The Preparation of Mesoporous Silica Gel and the Nature of the Modification of Its Surface with Organoalkoxysilane

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Mesoporous silica gel with a narrow pore-size distribution at the pore diameter of 200 Å has been prepared upon gelation in the presence of starch. Taking into account the effects on the geometrical properties of its surface, two typical surface-modifying procedures that utilize organoalkoxysilane were characterized. Procedure I retains the mesoporous structure, although the fixed amount of the organofunctional group is rather small. Procedure II introduces a large amount of the organofunctional group to the surface, but is accompanied by a pronounced reduction in both the B.E.T. surface area and the specific pore volume. The observed range of the apparent surface concentration of the organofunctional group and the scanning electron micrographs suggest that the surface is coated with highly crosslinked organosiloxane polymers in the latter case. Despite the contrasts between the two modified surfaces, the similarity of C-13 NMR line shapes, chemical shifts, and spin-lattice relaxation times between the respective surface organofunctional groups indicates that their microenvironment and mobility resemble each other.

The modification of the surface of porous adsorbents *via* the chemical bonding of the organofunctional group is now a common procedure to improve them for use as a stationary phase in liquid chromatography[1) or as a support of soluble complex catalysts.[2) A surface reaction with organoalkoxysilane is one of the most popular methods for this purpose, but scarcely physicochemical investigation has been undertaken to examine how the surface is actually "modified" by such a treatment.[1,3)

Since such geometrical properties as the specific pore volume and pore-size distribution govern the efficiency of chromatographic separations[4—6) and the activity and/or selectivity of catalytic reactions,[7) it is especially important to characterize appropriately the effect of the surface modification. From this viewpoint, we prepared mesoporous silica gel with a narrow pore-size distribution at the 200 Å pore diameter, and investigated the change in the geometrical properties associated with the coupling treatment with organoalkoxysilane. In an attempt to characterize the fixed organofunctional groups spectroscopically, C-13 NMR (CMR) spectroscopy was applied to them. Two typical procedures for fixation[8—11) were adopted, and the advantage of each procedure is discussed.

Experimental

Preparation of Mesoporous Silica Gel. Starch (15 g) was dissolved in warm water (500 cm^3), and the resulting solution was mixed with an aqueous solution of colloidal silica (Nissan Chem. Ind., Ltd.; Snowtex-30: SiO_2 content 30—31%; particle diameter 10—20 nm; pH 9.5—10.5; 500 cm^3). The mixed solution was poured into acetone (2.5 dm^3) with stirring and allowed to stand for 4 d with occasional stirring. During this procedure silica gel was precipitated, and the supernatant solution was replaced by acetone (2.5 dm^3) once a day. The silica gel thus formed was filtered, air-dried, milled in an α-alumina mortar, and calcined in air (120 °C, 24 h). After calcination, the color of the silica gel changed from white into light brown. It was decolorized by repeated washing with water, and then boiled three times. After cooling, the water was decanted and acid (concd HNO_3–concd H_2SO_4 150 cm^3; 9/1 Vol.) was added to the residual suspension of silica gel, which was then permitted to stand for 24 h. The treatment with acid was done twice. The sample was washed with water untill the solution became neutral and then dried in a drying oven. Silica gel was evacuated at 200 °C (4 h) immediately before the succeeding fixation treatment.

Procedure for the Fixation of Organofunctional Groups. The fixation of 3-aminopropyl or *N*-(2-aminoethyl)-3-aminopropyl groups to silica gel was effected in two ways. Procedure I: To a toluene solution (100 cm^3) of silane ($NH_2CH_2CH_2CH_2Si(OEt)_3$: Shin-Etsu Chem. Ind., Ltd.; 15.6 g), silica gel (10 g) was added with stirring, after which the suspended solution was refluxed for 24 h. The sample was then transferred to a Soxhlet apparatus, extracted with benzene for 24 h, and dried *in vacuo* (130 °C, 4 h). The fixation procedure for $NH_2CH_2CH_2NHCH_2CH_2CH_2Si(OMe)_3$ (Shin-Etsu Chem. Ind., Ltd.) was performed similarly using the following amounts of reagents: silane, 20.8 g; toluene, 100 cm^3, and silica gel, 15.0 g. Procedure II was the same as Procedure I except that water, in an amount equivalent to that necessary for hydrolyzing the alkoxyl group of the silane, was introduced into the toluene before the addition of silane. In Procedures I and II, about 20 and 70% of the added silane were consumed for fixation respectively.

