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RESEARCH NOTE

Source of Selectivity of *p*-Xylene Formation in the Toluene Disproportionation over HZSM-5 Zeolites

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Source of selectivity of *p*-xylene formation in the disproportionation of toluene was studied on more than 20 kinds of the synthesized ZSM-5 using multiple characterization techniques. Based upon the total characterization and its comparison with the selectivity, we found that the selectivity in disproportionation could be correlated with not only the diffusion rate but also the external solid acidity, except for unusual species of zeolites. Unusual low or high selectivity was caused by the high external surface acidity or by the slow diffusion rate. It was considered that these unusual properties were based on the nonhomogeneous distribution of Al or Si in the zeolite. Source of the selectivity, therefore, strongly depends on the physical and chemical zeolite property which is characteristic of each species of HZSM-5. An important experimental confirmation of the selectivity of *p*-xylene formation has been thus obtained. © 1999 Academic Press

Key Words: **ZSM-5; disproportionation; toluene; *p*-xylene; shape selectivity.**

Shape selectivity is the important catalytic function of a zeolite with the microporosity. There are many investigations, thereby, to reveal the generation of the shape selectivity on such a zeolite as ZSM-5. Among three kinds of selectivity, i.e., reactant selectivity, product selectivity, and transition-state selectivity, the latter two are usually difficult to be discriminated. In addition, it is difficult to decide which is a preferential parameter of the zeolite in obtaining the high selectivity, diffusion property, and external surface acidity because both parameters usually are correlated each other. Although correct understanding of the selectivity is necessary to design the selective catalyst, a controversy on this problem still remains unsolved.

In our previous paper (1), the generation of shape selectivity in the toluene alkylation was analyzed comprehensively using multiple characterization techniques. More than 20 kinds of ZSM-5 were synthesized, and these were characterized quantitatively. Melson and Schuth performed a study from a similar viewpoint in the disproportionation of ethylbenzene on HZSM-5 (2). In our study, the selectivity of *p*-xylene formation at 20% conversion of toluene was compared with the measured parameters, particularly the diffusion property and the external solid acidity. After all, we reached a conclusion; the diffusion property was a prevailing parameter to decide the selectivity of *p*-xylene formation. There was however an exceptional species of synthesized ZSM-5 named No. 15 where the solid acidity on the external surface was abundant. Acidity on the external surface was an important parameter for the selectivity only on the exceptional species.

Disproportionation of toluene is another important reaction path to produce *p*-xylene in which the shape selectivity of a zeolite is utilized (3–8). In the first step of this reaction, two molecules of toluene are dimerized into the reaction intermediate. Because the molecular size of toluene is close to the pore size of ZSM-5, the transition-state selectivity has been indicated. The selectivity in the disproportionation therefore could be different from that in the alkylation. Kaeding reported a different temperature dependence of ethylation and disproportionation of ethylbenzene (9). Klemm *et al.* explained the finding by Kaeding based on the change of the Thiele modulus with the reaction temperature (10). Kim *et al.* indicated that the selectivity in the disproportionation of toluene was generated by the so-called “product selectivity” and this was different from that in the alkylation with methanol (7). As a series of studies on the selective formation of *p*-xylene, the disproportionation of toluene was studied on the ZSM-5 which were synthesized, characterized, and used for the alkylation of toluene in the previous paper (1).

Disproportionation was performed using the usual pulse reactor. Prior to the reaction, helium gas was fed for 1 h at 773 K to dry the sample; the temperature was then cooled down to 723 K where the activity was measured. Then, 1.0 mm^3 of liquid toluene was injected, and the products were analyzed by gas chromatography with a Benton

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34 column. The weight of zeolite was adjusted to obtain the conversion of toluene, 1–3%, and the selectivity of *p*-xylene formation at the 1.5% conversion was taken as a parameter of selectivity on a zeolite. Preparation and characterization of zeolites ZSM-5 were described elsewhere (1) in detail.

The selectivity to form *p*-xylene in the disproportionation was 20–65% from species to species. The range of selectivity was broader than that in the alkylation with methanol previously reported (1).

The measured selectivity was plotted against the rate constant of *o*-xylene adsorption and the conversion of 1,3,5-triisopropylbenzene (1,3,5-TIPB) in Figs. 1 and 2, respectively. In Fig. 1, a clear relationship was observed between the selectivity and the diffusion constant; the smaller the diffusion constant, the higher the selectivity. There was, however, an exceptional species, No. 15, where the selectivity was lower than that expected from the adsorption constant. Aluminum atoms were enriched on the external surface of No. 15, and the external surface acid site was exceptionally abundant. It was revealed from the temperature-programmed desorption of ammonia that very strong acid sites were observed on the No. 15 as a small shoulder desorption peak at higher temperature, and the unusual strong acid site was generated by a combination of extra framework aluminum cations with the usual Brønsted acid sites (11). The strong acid sites on the external surface caused the low selectivity of No. 15.

