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New Method to Determine the External Surface Area of ZSM-5 Zeolite

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The external surface area of ZSM-5 zeolite obtained by the benzene filled-pore method is smaller than that by the electron micrograph method when the crystalline diameter is smaller than 0.3 μm. On the other hand, the surface area of ZSM-5 which contains template in its intra-crystalline micro-pores agrees well with the external surface area of calcined ZSM-5 obtained by the electron micrograph method in a whole range of crystalline diameters.

The external surface area (ESA) is an important parameter for characterization of zeolite, and the ESA often plays a significant role in the catalytic reactions such as the vapor phase Beckmann rearrangement over ZSM-5 zeolite, in which the active site is estimated to be the neutral silanols on the external surface of ZSM-5.[1,2] The ESA of ZSM-5 was measured for the first time by Suzuki et al. in 1983.[3] In previous works, the ESA of zeolite has been measured by one of the following four methods; the filled-pore method,[4,5] the BET method using large molecules,[6] the adsorption kinetics method[4] and the electron micrograph method.

Here, we report that the ESA of ZSM-5 can be determined by measuring the BET area of the uncalcined ZSM-5 which contains templates among its channels ("uncalcination method").

The ZSM-5s were hydrothermally synthesized according to (1) Yashima's method which utilizes sodium silicate as a silicon source and tetra-n-propylammonium bromide as a template (samples No. 3, 4, 5)[7] or to (2) DuPont's method which utilizes tetraethyl orthosilicate as a silicon source and tetra-n-propylammonium hydroxide as a template in a mixed solvent of ethanol and water (samples No. 1, 2).[8] The uncalcined samples were only dried at 120 ℃ for 12 h and they were not calcined. The calcined samples were treated in air stream at 450 ℃ for 3 h. The SEM images of ZSM-5 samples (No. 1 − 5) are shown in Fig. 1.

The pore size distribution and the BET plot were analyzed using SORPTOMATIC -1800 (CARLO ERBA corporation), and the surface areas (total and external) were measured using Monosorb (Quantachrome corporation). The benzene-filled-pore method was conducted according to the literature,[9] and the time for equilibrium adsorption of benzene was determined as 24 h by experiment. The geometrical ESA was calculated from the particle diameter obtained from the SEM image, on the assumption that the particle is spherical and its real density is 2.

Table 1 shows the ESAs obtained by (a) the benzene-filled-pore method, (b) the uncalcination method and (c) the electron micrograph method together with other data such as particle diameters, Si/Al atomic ratios and total surface areas. Figure 2 illustrates the relation between the particle diameter obtained by SEM image and the ESA obtained by each method. Whereas the ESAs obtained by

Table 1. External Surface Area (ESA) of ZSM-5

Sample No.	Si/Al Atomic ratio	Total surface area $/m^2 g^{-1}$	External surface area $/m^2 g^{-1}$ a) (a)	(b)	(c)	Diameter $/\mu m$
1	27500	382	11.3	11.7	9.1	0.33
2	2950	349	1.4	1.4	0.8	3.8
3	48.6	362	10.1	25.3	35.7	0.08
4	32.0	343	12.1	48.3	71.4	0.04
5	7.2	241	31.9	99.3	60.0	0.05

a) (a); benzene-filled-pore method, (b); uncalcination method, (c); electron micrograph method