Characterization of Silica Gels. The B.E.T. surface area (s_{BET}) was determined using the B.E.T. procedure (a_m (N_2) = 16.2 Å^2 molecule^{-1}). The specific pore volume (v_p) and the pore-size distribution were calculated from the nitrogen adsorption (or desorption) measurements at 77 K, based on the method of Cranston and Inkley,[12) or by means of mercury porosimetry (American Instrument Co., Ltd.; 60000 psi). The amounts of the fixed organofunctional groups were evaluated from the carbon and nitrogen contents of the modified silica gel, as determined from the elemental analysis. In the evaluation, alkoxyl carbons were omitted (*vide infra*), and the two values, coinciding within a 10% deviation, were averaged. Scanning electron micrographs were taken using a Hitachi HHS-2R SEM apparatus. CMR spectra were obtained with noise-modulated proton decoupling on a Fourier-transform pulsed NMR spectrometer (JEOL JNM-FX60), operating at 15.04 MHz.

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Results and Discussion

Geometrical Properties of the Surfaces. The prepared silica gel (original silica gel) has the values of $148\ \mathrm{m^2\,g^{-1}}$ for s_{BET} and $0.792\ \mathrm{cm^3\,g^{-1}}$ for v_p (calculated at the saturated vapor pressure). In particular, as revealed by mercury porosimetry, it has a maximum abundance of mesopores, amounting to $0.45\ \mathrm{cm^3\,g^{-1}}$, with an (entrance) pore diameter of about 200 Å (Fig. 1). This feature is probably derived from the effect of the incorporation of starch upon gelation.[13,14] The nitrogen adsorption and desorption isotherms on the silica gel showed hysteresis. The analysis of the isotherms gave the pore-size distributions depicted in Fig. 2. The cumulative pore volumes below 300 Å were 0.427 and $0.653\ \mathrm{cm^3\,g^{-1}}$ respectively. Since a distinctive peak with a maximum abundance at a pore diameter of about 200 Å appears only in the case of desorption, the mesopores with that pore diameter may be formed with various bottlenecks.

After the modification with Procedure I, the corresponding values became $0.332\ \mathrm{cm^3\,g^{-1}}$ (nitrogen adsorption), $0.483\ \mathrm{cm^3\,g^{-1}}$ (nitrogen desorption), and 0.46 $\mathrm{cm^3\,g^{-1}}$ (mercury porosimetry). As far as the 200 Å-mesopores are concerned, both the mercury porosimetry (Fig. 1) and the nitrogen desorption experiment (Fig. 2) showed distribution patterns similar to those of the original silica gel around this range, and their abundance, evaluated by the mercury porosimetry, was actually hardly affected at all. The application of the V_a-t plot,[15,16] however, showed that the micropores (<7 Å) present on the original silica gel with the surface area of $12\ \mathrm{m^2\,g^{-1}}$, where S_{total} was evaluated to be $151\ \mathrm{m^2\,g^{-1}}$, were lost after this modification. It can be said that Procedure I caused little change in the mesopore structure, although it disrupted most of the micropores.

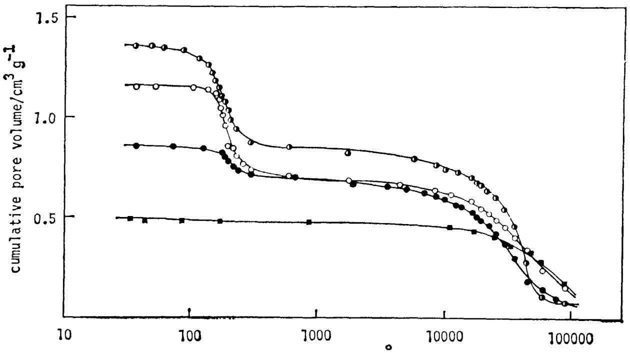

Fig. 1. Mercury intrusion pore size distribution of original and modified silica gels.
○: Original silica gel, ◑: after modification with Procedure I, ●: after modification with Procedure II, ■: Aerosil 380 after modification with Procedure II.

