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Generation of Shape-Selectivity of *p*-Xylene Formation in the Synthesized ZSM-5 Zeolites

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Quantitative study has been performed in order to reveal the generation of shape-selectivity of the zeolite ZSM-5 in the formation of *p*-xylene from the alkylation of toluene. More than 20 kinds of ZSM-5 species prepared at various hydrothermal conditions were characterized in views of crystal size, diffusion property, and the external surface acidity; then, the measured selectivity at a constant conversion of toluene was correlated with them. The size of zeolite crystal was 0.5 to 6 μm, and it was strongly correlated with the rate constant of adsorption of *o*-xylene. Distribution of acid sites in the zeolite crystal was estimated to be not homogeneous from measurements of acidity on the external surface. Selectivity in the *p*-xylene formation was clearly correlated with the rate constant of adsorption, except for only a species. It was thus concluded that the shape-selectivity strongly depended on the adsorption property on zeolites due to the size of crystal. Acidity on the external surface was not a prevailing factor, however, it was significant on the zeolite with the external surface acidity which was created by the nonframework aluminum atoms. © 1998 Academic Press

Key Words: **ZSM-5; shape-selectivity; zeolite crystal size; adsorption; external surface acid.**

INTRODUCTION

Formation of *para*-substituted alkyl-aromatics from alkylation or disproportionation is regarded as the industrially most important reaction in which the shape-selectivity of a zeolite is utilized. In order to enhance the selectivity, various methods of modification of the zeolite property have been proposed (1–7). The enhancement of the shape-selectivity was explained from the narrowing of the pore-opening size (1, 5), the inactivation of the external surface (3, 7), or the controlling of the zeolite acidity (2, 4, 6). The mechanism for the selectivity must be understood well, and, based on the properly explained mechanism, the selective catalyst is to be designed. However, the interpretation of the selective formation of the *para* isomer is complex, and the problem remains still unsolved completely.

The shape-selectivity was first explained based on the diffusion property by Mobil researchers (8, 9), and for the *p*-xylene formation, it was termed "product shape-selectivity." The mechanism based on the difference in diffusion rates of xylene isomers was supported by the kinetics model proposed by Wei (10), and later more precisely explained by Hashimoto, Masuda *et al.* (11). Although this model is highly accepted by the people in this field, another explanation prevails and is frequently made more recently (12, 13). It is the mechanistic interpretation based on the nonselective reaction on the external surface; i.e., *p*-xylene is isomerized on the external surface into two other isomers, and if it occurs, it results in the low selectivity. It should be pointed out that one has to take notice of the nonselective reaction on the outer surface. However, it is difficult, in different samples of zeolite, to identify the deterioration of selectivity by the external surface acid sites because the external surface area can be correlated to the crystal size of the zeolite and, thus, to the diffusion property of zeolite also. In addition, it is difficult in modified zeolites, also, because modifications of the zeolite usually change both parameters simultaneously.

Based on the consideration in our previous study (14), both the diffusion property and external surface acidity were characterized on the silica deposited HZSM-5 modified by a chemical vapor deposition method. From the obtained characterization, we concluded that the controlling the pore-opening size was more effective in enhancing the selectivity up to nearly 100% than the inactivation of the external surface acidity. This way of investigation about the shape-selectivity must be carried out, not only on the silica modified zeolite, but on the usual synthesized HZSM-5. In this investigation, therefore, various kinds of ZSM-5 will be synthesized and characterized; evidence for the generation of shape-selectivity will be shown from the dependence of the selectivity upon the zeolite property.

EXPERIMENTAL METHODS

Synthesis of ZSM-5

Zeolites ZSM-5 were synthesized under hydrothermal conditions as reported in Argaur and Landolt (15).

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Solution A was made by mixing $Al_2(SO_4)_3$, the organic template, tetrapropylammonium bromide, H_2SO_4, and water, solution B was made from sodium silicate solution (Nakalai Tesque; Na_2O, 13.9 wt%; SiO_2, 41.3 wt%; water; 44.8 wt%) and water; these were mixed into solution C, which was made from NaCl and water, and stirred using a Teflon rod stirrer for 3 h . The pH of the solution was then adjusted to 10.3 by dropping concentrated H_2SO_4, and the obtained gel was set in an autoclave kept at 443 K for 72 h with the 300-rpm rotator. After the synthesis, the precipitate was filtered and thoroughly washed with deionized water. It was heated to dryness at 383 K overnight and calcined in air at 813 K for 24 h. Finally, it was ion-exchanged with 0.5 M NH_4NO_3, followed by calcination at 813 K for 24 h to obtain the H-type ZSM-5. Twenty two experimental runs for the synthesis were performed with varied synthetic conditions, and the obtained zeolites were named No. 2 to 23 due to the sequence of synthesis; only one species of HZSM-5 (No. 1) was supplied from the Mobil Catalysts of Japan, as shown in Table 1.

