JOURNAL OF CATALYSIS **100**, 219–227 (1986)

Determination of External Surface Areas of Zeolites

ISAO SUZUKI,*,[1] SHOICHI OKI,* AND SEITARO NAMBA†

Department of Chemistry, Utsunomiya University, 350 Mine, Utsunomiya 321, Japan; and †Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Received October 7, 1985; revised January 30, 1986

The external surface areas of NaA, CaA, H mordenite, NaX, and NaY zeolites were determined from the amounts of nitrogen adsorbed at 77 K on zeolites, after their internal pores had been filled previously with water, ethane, propane, butane, or 2,2-dimethylpropane by adsorption. The amount of nitrogen adsorbed was measured with a temperature-compensated tensimeter having symmetrical design. When the change in the pressure due to the adsorption of nitrogen on the zeolite previously filled with a filling substance stopped in a short while, the linear BET plot was obtained and the monolayer volume of nitrogen adsorbed on the external surface of zeolite was evaluated from the BET plot (the filled-pore method). When the pressure due to the adsorption of nitrogen on the zeolite changed slowly, the monolayer volume of nitrogen adsorbed on the external surface was evaluated from the amount of nitrogen adsorbed rapidly on the zeolite (the adsorption kinetic method).

INTRODUCTION

It is well known that the internal pore structure of zeolite has precise dimensions characteristic to its individual species. Hydrocarbons can be separated from others by a competitive adsorption into some zeolites (*1*). Some hydrocarbons are able to diffuse into pores, reach a catalyst site, and undergo a reaction. The product may diffuse out, or other compounds or isomers may be too large to be formed easily or may diffuse out at greatly reduced rates.

Such molecular shape-selective catalyses, first reported by Weisz and Frilette (*2*) in 1960, have been demonstrated by many researchers. Recently, a new type of zeolite, ZSM-5, was reported to exhibit beautiful shape selectivities for methanol conversion into hydrocarbons (*3*), alkylation of methylbenzenes with methanol (*4*), and competitive cracking of paraffins (*5*).

When we consider the shape selectivity of a 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 external surface area of the zeolite is very important in discussing the shape selectivity and the deactivation rate. The external surface areas were determined for some ZSM-5 zeolites by two different methods, the filled-pore method and the adsorption kinetic method (*6*).

In this paper the external surface areas were determined for NaA, KA, CaA, H mordenite, NaX, and NaY zeolites.

EXPERIMENTAL

Materials

Two series of A type zeolites (NaA-1, KA-1, CaA-1; NaA-2, KA-2, CaA-2) were used here. The specially synthesized NaA-1 zeolite was kindly given to us by Toyo Soda Mfg. Company, Ltd. The crystallite sizes of the NaA-1, whose scanning-elec-

---

[1] To whom all correspondence should be addressed.