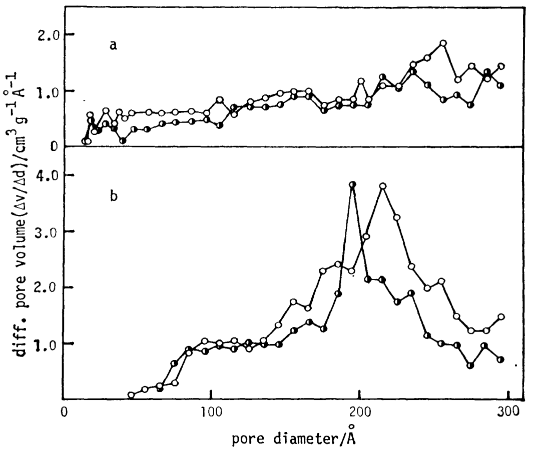

Fig. 2. Pore-size distributions determined from nitrogen adsorption (a) and desorption (b) isotherms.
○: Original silica gel, ◑: after modification with Procedure I.

It was found that Procedure II exerted a further influence on the surface geometrical properties because of the presence of water in the fixation treatment. Figure 1 shows that a large amount of mesopores of the original silica gel disappeared during the treatment. The cumulative pore volume below 300 Å was decreased as low as $0.082\ \mathrm{cm^3\,g^{-1}}$, and the V_a-t plot indicated that the micropores vanished also in this case. For reference, the result for the Aerosil 380 (Degussa) modified with Procedure II is shown in Fig. 1. Naturally, it exhibits no population in the mesopore range of about 200 Å. The distribution in the pore-size range around tens of thousands ång-

TABLE 1. GEOMETRICAL PROPERITIES OF MODIFIED SILICA GEL SURFACES AND THE AMOUNTS OF FIXED ORGANOFUNCTIONAL GROUPS

Fixation procedure	B.E.T. surface area	Pore volume$^{a)}$	Fixed organofunctional group	
			Amount	Apparent surface concentration$^{b)}$
	$\mathrm{m^2\,g^{-1}}$	$\mathrm{cm^3\,g^{-1}}$	$\mathrm{mmol\,g^{-1}}$	Group/100 Å^2
Procedure I	116	0.643	0.55	2.8
	95.7	0.566	0.85	5.3
	86.7	0.613	0.84	5.8
Procedure II	29.6	0.208	2.25	45.8
	13.1	0.128	2.70	124
	10.3$^{c)}$	0.055$^{c)}$	3.90$^{c)}$	228$^{c)}$

a) Evaluated at the saturated vapor pressure of nitrogen at 77 K. b) Calculated based on the B.E.T. surface area of modified surfaces. c) Modified with (3-aminopropyl)triethoxysilane.

stroms, which was observed in all the cases in Fig. 1, may correspond to the interstitial volume of agglomerated particles.

Table 1 presents the amount of the fixed organofunctional group, together with the values of s_{BET} and v_{p}, for the silica gels modified by the use of Procedure I or II in repeated runs. It is seen that Procedure II caused a pronounced reduction in both s_{BET} and v_{p}, but introduced an appreciable amount of organofunctional groups to the surface in comparison with Procedure I. The characteristic mesopores of the original silica gel are retained in Procedure I, whereas in Procedure II they are limited in return for the large amount of fixation. From this viewpoint, the trend shown in Table 1 is consistent with the data of the pore-size distribution.

The influence of these fixation procedures may be noticed plainly in the apparent surface concentration of the fixed organofunctional group (Table 1). In the case of Procedure I, the values have the same order of magnitude as the ordinary surface concentration of hydroxyl groups on silica gels (about 4.8 hydroxyl groups per 100 Å^2).[17] In contrast, Procedure II gave values far exceeding this value.

Scanning Electron Micrographs. Some representative scanning electron micrographs (SEM) of the original and modified silica gels are shown in Fig. 3. A remarkable feature is that the spherical shape of Aerosil 380 is completely lost by the modification with Procedure II. It appears that a number of Aerosil particles were combined and coated with a polymer-like substance, possibly an organosiloxane polymer. The marked decrease in s_{BET} (from 380 to 36 m^2 g^{-1}) seems to support this view. The SEM of the mesoporous silica gel modified with Procedure II also appears to indicate a similar surface coating. The observed range of the apparent surface concentration suggests that highly crosslinked organosiloxane polymers were formed as a result of the trifunctionality of the modifiers. The resemblance between the two silica gels, original and modified with Procedure I, is reasonable in view of the rather small change in the surface characteristics by this modification. It has been suggested that organoalkoxysilane molecules are fixed on silica surfaces in the monomeric form when the amount of physically adsorbed water is small.[1]

