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Behavior of Quinoline Derivatives as Poisons in Isomerization of *p*-Xylene on HZSM-5 Zeolite

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The influence of poisoning with quinoline derivatives having various molecular dimensions on the activity of HZSM-5 zeolite for the isomerization of *p*-xylene was studied. Quinoline can easily enter the pores of HZSM-5 and poison the catalyst completely. On the other hand, 2,4-dimethylquinoline and β-naphthoquinoline, which are the largest molecules in the quinoline derivatives used, cannot enter the pores and selectively poison the acid sites solely on the external surface of HZSM-5 crystallites. 4-Methylquinoline, which has an intermediate size, is adsorbed on the acid sites not only on the external surface but also near the pore entrances and inhibits the diffusion of xylenes through the pore entrances. Moreover, it can diffuse into the interior of the pore at a very slow rate.

INTRODUCTION

It has been reported that poisoning with 4-methylquinoline improves the shape selectivity of HZSM-5 zeolite for many reactions, e.g., the cracking of hexane and 2,2-dimethylbutane (*1*), the alkylation of toluene with methanol (*2*), methanol conversion (*3*), the alkylation of toluene with ethylene (*4*). It has also been reported that this kind of improvement in shape selectivity is attributed to selective poisoning solely on the external surface of zeolite crystallites (*1–3*). That is, it is thought that 4-methylquinoline is too large in molecular dimension to enter the pores of HZSM-5 zeolite and, consequently, selectively poisons the acid sites solely on the external surface of the zeolite crystallites. By poisoning only these acid sites, which are not responsible for the shape selectivity, the shape selectivity of HZSM-5 zeolite is improved.

In the present work, we wish to clarify the influence of poisoning with quinoline derivatives having various molecular dimensions on the activity of HZSM-5 zeolite for the isomerization of *p*-xylene. Moreover, we will discuss the significance of the location of the acid sites poisoned by the quinoline derivatives.

EXPERIMENTAL

Materials

Derivatives used as poisons were quinoline, 4-methylquinoline, β-naphthoquinoline, and 2,4-dimethylquinoline. These structures and the order of their molecular sizes are shown in Fig. 1. The reactant (*p*-xylene) and the quinoline derivatives were pure grade. They were supplied by the commercial source and were used without further purification.

Our ZSM-5 zeolites were prepared according to the procedure described by Argauer *et al.* (*5*) and were transformed into H-form by the cation-exchange procedure with 1 *N* HCl at 333 K. The Si/Al atomic ratios of the HZSM-5 zeolites were 16, 27, 48, and 90 and the Na/Al atomic ratios of the zeolites were less than 0.005. The crystallite sizes of the zeolites determined by the broadening of X-ray diffraction were 30–60 nm. The external surface area of the HZSM-5 with a Si/Al ratio of 48 was about 20 m^2/g which corresponded to about 4.5% of the total surface area (*6*). XPS studies showed that the Si/Al ratio at the external

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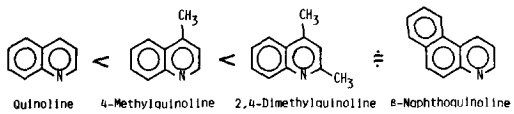

FIG. 1. Structures and the order of molecular sizes of quinoline derivatives used.

surface did not differ very much from the bulk Si/Al ratio (*7*).

Apparatus and Procedure

The isomerization of *p*-xylene was carried out in a fixed-bed-type apparatus with a continuous flow system at atmospheric pressure. The catalyst (0.5 g) was placed in a fused silica reactor with an electric heater. The dehydration of the catalyst was carried out in a helium stream for 1 h at 823 K and then the temperature was brought to the reaction temperature, 543 K. The reaction was started by adding the reactant into the helium stream. The feed rate of *p*-xylene was 0.105 mol · h^{-1} · g^{-1} and the initial partial pressure of *p*-xylene was 0.4 atm. The reaction products were analyzed by gas chromatography (column; Benton 34 (5%) and DIDP (5%) supported on Uniport KA, 4 m long, 3 mm diameter).

The poisoning with the quinoline derivatives was carried out in two manners, that is, the continuous method (the poisons were continuously added to the catalyst) and the pulse method (the poisons were pulsed into the catalyst). In the continuous method, the feed rates of quinoline derivatives were 9.0×10^{-4} mol · h^{-1} · g^{-1} and the initial partial pressures were 3.4×10^{-3} atm.

RESULTS AND DISCUSSION

It has been reported that the isomerization of xylene on HZSM-5 proceeds selectively with a very small extent of side reactions, dealkylation and transalkylation (*8*). In our study, the isomerization of *p*-xylene proceeded selectively and the total yield of side reaction products, benzene, toluene, and trimethylbenzenes was less than 0.2% at 30% of *p*-xylene conversion.