0021-9517/86 $3.00

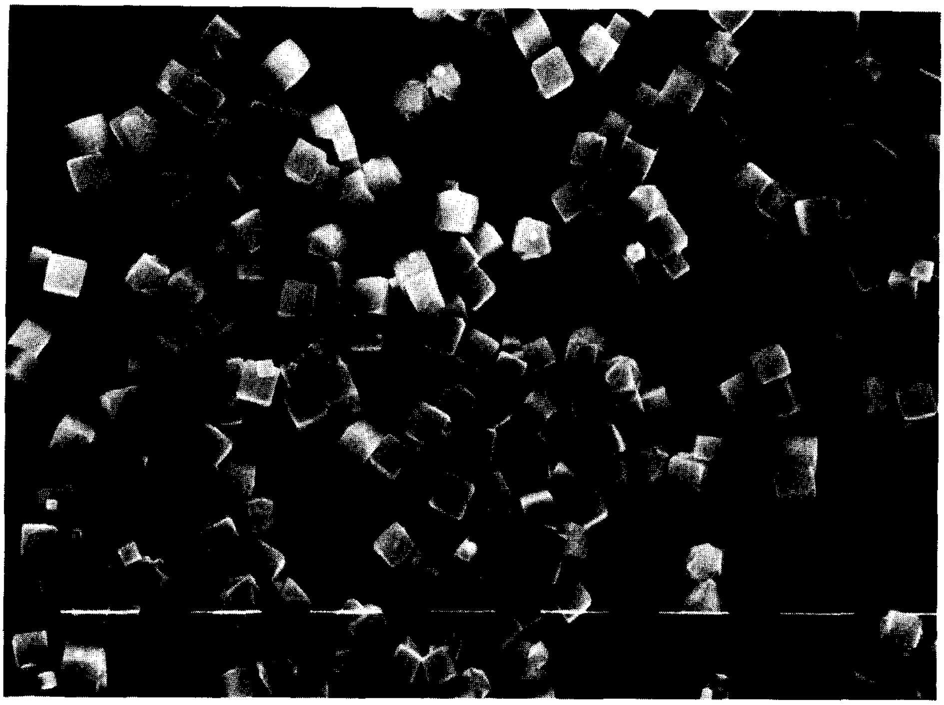

FIG. 1. Scanning-electron micrograph of NaA-1 zeolite. Each scale bar corresponds to 10 μm.

tron micrograph is shown in Fig. 1, were uniform and were about 4 μm. The KA-1 and CaA-1 zeolites were obtained by repeated ion exchange of NaA-1 with 1 *N* KCl and $CaCl_2$ aqueous solutions, respectively.

The NaA-2, KA-2, CaA-2, NaX, H mordenite, and NaY zeolites were designated as Linde Molecular Sieves 4A, 3A, 5A, 13X, Zeolon 100H, and SK-40, respectively, and they were commercial ones obtained from Nikka Seiko Company, Ltd. The crystallites of the NaA-2, KA-2, and the CaA-2 zeolites obtained from the scanning-electron micrograph are cubic in shape, and the NaA-2 is more fused and the CaA-2 is less fused than the KA-2 zeolite. These crystallites are not uniform in size and the average size of the cubes is about 1 ~ 2 μm. The crystallites of NaX, H mordenite, and NaY seem to be aggregations of small crystallites. Their crystallites are about 0.5 ~ 1 μm in size and the apparent order of the sizes of three samples is as follows; NaX $\geq$ H mordenite $\simeq$ NaY. Their total surface areas determined from the monolayer volumes of nitrogen with the Langmuir equation is tabulated in Table 1. About 0.1 ~ 0.2 g of zeolites were degassed for 2 h at 673 K and weighed before being used.

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. Ethane, propane, butane, and 2,2-dimethylpropane were obtained from Takachiho Chem. Ind. Company, Ltd., and were purified by repeated distillations. Water was used after repeated degassing.

Apparatus

The adsorption of nitrogen was measured by the temperature-compensated differential tensimeter having symmetrical design (7) as shown in Fig. 2. The apparatus consists of a differential micromanometer whose two arms are connected to a pair of

TABLE 1

The Monolayer Volumes of Nitrogen, V_m, the External Surface Areas, S, and the Total Surface Areas, S_t, of the Zeolites

Zeolite	Filling substance	Method[a]	V_m (STP cm^3/g)	S (m^2/g)	S_t (m^2/g)
KA-1	—	SA	0.22	0.9	
NaA-1	Ethane	FP	0.21	0.9	
	Water	FP	0.20		
CaA-1	Water	FP	0.21	0.9	790
KA-2	—	SA	0.39	1.7	
NaA-2	Ethane	FP	0.19	0.8	
CaA-2	Propane	FP	1.14	4.8	775
	Water	FP	1.08		
H Mordenite	Water	FP	0.90	3.6	576
	Butane	FP	0.77		
	2,2-Dimethylpropane	FP	0.82		
NaX	Water	FP	1.03	4.6	902
	Butane	FP	1.18		
NaY	Water	FP	1.02	3.7	886
	2,2-Dimethylpropane	FP	0.71		
	Butane	FP	0.76		
	Butane	AK	0.96		

[a] SA, simple adsorption method; FP, filled-pore method; AD, adsorption kinetic method.

