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NOTE

Preparation of Microporous Silica Powder by Fume Pyrolysis of Tetraethoxysilan Solution

Pores of solid catalysts not only offer large surface area but also affect mechanical strength and heat resistance. A more attractive role of the pores in catalysis is to provide shape-selective sorption and reaction. Zeolites have pores which are small and regular enough to sieve molecules by size, resulting in high shape selectivity in catalytic reactions. In order to alter the molecular sieving effect, porosity modification of zeolites has been attempted by cation exchange, chemical vapor deposition, and so on (1).

Since silica may have a porous network with large surface area, it is often used as a catalyst and a catalytic support. The molecular shape selectivity in catalytic reaction over silica, however, is not apparently observed, because silica generally has wide distribution of pore size compared to reaction molecules. Sol-gel process, in which the structure of precursory polymers of silica formed in the sol or gel is easily controlled by changing the preparation conditions such as solvent, catalyst, temperature, etc. (2, 3), has been applied to design morphology-controlled silica. Nakanishi *et al.* (4, 5) prepared dual-porosity silica gels by a polymer-incorporated sol-gel process and found that the micrometer-range pore size could be adjusted with molecular weight or concentration of the polymer added or reaction temperature, whereas the nanometer-range pores were varied by different solvent exchange of the wet gel. Toba *et al.* (6) also reported that the micropore size of the silica-alumina prepared by an advanced sol-gel method increased with kinetic diameter of the diols which were added to the solution as a pore-forming agent.

On the other hand, we previously synthesized various metal oxides by a fume pyrolysis technique using sols of metal alkoxides (7–9). Among them, the silica powder prepared from the aqueous solution of tetraethoxysilan (TEOS) was found to consist of the spherical particles with the following features (9): 1) the surface area and the pore volume increased with viscosity of the TEOS solution, and 2) the pore size was not affected by the solution viscosity but remarkably increased with combustion temperature; the silica obtained at 1023 K had the pores of about 1.5 nm in diameter, whereas elevating the temperature to 1123 K resulted in a pore expansion to 4–4.5 nm. In this work, we attempted to prepare the silica with pores of less than 1 nm which are expected to provide shape-selective reactions of micro-molecules. Furthermore, the mechanism of the pore expansion dependent on the combustion temperature was examined.

The preparation procedure was described in the previous paper (9). In brief, TEOS was dissolved in 120 times the molar quantity of water and stirred at 353 K after being adjusted to a pH of about 2 with nitric acid, becoming gradually white and viscous. The solution which reached a desired viscosity was supplied into the vessel of the fume pyrolysis apparatus and was fumed with a supersonic vibrator of 1.5 MHz. The fumes were carried with an oxygen stream of 15 dm^3/min into a quartz reactor (inside diameter of 32 mm) heated with an electric furnace of 600 mm in length. In this work, the furnace temperature was adjusted to 773 K instead to 1023 and 1123 K employed in the previous work. Because of the exist of the fumes and the oxygen stream, the temperature inside the reactor was lower than that on the outside and the maximum was 473 K. The silica particles dried and burned out instantaneously (within 2 sec) were collected in about 20 dm^3 of water, followed by filtration, drying at 383 K for 24 h, and calcination at 773 K for 4 h. The surface porosity of the silica was estimated by nitrogen adsorption measurement at the liquid nitrogen temperature. After evacuating the sample at 573 K for 1 h, the adsorption and desorption curves were obtained by use of a vacuum system equipped with a Baratron manometer and valves controlled by a microcomputer.

It was confirmed from microscopic observation that the silica powder obtained at 773 K consisted of spherical particles of 0.5–3 μm in diameter similarly to those obtained at 1023 and 1123 K. Fig. 1 shows the nitrogen adsorption-desorption isotherms of the silicas prepared from the TEOS solutions of different viscosities. All of the adsorption profiles belonged to Type I in the IUPAC classification (10) which is characteristic of microporous materials. As the solution viscosity increased, although the type of the isotherm did not change, the amount of adsorbed nitrogen increased. This means that the pore volume can be raised with the pore opening size being kept in the micropore region.

Fig. 2(a) shows the pore size distributions calculated using Barrett–Joyner–Halenda (BJH) theory (11) from the desorption curves in Fig. 1. Those of the silicas prepared at 1023 and 1123 K are also given in Fig. 2(b) for comparison.

