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# Determination of External Surface Area of ZSM-5 Type Zeolite

A ZSM-5-type zeolite exhibits beautiful shape selectivities for methanol conversion into hydrocarbons (*1*), alkylation of toluene with methanol (*2*), and competitive cracking of paraffins (*3*). These shape selectivities are caused by the characteristic pore dimension and structure of ZSM-5-type zeolite. When we consider the shape selectivity of ZSM-5-type zeolite, the smaller external surface area of the zeolite may provide the higher shape selectivity, because the active sites on the external surface may be independent of the shape selectivity. On the other hand, when we consider the catalyst life, the smaller external surface area may provide the higher deactivation rate, because the external surface area corresponds to the number of pore entrances. Therefore, the determination of the external surface area of ZSM-5-type zeolite is very important in discussing the shape selectivity or the catalyst life.

In this note both total and external surface areas were determined for some ZSM-5-type zeolites. The total areas were determined in the usual way for adsorbents having Langmuir isotherms. The external areas were determined by two different methods. One method was the measurement of the amount of nitrogen adsorbed at 77 K on the external surface of the zeolite, after its internal pores had been filled with butane (filled pore method). The other method was the measurement of the amount of 2,2-dimethylpropane that adsorbed rapidly on the zeolite.

The samples used in this work were three kinds of ZSM-5-type zeolite, HZSM-5(a), HZSM-5(b), and NaZSM-5, whose scanning-electron micrographs are shown in Fig. 1. The sample of HZSM-5(a) seems to be an aggregation of small crystallites whose size, determined from the broadening of X-ray diffraction, is about 57.6 nm. The crystallite shapes of HZSM-5(b) and NaZSM-5 are a flat hexagonal prism and a partially fused rectangular parallelepiped, respectively. The apparent order of the crystallite sizes of three samples is as follows:

HZSM-5(b) > NaZSM-5 > HZSM-5(a).

Helium and nitrogen from tanks were purified by passing them through tubes filled with copper powder at 773 K and activated carbon at 77 K. Butane and 2,2-dimethylpropane were obtained from Takachiho Chem. Ind. Ltd. and Tokyo Kasei kogyo Company Ltd., respectively. They were purified by repeated distillations. The samples were calcined at 773 K in air for 1 h and degassed at the same temperature for 2 h before making the adsorption experiments.

The total surface areas of HZSM-5(a), HZSM-5(b), and NaZSM-5, obtained from the adsorption of nitrogen at 77 K using the conventional volumetric method for Langmuir adsorption isotherms, are shown in Table 1.

If the adsorption of nitrogen on the ZSM-5-type zeolite, whose internal pores have been filled with butane, is carried out at 77 K, the ∞-form BET isotherm will be obtained and the external surface area of the zeolite will be determined from the BET plot.

The Langmuir isotherm was obtained for the adsorption of butane on HZSM-5(a) at 273 K, and the amount adsorbed at saturation was 42.3 STP cm$^3$/g. After the adsorption equilibrium was attained at a pressure of 52.4 kPa, helium was introduced into the adsorption cell to reach 1 atm in total pressure. The amount adsorbed at 52.4 kPa cor-