Fundamental Characterization Techniques

The content of Al and Na in the synthesized HZSM-5 was analyzed using induced coupled plasma spectroscopy (Shimadzu ICPS-1000) after digestion of the zeolite sample by HF. Chemical composition of the zeolite sample was determined based on the usual assumption; Si was removed as the gaseous fluoride during the analysis procedure, and the sum of Na and proton balanced the Al in the zeolite.

X-ray diffraction was measured to identify the zeolite crystal (Rigaku Miniflex). D-spacing of the (1000) plane of MFI was measured from the degree of diffraction without an internal standard.

Surface area of the zeolite was measured from the adsorption of nitrogen at 77 K and ca 0.3 atm of partial pressure, where the type-I isotherm was applied to the adsorbed amount. Scanning electron microscope (SEM) was measured to determine the morphology and the crystal size of zeolite (JEOL, JSM-5800). Zeolite powder was loaded on the mounted plastic tape, and Au vapor was deposited *in vacuo* thereon. SEM was taken at 20 kV of the accelerated voltage with the magnification of 3000 to 10000. To average the size of crystal, 50 crystals were measured.

External Surface Acidity Measurements

Acidity on the external surface of the zeolite was measured by a pulse method using cracking of 1,3,5-triisopropylbenzene (TIPB) which was too large to enter the pore (16). Zeolite sample (5 mg) installed in Pyrex glass tube was heated at 773 K for 1 h in a flow of helium (27 $cm^3\ min^{-1}$), and TIPB (1 mm^3) was injected into the catalyst at 623 K. Products of the cracking were propylene, benzene, mono-, and di-isopropylbenzene. The external surface acidity was

TABLE 1

Conditions for Synthesis and Characterization of Zeolites

	Conditions for synthesis										
No.	H_2O/SiO_2	NaCl/g	Temp./°C	Rotate/rpm	Si/Al_2	Surface area/$m^2\ g^{-1}$	Crystal size/μm	Ads. rate const./$\mu mol/gsec^{1/2}$	Conv. of TIPB/%	Rate, toluene/mol/h/g	Select., *p*-xylene/%
1	Provided				73	442	0.5	9	9.13	0.20	63
2	42	25.9	170	300	69	413	0.5	8.5	4.2	0.18	67
3	42	25.9	170	300	53	387	3	2.5	0.19	0.08	82
4	42	25.9	170	300	86	431	0.7	11.8	5.06	0.14	64
5	20	25.9	170	300	63	418	0.8	4.5	1.05	0.16	69
6	20	25.9	170	300	67	407	1	8.2	1.82	0.12	68
7	30	25.9	170	300	103	389	4.5	2	0.18	0.05	83
8	15	25.9	170	300	70	418	1.1	6.5	1.94	0.15	72
9	30	25.9	170	300	68	391	1.2	3.3	0.68	0.15	77
10	42	5.2	200	100	85	424	2.1	3.4	0.44	0.10	73
11	42	13	200	100	78	412	1.4	5.1	1.13	0.09	69
12	42	2.6	200	100	99	433	6	0.9	0.14	0.05	82
13	42	25.9	200	500	86	388	5	2	0.19	0.08	78
14	42	2.6	200	50	77	414	1	7.5	3.58	0.15	67
15	42	2.6	170	50	91	440	1	10	18.3	0.12	54
16	42	2.6	140	50	205	409	—	—	—	—	—
17	42	K	170	300	109	413	2	3.8	2.3	0.09	74
18	42	Li	170	300	96	330	—	—	—	—	—
19	42	5.2	170	0	105	416	1.5	3.2	3.02	0.10	76
20	60	5.2	170	300	73	447	0.7	5.2	1.5	0.14	69
21	80	5.2	170	500	74	446	0.9	12.5	4.2	0.12	62
22	80	5.2	170	300	75	455	0.5	12.5	9.3	0.15	63
23	80	5.2	170	50	77	433	0.8	14	11	0.16	64

evaluated from the conversion of TIPB, i.e.,

$$(1 - \mathrm{TIPB}_{\mathrm{unreacted}}/\text{sum of products including benzene ring} + \mathrm{TIPB}_{\mathrm{unreacted}}) \times 100.$$