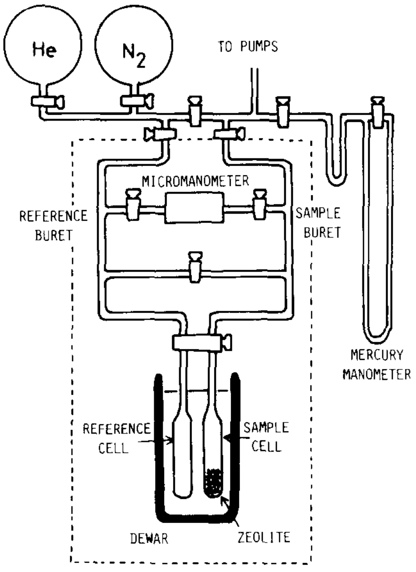

FIG. 2. Scheme of apparatus.

sample and reference burettes of nearly equal volume. Both burettes and cells are constructed to be as symmetrical as possible. The cells are immersed about 6 cm deep below the surface of liquid nitrogen which is used as a thermal bath.

This design allows that any changes in pressures due to temperature fluctuations can be compensated for by accompanying changes in the reference pressures. The volume of burettes and cells used were about 45 and 30 cm^3, respectively. The apparatus within the dotted lines in Fig. 2 was covered with a piece of transparent plastic which was used as thermal insulation. If necessary, the differential pressure was recorded with an electric recorder.

Surface areas as small as 0.03 m^2 can be measured through volumetric measurements of nitrogen uptake at liquid-nitrogen temperature with the apparatus described here (*7*). The external surface areas of zeolite catalysts are generally much smaller than the internal surface areas or the total surface areas. This makes the apparatus described here the convenient tool for determining the external surface areas of the zeolite catalysts. The micromanometer, its response, the method of adsorption measurements, and the calculation of amount adsorbed were described elsewhere (*7*).

Method

The external surface areas of zeolites were determined by three different methods according to their pore sizes.

Simple adsorption method. In the case that the dimension of the pore of the zeolite is smaller than that of adsorbate (nitrogen) molecules, the external surface area can be determined from the monolayer volume of nitrogen evaluated from the BET plot. The external surface areas of the KA zeolites were determined by this method.

Filled-pore method. In the case where the dimension of the pores of the zeolites is larger than that of the adsorbate (nitrogen) molecules, we determined the external surface area from the monolayer volume of nitrogen evaluated from the BET plot, after the internal pores had been filled with water, ethane, propane, butane, or 2,2-dimethylpropane by adsorption. The adsorption of water, ethane, propane, butane, or 2,2-dimethylpropane was carried out at 293 K (water) or at 273 K (ethane, propane, butane, or 2,2-dimethylpropane) with a conventional adsorption apparatus.

After the adsorption equilibrium was attained at a pressure of about 1 kPa with water or about 30 ~ 50 kPa with ethane, propane, butane, or 2,2-dimethylpropane, helium was introduced into the adsorption cell to reach 100 kPa in total pressure. Helium was used as a heating medium to cool the zeolite quickly to 77 K, so that the filling substance such as water, ethane, propane, butane, or 2,2-dimethylpropane would not be desorbed from the zeolite. In order to quickly cool the zeolite catalyst to 77 K, about 0.1 ~ 0.2 g of zeolite catalyst was used here, because a large amount of zeolite catalyst may be difficult to cool quickly.