Figure 2 shows the effect of the continuous addition of quinoline derivatives on the conversion of *p*-xylene. In the case of quinoline, whose molecular size was the smallest of the quinoline derivatives used, the conversion reached almost zero at 60 min after the addition. The number of quinoline molecules added for 60 min corresponded to about three times as much as the number of aluminum atoms in the HZSM-5. The activity of the catalyst poisoned completely with quinoline did not recover by treatment with flowing helium at 543 K for 3 h. Therefore, it is concluded that quinoline can easily enter the pores of HZSM-5 and poison all acid sites. Moreover, quinoline is irreversibly adsorbed on the acid sites at 543 K.

In the cases of β-naphthoquinoline and 2,4-dimethylquinoline, the conversion of *p*-xylene dropped at the initial stage of the addition and then did not decrease remarkably with process time. It is suggested that these two bases are too large in molecular size to enter the pores of HZSM-5 and, therefore, poison only the acid sites on the external surface of the zeolite crystallites.

In the case of 4-methylquinoline, the conversion of *p*-xylene dropped rapidly at the

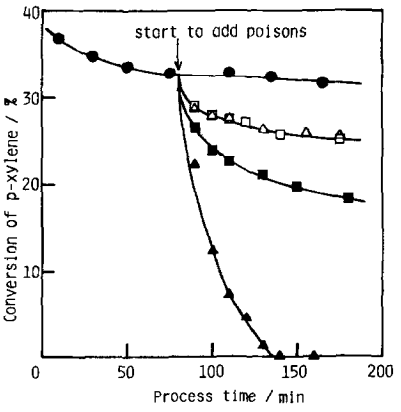

FIG. 2. Effect of continuous addition of quinoline derivatives on the conversion of *p*-xylene. ●, Without poison; ▲, quinoline; ■, 4-methylquinoline; □, 2,4-dimethylquinoline; △, β-naphthoquinoline. Catalyst, HZSM-5 (Si/Al = 48); reaction temperature, 543 K; W/F = 3.8 g · h · mol^{-1}; partial pressure of xylene, 0.40 atm.

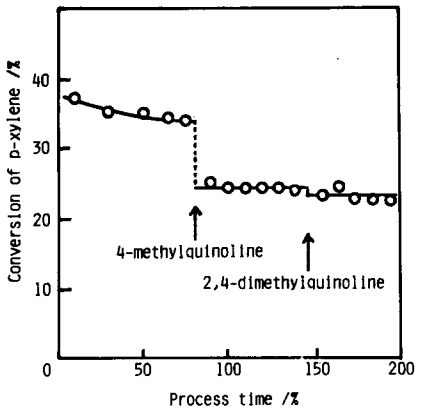

FIG. 3. Effect of pulses of 4-methylquinoline and 2,4-dimethylquinoline on conversion of *p*-xylene. Catalyst and reaction conditions are described in Fig. 2.

initial stage of the addition and then gradually decreased with process time. These results show that 4-methylquinoline can enter the pores of HZSM-5 and that the rate of diffusion of 4-methylquinoline within the pore is very slow.

The drop in conversion at the initial stage by the continuous addition of 2,4-dimethylquinoline is less than that by the continuous addition of 4-methylquinoline. If the poisons are pulsed, the difference of the drop in conversion at the initial stage between 4-methylquinoline and 2,4-dimethylquinoline will be shown more clearly. The effect of the slow step in poisoning by the slow diffusion of 4-methylquinoline in the zeolite pore can be excluded to a considerable extent.

The effect of pulse addition of 4-methylquinoline and 2,4-dimethylquinoline on the conversion of *p*-xylene was examined. Each pulse size was 100 μl per unit weight of the catalyst and was sufficient for all acid sites in the catalyst. As shown in Fig. 3, the conversion of *p*-xylene dropped moderately by the addition of a 4-methylquinoline pulse, but little effect was noted by the subsequent addition of a 2,4-dimethylquinoline pulse. On the other hand, the conversion of *p*-xylene was lowered slightly by the first 2,4-dimethylquinoline pulse and was virtually unaffected by a second addition of 2,4-dimethylquinoline. However, it was lowered considerably again by the subsequent addition of a 4-methylquinoline pulse as shown in Fig. 4. Thus, 2,4-dimethylquinoline cannot poison the catalyst poisoned already with 4-methylquinoline, but 4-methylquinoline can poison the catalyst poisoned with 2,4-dimethylquinoline. These facts show that 4-methylquinoline can reach the acid sites on which 2,4-dimethylquinoline cannot be adsorbed. These acid sites may exist in the pores near the external surface of HZSM-5 crystallites. The addition of a 4-methylquinoline pulse lowers the conversion of *p*-xylene more severely than that of 2,4-dimethylquinoline pulse, probably because 4-methylquinoline adsorbed on the acid sites in the pores near the external surface inhibits the diffusion of xylene.

