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Spherical Particles and Their Surface Properties. I. Interaction of Water with the Surface of Spherical Silica

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Spherical particles of silica were prepared by passing fine silica material through the O_2–H_2 flame. Spherical particles obtained were amorphous, creviceless, and very large in size compared to those of the starting material which indicates that spheres are made by complete comelting of a large number of fine particles. Water adsorption measurements showed that the rate of rehydration of the dehydroxylated silica surface is very slow, especially at low water pressures, and that the spherical silica has a heterogeneous surface, this heterogeneity being enhanced when the sample is heated at elevated temperatures. The ratio of the number of water molecules adsorbed in the first physisorption layer to that of the underlying surface hydroxyls was found to be 1:1.

Particles of most powders employed in industry and surface chemical researches have irregular shapes and inhomogeneous surfaces. Since an ideally spherical particle of any solid substance, if available, will have a physically and chemically homogeneous surface, the usage of such a particle should simplify the surface phenomena and therefore permit exact theoretical treatment. Thus, spherical particles will represent the reference sample for the surface chemistry of powders.

The preparation of spherical particles can be carried out by two methods. The first is the reaction in the liquid phase, that is, the precipitaion of sparingly soluble salts,[1,2)] hydrous metal oxides,[3–5)] and polystyrene lattices.[6)] The particles formed by this method usually contain reagents and by-products as impurities. The second method consists of melting of powders at elevated temperature and solidification on cooling at a lower temperature.[7,8)] This procedure should give particles whose purity depends on the purity of the raw materials.

Silica is used in a variety of industrial fields as mixed catalysts, carriers of catalyst, fillers and drying materials, and has been extensively studied from the surface-chemical stand point. Generally, surface hydroxyls are present on metal oxides as the result of chemisorption of water in the atmosphere,[9–11)] and it has been found that surface hydroxyls on silica show characteristic behavior[11)] which differs from that of most oxides[10,11)] in the following points: a small rate of hydroxylation, a small surface density of the hydroxyls, and the 1:1 ratio between the amounts of physisorbed water and the underlying hydroxyls. In the present work we have undertaken the preparation of spherical silica particles by passing fine silica powders through the O_2–H_2 flame in order to investigate the interaction of the surface with water.

Experimental

Preparation of Spherical Particles of Silica. The apparatus for preparing spherical particles is illustrated schematically in Fig. 1. Raw material of silica was melted by the O_2–H_2 flame in a cylindrical furnace tube made of high alumina, 30 mm in diameter and 250 mm in length, where O_2 and H_2 were introduced at the rate of 14 and 10 l min^{-1}, respectively. A sample bucket was vibrated electrically to permit the sample to fall through the 150 mesh sieve placed at the bottom of the bucket, and the sample was passed into the furnace by the O_2 stream. H_2 was emitted into the furnace at the entrance. After passing through the furnace, the sample was pumped out; the major part of spherical particles formed sedimented on the bottom of the ducts D_1, D_2, and D_3, of 1000 mm each in length, and a minor part was collected on the 100 mesh stainless steel net N and cotton gauze G.

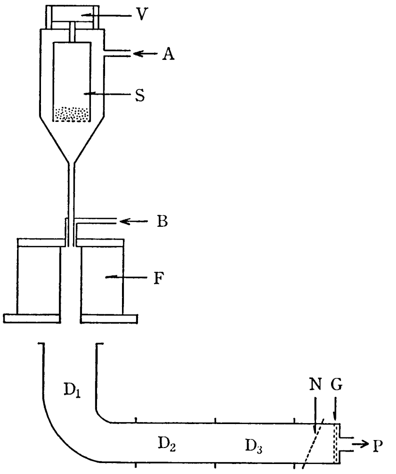

Fig. 1. Diagram of the apparatus for preparing spherical particles by fusion in the O_2–H_2 flame. A, O_2 inlet tube; B, H_2 inlet tube; V, vibrator; S, sample bucket (with 150 mesh net); F, furnace; D_1, D_2, D_3, ducts; N, stainless steel net (100 mesh); G, cotton gauze; P, pump.

Materials. The raw material of silica used in this study was Aerosil 200 made by Japan Aerosil Co., having a specific surface area of about 200 m^2 g^{-1}. Since the sample was too light to pass through the sieving mesh, it was sintered by heating it at 1220 °C for 3 h in an electric furnace; the particles formed had a specific surface area of about 31 m^2 g^{-1}, and could pass easily through the mesh.