After the cell was immersed in a Dewar vessel containing liquid nitrogen, the helium was pumped out. At that time, some of the filling substance in the gas phase would condense on the zeolite surface or adsorption cell walls, but the rest of the filling substance would be pumped out with the helium. Then the adsorption of nitrogen was carried out at 77 K.

Adsorption kinetic method. In the case where the nitrogen molecules could diffuse into the pores through the intercrystalline channels even though the pores were already filled with the filling substance by adsorption, the external surface area was determined from the amount of nitrogen that adsorbed rapidly on the zeolite.

If the rate-controlling process in the adsorption is the activated diffusion of adsorbate molecules into the pores through the intercrystalline channels, the process may be described by the following equation for small values of time t, after an initial stage (*8*):

$$V_t = Ct^{1/2} + V_0 \qquad (1)$$

where V_t is the amount adsorbed at time t, and C and V_0 are constants. The constant V_0 is the amount of nitrogen adsorbed rapidly on the external surface. This value is found from the intercept of the linear portion of the V_t vs $t^{1/2}$ plot.

RESULTS AND DISCUSSION

KA-1 Zeolite

The change in the differential pressure due to the adsorption of nitrogen on the KA-1 zeolite stopped within 50 s, which shows nitrogen molecules did not diffuse into the pores through the intercrystalline channels. This means the amount of nitrogen adsorbed corresponds to that adsorbed on the external surface of the KA-1 zeolite, and the external surface area of the KA-1

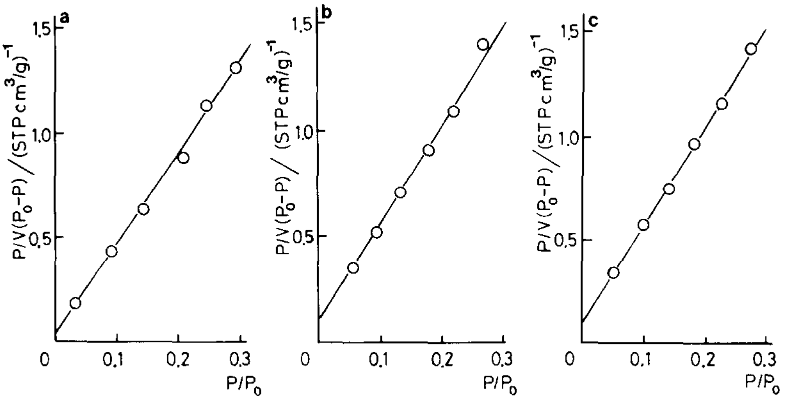

FIG. 3. The BET plots for nitrogen adsorption at 77 K (a) on KA-1 zeolite, (b) on NaA-1 zeolite filled previously with ethane, and (c) on CaA-1 zeolite filled previously with water.

zeolite can be determined by the simple adsorption method. The linear BET plot obtained from the adsorption isotherm for nitrogen is shown in Fig. 3a. The monolayer volume of nitrogen evaluated from the BET plot was 0.22 cm^3 (STP)/g. Therefore the external surface area of the KA-1 zeolite is estimated at 0.9 m^2/g.

NaA-1 Zeolite

The change in the differential pressure due to the adsorption of nitrogen on the NaA-1, on which ethane or water had been adsorbed previously, stopped within 200 s. This result suggests that the internal pores of the NaA-1 zeolite have been filled perfectly with ethane or water. The linear BET plot was obtained from the adsorption isotherm for the adsorption of nitrogen on the NaA-1 previously filled with ethane or water. One of them is shown in Fig. 3b. The linear BET plot also shows that the internal pores of the NaA-1 zeolite have been filled with ethane or water. The monolayer volumes of nitrogen evaluated from the BET plots with the NaA-1 previously filled with ethane and water were 0.21 and 0.20 cm^3 (STP)/g, respectively.

These monolayer volumes of nitrogen were equal to each other within experimental errors. The external surface areas of the NaA-1 can be determined from the monolayer volume of nitrogen and was estimated at 0.9 m^2/g.