On the other hand, plots of the selectivity with the external surface acidity seemed to show a simple relationship, as shown in Fig. 2, when the species Nos. 17 and 19 were excluded. Based upon the relationship, the low selectivity of No. 15 could be explained due to the high external surface acidity. However, we were faced with another problem of the deviation from the relation on Nos. 17 and 19. Then, we will reconsider the parameters obtained in the former paper (1).

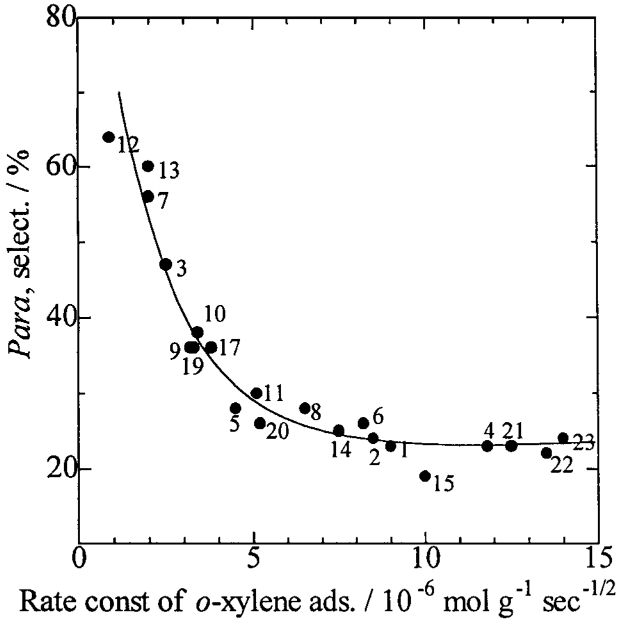

FIG. 1. Relation of the selectivity of *p*-xylene formation with the rate constant of *o*-xylene adsorption. The number shows the serial number of ziolite species ZSM-5 prepared in the previous paper (1).

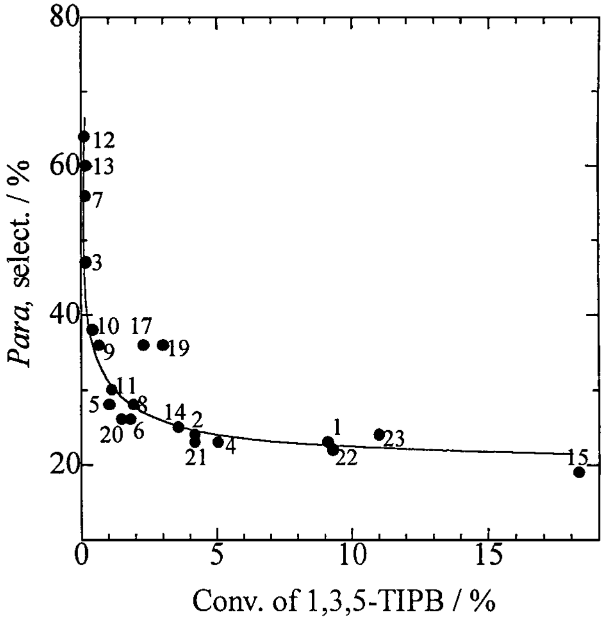

FIG. 2. Relation of the selectivity of *p*-xylene formation with the conversion of 1,3,5-triisospropylbenzene.

The rate constant of adsorption *k* is theoretically correlated with 1/*r* (*r*, crystal radius). On the other hand, the cracking of 1,3,5-TIPB is correlated with the external surface area and the density of the acid site. Thus, the cracking rate can be related to 1/*r* and the surface density of Al, i.e., Al/(Si + Al), because the external surface area is proportional to 1/*r* on the basis of zeolite morphology (cube or sphere), and the acid site is generated by the Al cation. The rate of cracking of 1,3,5-TIPB normalized by the Al density, therefore, should be linearly proportional to the adsorption rate constant. The normalized conversion of cracking of 1,3,5-TIPB, named external surface acidity parameter, was thus plotted against the rate constant of *o*-xylene adsorption, as shown in Fig. 3. Both parameters were, however, not linearly correlated, and it was unexpected from the above consideration. Note that this is a theoretically unexpected finding, but a usual trend observed in the synthesized zeolites. In other words, there is a trend in the synthesized HZSM-5 that the external surface acid site becomes abundant on the small crystal of zeolite. In addition, it is important to take notice that some ZSM-5 species do not follow the simple relation. For these species, Nos. 1, 15, 17, and 19, two kinds of deviations could be indicated; i.e., (1) the number of external acid sites is too large, when the plot