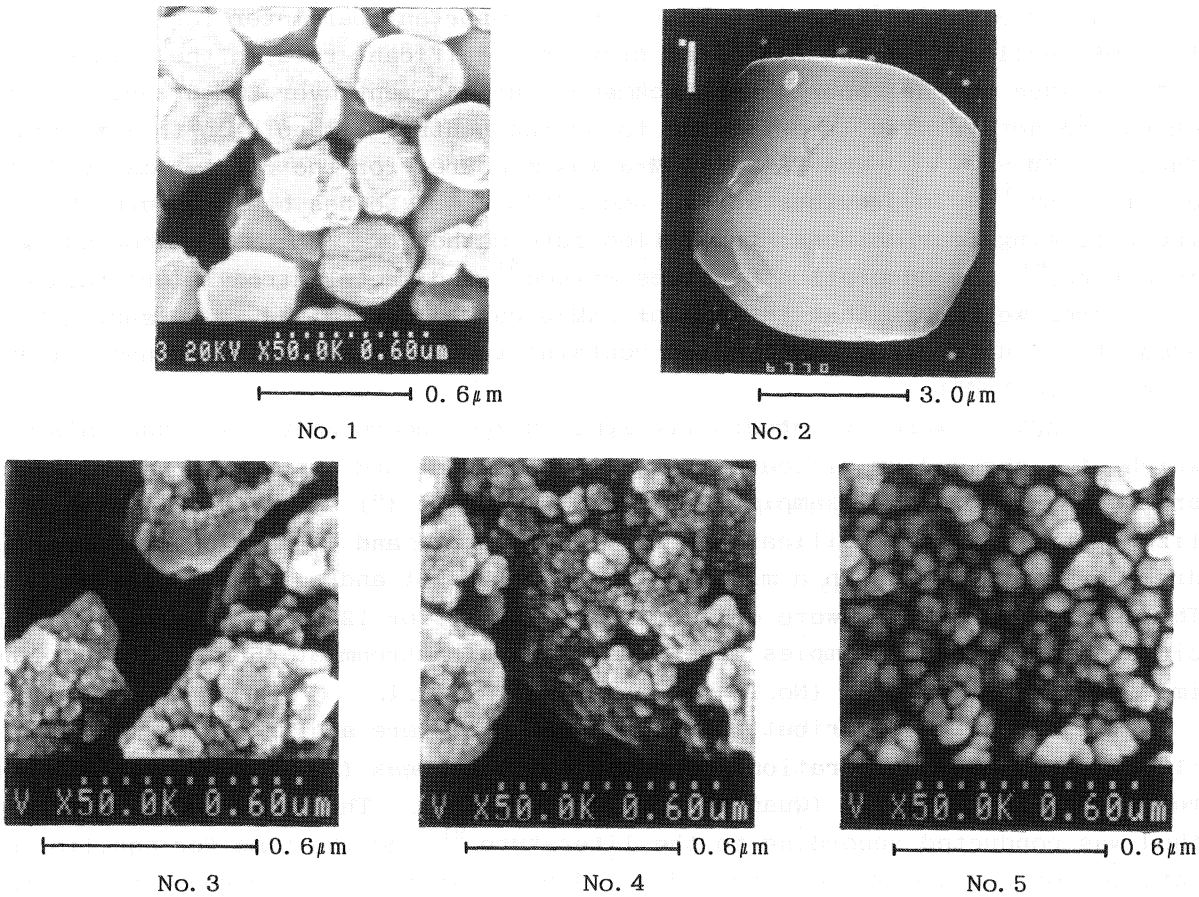

Fig. 1. SEM images of ZSM-5 samples No.1– 5.

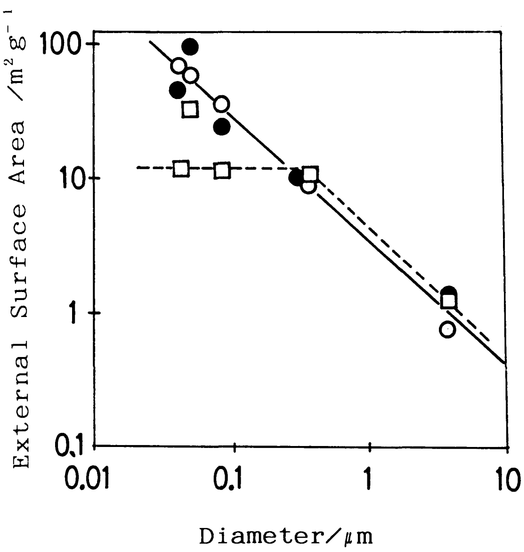

Fig. 2. Dependency of ESA on particle diameter.
□ ; Benzene-pore-filled method,
● ; Uncalcination method,
○ ; Electron micrograph method.

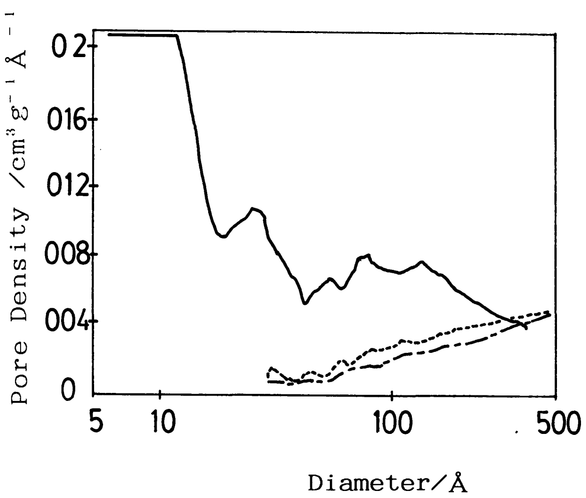

Fig. 3. Pore size distribution. Sample No. 4.
———; Calcined
– – –; Benzene-pore-filled
-------; Uncalcined

(b) the uncalcination method and (c) the electron micrograph method agree well with each other, the ESA obtained by (a) the benzene-filled-pore method deviates from the formers and becomes constant (≒ $10 m^2/g$) when the particle diameter is smaller than 0.3 μm.