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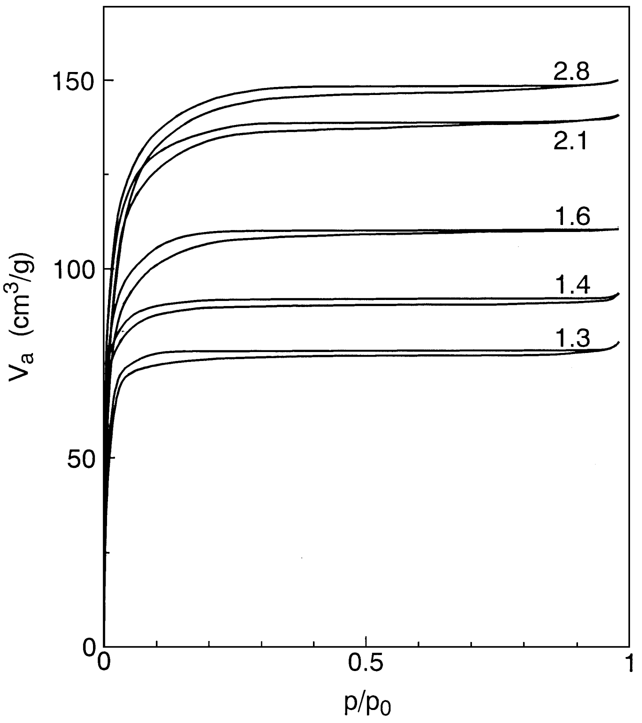

FIG. 1. Nitrogen adsorption-desorption isotherms of the silicas prepared at 773 K. The values in the figure represent the viscosities of the TEOS solutions employed in mPa · s.

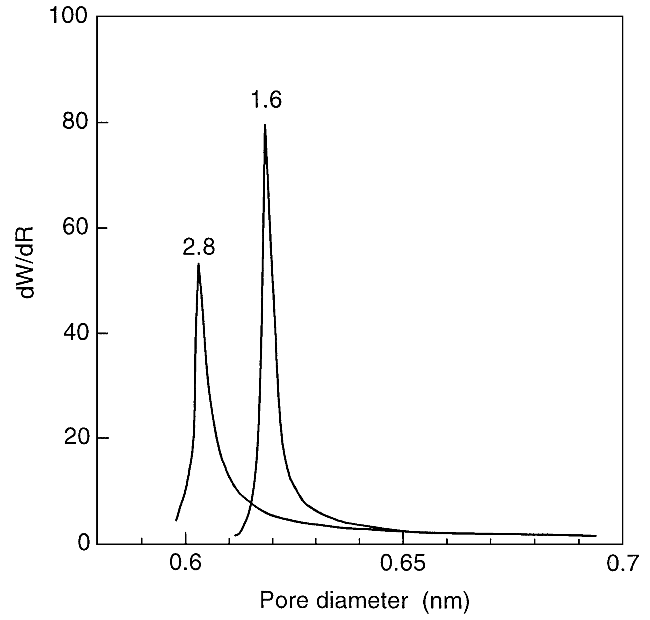

FIG. 3. Micropore size distributions of the silicas prepared at 773 K from the TEOS solutions of 1.6 and 2.8 mPa · s.

The peak was shifted to the smaller side with decreasing combustion temperature and the peak tops of the silicas prepared at 773 K ultimately existed at less than 1.5 nm below which the BJH method cannot be applied. For some of the samples, the micropore size distributions were also calculated according to the Horvath-Kawazoe (HK) theory (12) from the highly accurate adsorption data measured with an OMNISORP-2000 (COULTER) instrument. The results are shown in Fig. 3. The peaks were very sharp and the pore diameters were estimated to be 0.62 and 0.60 nm for the silicas prepared from the TEOS solutions of 1.6 and 2.8 mPa · s, respectively, indicating that the pore size was scarcely affected by the solution viscosity. The porosity data obtained, which are summarized in Table 1, suggests that the surface morphology of the silica is easily controlled by adjusting the solution viscosity and the combustion temperature. The internal surface areas calculated by Va-t plot analysis were 94–99% of the total values for all the samples; therefore the surface of the silica obtained was almost made up of the internal walls in the pores.