Adsorption of o-Xylene

Rate of adsorption of *o*-xylene was measured by a gravimetric method using quartz micro balance at 393 K with the xylene pressure of 4 Torr (1 Torr = 133.3 Pa) on the zeolite evacuated at 673 K. Equilibrium amount of adsorbed *o*-xylene was measured on some samples for 17 h. Rate constant of adsorption was measured from the theoretical equation (*vide infra*).

Alkylation of Toluene with Methanol

Alkylation of toluene with methanol was carried out at 673 K with a continuous flow method under the atmospheric pressure. Before the reaction, the zeolite was activated at 773 K for 1 h with dried nitrogen as a carrier gas. The mixture of toluene and methanol was fed into the catalyst by a micro feeder with the molar ratio, toluene/methanol/N_2 = 1/1/10; the liquid product was collected in the exit and analyzed by gas chromatography with a Benton 34 column. The amount of catalyst was varied in order to change the conversion of toluene at the conditions of W/F from 0.079 to 0.336 g h/mol; the selectivity to form *p*-xylene was determined at the 20% conversion of toluene from the linear plot of the selectivity against the conversion.

RESULTS

Fundamental Data for the Characterization of Zeolites

Synthesized ZSM-5 was characterized, as listed in Table 1. The silica to alumina molar ratio of the synthesized zeolites was ca 50 to 100, and the surface area was 380 to 450 $m^2\ g^{-1}$. XRD showed that the structure was identified as MFI in all samples. Intensity of diffraction of the (501) face of MFI structure was at least 75% of the highest one. Only two of them (Nos. 16 and 18) were out of the criteria from the adsorption capacity and X-ray diffraction, and these were excluded in the following experiments because of low crystallinity.

SEM photographs showed that the morphology of crystals was cubic or sphere, as shown in Fig. 1, except for two

