

STUDY OF THE NATURE OF SILICA GEL ACTIVE CENTERS FOR WATER ADSORPTION BY INFRARED SPECTROSCOPY. INTERACTION WITH PYRIDINE-WATER MIXTURE

L. KUBELKOVÁ and P. JÍRŮ

*Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, Prague 2*

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The adsorption of pyridine-water mixture (partial pressures 9–12 and 4–13.5 Torr, respectively) on silica gel previously dehydrated at 400°C has been studied at room temperature by infrared spectroscopy. The adsorption of single components has been also examined. Pure pyridine is adsorbed on the "free" OH groups of the adsorbent under hydrogen bonds formation. It was found that the presence of water in the gas phase has no significant effect on the concentration and the structure of the surface complexes of pyridine. Water interacts with silica gel even after blocking of the "free" surface OH groups with pyridine. The "bound" OH groups are preferentially formed probably by the reaction of water with siloxane bridges of the surface. Simultaneously the number of "intraglobular" OH groups increases by diffusion of water into the intercrystallite space of silica gel. The "bound" hydroxyl groups are probably active in the physical adsorption of water, which also affects in certain extent the "free" OH groups of the adsorbent.

Although many papers were devoted to the study of the silica gel dehydration¹⁻⁵, the question of the nature of active centers in the inverse process (*i.e.* in the adsorption of water) has not been definitively answered yet. We believe that using the results of the study of the interaction of pyridine-water mixture with silica gel by infrared spectroscopy can help in solution of this problem. Our interpretation of the absorption bands of the silica gel OH groups is based on the previous papers⁴⁻⁷, from which we also take the terminology.

EXPERIMENTAL

Silica gel — Cabosil M5 (Cabot Corporation, Boston, U.S.A.) with specific surface area 200 m²/g was pressed under 1000 kg/cm² pressure into plates of 7–15 mg/cm² area density. The sample was then dehydrated in the infrared cell⁸ under vacuum for 2 h at room temperature and at 400°C. The heating for 17 h at 400°C in the oxygen atmosphere (pressure of oxygen 20–30 Torr) then followed. The gas was removed from the cell at room temperature and the spectrum of silica gel was recorded. The sample (silica gel — 400) was then allowed to interact with pyridine, water, and pyridine-water mixture, respectively, for more than 17 h at room temperature and corresponding spectra were taken. The absorption bands of the gas phase were compensated by putting

the second cell without sample into the reference beam of the spectrometer. The detailed description of the vacuum apparatus and of the pressure determination (minimum pressure reached in the cells was 10^{-5} Torr), the data about the purity and the preparation of the adsorbates are given elsewhere⁹.

The spectra were recorded on a double-beam infrared spectrometer Zeiss-Jena model UR-10 in the range of $4300-700\text{ cm}^{-1}$. The spectral slit-width of the instrument varied between 4 and 12 cm^{-1} . Strong bands assigned to the silica gel skeletal vibrations made impossible the measurement in the regions of $1320-980\text{ cm}^{-1}$ and $860-780\text{ cm}^{-1}$. The same sample transmission was adjusted at 4250 cm^{-1} for each run of experiments by a screen placed in the reference beam of the spectrometer. In some cases the spectra measured in % of transmission were converted to the absorbancy scale. The following difference spectra were then obtained after suitable subtraction: a) the spectrum of silica gel after the interaction with water against silica gel dehydrated at 400°C ; b) the spectrum of silica gel after the interaction with pyridine-water mixture against silica gel with adsorbed pyridine only. A decrease of the band intensity in the original spectrum was expressed as a "negative" absorption in the difference spectrum whereas an increase of the intensity or a new band formation gave rise to a "positive" absorption.

RESULTS AND DISCUSSION

The silica gel - 400 contained mainly surface "free" OH groups which are not mutually influenced by hydrogen bonding. These groups are characterized in the spectrum by a sharp band at 3745 cm^{-1} (Fig. 3, curve 1). The bulk "intraglobular" OH groups of silica gel, manifested by a shoulder at 3660 cm^{-1} , were also detected. The spectral data did not exclude also the presence of a relatively small amount of the "bound" OH groups on the surface of the sample.