CaA-1 Zeolite

The change in the differential pressure due to the adsorption of nitrogen on the CaA-1, on which water had been adsorbed previously, stopped within 200 s, which suggests the internal pores of the CaA-1 zeolite have been filled perfectly with water by adsorption.

As shown in Fig. 3c, the linear BET plot was obtained from the adsorption isotherm for the adsorption of nitrogen on the CaA-1, whose pores had been previously filled with water. The linear BET plot also shows that the internal pores of the CaA-1 have been filled with water. The monolayer volume of nitrogen evaluated from the BET plot was 0.21 cm^3 (STP)/g. Thus the external surface area of the CaA-1 is estimated at 0.9 m^2/g.

The crystallite sizes of the CaA-1 should be similar to those of the KA-1 or the NaA-1, because the KA-1 and the CaA-1 were prepared from the NaA-1 by a conventional ion-exchange method. The monolayer volumes of nitrogen evaluated from the BET plots for the KA-1, the NaA-1, and the CaA-1 are described in Table 1. These values were nearly equal to each other. Moreover, the external surface area estimated from the nitrogen adsorption is in good

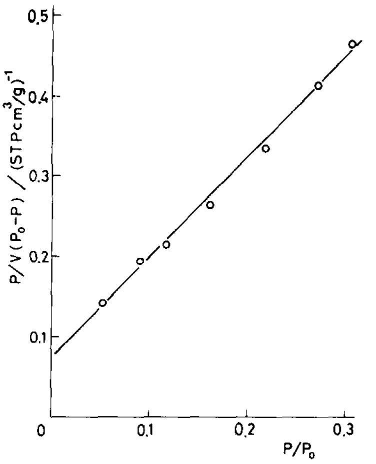

FIG. 4. The BET plot for nitrogen adsorption at 77 K on H mordenite, after its pores were filled with butane.

agreement with the geometrical surface area, 0.8 ± 0.1 m^2/g, estimated from the scanning-electron micrograph in Fig. 1. Therefore the external surface area of A type zeolites can be determined by the filled-pore method as described above.

KA-2, NaA-2, and CaA-2 Zeolites

The external surface areas of the commercial A type zeolites were also determined by the same method as described above. The linear BET plots were obtained from the adsorption isotherms for the adsorption of nitrogen on the KA-2, on the NaA-2 previously filled with ethane, and on the CaA-2 previously filled with propane or water. The monolayer volumes of nitrogen evaluated from the BET plots and the external surface areas estimated from the monolayer volumes of nitrogen are described in Table 1.

H Mordenite

The change in the differential pressure due to the adsorption of nitrogen on the H mordenite on which water, butane, or 2,2-dimethylpropane had previously been adsorbed stopped within 200 s, which suggests the internal pores of the H mordenite have been filled with water, butane, or 2,2-dimethylpropane. The linear BET plot was obtained from the adsorption isotherm for the adsorption of nitrogen on the H mordenite previously filled with water, butane, or 2,2-dimethylpropane. One of them is shown in Fig. 4. The monolayer volumes of nitrogen evaluated from the BET plots were 0.90, 0.77, and 0.82 cm^3 (STP)/g for the H mordenite previously filled with water, butane, and 2,2-dimethylpropane, respectively. These values were nearly equal to each other. Thus the external surface area of the H mordenite is estimated at 3.6 m^2/g.

NaX Zeolite

The change in the differential pressure due to the adsorption of nitrogen on the NaX zeolite, on which butane or water had previously been adsorbed, stopped within 200 s. The linear BET plot was obtained from the adsorption isotherm for the adsorption of nitrogen on NaX previously filled with water or butane. This BET plot is shown in Fig. 5a.

The monolayer volumes of nitrogen evaluated from the BET plots were 1.03 and 1.18 cm^3 (STP)/g for NaX filled with water and butane, respectively. These values were nearly equal to each other. Thus the external surface area of the NaX zeolite is estimated at 4.6 m^2/g.