Measurement of the Water Adsorption Isotherm and Surface Water Content. The adsorption isotherm of water on spherical silica was measured volumetrically by using a conventional adsorption apparatus equipped with an oil manometer. Prior to the adsorption measurement, the spherical sample was treated at 25, 300, 500, 900, and 1200 °C, respectively for 4 h each in a vacuum of 10^{-6} Torr.[†] After the measurement of the water adsorption isotherm at 25 °C, the sample was exposed to the saturated water vapor for 12 h at room temperature in order to ensure the complete hydroxylation of the surface, followed by the evacuation at 40 °C to leave chemisorbed water on the surface. The second adsorption isotherm was then measured on the fully hydroxylated surface of silica. In order to obtain the isosteric heat of physisorption of water, the second adsorption isotherm was measured over a range of temperatures 10, 15, 20, and 25 °C. The time required of reaching the adsorption equilibrium was about 2 h and 30 min for the first and second adsorption, respectively.

The surface water content was measured by means of the successive-ignition-loss method,[12] and the N_2-BET method was used for the determination of surface area. Electron microscopes were Hitachi HU-11E and JEOL JSM-35.

Results and Discussion

Formation of Spherical Silica. Electron micrographs of sintered silica used as starting material and of spherical silica particles obtained are shown in Fig. 2. It is clear from Fig. 2 that the spherical particles obtained have smooth surfaces. Furthermore, observation of fracture of crushed particles of spherical silica under the field of a scanning electron microscope showed the inner part of the particle to have no crevices, in contrast to TiO_2.[13] X-Ray analysis proved the spherical particles of silica to be amorphous. The mean surface area of the particles obtained was 0.315 $m^2\,g^{-1}$ as shown in Table 1, indicating that the size of the spherical particles is very much larger than that of the sintered sample. This fact manifests that a large number of sintered particles form a drop of melted silica in the flame, and the state of agglomeration of silica at the time when it enters the furnace determines the size of the silica sphere formed.

Adsorption Isotherm of Water and Isosteric Heat of Adsorption. The adsorption isotherm of water on spherical silica is given in Fig. 3. It can be seen from Fig. 3 that the isotherms belong to type II according to Brunauer's classification,[14] and that the second adsorption isotherms on the same sample almost coincide with each other when they are plotted against the relative pressure of water. Furthermore, Fig. 3 shows that the first adsorption isotherm lies above the second one except for the sample treated at 25.0 °C. In addition, the first and second adsorption isotherms measured at the same temperature do not go parallel, but deviate from each other with increasing relative pressure.

This can be explained by the idea that the rate of rehydration of the siloxane surface formed by dehydration of silanols is very slow at lower pressure and gradually increases with increasing relative humidity. This is in contrast to the behavior of most metal oxides where the two isotherms go parallel because of fast rehydration of the dehydrated surface

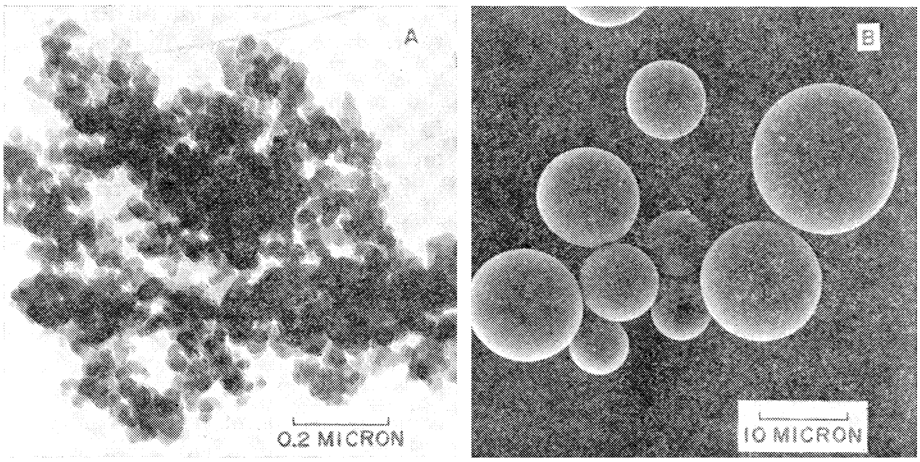

Fig. 2. Electron micrograph of starting material of SiO_2(A) and scanning electron micrograph of spherical SiO_2(B).