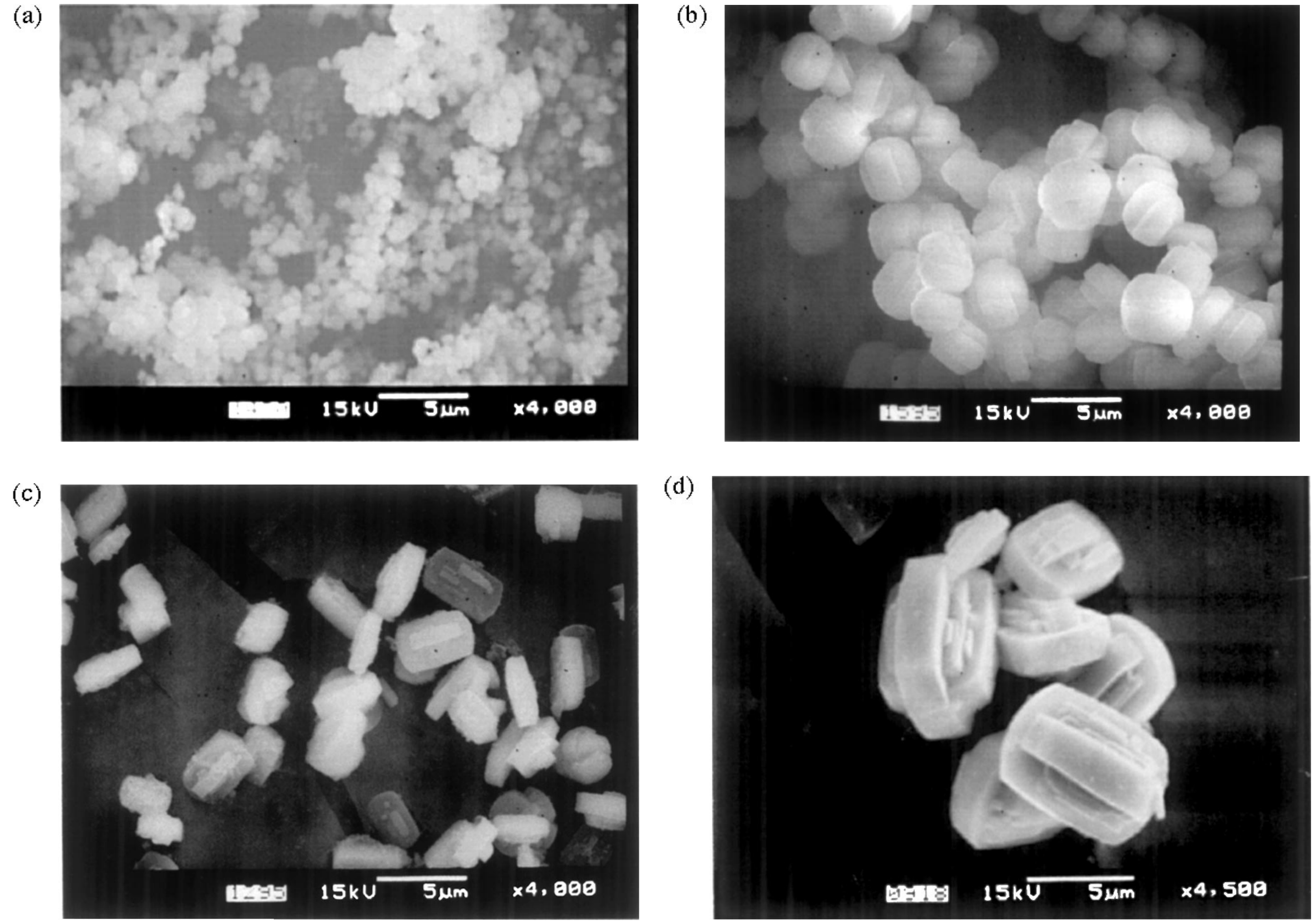

FIG. 1. Morphology of ZSM-5 crystals: (a), No. 2; (b), No. 3; (c), No. 10; (d), No. 12.

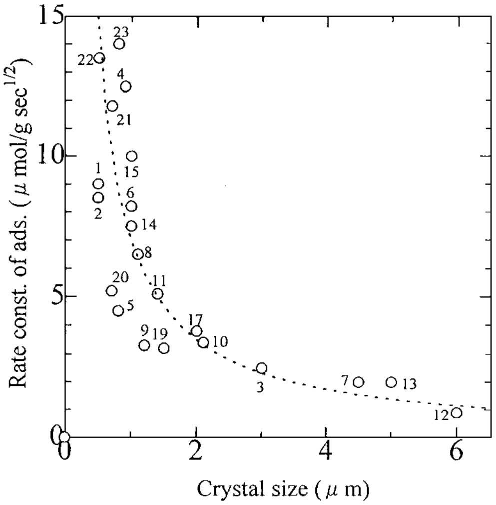

FIG. 2. Correlation between the rate constant of *o*-xylene adsorption and crystal size of zeolites.

species; No. 13 was a rod-like crystal and No. 20 was apparently a large single crystal, but it was composed of clustered small ones. The size of crystal was thus measured from the SEM photographs and found to be 0.5 to 6 μm.

Adsorption of *o*-xylene was measured, and the rate constant of adsorption was determined from the root *t* plot; the rate constant was calculated from the curvature of the adsorbed amount against $t^{1/2}$ at the initial stage of adsorption. The obtained rate constant *k* was plotted against the size of crystal, as shown in Fig. 2. These were inversely correlated; i.e., the larger the crystal size, the smaller the rate constant.

The rate of adsorption can be analyzed based on the equation (17).

$$\frac{M_t}{M_e} = \left(\frac{2A_p}{V_p}\right)\left(\frac{D}{\pi}\right)^{1/2} t^{1/2}, \qquad [1]$$

where M_t and M_e are the amounts adsorbed at time t and at equilibrium, A_p is the external surface area, V_p is the volume of the adsorbent, and D is the diffusion constant. Because A_p and V_p can be replaced by the assumption of a spherical adsorbent of radius r, we have

$$k = M_e\left(\frac{6}{r}\right)\left(\frac{D}{\pi}\right). \qquad [2]$$

The relation between k and r was simulated based on Eq. [2] with parameters D, 6.37×10^{-18} m^2 s^{-1} and M_e, 405 μmol^{-1}. The simulated curve shown in Fig. 2 fairly agreed with the experimental data. Thereby, the fundamental data for characterization of the physical property of zeolite were explained from simple consideration of the adsorption behavior.