Sometimes, a slightly U-shaped BET plot was obtained from the adsorption isotherm for the adsorption of nitrogen on the NaX zeolite previously filled with butane as shown in Fig. 5b. This may suggest that the internal pores of the NaX zeolite have not been filled perfectly with butane. In such a case, the amount of nitrogen adsorbed is the summation of the amount of nitrogen adsorbed on the external surface and that on the internal surface. The adsorption on the external surface should obey a BET equation. On the other hand, the adsorption on the internal surface should obey a Langmuir equation. Thus the U-shaped curve is obtained if the BET plot is applied to the total adsorption of nitrogen on the

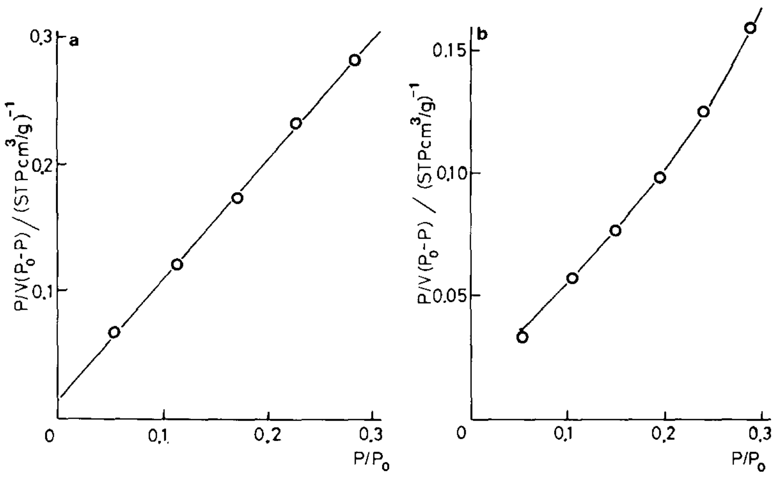

FIG. 5. The BET plot for nitrogen adsorption at 77 K on NaX zeolite, (a) a linear BET plot obtained after its pores were filled previously with water; (b) a U-shaped BET plot obtained after its pores were not filled perfectly with butane.

NaX zeolite, on which butane have not been filled perfectly.

The monolayer volumes evaluated from the U-shaped BET plots are much larger than those evaluated from the linear BET plots. Thus the linearity of the BET plot shows that the amount of nitrogen adsorbed on the internal surface is negligibly small in comparison with that adsorbed on the external surface. That is, the linear BET plot shows that the internal pores of the zeolite have been filled perfectly with the filling substance.

NaY Zeolite

The change in differential pressure due to the adsorption of nitrogen on the NaY, on which water or 2,2-dimethylpropane had been adsorbed previously, stopped within 200 s. The linear BET plots were obtained from these adsorption isotherms. The monolayer volumes of nitrogen evaluated from the BET plots for the NaY zeolites previously filled with water and 2,2-dimethylpropane were 1.02 and 0.71 cm^3 (STP)/g, respectively.

The differential pressure due to the adsorption of nitrogen on the NaY zeolite on which butane had been adsorbed previously changed slowly or sometimes stopped within 200 s. It is suggested that the internal pores of the NaY zeolite had been filled with butane perfectly when the differential pressure due to the adsorption of nitrogen stopped within 200 s as shown in Fig. 6. In such a case, the obtained linear BET plot is shown in Fig. 7. The monolayer volume of the nitrogen evaluated from the BET plot was 0.76 cm^3 (STP)/g.

