JOURNAL OF CATALYSIS **100**, 264–269 (1986)

# NOTES

## Benzene-Filled Pore Method: A Method of Measuring External Surface Areas Applicable to Zeolites with Low-to-High Si-to-Al Ratios

### INTRODUCTION

The external surface area is one of the most significant physical properties of zeolite, since it is relevant to such basic properties as the size and shape of the zeolite crystal. Moreover, external surface area measurements are of importance in understanding the catalytic activity and adsorptive properties, since the external surface contributes only to the nonselective reaction or adsorption. It has been reported (*1*) that the life of ZSM-5 containing catalysts, when used in conversion reactions, depends upon the size of the zeolite crystals. In spite of this significance, the external surface area is often neglected, and relatively few studies have been reported.

In previous works, the external surface area of zeolite has been measured by (a) the filled-pore method (*2*), (b) the BET method using large molecules (*3*), or (c) the sorption kinetics so-called "foot method," or, when possible, by (d) electron microscopy. There have been only a few reports about the BET method using large molecules, probably because of the low vapor pressure of the larger compounds. Barrer used the foot-method to measure the external area of mordenite and chabazite (*3*). Since the adsorbate organic molecule has to be adsorbed slowly in this method, the molecule which is exactly fitted to the zeolite pore must be chosen. Suzuki *et al.* (*4*) proposed neopentane for measurement of the external surface area of ZSM. In contrast to problems encountered with these methods, the filled-pore method appears to be the most direct in determining the external surface area. The principle of the pore-filling method is that an adsorbate is first used to fill the internal pore structure. The sample is then lowered to a temperature of 77 K where the accessible surface is measured by nitrogen BET. Water is usually recommended as an adsorbate (*2*). The pores of fully hydrated zeolite are believed to be sufficiently filled to inhibit the penetration of nitrogen.

However, as reported in this study, the ZSM-5 pore was not filled with water because of its hydrophobicity; therefore the external surface area of the ZSM-5 zeolites could not be measured by the water-filled pore method. However, no appropriate adsorbate has been identified so far for the ZSM-5 zeolite, although such hydrocarbons as benzene and hexane might be considered. Furthermore, the adsorbate which could be used with various different zeolites should be chosen, if possible. Otherwise, an adsorbate appropriate for the measurement of each kind of zeolite would have to be selected. The purpose of this study is therefore twofold: first, to investigate different adsorbates which might be applied to various kinds of zeolites including Y, mordenite, and ZSM-5; and, second, to evaluate the proposed method of measurement.

### EXPERIMENTAL

Zeolites ZSM-5 were prepared according to the Mobil patent (*1*). The ammonium form of ZSM was converted into the hydrogen type by calcining at 673 K in flowing $N_2$. Mordenite and Y zeolites of both Na and H types were supplied by the Catalysis Society of Japan as reference catalysts. The atomic ratio of Si to Al and the total surface

0021-9517/86 $3.00

TABLE 1

External Surface Area of Zeolite

| Zeolite | Ratio (Si/A) | Surface area ($m^2/g$) | | | | | Shape |
|---|---|---|---|---|---|---|---|
| | | Total | External | | | | |
| | | | Filled-pore method | | | SEM geometrical[a] | |
| | | | Benzene | Water | Hexane | | |
| HZSM-5 (A) | 19 | 389 | 19.2 | 28 | | | |
| (B) | 33.6 | 367 | 11.2 | 66 | | 11.3 | Cube |
| (C) | 50 | 365 | 12.5 | 159 | | 11.3 | Cube |
| (D) | 74 | 335 | 1.3 | 163 | 1.2 ± 0.1 | 0.82 | Plate |
| (E) | 77 | 357 | 4.8 | 166 | | — | Unresolved |
| Mordenite | | | | | | | |
| JRC-Z-M10 | 4.9 | 267 | 8.9 | 9.0 | | | |
| JRC-Z-M15 | 7.5 | 292 | 11.0 | 14.7 | | | |
| JRC-Z-M20 | 10.05 | 266 | 13.0 | 19.4 | | | |
| JRC-Z-HM10 | 4.95 | 187 | 9.8 | 10.7 | 10.1 | | Rod |
| JRC-Z-HM15 | 7.45 | 309 | 13.5 | 13.4 | | | |
| JRC-Z-HM20 | 9.95 | 299 | 15.2 | 16.9 | | 15.0–16.9 | Cube |
| Y | | | | | | | |
| JRC-Z-Y4.8 | 2.4 | 636 | 6.9 | 6.5 | | 6.7–8.4 | Sphere |
| JRC-Z-Y5.6 | 2.8 | 628 | 7.2 | 6.0 | 12.6 ± 1.6 | 6.7–8.4 | Sphere |
| JRC-Z-HY4.8 | 2.6 | 646 | 17.0 | 12.2 | | | |
| JRC-Z-HY5.6 | 2.8 | 634 | 10.6 | 8.1 | | | |