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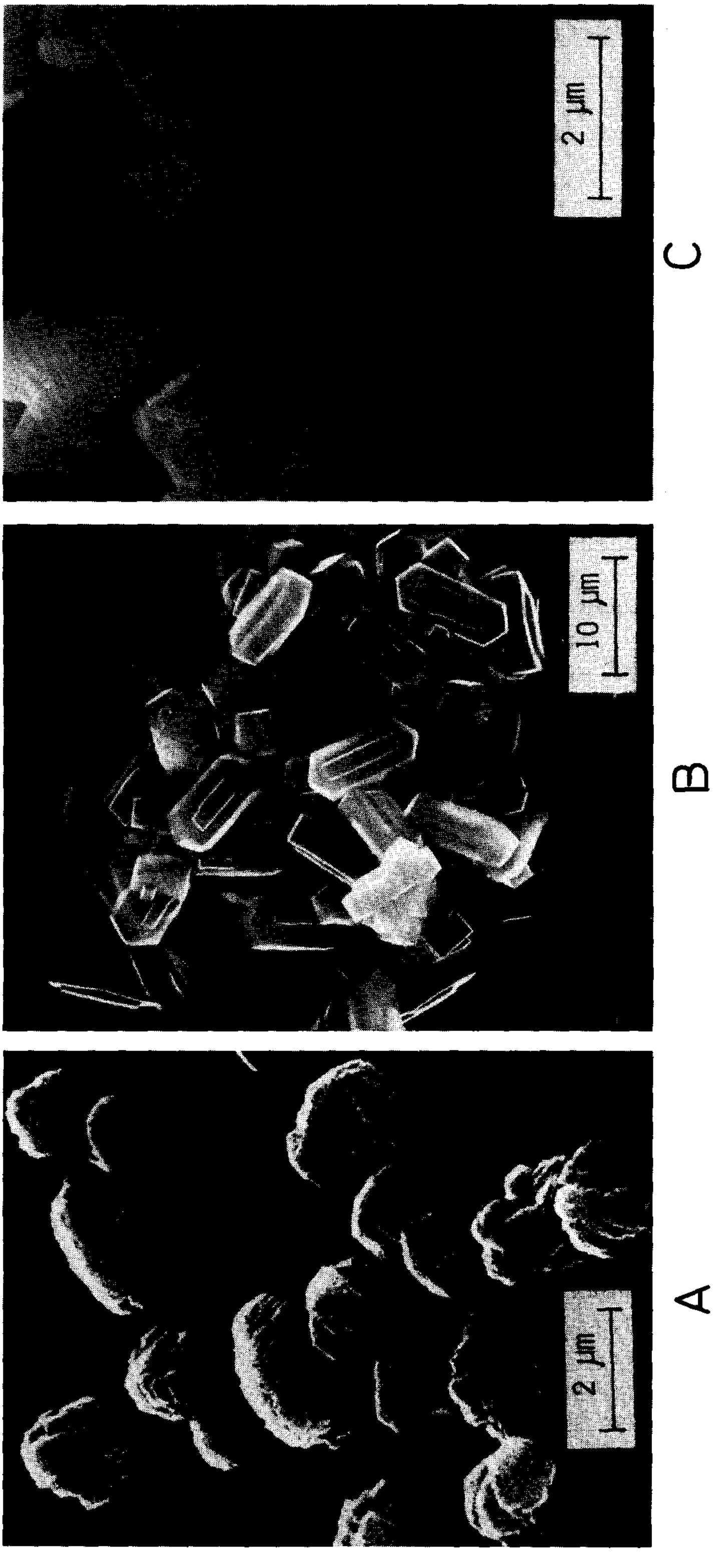

FIG. 1. Scanning-electron micrographs of (A) HZSM-5(a), (B) HZSM-5(b), and (C) NaZSM-5.

TABLE 1

Total and External Surface Areas of ZSM-5-Type Zeolites

| Sample | Total surface area ($m^2 \cdot g^{-1}$) | External surface area ($m^2 \cdot g^{-1}$) | |
|---|---|---|---|
| | | Filled pore method | Adsorption kinetics |
| HZSM-5(a) | 447 | 24.5 | 19.8 |
| HZSM-5(b) | 422 | — | 1.1 |
| NaZSM-5 | 359 | — | 8.3 |

responds to 99.3% of that at saturation. After the cell was immersed in a Dewar vessel containing liquid nitrogen, the helium was pumped out. The residual pressure of butane adsorbed on the zeolite at 77 K was too small to be removed from the zeolite. Then the nitrogen adsorption on the HZSM-5(a), whose internal pores had been filled with butane, was carried out at 77 K. As expected, the ∞-form BET isotherm was obtained for the adsorption of nitrogen and the BET plot is shown in Fig. 2. Therefore, with the pores of the HZSM-5(a) almost filled with butane, the external surface area of the HZSM-5(a) was calculated at 24.5 $m^2/g$ from the monolayer volume, 5.62 STP $cm^3/g$, obtained from the BET plot.

When the rate controlling process in the adsorption on a zeolite is the activated diffusion of the adsorbate molecule through intracrystalline channels, then the process may be described by the following equation for small values of time $t$, after an initial stage (*4*)

$$Q_t = B \cdot t^{1/2} + C \qquad (1)$$

where $Q_t$ is the amount adsorbed at time $t$, and $B$ and $C$ are constants. Based on Eq. (1), a plot of the amount adsorbed $Q_t$ versus $t^{1/2}$ should yield a straight line except for a "foot," which may occur near the start of the curve and which results from the very rapid adsorption that occurs on the external surface of the zeolite crystal at the initiation of the experiment (*4*, *5*). The constant $C$, the amount of adsorbate adsorbed on the external surface of the zeolite, is found from the intercept of the linear portion of the $Q_t$ vs $t^{1/2}$ plot at the $Q_t$ axis.