The pulsed 2,4-dimethylquinoline poisons only the active sites on the external surface of HZSM-5 crystallites. On the other hand, the pulsed 4-methylquinoline poisons not only these acid sites but also the acid sites in the pores near the entrances. The adsorption of 4-methylquinoline on the later acid sites is a fast process compared to the diffusion into the interior of the pore. If 2,4-dimethylquinoline adsorbed on the external surface does not affect the diffusion of xylenes through the pore entrances, the percentage deactiva-

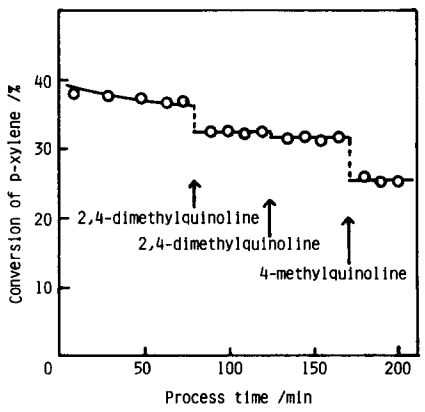

FIG. 4. Effect of pulses of 2,4-dimethylquinoline and 4-methylquinoline on conversion of *p*-xylene. Catalyst and reaction conditions are described in Fig. 2.

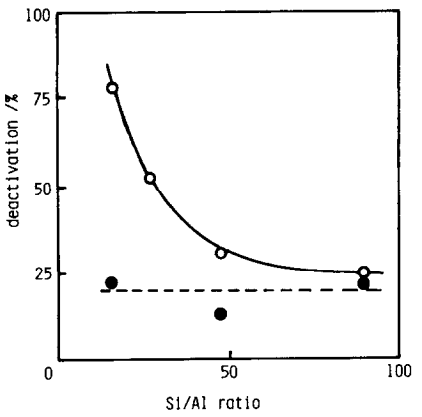

FIG. 5. Effect of Si/Al ratios of HZSM-5 on percentage deactivation by adding 4-methylquinoline and 2,4-dimethylquinoline pulses. ○, 4-Methylquinoline; ●, 2,4-dimethylquinoline. Reaction temperature, 543 K; partial pressure of xylene, 0.40 atm W/F = 1.1–6.8 g · h · mol^{-1}.

tion, by addition of 2,4-dimethylquinoline pulse, will not be strongly dependent on the Si/Al ratio of HZSM-5. The percentage deactivation is defined as

$$\text{Percentage deactivation} = \frac{\text{Drop in conversion by poisoning}}{\text{Conversion just before poisoning}} \times 100\%$$

On the other hand, 4-methylquinoline adsorbed on the acid sites near the pore entrances lowers the rate of xylene diffusion through the pore entrances. The probability that the acid sites, on which 4-methylquinoline can be adsorbed, exist near the pore entrances decreases with increasing Si/Al ratios of HZSM-5. Consequently, the percentage deactivation by adding a 4-methylquinoline pulse will be lowered with increasing Si/Al ratios.

The effect of Si/Al ratios of HZSM-5 on the percentage deactivation by adding 4-methylquinoline and 2,4-dimethylquinoline pulses was examined. The conversion just before poisoning was adjusted to 25–40% by changing W/F. The results are shown in Fig. 5. The percentage deactivation by poisoning with 4-methylquinoline decreased remarkably with increasing Si/Al ratios as expected. That is, at a Si/Al ratio of 16, the percentage deactivation was about 80% and at a Si/Al ratio of 90 it reached about 25%. On the other hand, the percentage deactivation by poisoning with 2,4-dimethylquinoline did not change remarkably with the Si/Al ratios and was about 20% throughout the range tested. This result may be explained by assuming that about 20% of the acid sites are external or that the rate of the *p*-xylene isomerization is diffusion-controlled and the effectiveness factor of the catalyst is about 0.2. (It is noted that the external surface area of our HZSM-5 is about 4.5% of the total surface area (*6*) and that the surface Si/Al ratio did not differ much from the bulk Si/Al ratio (*7*).)

In conclusion, 4-methylquinoline is adsorbed on the acid sites not only on the external surface but also near the pore entrances and influences the diffusion of xylenes through the pore entrances. Moreover, it can diffuse into the interior of the pores at a very slow rate. On the other hand, 2,4-dimethylquinoline and β-naphthoquinoline, whose molecular sizes are larger than that of 4-methylquinoline, is adsorbed on the acid sites solely on the external surface. Quinoline can easily enter the pores of HZSM-5 and kill the isomerization activity of HZSM-5 completely.

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