[a] (ZSM) 1.79, (mordenite) 1.7, of (Y) 1.27 g $cm^{-3}$ of zeolite density was used.

area (determined by $N_2$ adsorption) are summarized in Table 1.

External surface area was measured by the BET method for zeolites with pores which were formerly thought to be filled with water, benzene, or hexane. The zeolite is usually stored in a desiccator with saturated ammonium chloride solution to maintain constant humidity. In the benzene- or hexane-filled pore method, the sample was pretreated by calcining at 673 K in a flow of nitrogen. The sample was kept in the desiccator with benzene or hexane at room temperature for at least 10 h. The zeolite sample in a glass cell was connected to the flow-type BET apparatus, cooled to 195 K by dry ice–ethanol, and exposed to a flow of $N_2$ and He gas mixture ($N_2$ content, 29.1%). The sample was next chilled to 77 K to adsorb nitrogen, and then flashed by the dry ice–ethanol to desorb the nitrogen. The amount of nitrogen adsorbed was determined by measuring the amount of nitrogen desorbed. In some cases, the cycle was repeated to obtain the averaged value. When water was used as an adsorbate, the zeolite was stored in the desiccator with saturated ammonium chloride solution for at least 20 h before use.

The amount of sorbed water and benzene was measured by gravimetry. Benzene vapor was admitted to the zeolite by using a saturator at room temperature, and the amount sorbed was measured in the saturated condition.

Scanning and transmission electron micrographs of zeolites were obtained using a Hitachi H-700H analytical electron microscope. The zeolite material was embedded in plastic resin, and this was sliced by an ultramicrotome into a plate of ca. 0.05 μm in thickness. The shape and size of the