External surface acidity was then measured by a pulse method, and the conversion of TIPB as a parameter of the external acidity was plotted against the $1/r$ which was approximately proportional to the external surface area. It was found that some of experimental data largely deviated from the expected relationship, as shown in Fig. 3. In particular, the acidity was enriched on the external surface of sample Nos. 15 and 23, whereas it was less than expected on sample Nos. 5, 9, and 20. Scattered behavior between them suggests an inhomogeneous distribution of acid sites in some synthesized zeolites.

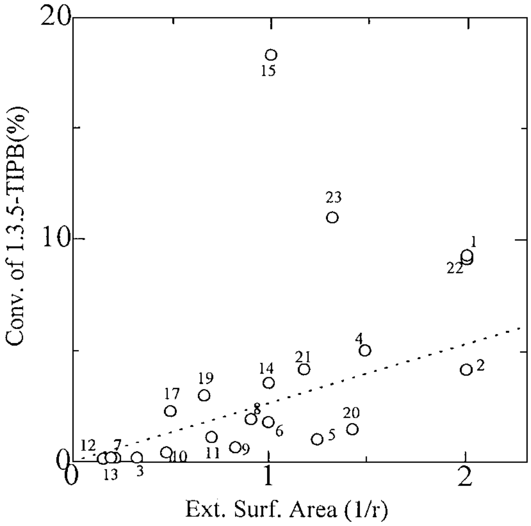

FIG. 3. Correlation between the acid amount and the area on the external surface.

In order to reveal the site of aluminum, XRD was precisely taken on the HZSM-5 and the *d*-spacing size was compared with the data for characterization. Figure 4 shows the correlation between the aluminum content and *d*-spacing

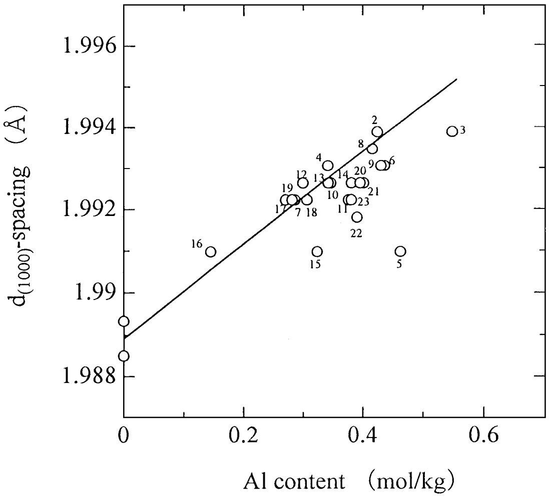

FIG. 4. Correlation between the *d*-spacing and aluminum content; Nos. 16 and 18 were plotted only in this figure, and data for two samples of silicalite were added.

size of (1000); the size of *d*-spacing increased with the Al content roughly. However, there were plots that strongly deviated from the relationship, i.e., Nos. 15 and 5. Increase in the size of *d*-spacing with an increase of aluminum content in the framework is well known. Deviations from the relationship thereby indicate the existence of Al atoms outside of the zeolite framework.

When these were compared with the measurements of external surface acidity in Fig. 3, two extreme cases were found; i.e., one case was observed on the sample of No. 15 in which the unexpectedly high external surface acidity was detected, and another on sample No. 5 with low external surface acidity, to the contrary. Based on the observation, the site of aluminum atoms outside of the framework was expected; nonframework Al atoms were enriched on the external surface of No. 15, whereas these were occluded inside the zeolite of No. 5.

Selectivity in p-Xylene Formation

Alkylation of toluene was performed on these synthesized HZSM-5. The conversion of toluene was varied by varying the amount of catalyst. The catalytic activity showed almost a constant value for 2 h, and the decay in activity was 2% at most. Table 1 shows the rate of toluene alkylation and the selectivity at the 20% conversion. Generally speaking, the selectivity in the *p*-xylene formation decreased with increasing the rate of toluene alkylation.

The selectivity to form *p*-xylene at the 20% conversion was plotted against the rate constant of adsorption of *o*-xylene. As shown in Fig. 5, the selectivity was closely related to the rate constant, except on sample No. 15, where the external acidity was exceptionally high, in Fig. 3; the selectivity decreased gradually with increasing the adsorption rate constant. Because the adsorption rate constant was related to the size of zeolite crystal, as shown above, the selectivity was related also with the size of zeolite crystal.