Figure 3 illustrates the pore size distributions of ZSM-5 (No. 4) calculated by the Dollimore-Heal method for the calcined sample, the calcined sample, in which the pores have been filled up with benzene and the uncalcined sample. There exist intra-crystalline micro-pores smaller than 20Å in the calcined ZSM-5, but there is no micro-pore smaller than 20Å in both the uncalcined ZSM-5 and the calcined, in which the pores have been filled up with benzene.[10] It is considered that templates occupy all the intra-crystalline micro-pores only in the uncalcined ZSM-5. On the contrary, considering the data in Fig. 2, benzene is regarded as occupying not only all the intra-crystalline micro-pores but also the inter-crystalline semimicro-pores when the particle diameter is smaller than 0.3 μm.

Figure 4 illustrates the BET plots for calcined and uncalcined ZSM-5 (No. 4). A slight upward slope of the BET plot for calcined ZSM-5 (Fig. 4A) reflects the adsorption both on micro-pores (Langmuir type) and on external surface (BET type) of ZSM-5. On the other hand, the straight line BET plot for uncalcined ZSM-5 (Fig. 4B) indicates adsorption on the external surface of ZSM-5 only.

We further measured the amount of N_2 gas adsorbed on uncalcined ZSM-5 (No. 4) by benzene-filled-pore method. The adsorbed amount corresponded to $10.4 m^2/g$, which was nearly equal to the value obtained by benzene-filled-pore method for calcined ZSM-5. This fact also suggests that benzene fills not only the intra-crystalline micro-pores but also the inter-crystalline semimicro-pores whose diameter is smaller than that decided by Kelvin's formula (1).

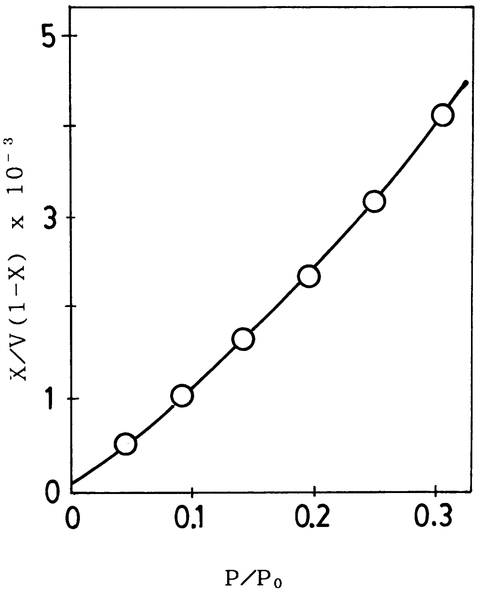

Fig. 4A. BET plot for calcined ZSM-5.

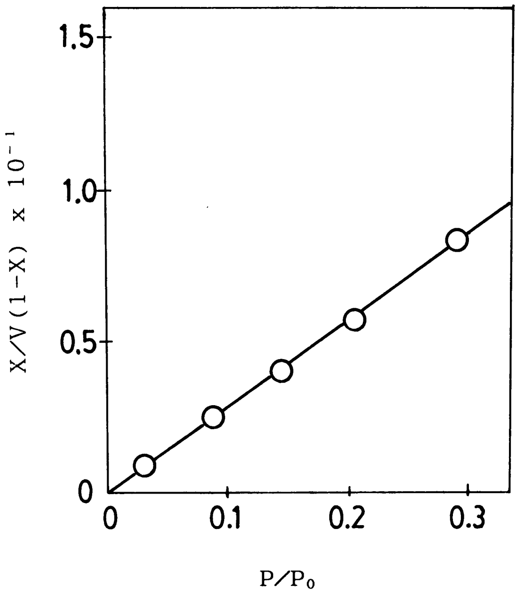

Fig. 4B. BET plot for uncalcined ZSM-5.

Sample No. 4, P/P_0; Partial pressure, $X=P/P_0$, V; Volume/cm^3 of adsorbed nitrogen

$$RT\ln(P_0/P\infty)=4\gamma\, v/D; \quad (\gamma\text{ ;surface energy, } v\text{; molar volume, } D\text{; diameter}) \qquad (1)$$

In conclusion, we have proposed here a new method ("uncalcination method") to determine the external surface area (ESA) of ZSM-5 zeolite, and this method is considered to be applicable to other zeolites which contain templates within their intra-crystalline micro-pores.

References

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10) In this method, the pores smaller than about 20Å can not be distinguished from each other. Therefore, when the channel of ZSM-5 (whose diameter is 5.5-6.0 Å) is filled up with templates or benzene, a pore density smaller than 20Å drops to a false zero.

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