Table 1. Relation between the amounts of physisorbed and chemisorbed water on spherical SiO_2

Treatment temperature	Specific surface area	V_m	V_p	V_c	V_h	V_c+V_h	$\frac{V_p}{V_c+V_h}$
°C	$m^2\,g^{-1}$	ml(STP)m^{-2}	$H_2Os\cdot nm^{-2}$	$OHs\cdot nm^{-2}$			$(H_2O)\cdot(OH)^{-1}$
25	0.315	0.0948	2.55	0	2.63	2.63	0.970
300	0.315	0.1391	2.56	2.36	0.35	2.71	0.945
500	0.300	0.1439	2.59	2.56	0	2.56	1.012
900	0.279	0.1500	2.60	2.91	0	2.91	0.893
1200	0.231	0.1349	2.36	2.52	0	2.52	0.937
500[a]	31.1	0.0868	2.34	0	—	—	—

a) Starting material of SiO_2 (sintered).

[†] 1 Torr=133.322 Pa.

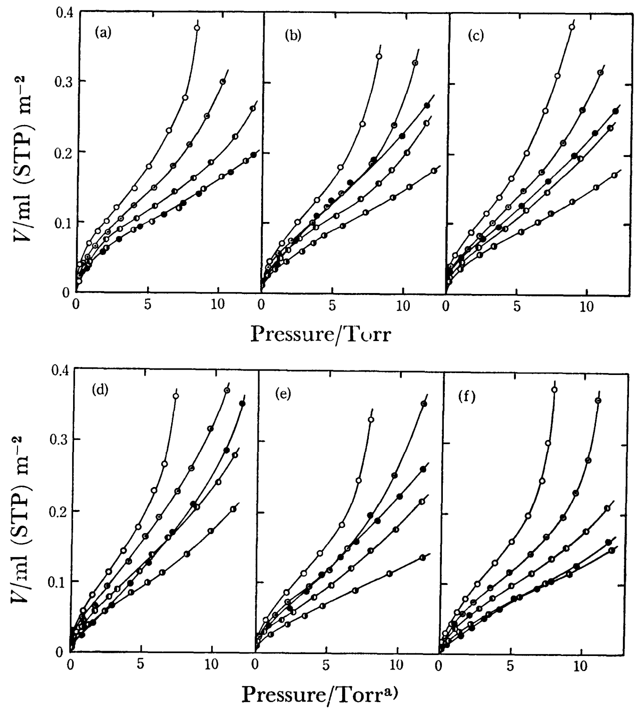

Fig. 3. Adsorption isotherms of water on spherical SiO_2 pretreated at (a) 25, (b) 300, (c) 500, (d) 900, (e) 1200 °C, and (f) starting material of SiO_2 treated at 500 °C. First adsorption ● at 25 °C; second adsorption ○ at 10 °C, ⊙ at 15 °C, ◐ at 20 °C, and ◑ at 25 °C. a) 1 Torr=133.322 Pa.

even at the initial pressure of water.[10]

For comparison, the water adsorption isotherms measured on the sintered silica are illustrated in Fig. 3. The results show that the adsorbed amounts for the second isotherm are almost equal to those in the case of spherical silica, but the first adsorption isotherm lies below that of the spherical silica. In other words, the extent of rehydroxylation differs from sample to sample, and the rehydroxylation rate is faster for the spherical sample than for the sintered one. This better hydrophilicity of spherical silica may be due to the history of the sample, *i.e.* the steam treatment by the O_2–H_2 flame at a very high temperature during the preparation.

As stated above, the first adsorption isotherm obtained includes physisorption and chemisorption of water, the latter of which is irreversible and increases in quantity with increasing pressure of water. This leads to a conclusion that the measurement of isosteric heat of adsorption q_{st} from the first adsorption isotherms by applying the Clausius-Clapeyron equation is unexpectable. On the other hand, the second adsorption isotherm measured on the fully hydroxylated surface of metal oxide has been found to be reversible and reproducible. Thus, we usually measure q_{st} values of water on the fully hydroxylated surface of metal oxide, though the surface heterogeneity discussed by the q_{st} values might be a little of quite different from that on the bare surface.

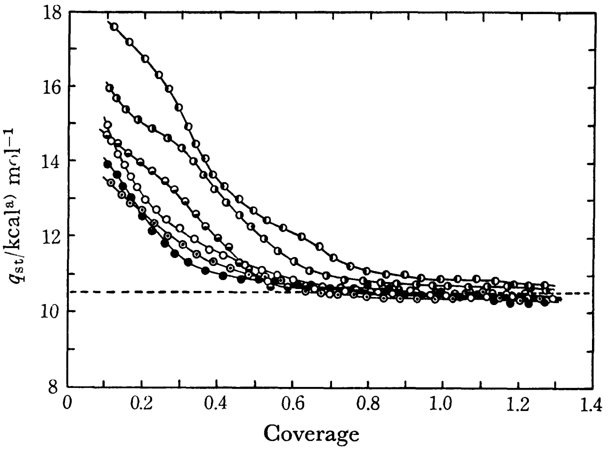

Fig. 4. Isosteric heat of adsorption of water on spherical SiO_2 pretreated at ○ 25 °C, ● 300 °C, ⊙ 500 °C, ◑ 900 °C, ◐ 1200 °C, and ◒ starting material of SiO_2 treated at 500 °C. Broken line represents the heat of liquefaction of water 25 °C. a) 1 cal (thermochemical)=4.184 J.