It is also suggested that the internal pores of the NaY zeolite had not been filled perfectly with butane when the differential pressure due to the adsorption of nitrogen changes slowly for a long time. In such a case, the linear BET plot was obtained form the amount adsorbed, V_t, and square

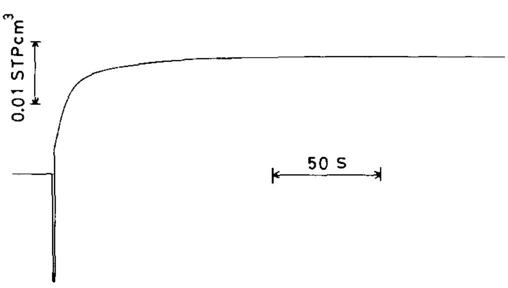

FIG. 6. Pressure change due to nitrogen adsorption at 77 K on NaY zeolite, after its pores were filled perfectly with butane. Weight of NaY, 0.0521 g; equilibrium pressure of butane, 5.12 kPa.

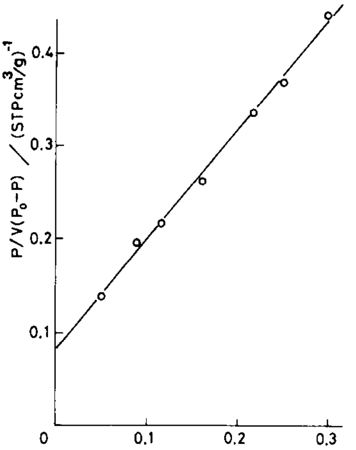

FIG. 7. The BET plot for nitrogen adsorption at 77 K on NaY zeolite when pressure change due to nitrogen adsorption stopped in a short while as shown in Fig. 6, after its pores were filled perfectly with butane.

root of time, $t^{1/2}$, except in the initial stage of the adsorption as shown in Fig. 8. The amount of nitrogen adsorbed, V_0, on the external surface determined from the intercept of Fig. 8 was 1.31 cm³ (STP)/g, at pressure P of 26.16 kPa.

The monolayer volume of the nitrogen, V_m, was evaluated by the "single point" method using the equation

$$\begin{aligned} V_m &= V_0(1 - P/P_0) \\ &= 1.31(1 - 26.16/99.93) \\ &= 0.96 \text{ cm}^3 \text{ (STP)/g} \qquad (2) \end{aligned}$$

where $P_0 = 99.93$ kPa is the saturated vapor pressure of nitrogen under experimental conditions. The monolayer volume of nitrogen determined by the adsorption kinetic method was nearly equal to the monolayer volumes of nitrogen determined by the filled-pore method. In this case the external surface area of the NaY zeolite is estimated at 3.7 m²/g.

The monolayer volumes of nitrogen adsorbed on the external surface of the zeolites and the external surface areas of the zeolites are tabulated in Table 1. The external surface area of the NaA-1 zeolite obtained by the filled-pore method is in good agreement with the geometrical surface area estimated from the scanning-electron micrograph, and the external surface areas of the CaA-1 and the KA-1 zeolites obtained from the NaA-1 by a conventional ion-exchange method were also in good agreement with that of the NaA-1. The crystallites of the NaA-2, KA-2, CaA-2, NaX, H mordenite, and the NaY obtained from the scanning-electron micrograph were not uniform either in size or in shape, and then the external surface areas could not be estimated from their geometrical surface areas.

When the differential pressure due to the adsorption of nitrogen stops in a short while and the linear BET plot is obtained from the adsorption isotherm for the adsorption of nitrogen on the zeolite, on which a filling substance has been adsorbed previously, then the internal pores of the zeolite are suggested to have been filled perfectly. The monolayer volume of nitrogen evaluated from the linear BET plot corresponds to the external surface area.

When the differential pressure due to the adsorption of nitrogen changes for a long time for the zeolite, on which a filling substance was previously adsorbed, the internal pores of the zeolite are suggested not to have been filled perfectly. The amount of nitrogen adsorbed rapidly on the zeolite can then be evaluated from the linear plot of V_t vs $t^{1/2}$ in Eq. (1) and corresponds to that adsorbed on the external surface.

