

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 33—37 (1971)

Infrared Absorption Spectra of Silica Gel - H_2^{16}O , D_2^{16}O , and H_2^{18}O Systems

Masao HINO and Toshio SATO

Government Industrial Development Laboratory, Hokkaido, Higashi-Tsukisamu, Sapporo

(Received July 4, 1970)

Infrared absorption spectra of the systems of silica gel - H_2^{16}O , D_2^{16}O , H_2^{18}O , and some organic vapors were measured in order to assign the bands sensitive to adsorption at 870 and around 950 cm^{-1} . Deuteration of silica gel caused the absorption decrease at 870 cm^{-1} and the appearance of a band at 620 cm^{-1} . The band around 950 cm^{-1} appearing by adsorption not only of water but also of organic vapors showed no shift on deuteration, but shifted toward low frequency side by 25 cm^{-1} on the substitution of ^{16}O of surface silanol groups with ^{18}O . From these facts the bands at 870, 620 and 950 cm^{-1} were assigned to Si-OH bending, Si-OD bending and Si-O stretching vibrations of surface silanol groups, respectively. The oxygen atom of silanol groups of silica gel was found to exchange with that of adsorbed water molecules even at room temperature for a sample treated at temperature below 300°C. On the other hand, higher reaction temperature of *ca.* 200°C was necessary for a sample calcined at 800°C. Mechanism of the oxygen atom exchange reaction was discussed.

A number of investigations have been carried out to elucidate the structure and properties of silica gel surface by use of infrared spectroscopy.¹⁻³⁾ They were concentrated on measurement of the OH stretching band between 4000 and 2500 cm^{-1} . However, there are very few investigations in other spectrum regions.

Beutelspacher⁴⁾ first pointed out that a wet silica gel had a 950 cm^{-1} band, which vanished by heat treatment at 1000°C. Soda⁵⁾ also found a 950 cm^{-1} absorption band sensitive to desiccation for a finely ground quartz powder sample. He assumed that it was due to the bending vibration of Si-OH groups on the surface of the particles. On the other hand, Benesi and Jones⁶⁾

1) M. L. Hair, "Infrared Spectroscopy in Surface Chemistry," Marcel Dekker, Inc., New York (1967), p. 79.

2) M. R. Basila, "Applied Spectroscopy Reviews," Vol. 1, Marcel Dekker, Inc., New York (1968), p. 296.

3) A. V. Kiselev and V. I. Lygin, *Russian Chem. Rev.*, **31**, 175 (1962).

4) H. Beutelspacher, VI Congress International de la Science du sol, Vol. B 329 (1956).

5) R. Soda, This Bulletin, **34**, 1491 (1961).

6) H. A. Benesi and A. C. Jones, *J. Phys. Chem.*, **63**, 179 (1959).

assigned this bending vibration to the band at 870 cm^{-1} , from the fact that it disappeared on deuteration.

The purpose of the present work is to establish the assignment of these two bands more directly by measuring the isotopic shift in wider frequency region when H and ^{16}O atoms of silica gel are substituted with D and ^{18}O atoms, respectively, and also by measuring the adsorption effects of various vapors on the surface. The reactivity of the silica gel surface was also studied through the exchange reaction of water with surface silanol groups.

Experimental

Materials. Silica gel for chromatography (Kanto Chemical Co., Inc.) made from sodium silicate and sulfuric acid was ground in an agate mortar and then suspended in deionized water to get a very fine powder sample. The surface area of this material was $450\text{ m}^2/\text{g}$, independent of the heat treatment at temperature lower than 600°C . D_2^{16}O (Showa Denko Co., Ltd.) of 99.75 atom % in purity and H_2^{18}O (Yeda R. & D., Co. Ltd.) of 97.9 atom % were used. Methanol, diethyl ether, acetone, and carbon disulfide, all of guaranteed reagent grade, were dried, distilled and degassed before the adsorption experiment. Pure hydrogen sulfide (Takachiho Chemical Industrial Co.) was used without further purification.