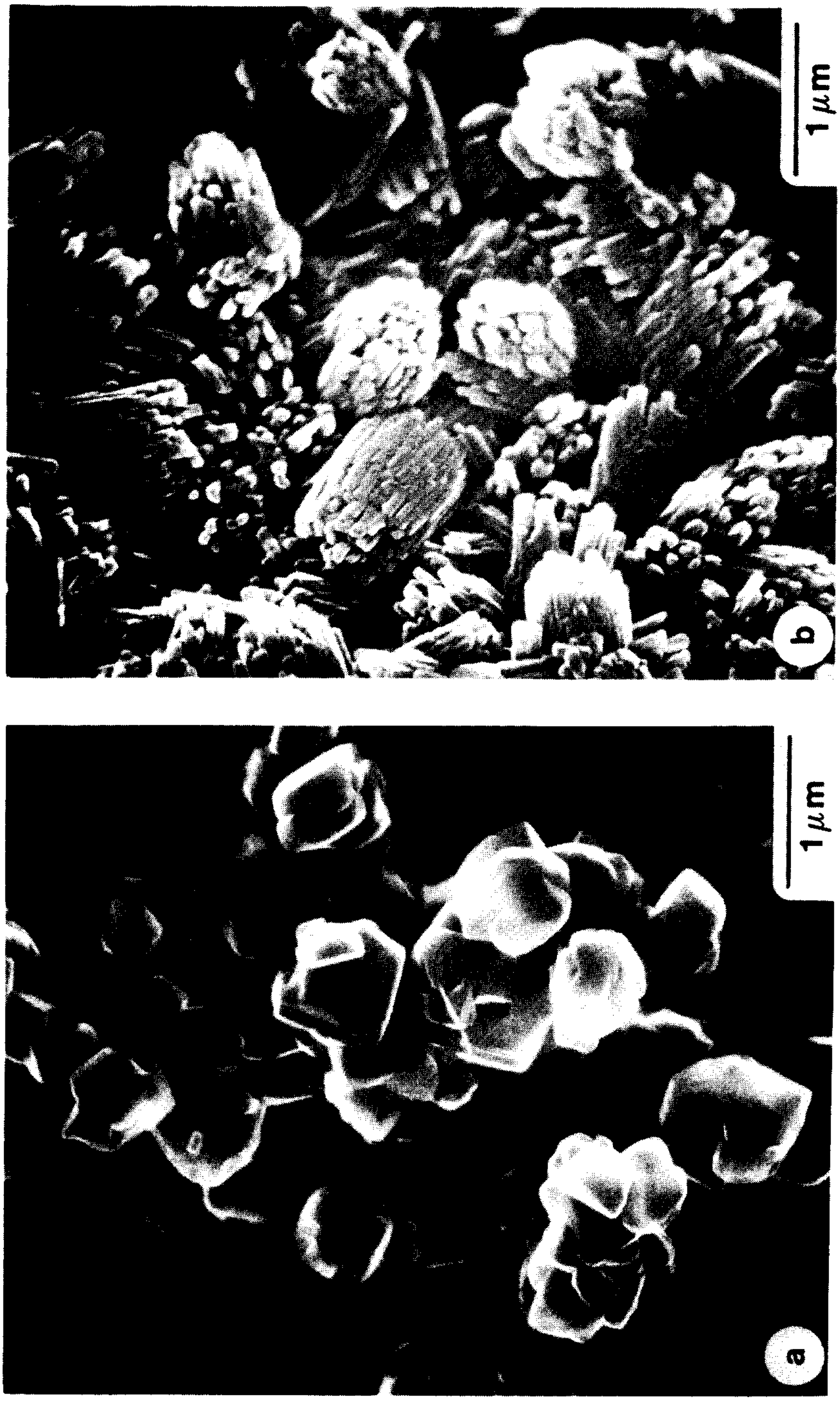

FIG. 1. SEM images of zeolites; (a) Y4.8, (b) HM10, (c) HZSM-5 (D), (d) HZSM-5 (C).