By applying the Clausius-Clapeyron equation to the second adsorption isotherm in Fig. 3, we can obtain the isosteric heat of adsorption q_{st} as given in Fig. 4. The results reveal that the adsorption energy of water onto the hydroxylated surface of the original spherical silica decreases with the coverage of water indicating some heterogeneity of the surface, and that the extent of heterogeneity depends on the pretreatment temperature of the sample. The q_{st} curves change little until the pretreatment temperature of 500 °C is reached, but further increase in temperature raises the q_{st} values. Additional data of the q_{st} value of the sintered silica give an intermediate curve as shown in Fig. 4, which indicates that the surface heterogeneity of silica was clearly decreased by the formation of spheres. Thus, it is found that the surface activity and surface heterogeneity of fully hydroxylated surface of spherical silica for water adsorption were less than that of the raw material, though they were not so low as those expected. This can be elucidated as follows. When liquid spherical particles of silica melted in the O_2–H_2 flame are quenched, the solid particles formed will have surface state close to that of the liquid, including a small amount of water from the environment. Also on the fully hydroxylated surface of the spherical silica, there will exist the network of SiO_2 including Si atoms of the coordination number 4, which have at least one or two hydroxyls per Si atom. The variety of the direction and surface density of these hydroxyls can be considered to bring about the heterogeneity of hydroxylated spherical silica surface for water adsorption.

It is interesting to note that the surface becomes more active when spherical silica is treated at higher temperature *in vacuo*. The heat treatment at higher temperature naturally causes the migration of atoms in solid toward the direction of more stable state of the solid, *i.e.* toward crystallization, though it be very slow, accompanied by the evolution of bonded water molecules. This may produce more active sites such as corners and edges on the surface.

Surface Water Content on Spherical Silica. Figure 5 gives the surface water content on the spherical silica

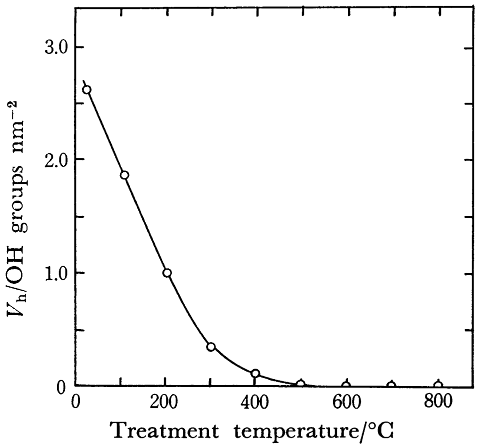

Fig. 5. Surface water content of spherical SiO_2.

which was obtained by the successive-ignition-loss method. The data obtained show that the surface water content at room temperature is almost the same as that reported on various other silica samples,[11] and very much smaller than that on most metal oxides.[10,11] The value 2.55 is almost one half of the calculated theoretical value.

Relation between the Amounts of Physisorbed Water and the Underlying Hydroxyls. The data obtained by the analysis of water adsorption isotherms of spherical silica are listed in Table 1. V_m and V_p are the monolayer capacities obtained by applying the BET method to the first and second isotherms, respectively. V_p contains only the physisorbed amount, but V_m both physisorbed and chemisorbed ones, and the difference between V_p and V_m therefore represents the amount of chemisorption V_c. We have another component of chemisorbed water, that is, the surface water content V_h which exists on the surface before the measurement of the first adsorption isotherm.

The sum V_c+V_h, therefore, represents the total amount of chemisorbed water. In the last column in Table 1, we can see the ratio of H_2O:OH to be 1:1, which shows a good agreement with the value obtained on fine silica particles.[11] In other words, a water molecule is physisorbed on a surface silanol group by hydrogen bonding on any kind of silica, contrary to the case of metal oxides, where a water molecule is adsorbed by two surface hydroxyls forming a tetrahedral coordination of the oxygen atom in an adsorbed water molecule. This interesting phenomenon of the silica surface may be attributed to a dilute population of surface silanols on the surface as was stated above, so that the neighboring two hydroxyls on silica are located too far apart for the bridging of a water molecule by two hydroxyls.

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