Apparatus and Procedure. A JASCO Model 402-G double beam infrared spectrometer was used for recording the spectra in the wave number region between 4000 and 430 cm^{-1} . An all metal *in situ* cell used for measurement at room temperature is shown in Fig. 1. Another infrared cell with liquid

nitrogen cooling system was also constructed by modifying the cell in Fig. 1 for measuring the adsorption of organic vapors and hydrogen sulfide at lower temperature down to -130°C .

A sandwich method was used for sample preparation; 6 to 20 mg of silical gel powder dispersed in a few drops of methanol was spread on the transparent KBr plate of $34\text{ mm} \times 12\text{ mm} \times 4\text{ mm}$. After the methanol was evaporated, the silica powder on the plate was made even with a spatula and sandwiched by facing another KBr plate on the sample. As far as infrared spectrometer was used as a monitor, the silica gel was found not to react with methanol during the course of preparation. A vacuum reference cell was set in the light path of the reference side to eliminate the background effect of the spectra. To prepare a sufficiently deuterated silica gel sample, the sample was exposed to D_2^{16}O vapor at 10 mmHg for 30 min and then evacuated, both at room temperature. The procedure was repeated six times.^{6,7)}

Results

1. Silica Gel - H_2^{16}O System. Measurement of the spectra was carried out on the silica gel sample after evacuation at various temperatures and also on successive exposure to water vapor at room temperature. As shown in Fig. 2, evacuation at room temperature gave marked decrease of the OH stretching band at 3400 cm^{-1} and the HOH bending band at 1630 cm^{-1} , which were attributed to the hydrogen-bonded hydroxyl groups and physically adsorbed water molecules, respectively. A simultaneous decrease of the absorption at 950 cm^{-1} was observed, while the absorption at 870 cm^{-1} increased in intensity and a sharp OH stretching band at 3748 cm^{-1} due to the "free" silanol groups appeared. Evacuation at elevated temperatures, as represented by Curves 4 and 6 in Fig. 2, produced a similar but stronger effect in the spectral changes, although the band at 870 cm^{-1} exceptionally decreased in intensity. Admission of water vapor on these evacuated surfaces produced the reverse effect on the spectral changes (Curves 3, 5, and 7). However, these five absorptions were completely restored only when the sample was evacuated at room temperature (Curve 3). A small band shift from 950 to 960 cm^{-1} was observed, when the sample was evacuated at 200 and 300°C and then rehydrated at room temperature.

Organic vapors and hydrogen sulfide, which have no absorption around 960 cm^{-1} , were then admitted at low temperatures onto the silica gel samples evacuated at 200°C . In each case, as seen in Table 1, bands were found to come out around 960 cm^{-1} and in the wave number region from 3680 to 3300 cm^{-1} , the peak positions depending on the kind and the amount of adsorbate.

2. Silica Gel - D_2^{16}O System. Appearance of a strong ^{16}OD stretching band at 2480 cm^{-1} together with the disappearance of the bands of ^{16}OH at 3400 and 1630 cm^{-1} after deuteration confirmed that the deuteration of the present silica gel sample was completed.^{6,7)} It should be emphasized that this treatment induced no spectral change at the 950 cm^{-1} band and