The measurements of the adsorption kinetics for the 2,2-dimethylpropane were conducted by the volumetric method using the temperature-compensated, differential tensimeter invented by Suzuki (*6*). The relation of $Q_t$ and $t^{1/2}$ on the HZSM-5(a) and HZSM-5(b) at 283 K are shown in Fig. 3. The estimated values of $C$ on HZSM-5(a) and HZSM-5(b) obtained from Fig. 3 were 2.89 and 0.161 STP $cm^3/g$ at the pressures $P$ of 30.75 and 29.94 kPa, respectively. The volume required to cover the external surface with monomolecular layer of 2,2-dimethylpropane $v_m$ was approximately obtained by the "single point" method (*7*) using the following equation

$$v_m = (1 - P/P_0)C \qquad (2)$$

where $P_0$ is the saturated vapor pressure of 2,2-dimethylpropane at 283 K and is 101.3 kPa. The cross-sectional area of the 2,2-dimethylpropane calculated from its density (*8*) was 0.367 $nm^2$. The external surface ar-

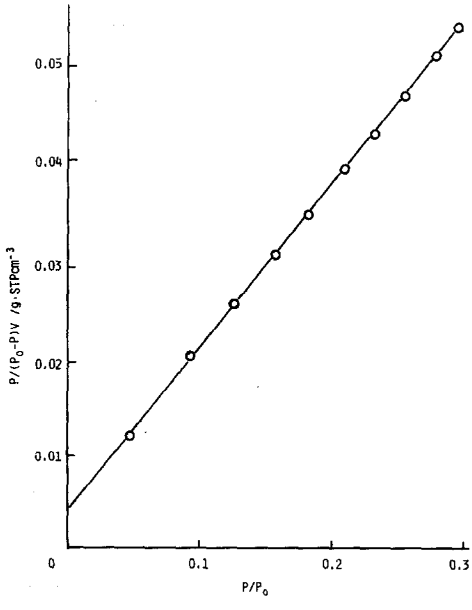

FIG. 2. BET plot for nitrogen adsorption at 77 K on HZSM-(a), after its pores were filled with butane.

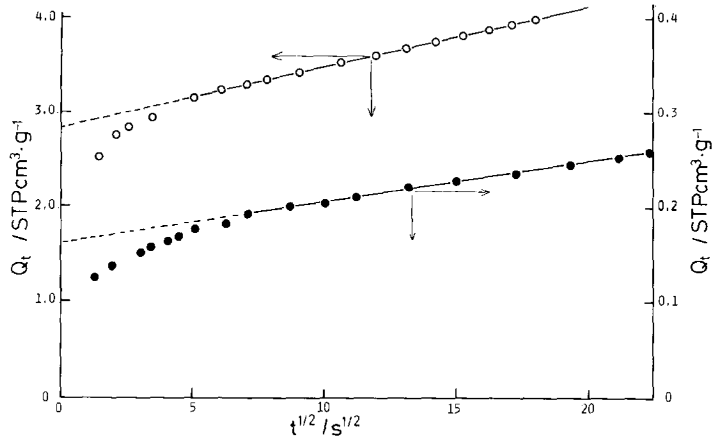

FIG. 3. The relations between $Q_t$ and $t^{1/2}$ on (○) HZSM-5(a) and (●) HZSM-5(b).

eas obtained with these values and the value for NaZSM-5 are summarized in Table 1.

For the HZSM-5(a), the external surface areas obtained by both methods, the filled pore method and the adsorption kinetics method, are in fairly good agreement with each other, and are about 4.5% of the total surface area. For the HZSM-5(b), the external surface area obtained by the adsorption kinetics method is 0.26% of the total surface area, and is in good agreement with the geometrical external surface area, 0.8 m$^2$/g, estimated from the scanning-electron micrograph in Fig. 1. The external surface area of NaZSM-5 is intermediate between those of HZSM-5(a) and HZSM-5(b).

The filled pore method consists of two processes, the adsorption of butane at 273 K and the adsorption of nitrogen at 77 K. Therefore, the kinetic method, which consists of the adsorption of 2,2-dimethylpropane at 283 K, is simpler than the filled pore method for determining the external surface area of the zeolite.

The external surface area of the HZSM-5(a) is about 20 times larger than that of the HZSM-5(b). Consequently, the catalytic properties of these two samples might be different from each other.

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