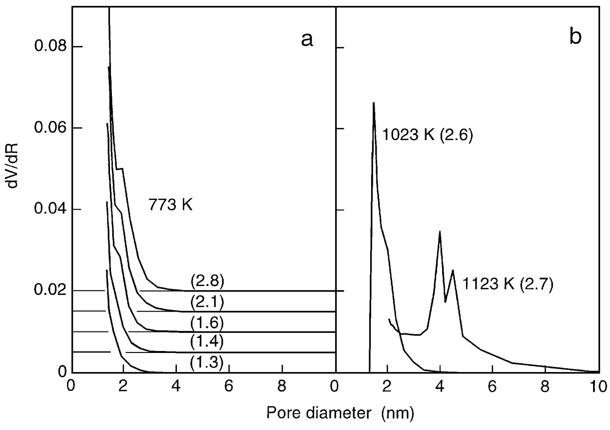

FIG. 2. Pore size distributions of the silicas prepared at 773, 1023, and 1123 K. The values in the parentheses represent the viscosities of the TEOS solutions employed in mPa · s.

TABLE 1

Porosity Data of the Silicas Prepared by the Fume Pyrolysis Method

F.P. temp. (K)	Solution viscosity (mPa · s)	Boiling temp. (K)	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
	1.3	—	220	0.12	<1.5
	1.4	—	250	0.15	<1.5
773	1.6	—	330	0.17	0.62
	2.1	—	400	0.22	<1.5
	2.8	—	420	0.23	0.60
1023	2.6	—	450	0.23	1.5
1123	2.7	—	350	0.44	4.0, 4.5
	2.4	Not boiled	360	0.22	<1.5
1123[a]	2.4	373	360	0.21	1.6
	2.4	423	330	0.21	1.5–4.0
	2.4	463	43	0.12	4.6

[a] The silica collected with a paper filter.

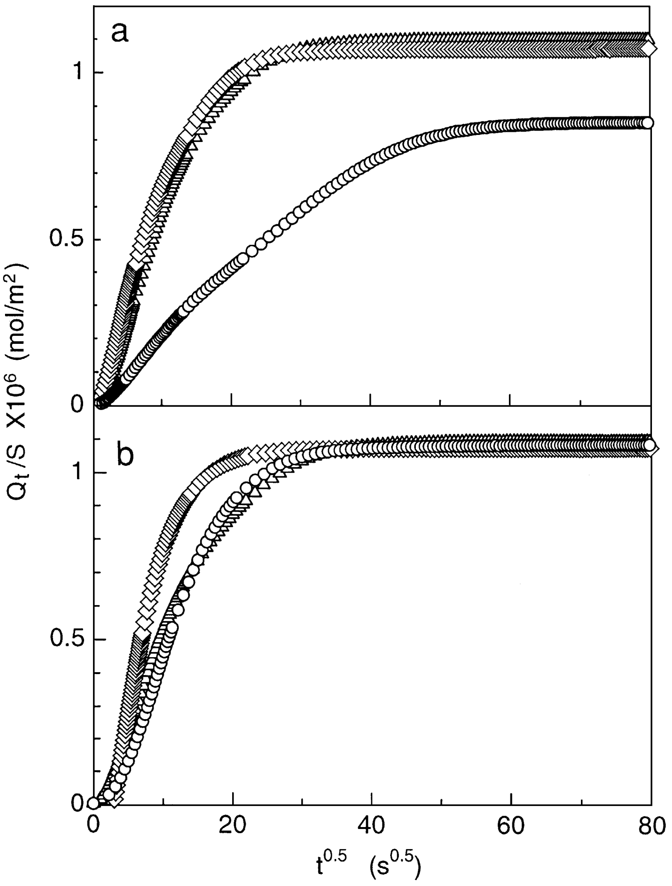

FIG. 4. Changes in amounts of (◇) water, (△) benzene, and (○) o-xylene adsorbed on the silicas prepared (a) from the 2.8 mPa · s solution at 773 K and (b) from the 2.6 mPa · s solution at 1023 K.

In order to evaluate the molecular sieving effect of the silica, adsorption measurements of water, benzene, and o-xylene were carried out at 313 K with a constant volume but variable pressure sorption system. The solvent volume introduced to the system was adjusted to be less than 30% of the total pore volume of the sample. The amount occluded at time t, Q_t, was divided by the surface area of the silica, S, and plotted as a function of $\sqrt{t}$ in Fig. 4(a). For comparison, the silica prepared at 1023 K was also subjected to the same measurements (Fig. 4b). The adsorption onto the silica obtained at 1023 K reached equilibrium within 20 min for all the molecules and the initial slopes were comparable to each other. On the other hand, the adsorption rate of o-xylene onto the silica obtained at 773 K was very slow and the equilibrium was achieved after more than 60 min, whereas water and benzene exhibited the adsorption profiles similar to those in Fig. 4b. Furthermore, the amount of o-xylene adsorbed at the equilibrium was less than the others. These mean that the pore size of the silica obtained at 773 K was very close to the molecular size of o-xylene (0.58 nm) and a part of the pores was smaller than the size, supporting the value estimated by the HK method.