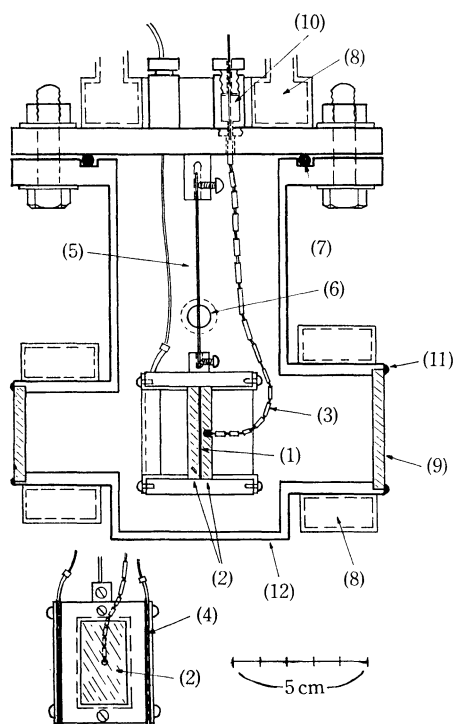
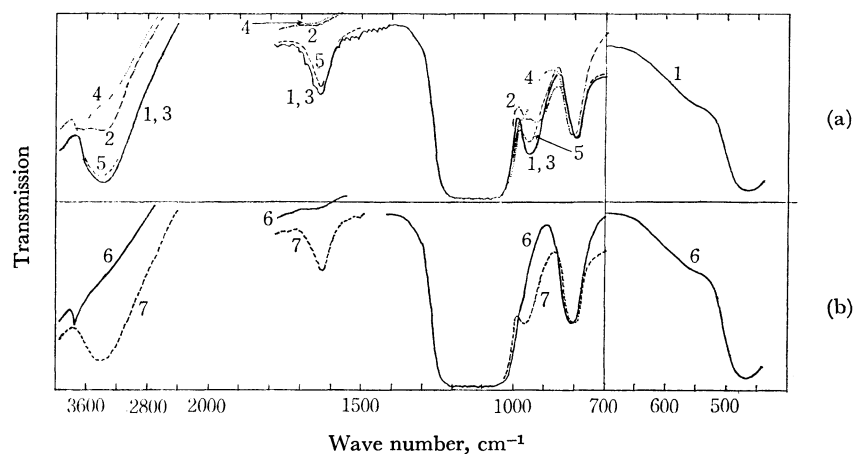


Fig. 1. All metal *in situ* cell.

- 1, adsorbent sample; 2, KBr plate; 3, thermocouple;
- 4, nichrome wire heater; 5, nichrome wire hanger;
- 6, evacuation outlet; 7, O-ring seal; 8, water jacket;
- 9, KBr window; 10, silicone rubber packing;
- 11, elastic epoxide resin seal; 12, chromium plated steel

7) V. Ya. Davydov, A. V. Kiselev, and L. T. Zhuravlev, *Trans. Faraday Soc.*, **60**, 2254 (1964).

Fig. 2. Spectra of silica gel - H_2^{16}O system.

- a) 1—, before evacuation; 2-•-•-, evacuated at room temperature for 26 hr; 3—, 5-----, exposed to H_2^{16}O at 12 mmHg; 4-----, evacuated at 200°C for 5 hr
 b) 6—, evacuated at 300°C for 5 hr; 7-----, exposed to H_2^{16}O at 12 mmHg

Experiments were carried out in the order from 1 to 7. The spectra of lower wave number than 1400 cm^{-1} were recorded after the background was adjusted to a constant level at 1400 cm^{-1} .

TABLE 1. PEAK POSITION OF THE BANDS PRODUCED BY ADSORPTION OF ORGANIC VAPORS

Adsorbate	OH stretching band of the surface silanol groups (cm^{-1})	The band around 960 cm^{-1} (cm^{-1})
CS_2	3680	970
H_2S	3460	914
$(\text{C}_2\text{H}_5)_2\text{O}$	3300	937
$(\text{CH}_3)_2\text{CO}$	3300	945
CH_3OH	a)	955

a) Not distinguishable from the OH stretching band of CH_3OH .

also much decrease of the absorption at 870 cm^{-1} . On evacuation of the sample at elevated temperatures, the band intensity at 950 cm^{-1} decreased and a new band

grew up at 620 cm^{-1} (Curve 3 in Fig. 3). Introduction of D_2^{16}O vapor to this evacuated sample gave a reverse spectral change, although the band at 950 cm^{-1} finally settled down to 960 cm^{-1} as in the case of silica gel - H_2^{16}O system. The original spectra illustrated in Fig. 2 were restored by treating the deuterated sample with light water vapor.