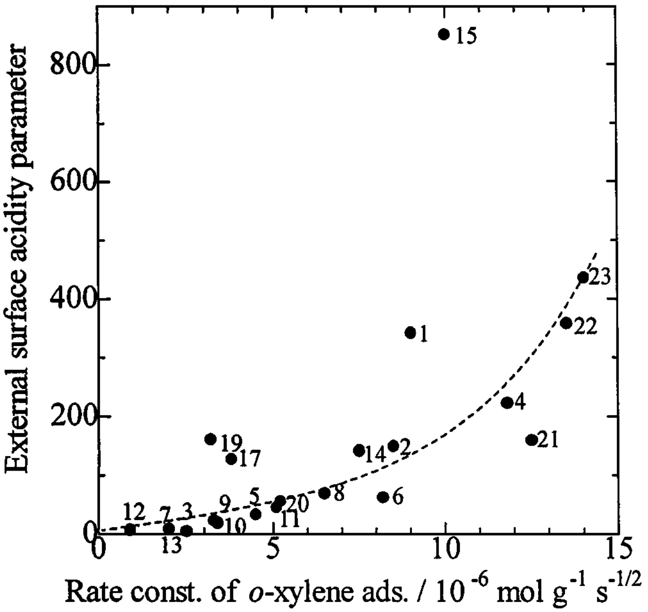

FIG. 3. Relation between the rate constant of *o*-xylene adsorption and the external surface acidity parameter which was defined as the conversion of 1,3,5-TIPB divided by Al/(Si + Al).

deviates vertically, or (2) the rate constant of adsorption is too small, when the plot deviates horizontally.

Based on this consideration, we can discuss the unusual selectivity. The low selectivity of No. 15 has already been explained due to the high external surface acidity. On the other hand, the selectivity on Nos. 17 and 19, which was higher than expected from the relation in Fig. 2, cannot be explained by the high external surface acidity, but by the unusual slow diffusion rate. Maybe some amorphous deposits in the pore narrow the pore size of these zeolites. The silica-to-alumina ratio of both zeolites, 105 and 109, were higher than others; i.e., the high concentration of Si may affect the diffusion rate. Therefore, the selectivity shown in Fig. 2 can be explained from the parameter of external surface acidity, except for the unusual species of Nos. 17 and 19 with the suppressed diffusion rate. A deviation of No. 1 in Fig. 3 does not seem to be so large as to affect the selectivity.

Dependence of the property on the synthesis conditions is not certain. However, the unusual property of the zeolite might be related to the preparation conditions. For Nos. 15 and 19, the stirrer in the autoclave rotated at a slow rate, 50 and 0 rpm, respectively. KCl was used only for No. 17 in place of NaCl. These conditions of preparation may cause the nonhomogeneous distribution of zeolite cations.

In conclusion, the selectivity in disproportionation can be correlated with not only the diffusion rate but also the external solid acidity, except for unusual species of zeolites. Unusual behavior of the zeolite is caused by the high external surface acidity or by the slow diffusion rate. The latter property may be related to the presence of deposits in the pore to suppress the diffusion of the molecule. In other words, these unusual properties may be correlated with nonhomogeneous distribution of cation Al or Si in the zeolite. These zeolite properties affect the selectivity so significantly. Therefore, the source of selectivity strongly depends on the physical and chemical properties of the zeolite. One can thus understand that the identification of the generation of shape selectivity needs total and precise characterization of zeolites.

From the present observation, it is concluded that the selectivity of *p*-xylene formation is not governed primarily by the first step of the disproportionation; rather, the following step of diffusion or isomerization of product xylene isomers decides it, as described in the literature (4).

REFERENCES

1. Kim, J.-H., Kunieda, T., and Niwa, M., *J. Catal.* **173**, 433 (1998).
2. Melson, S., and Schuth, F., *J. Catal.* **170**, 46 (1997).
3. Kaeding, W. W., Chu, C., Young, L. B., and Butter, S. A., *J. Catal.* **69**, 392 (1981).
4. Olson, D. H., and Haag, W. O., *in* "Catalytic Materials" (T. E. Whytes, Jr., Ed.), ACS Symposium Series **248**, p. 257. American Chemical Society, Washington, DC, 1984.
5. Kaeding, W. W., *J. Catal.* **95**, 512 (1985).
6. Hibino, T., Niwa, M., and Murakami, Y. *J. Catal.* **128**, 551 (1991).
7. Kim, J.-H., Namba, S., and Yashima, T., *Appl. Catal. A* **83**, 51 (1992).
8. Wu, P., Komatsu, T., and Yashima, T., *Microporous Mesoporous Mater.* **22**, 343 (1998).
9. Kaeding, W. W., *J. Catal.* **95**, 512 (1985).
10. Klemm, E., Wang, J., and Emig, G., *Chem. Eng. Sci.* **52**, 3173 (1997).
11. Kunieda, T., Katada, N., and Niwa, M. "Proceedings of 12th International Zeolite Conference, Baltimore" (M. M. J. Treacy, B. K. Marcus, M. E. Bisher, and J. B. Higgins, Eds.). IV-2549, MRS, Warrendale, 1999.