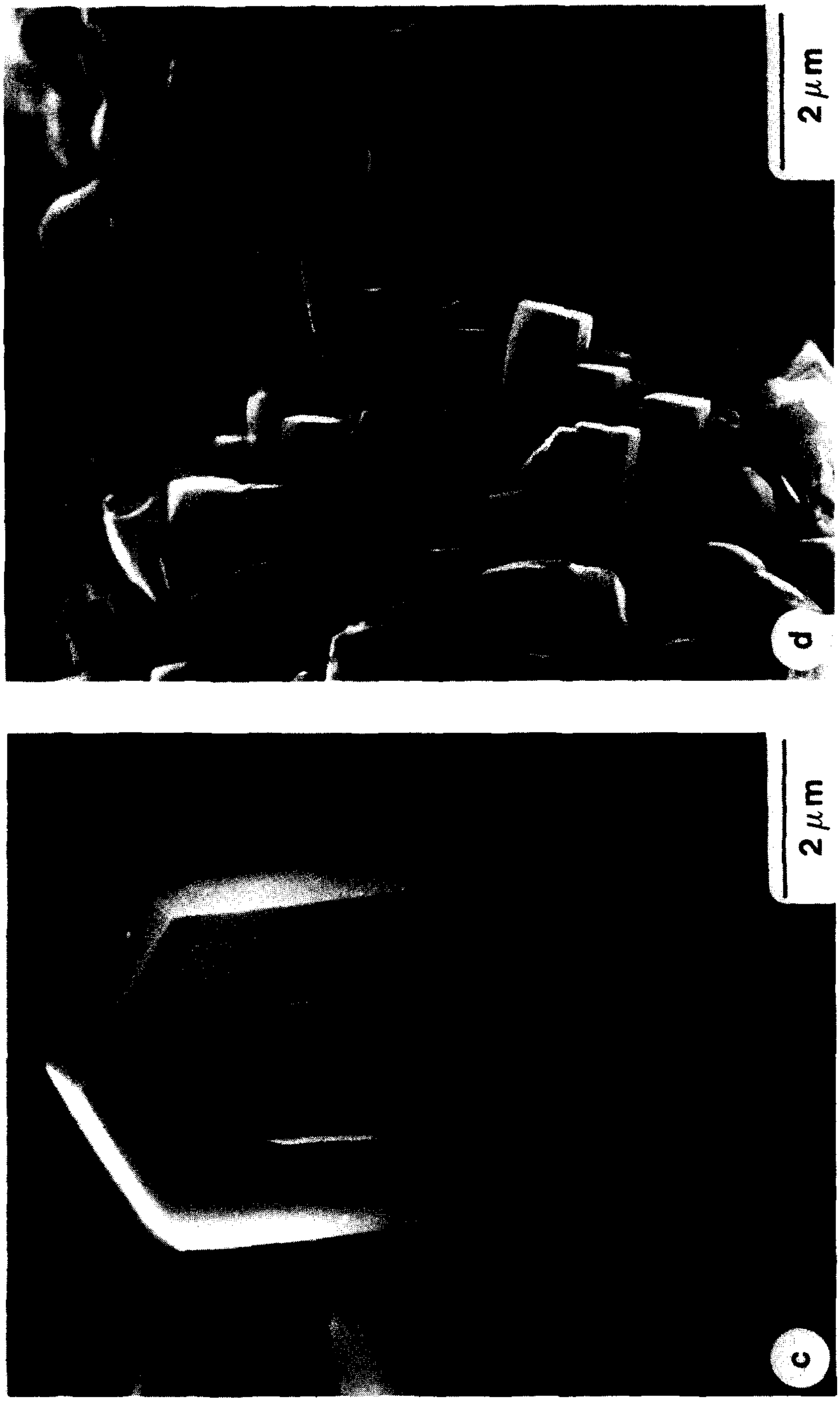

FIG. 1—*Continued.*

crystal were measured, and the geometrical external surface area was calculated only when the crystals were discrete and relatively homogeneous.

## RESULTS AND DISCUSSION

The external surface areas of zeolite were first measured geometrically by SEM images, and compared with those obtained by the water-filled method. Typical electron micrographs of zeolites are shown in Fig. 1. SEM pictures of zeolite revealed identifiable cube, sphere, or rod forms. Both samples of Y zeolite exhibited sphere-like crystals of 0.55 to 0.75 μm in diameter (Fig. 1a). Mordenite HM20 consisted of cubic crystals of 0.2 μm in height. HM10 appeared to be a bundle of rod-like crystals, but differentiation between unit crystal and secondary clustered oxide was difficult (Fig. 1b). On the other hand, the ZSM-5 crystals were cube- or plate-shaped. Exceptionally, one species, ZSM-5 (D), formed a large flat plate of $7 \times 4.5 \times 2.5$ $\mu m^3$ (Fig. 1c). Based on these SEM images, the external geometrical surface area could be calculated (Table 1).

In contrast, the external surface area was measured by the water-filled pore method. Although external surface areas by this method agreed with the geometrical values obtained from mordenite and Y zeolites, a large difference was observed in the case of ZSM-5. The values obtained by the water-filled pore method were too large, between about one-fifth and one-half of the total surface area; it was therefore presumed that the pores of the ZSM-5 did not fill with water, and that nitrogen penetrated the pore. It can therefore be concluded that water is not always a suitable adsorbate.