3. *Silica Gel - H_2^{18}O System.* A preliminary experiment showed that the introduction of H_2^{18}O to a silica gel sample evacuated at 300°C for several hours gave small but definite isotopic shifts at the 3750 and 950 cm^{-1} bands, but not at any other bands. Evacuation and introduction of H_2^{18}O were then repeated in the order from Curve 1 to Curve 12 in Fig. 4 in order to observe more precise spectral changes with time. As illustrated by Curve 3 of Fig. 4 (b), the band at

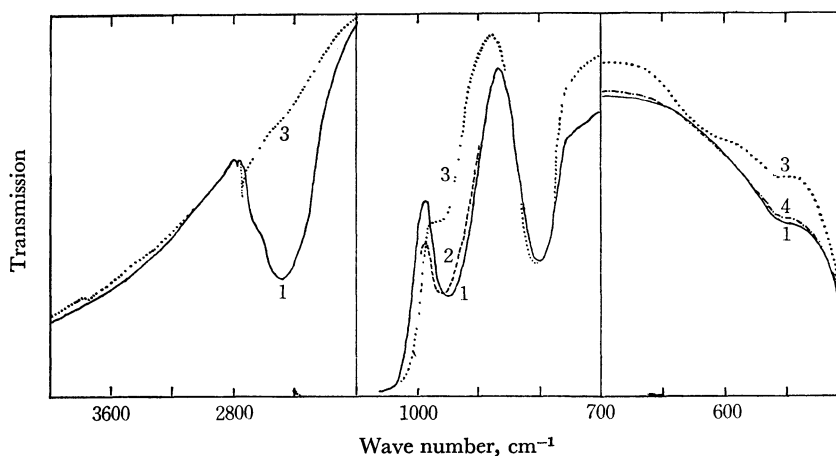


Fig. 3. Evacuation effect of a deuterated silica gel sample.

- 1—, on exposure to D_2^{16}O at 5 mmHg; 2-----, on exposure to D_2^{16}O at 9 mmHg after being evacuated at 200°C for 5 hr; 3....., after being evacuated at 300°C for 5 hr; 4-•-•-, on exposure to D_2^{16}O at 12 mmHg after the 300°C evacuation

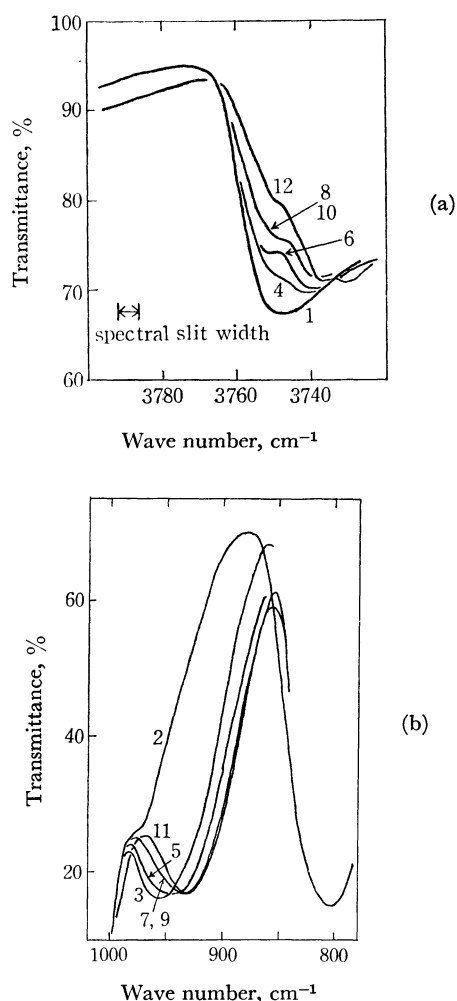


Fig. 4. Spectra of silica gel - H_2^{18}O system.

1, evacuated; 2, evacuated at 200°C ; 3, exposed to H_2^{18}O vapor for 6 min; 4, evacuated; 5, exposed to H_2^{18}O vapor for 25 min; 6, evacuated; 7, exposed to H_2^{18}O vapor for 40 min; 8, evacuated; 9, exposed to H_2^{18}O vapor for 100 min; 10, evacuated; 11, exposed to H_2^{18}O vapor at 100°C for 1 hr and cooled to room temperature in the vapor atmosphere; 12, evacuated.

Evacuation was conducted at room temperature for 5 hr and H_2^{18}O vapor of 10 mmHg was introduced also at room temperature unless otherwise described.