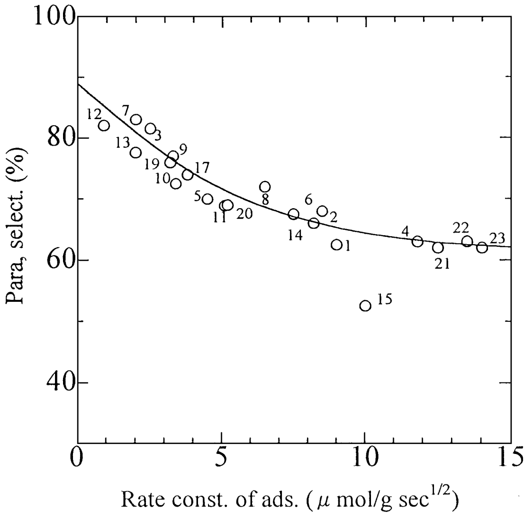

FIG. 5. Dependence of the selectivity of *p*-xylene formation upon the rate constant of *o*-xylene adsorption.

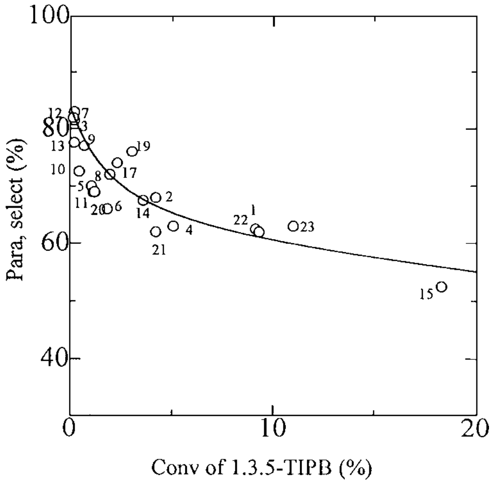

FIG. 6. Dependence of the *p*-xylene selectivity upon the external surface acidity.

On the other hand, plots of the selectivity against the external surface acidity showed a somewhat scattered relation as shown in Fig. 6. Although a simple relation appeared between them, lots of experimental data, particularly in the small conversions of TIPB, deviated from the simple relationship. The apparently observed relation in Fig. 6 can explain only the experimental data at the high conversion of TIPB like on sample Nos. 15 and 23.

Thus, we reach a conclusion about the relationship of the selectivity with the properties of synthesized zeolites. The selectivity is closely related with the adsorption behavior, but not sufficiently related with the acidity on the external surface. The external surface acidity affects the selectivity strongly only in the exceptional case. Also in the disproportionation of toluene, we have reached a similar conclusion (18).

DISCUSSION

Generation of the Shape-Selectivity

In this investigation, ZSM-5 was prepared under various conditions for the synthesis in order to obtain many kinds of zeolites with different properties. The size of zeolite crystal was varied, and different adsorption properties were expected from its different sizes. The expectation about the relationship between the size of crystal and the adsorption property was clearly identified, as shown above. The observation is usually expected, as long as the adsorbent has the same zeolite structure. The rate of adsorption may not be strongly affected by both the composition of zeolite and the distribution of aluminum cations. The simple relation between the size of crystal and the rate of adsorption is therefore a strong certificate for the accurate and properly controlled experiment.

On the other hand, heterogeneous or, in other words, local distribution of the solid acidity was identified in some prepared zeolites. The abundant solid acidity on the external surfaces of Nos. 15 and 23 samples was particularly noteworthy. As observed on No. 15, such a nonselective site with high external acidity is caused by the nonframework aluminum atoms on the external surface. It has been previously reported that the combination of acid sites with nonframework aluminum atoms forms the strong acid site (19). Also in the synthesis of No. 15 sample, the strong acid sites may be created on the external surface in a similar way. The nonselective site was identified, but it was an exceptional site with the nonframework Al on the external surface.