The adsorption of water at low pressures was followed by the formation of a broad band at 3520 cm^{-1} , by the increase of the intensity of the 3660 cm^{-1} band, and by the decrease of the 3745 cm^{-1} band intensity (Fig. 1, curve 1). Under high pressures of water, two new bands were detected: a broad one at 3430 cm^{-1} and a weak one at 1630 cm^{-1} . This process was also accompanied by the intensity decrease of the 3745 cm^{-1} band and with the intensity increase of the 3660 cm^{-1} band (Fig. 2, curve 1). Both new bands disappeared after the desorption of water at room temperature and a spectrum containing the band at 3530 cm^{-1} with the shoulder at 3660 cm^{-1} was obtained. The desorption also affected the intensity of the 3745 cm^{-1} band (Fig. 2, curve 2). The changes of the 3745 cm^{-1} band intensity due to the silica gel-water interaction were found to be smaller than $1/7$ of the band height (measured in the absorbancy scale) before the adsorption experiments.

The band with the maximum at $3550-3500\text{ cm}^{-1}$ in the silica gel spectrum is assigned to the stretching vibration of surface "bound" OH groups⁴⁻⁶ which are mutually hydrogen bonded. The positions of the bands at 3430 and 1630 cm^{-1} are very close to the positions of the bands of liquid water¹⁰. These facts led us to the following explanation of the above mentioned experimental data. The interaction of water with silica gel - 400 carried out at room temperature results at first in the formation of "bound" OH groups. This process is accompanied by the small de-

crease of the number of "free" hydroxyls. At the same time, the number of "intraglobular" silica gel OH groups rises. Then physical adsorption of water follows, which affects also a part of "free" OH groups. The physically adsorbed water can be removed by the desorption for several hours at room temperature whereas the "bound" and the "intraglobular" hydroxyls of silica gel are stable under these conditions.

Thus, the interaction of water with silica gel — 400 involves "free" OH groups of the adsorbent surface. If the existence of another silica gel active centers is to be demonstrated, the "free" hydroxyls must be blocked. We used the adsorption of pyridine for this purpose. Pyridine is adsorbed on "free" hydroxyls of silica gel under hydrogen bonds formation¹¹. This process is followed by a decrease of the intensity of the 3745 cm^{-1} band of the "free" OH groups and by the formation of a new very broad band of the OH groups¹² at 3000 cm^{-1} . The surface complexes of pyridine manifest themselves in the spectrum by the bands shown in the Fig. 3, curve 2 and by the bands at 1630 , 1597 , 1447 , 750 , and 700 cm^{-1} . The 1447 cm^{-1} band was chosen as the most suitable for the study of the changes both of the number of adsorbed particles and of the mode of pyridine bonding to the surface⁹ in the course of the experiment. The intensity of the 3745 cm^{-1} band depends on the amount of adsorbed species and therefore decreases with increasing pressure of pyridine (the pressure of 12 Torr is sufficient for disappearance of this band). The desorption of pyridine

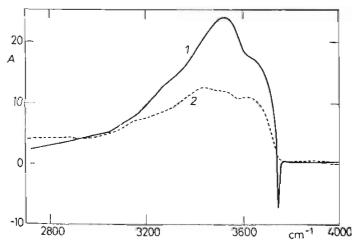


FIG. 1

Difference Spectrum of Silica Gel — 400 after Interaction at Room Temperature

1 With water (4 Torr, 19 h) against the silica gel dehydrated at 400°C ; 2 with water and pyridine (4 Torr water, 12 Torr pyridine, 19 h), against the silica gel with adsorbed pyridine (12 Torr, 17 h).

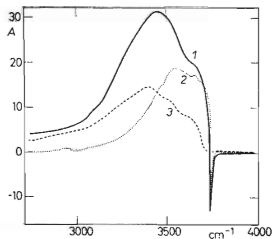


FIG. 2

Difference Spectrum of Silica Gel — 400 after Interaction at Room Temperature

1 With water (13.5 Torr, 19 h); 2 the same after 19 h of desorption, against the silica gel before adsorption; 3 with water and pyridine (partial pressures 13.5 and 12 Torr, 17 h), against the silica gel with adsorbed pyridine (12 Torr, 19 h).

undergoes relatively easily. Under our experimental conditions, pyridine was removed from the surface of silica gel by evacuation of the cell at room temperature (2.5 h) followed by heating of the sample by infrared rays (0.5 h). The spectrum of silica gel obtained after this procedure was then identical with the spectrum measured before adsorption.