960 cm^{-1} was produced immediately after the introduction of H_2^{18}O at room temperature. This band, however, shifted to the lower wave number side with time and reached almost a steady value of 935 cm^{-1} after about 70 min. Successive treatment with H_2^{18}O at 100°C gave more shifts, as seen in Curve 11. In a quite similar way, a new band around 3740 cm^{-1} grew up in accordance with the decrease of the OH stretching band at 3748 cm^{-1} with time and reached a steady state after 70 min (Curves 8 and 10, Fig. 4(a)). Treatment with H_2^{18}O at 100°C gave a more distinct spectral change, as seen in Curve 12.

The exchange reaction with H_2^{18}O was also conducted on a silica gel sample preliminarily calcined at 800°C for 30 hr, which gave very sharp free OH absorption on account of almost complete lack of background due to the broad hydrogen-bonded OH

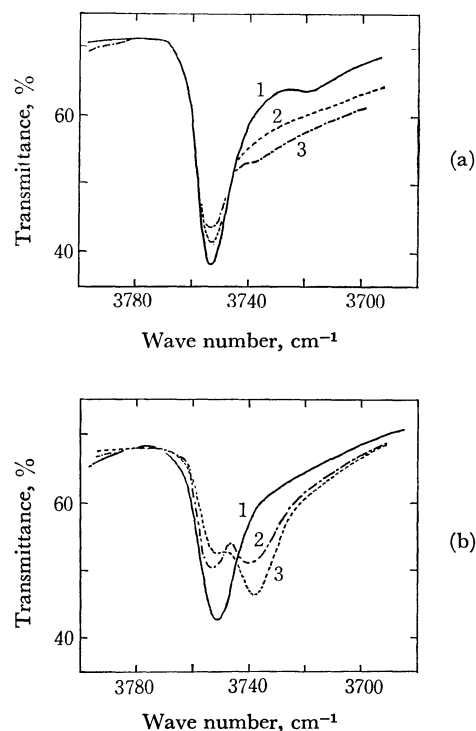


Fig. 5. Spectral changes in free OH stretching band of silica gel calcined at 800°C on exposure to H_2^{18}O vapor at room temperature (a) and at higher temperatures (b).

a) before exposure (1), exposed to H_2^{18}O vapor for 25 min (1), 2 hr more (2), 15 hr more (3), and 15 hr more (3). Each spectrum was recorded after evacuation at room temperature.

b) before exposure (evacuated at room temperature) (1), exposed to H_2^{18}O vapor at 200°C for 20 hr and evacuated at room temperature (2), exposed at 260°C for 8 hr and evacuated at the same temperature (3).

absorption around 3600 cm^{-1} . After the sample was evacuated at room temperature, it was exposed in H_2^{18}O vapor at room temperature. As seen in Fig. 5(a), the free ^{16}OH absorption at 3751 cm^{-1} decreased very slowly in intensity and reached a steady state after 17 hr. A very small ^{18}OH absorption at 3737 cm^{-1} was observed. The result confirmed that the oxygen of the surface silanol groups was only partially exchanged by oxygen of H_2^{18}O in adsorbed state at room temperature. Figure 5(b) shows the result on the same sample exposed in H_2^{18}O vapor at 200 and 260°C and then evacuated. It turned out that the higher the temperature treatment with H_2^{18}O the more promoted the oxygen exchange reaction.

Discussion

1. *Assignment of the Bands at 960 and 870 cm^{-1} .* The band at 870 cm^{-1} can definitely be attributed to the bending vibration of free Si-O-H groups on the surface, because the band increased in intensity on evacuation, at least at room temperature, and shifted to the position of 620 cm^{-1} on deuteration, its frequency being almost consistent with that calculated under the assumption that the band at 870 cm^{-1} was associated with Si-O-H bending vibration and that this can be