The selectivity to form *p*-xylene from the alkylation of toluene can be thus explained mainly from the adsorption property which can be related to the crystal size. The isomerization of xylene isomer, particularly the location of site for the isomerization is another key problem to understand the mechanism of selective formation of *p*-xylene (20, 21). However, ir observation by Mirth and Lercher indicated strongly the possible occurrence of isomerization within the pore (22). The selectivity of the *p*-xylene formation may be thus generated, based on the following mechanism. Reaction of methanol with toluene on the acid sites of zeolite forms *p*-xylene preferentially due to the restricted pore size of ZSM-5 zeolite. However, *p*-xylene can be isomerized into *o*- and *m*-xylenes, because the solid acidity is active enough to isomerize the *p*-xylene. Simultaneously, these xylene isomers diffuse out from the pore of zeolite. The selectivity of *p*-xylene formation is generated based on the difference in rates of diffusion and of isomerization of each xylene isomer. The selectivity to form *p*-xylene was mathematically analyzed, as shown in Fig. 7 (11), where the length of zeolite crystal and the ratio of acid sites on the external surface against the total amount of acid sites were used as parameters. In this figure, however, the ratio of external and total surface areas was used in place of the ratio of solid acid sites. The values of selectivity obtained in the present investigation were plotted in the figure, and these followed the theoretical expectation almost satisfactorily. Thereby, the present investigation adds support to the theoretical analysis based on the proposed mechanism.

As long as the same species of zeolite was used, the change of acid strength could be neglected, because the acid strength is mainly determined by the structure of zeolite (23). Effect by the acid strength on the selectivity is therefore not taken into consideration in the present investigation.

The mechanism of generation of selectivity is no other than that previously proposed (9–11). Recent investigations, however, indicated strongly the importance of the external acidity as the factor determining the selectivity. Paparatto *et al.* studied the ethylation of toluene on the synthesized ZSM-5 zeolite and concluded that the external surface acidity was a prevailing factor to decide the selectivity (12). However, they measured the size of zeolite crystal only and reached the conclusion without considering the diffusion. Usually, it is difficult to study two different parameters independently, because these are often correlated to each other. Present investigation, on the other hand, succeeded in studying the adsorption property and external solid acidity independently, because many kinds of zeolite were prepared, and these parameters were not well correlated. By utilizing the simple conclusion of the adsorption property and the observation of the unusual strong acidity on the external surface, we reached a conclusion about the generation of the selectivity.

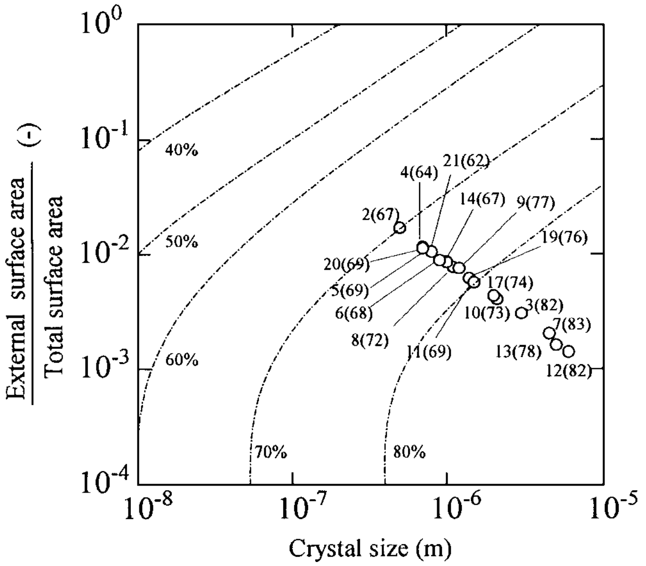

FIG. 7. Comparison between theoretical and experimental values of selectivity of *p*-xylene formation.

Control of the Zeolite Property

Another interesting observation is the effect of the synthetic conditions on the property of a zeolite. However, the synthesis of zeolite ZSM-5 was not completely controlled in this study. There are examples to show the low degree of reproducibility, i.e., Nos. 2 to 4 samples showed different character, although these were prepared under the same conditions. Another unknown parameter which was not controlled precisely may affect the zeolite property. On the other hand, there is a strong tendency in sample Nos. 12, 15, and 16 which were prepared under conditions of low concentration Na added in the gel; at the conditions, the low crystallinity was obtained at 140°C (16), the high external acidity due to the nonframework Al was obtained at 170°C

(15), and the largest crystal of zeolite was prepared at 200°C (12). In other words, the zeolite with unique character was prepared at small concentration of Na. On the other hand, under the conditions of high concentration of Na, the unusual character of zeolite was not obtained. The condition for the synthesis of the high Na concentration was adopted by Mobil patent (15) and supposed to have been used in many previous investigations. One can suspect that the zeolite ZSM-5 prepared under the usual conditions does not have a property which is correlated with the low selectivity in the methylation of toluene.

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