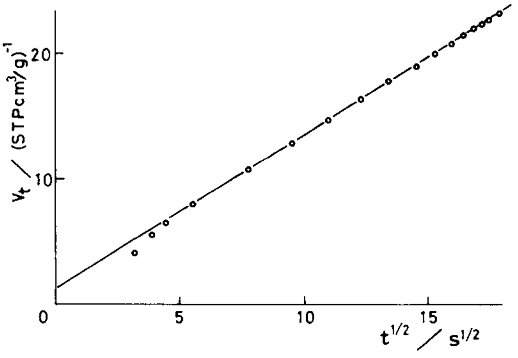

FIG. 8. The relation between V_t and $t^{1/2}$ on NaY zeolite, after its pores were not filled perfectly with butane.

The filled-pore method with butane can be easily applied to the NaX zeolite but sometimes cannot be applied to the NaY zeolite despite the similarity in the crystal morphology of the faujasite zeolites. This comes from the fact that the pore dimensions are also dependent to a small extent on the Si/Al ratio. The filled-pore method with butane could be applied to the mordenite with low Si/Al ratio (SiO_2/AlO_3 = 10), but it could not be applied to the mordenite with high Si/Al ratio (SiO_2/Al_2O_3 = 20) (*9*). Unfortunately at present it is very difficult to offer insight into the selection criteria for applying each of the three methods.

The external surface areas of the A, X, and Y type zeolites, and H mordenite can be determined by the filled-pore method or the adsorption kinetic method. Even if the internal pores of the zeolite cannot be filled perfectly by the adsorption, the external surface area of the zeolite can be determined by the adsorption kinetic method.

ACKNOWLEDGMENTS

The authors thank Dr. K. Igawa and Dr. M. Obara of Toyo Soda Mfg. Co., Ltd. for giving us the NaA-1 zeolite.

REFERENCES

1. Barrer, R. M., *J. Soc. Chem. Ind.* **44,** 130 (1945); Barrer, R. M., and Belchetz, L., *J. Soc. Chem. Ind.* **44,** 131 (1945); Namba, S., Yoshimura, A., and Yashima, T., *Chem. Lett.* **1979,** 759 (1979); Dessau, R. M., *ACS Symp. Ser.* **135,** 123 (1980); Namba, S., Kanai, Y., Shoji, H., and Yashima, T., *Zeolites* **4,** 77 (1984).

2. Weisz, P. B., and Frilette, V. J., *J. Phys. Chem.* **64,** 382 (1960).

3. Chang, C. D., and Silvestri, A. J., *J. Catal.* **47,** 249 (1977).

4. Chen, N. Y., Kaeding, W. W., and Dwyer, F. G., *J. Amer. Chem. Soc.* **101,** 6783 (1979); Kaeding, W. W., Chu, C., Young, L. B., Weinstein, B., and Butler, S. A., *J. Catal.* **67,** 159 (1981); Yashima, T., Sakaguchi, Y., and Namba, S., *Stud. Surf. Sci. Catal.* **7,** 739 (1981); Namba, S., Inaka, A., and Yashima, T., *Zeolites* **3,** 106 (1983); Yashima, T., Inaka, A., and Namba, S., *Sekiyu Gakkaishi* **28,** 13 (1985).

5. Namba, S., and Yashima, T., *Chem. Lett.* **1978,** 1261 (1978); Weisz, P. B., *Stud. Surf. Sci. Catal.* **7,** 3 (1981).

6. Suzuki, I., Namba, S., and Yashima, T., *J. Catal.* **81,** 485 (1983).

7. Suzuki, I., *Rev. Sci. Instrum.* **53,** 1061 (1982).

8. Breck, R. M., "Zeolite Molecular Sieves," p. 672. Wiley, New York, 1974.

9. Suzuki, I., and Ezure, H., Prep. of the 1st Zeolite Meeting, Tokyo, p. 144, 1985.