CMR Properties. The C-13 nuclear magnetic resonance of the fixed organofunctional group is detectable with high resolution if the solvent used to suspend the modified silica gel is properly chosen.[18] The CMR spectra of the fixed 3-aminopropyl groups are shown in Fig. 4. The absence of ethoxyl carbon resonances confirms that the ethoxyl groups were completely removed in the course of the fixation treatment. It is apparent that the two modified silica gels gave essentially identical spectra despite the salient contrasts between the geometrical properties of their surfaces. The situation was unaltered for the *N*-(2-aminoethyl)-3-aminopropyl group. The chemical shift data are tabulated in Table 2. The observed substantial low-field shift of the C_1 carbon atom seems reasonable in view of the fact that 2-butenes[19] and toluene[20] adsorbed on silica gel or Zeolite show low-field shifts for the carbon atoms pertinent to adsorption.

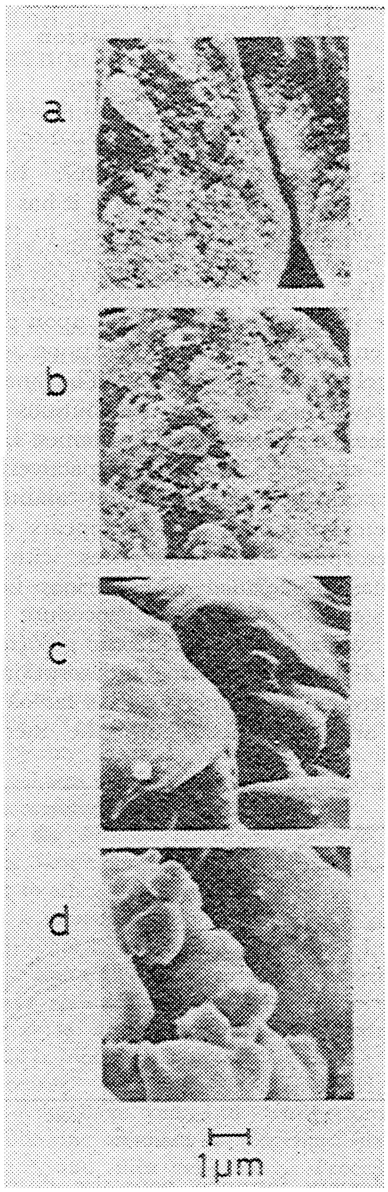

Fig. 3. Scanning electron micrographs of original and modified silica gels.
a: Original silica gel, b: after modification with Procedure I, c: after modification with Procedure II, d: Aerosil 380 after modification with Procedure II.

For the same samples, the spin-lattice relaxation times (T_1) of the carbon atoms were determined by the inversion-recovery method.[21] Table 3 shows that fixation caused a considerable reduction in T_1 values; here, too, there is no distiguishing difference between the two procedures.

The effect of possible paramagnetic impurities in the silica gel on the spin-lattice relaxation is small for the following reasons: (i) for both modified silica gels, the T_1 values of the C_1 carbon atom are significantly different between the two kinds of organofunctional groups, and (ii) the values of the ^{13}C–^{1}H nuclear Overhauser effect were determined to be 1.3 (C_1) and 1.6 (C_2) for the *N*-(2-aminoethyl)-3-amino-

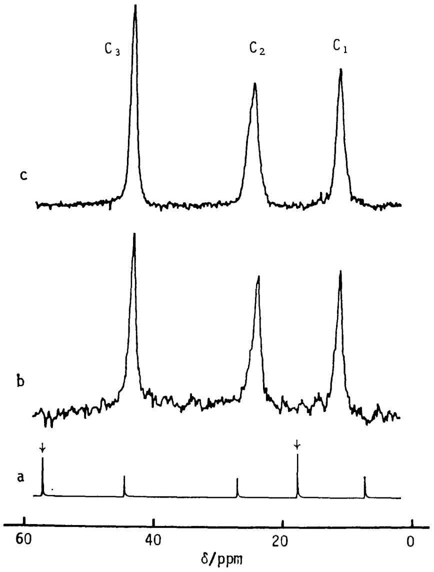

Fig. 4. C-13 NMR spectra of the 3-aminopropyl groups fixed on silica gel and of original alkoxysilane (15 MHz, 10 μs pulse width, 2.0 s pulse interval).
a: 3-Aminopropyltriethoxysilane (neat liquid, 1000 scans), b: fixed with Procedure I (0.96 mmol g^{-1}, D_2O suspension, 69000 scans), c: fixed with Procedure II (3.90 mmol g^{-1}, D_2O suspension, 22000 scans). Numbers are designated from the silicon atom. Arrows indicate the ethoxyl carbon resonances.