TABLE 2. SUMMARY OF THE INFRARED ABSORPTION BANDS OF SILICA GEL - WATER SYSTEM

Silica gel- H_2^{16}O system (cm^{-1})	Silica gel- D_2^{16}O system (cm^{-1})		Silica gel- H_2^{18}O system (cm^{-1})		Assignment
	Obsd	Calcd	Obsd	Calcd	
* a) 3748	2755	2728	3740	3735	OH (or OD) stretching of free silanol groups
* b) 3751	—	—	3737	3737	
* 3400	2500	2474	**3400	3389	OH (or OD) stretching of water and hydrogen bonded silanol groups
* —	2780	—	—	—	OD asymmetric stretching of D_2O vapor
1870	1870	—	1870	—	Skeletal Si-O combination ^{c)}
1640	1640	—	1640	—	Skeletal Si-O overtone ^{c)}
* 1630	—	—	1630	—	HOH deformation of water
—	1440	—	—	—	HOD deformation ^{c)}
1050	1050	—	1050	—	Skeletal Si-O stretching ^{c,d)}
~1200	~1200	—	~1200	—	
* 950	950	—	935	916	Si-O stretching of silanol groups
~960	~960	—	—	~925	
* 870	620	633	870	—	Si-OH (or Si-OD) bending
805	805	—	805	—	Skeletal Si-O stretching ^{c,d)}
560	560	—	560	—	Unknown, some skeletal vibration ?
470	470	—	470	—	Skeletal Si-O ^{d)}

a) For silica gel without heat-treatment.

b) For silica gel calcined at 800°C.

c) Ref. 6.

d) Ref. 5.

* Adsorption sensitive bands.

**The band was so broad that an accurate determination of the small isotope shift was impossible.

treated by a simple harmonic oscillator model (Table 2).

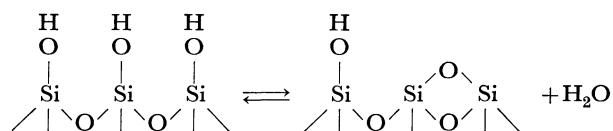
The band at 960 cm^{-1} is conclusively assigned to the Si-O stretching vibration in surface silanol groups because of the following evidences. 1) No hydrogen isotopic effect was observed for this band. 2) The free OH stretching band and this band shifted quite simultaneously during the course of oxygen exchange reaction. 3) The observed values of the oxygen isotopic shift for these two bands were in harmony with those calculated according to a simple harmonic oscillator model, as illustrated in Table 2.

It should be pointed out, however, that no shift of the band at 960 cm^{-1} was observed immediately after the introduction of H_2^{18}O on a silica gel sample. In other words, the band at 960 cm^{-1} was produced by rapid adsorption of H_2^{18}O on the surface as in the case of H_2^{16}O -silica gel system and then shifted gradually with the progress of the exchange reaction. The band is thus expected to be induced indirectly by the hydrogen bond formation of Si-OH with adsorbed water. This explanation was supported by the fact that the band around 960 cm^{-1} was produced by the introduction of various organic vapors which formed more or less hydrogen bonding with silanol groups. Such a stretching vibration sensitive to hydrogen bonding is not so strange; it is known that Si-O stretching vibration in silanol compounds⁸⁾ as well as C-O stretching vibration in alcohols⁹⁾ have a big dilution effect

in nonpolar solvents.

We can safely rule out the possibility that the two bands at 960 and 870 cm^{-1} are associated with the overtone and combination of Si-O skeletal vibration, judging from their position and sensitivity to adsorption.

2. *Reactivity of Silica Gel Surface.* Mills and Hindin¹⁰⁾ have concluded indirectly from mass spectrometric analysis that the oxygen exchange reaction between surface silanol groups of silica gel and water takes place at a temperature above 100°C . The present work confirmed directly that the reaction proceeded considerably, but not completely, at room temperature on a silica gel treated at a low temperature below 300°C . Such a silica gel is readily dehydrated and rehydrated. The result can be explained as a consequence of the repetition of these two reactions according to the following scheme hitherto accepted¹⁾



viz., the production of strained siloxan type species and some free OH groups from the clusters of OH groups adjacent to each other and the reverse reaction. Incomplete exchange of oxygen in the present case would be due to the presence of some genuinely free silanol groups, predominant for the silica gel treated at such a high temperature as 800°C .

8) K. Licht and H. Kriegsmann, *Z. Anorg. Allgem. Chem.*, **323**, 190, 239 (1963).

9) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman & Company, San Francisco & London (1960), p. 140.

10) G. A. Mills and S. G. Hindin, *J. Amer. Chem. Soc.*, **72**, 5549 (1950).