The pores in the silica prepared by the fume pyrolysis method can be regarded as openings between the siloxane particles aggregated. The structure of the siloxane polymer produced in TEOS sol is well known to be affected by pH and concentration (13, 14). The acidic condition and the large excess of water to TEOS employed in this work are likely to form small particles composed of the densely crosslinked siloxane polymers in the initial stage of the preparation. The siloxane particles produced are further aggregated by the condensation of surface silanol groups to build up three-dimensional networks, resulting in an increase in the solution viscosity (15). Therefore, the fumes generated from the solution involve many networked clusters of siloxane between which the solvent is filled. By heating the liquid particles, openings are formed between the clusters with evaporation and combustion of the solvent and then shrunk by aggregation and sintering of the siloxane clusters. It is expected that the growth of the siloxane network prevents the clusters from dense aggregation and the openings from shrinking. Consequently, raising the solution viscosity leads to increases in the pore volume and the surface area as observed in Table 1.

We also attempted to elucidate the mechanism of the pore expansion with combustion temperature through the following experiments: the silica was prepared by burning out the TEOS solution of 2.4 mPa · s at 1123 K and collected with a paper filter instead of the water collector, and then boiled in water at 373, 423, and 463 K under the saturation vapor pressures for 2 h. The samples before and after boiling were dried at 383 K for 24 h and calcined at 773 K for 4 h, followed by nitrogen adsorption measurements. Fig. 5 shows a change in the pore size distribution with boiling temperature. In spite of furnace temperature of 1123 K, the silica before boiling had the pores whose diameters were less than 1.5 nm in contrast to 4–4.5 nm for the sample obtained at the same temperature with the water collector. As the boiling temperature was raised, the peak was shifted to the larger side and remarkably reduced, indicating strongly that the pore expansion was caused by dissolution and deformation of the silica surface in water. The porosity data are summarized in Table 1. The silicas boiled at 373 and 463 K had the pores of 1.6 and 4.6 nm, respectively, which were close to those of the samples obtained at 1023 and 1123 K with the water collector. The pore volume and the BET surface area, however, were remarkably reduced by boiling at 463 K. This suggests that the silica suffered the significant modification from the boiling compared with the water-collected silica.

The differences between both the pore-expansion processes are attributable to temperature, pressure and time in the surface modifications; in the fume pyrolysis with the water collector, silica particles produced through the preparation reactor are heated up to higher temperature than

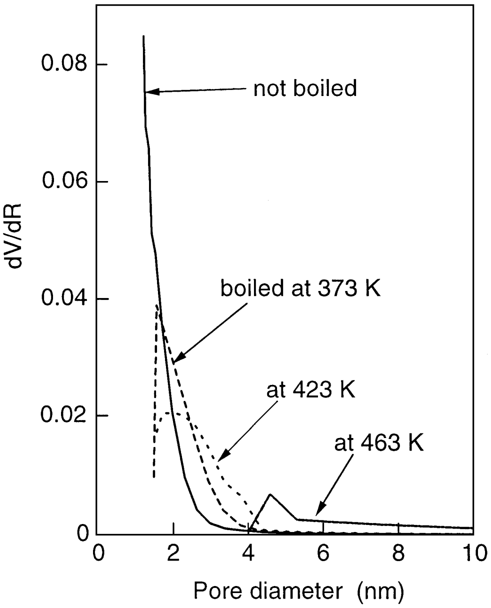

FIG. 5. Pore size distributions of the silicas obtained at 1123 K with a paper filter, and followed by boiling in water at 373, 423, and 463 K.

the boiling temperatures employed and the modification is accomplished under the atmosphere pressure for an instant until the hot particles are rapidly cooled in water. This can induce a slight erosion of the internal walls of the pores and consequently result in a pore expansion. This inference was supported from a fact that the pore volume of the silica which was prepared at 1123 K and collected in water was much larger than the filter-collected one.

At furnace temperature of 773 K, it is presumed that since the silica particles were not heated satisfactory to dissolve the surface, the pores were kept in the micropore region similarly to the filter-collected silica. In addition, the surface areas and the pore volumes of the silicas prepared from the solutions of 2.1 and 2.8 mPa · s were close to those of the sample obtained from the 2.4 mPa · s solution using a paper filter, suggesting that the morphology of the silica before immersion in water is scarcely affected by the combustion temperature. Elevating the temperature, however, raised the surface temperature of the silica particles produced and consequently causes the surface modification in water.

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