Moreover, it was found that the external surface area of the ZSM-5 was proportional to the Si-to-Al ratio of the zeolite bulk. It was observed that as the amount of adsorbed water decreased so did the ratio of Si to Al (Fig. 2), this being consistent with the hydrophobic property of the ZSM-5 (*5*). This strongly suggests that the extent of pore filling by water depends upon the Si-to-Al ratio of the zeolite bulk. If the pore volume is assumed to be constant, the unfilled volume of the ZSM-5 pore increases with the Si-to-Al ratio, and nitrogen sorption increases in proportion to the unfilled volume. This is the reason why the external surface of the ZSM-5 as measured by the water-filled pore method is proportional to the Si-to-Al ratio.,

We next sought to identify an adsorbate suitable for use with ZSM-5 as well as Y and mordenite. As understood from the discussion above, the adsorbate in the filled-pore method has to be adsorbed sufficiently to fill the pore, and yet remain undesorbed during the BET measurement.

Nakamoto and Takahashi reported (*6*) that the adsorbed amount of benzene or hexane on ZSM-5 was almost independent of the bulk compositions. The relationship between the adsorbed amount of benzene and the Si-to-Al ratio was also measured in the present study (Fig. 2). It seems that the dependence observed for ZSM-5 zeolites could be extrapolated to the Y zeolite. It was therefore found that benzene uptake by zeolites was almost independent of their composition. Furthermore, benzene is appropriate in the present method, since it is chilled from 195 to 77 K (the melting point of benzene is 278 K) during the measurement. Based on the sorption profile and melting point of benzene, it was used as an adsorbate to fill the pores.

External surface area measurements obtained by the benzene-filled pore method were in agreement with geometrical values obtained from ZSM-5, as well as those on mordenite and Y zeolites, by the water-filled pore method (Table 1). Therefore, one can use the benzene-filled pore method not only on hydrophobic ZSM-5 or high siliceous zeolites, but also on typical nonhydrophobic zeolites, to measure the external surface area.

Hexane was also used in order to compare its adsorptive properties with those of benzene. As shown in Table 1, the external

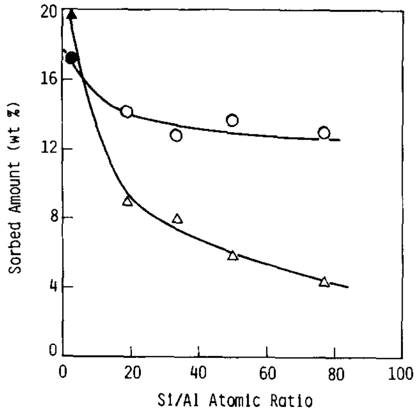

FIG. 2. Sorption property of zeolites HZSM-5 (open symbol) and HY-5.6 (closed symbol) for water (△) and benzene (○) as adsorbates.

surface area of ZSM-5 and mordenite by the hexane-filled pore method agreed well with those obtained by other methods, whereas a difference was found in the Y zeolite.

In conclusion, water cannot be used in the hydrophobic ZSM-5, while hexane is not appropriate for the Y zeolite. However, benzene can be used in not only ZSM-5 but also Y and mordenite. It may therefore be concluded that benzene is the most widely applicable to various kinds of zeolites: the broad applicability of the benzene-filled pore method is thus demonstrated. This may be the result of the property of benzene as an adsorbate in the zeolite and by the strongly adsorbed state under the present conditions. The slight solubility of benzene in water (soluble in 1430 parts water) may account for its having properties intermediate between water and hexane (insoluble in water). Benzene can be regarded as a nonpolar, but nevertheless slightly polar, molecule. Such an adsorptive property may result from the presence of the $\pi$-electron and the nonpolar structure of benzene. Additionally, benzene is sorbed in the pore completely, since the sample is kept below the melting point. Therefore, the selection of not only adsorbate benzene but also the experimental conditions, especially working at temperatures below 195 K, may be key contributors to the efficacy of this proposed method.

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*Received October 18, 1985*

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