propyl group (fixed with Procedure II; $CDCl_3$ solvent), values which are close to the maximum value of this effect (1.988) and which indicate the predominance of ^{13}C–^{1}H dipole-dipole interactions in the relaxation of these carbon atoms.[21] We consider that the observed enhancement of relaxation rates is ascribable to the decrease in the freedom of motion of the organofunctional groups resulting from the anchoring of the silicon atom. The magnitude of T_1 is reasonable for the aliphatic carbon chain, whose translational motion is hindered, but whose internal rotation is almost free, when compared with those for the butyl group anchored in poly(butyl methacrylate) (T_1 in s: C_1 0.12, C_2 0.13, *etc.*).[22] The increase in T_1 from C_1 to C_2 to C_3 reflects the ease of motion, in that order.

It should be noted that the resemblance of line shapes between the spectra suggests that the fixed organofunctional groups obtained with Procedure II have a homogeneity similar to those obtained with Procedure I. This similarity seems noticeable in view of the high crosslinkage of organosiloxane polymers, which was suggested for the former case. Based on the CMR properties reported above, it may be concluded that the microenvironment and the mobility of the fixed organofunctional groups resemble each other in the D_2O solvent, irrespective of the difference in the method of surface modification.

Comparison of the Two Surface-modifying Procedures. The two procedures for surface modification have thus been characterized. In the case of Procedure

TABLE 2. C-13 CHEMICAL SHIFTS OF THE ORGANOFUNCTIONAL GROUPS FIXED ON SILICA GEL AND OF ORIGINAL ALKOXYSILANE[a)]

Sample		Medium	Chemical shift/ppm[b)]				
Organofunctional group	State		C_1	C_2	C_3	C_4	C_5
$NH_2CH_2CH_2CH_2Si$–	Silane	neat	7.3	27.2	44.8		
	Silica (Procedure I)	D_2O	11.4	24.2	43.6		
	Silica (Procedure II)	D_2O	11.5	24.8	43.7		
$NH_2CH_2CH_2NHCH_2CH_2CH_2Si$–	Silane	neat	6.4	23.1	52.3	52.7	41.8
	Silica (Procedure I)	D_2O	11.6	22.6	50.6	51.8	40.0
	Silica (Procedure II)	D_2O	11.7	23.0	51.0	52.0	40.4

a) Numbers are designated from the silicon atom. b) Downfield from Me_4Si, where the original data, measured relative to 1,4-dioxane present in a concentrically placed capillary tube, are converted using $\delta_{\text{dioxane}}=67.4$ ppm. Accurate to ±0.3 ppm.

TABLE 3. SPIN-LATTICE RELAXATION TIMES OF THE ORGANOFUNCTIONAL GROUPS FIXED ON SILICA GEL AND OF ORIGINAL ALKOXYSILANE[a)]

Sample		Medium	T_1/s[b)]				
Organofunctional group	State		C_1	C_2	C_3	C_4	C_5
$NH_2CH_2CH_2CH_2Si$–	Silane	neat	2.27	3.03	3.16		
	Silica (Procedure I)	D_2O	0.25	0.36	0.36		
	Silica (Procedure II)	D_2O	0.21	0.35	0.36		
$NH_2CH_2CH_2NHCH_2CH_2CH_2Si$–	Silane	neat	0.98	0.98	0.97	1.28	1.49
	Silica (Procedure I)	D_2O	0.11	0.14	0.14	0.14	0.18
	Silica (Procedure II)	D_2O	0.10	0.14	0.20	0.14	0.37

a) Numbers are designated from the silicon atom. b) Accurate to ±0.02 s.

II, pores of silica gel as large as 200 Å in pore diameter are covered with organosiloxane polymers, but this procedure has the merit of producing a large quantity of fixation. This may be advantageous for its use as a silica support for preconcentration of trace metals,[23] affinity chromatography, or the immobilization of soluble complex catalysts with high density of active sites.

In contrast, modification with Procedure I retains the mesoporous structure of the silica gel surface. In this case, the ability to separate substances or to select substrates, through differentiating their molecular sizes, can be expected. If this characteristics is employed properly, the utility of the surface organofunctional groups may be enlarged.

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