-opening size.

REFERENCES

1. Chen, N. Y., Kaeding, W. W., and Dwyer, F. G., *J. Am. Chem. Soc.* **101**, 6783 (1979).
2. Kaeding, W. W., Chu, C., Young, L. B., Weinstein, B., and Butter, S. A., *J. Catal.* **67**, 159 (1981).
3. Young, L. B., Butter, S. A., and Kaeding, W. W., *J. Catal.* **76**, 418 (1982).
4. Yashima, T., Sakaguchi, Y., and Namba, S., *in* "Proc. 7th Int. Congr. Catal." (T. Seiyama and K. Tanabe, Eds.), Kodansha, 1981.
5. Kim, J.-H., Namba, S., and Yashima, T., *Bull. Chem. Soc. Jpn.* **61**, 1051 (1988).
6. Olson, D. H., and Haag, W. O., *in* "Catalytic Materials: Relationship between Structure and Reactivity," (T. E. Whyte, Jr., Ed.), p. 275, ACS Symposium Series, Vol. **248**, Amer. Chem. Soc., Washington, DC, 1984.
7. Haag, W. O., *in* "Proc. 6th Int. Zeolite Conf." (D. Olson and A. Bisio, Eds.), p. 466, Butterworths, London, 1984.
8. Derouane, E. G., *in* "Zeolites: Science and Technology," R. Ribeiro *et al.,* Eds.), p. 347, Nijhoff, The Hague 1984.
9. Paparatto, G., Moretti, E., Leofanti, G., and Gatti, F., *J. Catal.* **105**, 227 (1987).
10. Wang, I., Ay, C. L., Lee, B. J., and Chen, M. H., *Appl. Catal.* **54**, 257 (1989).
11. Niwa, M., Kato, S., Hattori, T., and Murakami, Y., *J. Chem. Soc. Faraday Trans. 1* **81**, 2757 (1985).
12. Niwa, M., Kato, M., Hattori, T., and Murakami, Y., *J. Phys. Chem.* **90**, 6233 (1986).
13. Inomata, M., Yamada, M., Okada, S., Niwa, M., and Murakami, Y., *J. Catal.* **100**, 264 (1986).
14. Namba, S., Inaka, A., and Yashima, T., *Zeolites* **6**, 107 (1986).
15. Niwa, M., Kawashima, Y., Hibino, T., and Murakami, Y., *J. Chem. Soc. Faraday Trans. 1* **84**, 4327 (1988).
16. Hibino, T., Niwa, M., and Murakami, Y., unpublished results.