We want to point out at this place in connection with our work⁹ that the exchange of silica gel OH groups for the OD groups does not produce any substantial changes as to the positions of the bands of adsorbed pyridine. The intensity of the 2760 cm^{-1} band, which is assigned to the stretching vibration of "free" OD groups of the adsorbent, decreases as a result of the interaction of these groups with pyridine and a new band appears at 2240 cm^{-1} .

The partial pressure of pyridine in the study of pyridine-water interaction with silica gel was chosen on the basis of results of pure pyridine adsorption. The main criterion was the disappearance of the 3745 cm^{-1} band from the spectrum in the latter case (Fig. 3), *i.e.* the pyridine pressure of 12 Torr was used (the pressure of water varied between 4 and 13.5 Torr). It follows from the experimental data that neither concentration nor structure of surface pyridine complexes are affected by the presence of water in the gas phase and that the "free" OH groups are again occupied by pyridine. (Fig. 3, curves 2, 3; no significant changes in the position or the intensity of the 1447 cm^{-1} band were observed when comparing the results of pure pyridine adsorption and pyridine-water adsorption under the same pyridine pressure). However, the interaction of pyridine-water mixture with silica gel gives rise to the new bands whose positions coincide with the positions of the bands formed during the adsorption of water alone (Fig. 1, curve 2; Fig. 2, curve 3). That means that the

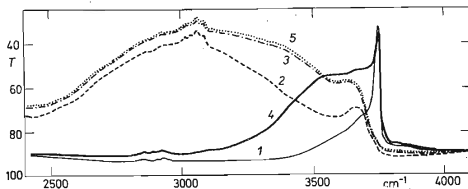


FIG. 3

Spectrum of Silica Gel - 400 after Interaction at Room Temperature

1 The initial spectrum of silica gel - 400; 2 with pyridine (12 Torr, 19 h); 3 with water and pyridine (partial pressures 13.5 and 12 Torr, 86 h); 4 after following desorption at room temperature (3 h) and after heating by IR rays (30 min); 5 after re-adsorption of water and pyridine (partial pressures 13.5, 12, and 21 Torr, for water, pyridine, and oxygen, respectively, 188 h).

interaction between water and silica gel takes place even if the "free" OH groups of silica gel are occupied by pyridine. The "bound" and the "intraglobular hydroxyls" are formed and also undergoes the physical adsorption of water.

After the desorption, during which pyridine and water both from the gaseous phase and liberated from the silica gel surface were frozen out at the liquid nitrogen temperature, a spectrum, similar to that obtained after the removal of the physically adsorbed water in the experiment with the adsorption of pure water at the same pressure, was recorded (Fig. 3, curve 4; Fig. 2, curve 2). The desorption of pyridine and of the physically adsorbed water was *inter alia* accompanied by an intensity increase of the 3745 and 3530 cm^{-1} bands with the shoulder at 3660 cm^{-1} . The reversibility of this process was confirmed by the re-adsorption of the frozen-out pyridine and water (Fig. 3, curve 5). These spectral changes can be explained by the physical adsorption of water on the "bound" OH groups which accompanies the interaction of pyridine with the "free" OH groups. The participation of "intraglobular" hydroxyls in the interaction with water is uncertain.

Following conclusions about the interaction of water at a room temperature with silica gel dehydrated at 400°C can be made on the basis of the above described results: 1. The "bound" and "intraglobular" OH groups are formed at first; the former probably by the reaction of water with siloxane bridges which originated during the initial dehydration at 400°C. A part of the "free" OH groups are converted to the "bound" hydroxyls, as well. The diffusion of water into the intercrystallite space of silica gel is believed to be responsible for the formation of the "intraglobular" hydroxyls; 2. The "bound" OH groups are active in the physical adsorption of water. The physically adsorbed water effects also a part of the "free" OH groups.

REFERENCES

1. Little L. H.: *Infrared Spectra of Adsorbed Species*. Academic Press, London 1966.
2. Hair M. L.: *Infrared Spectroscopy in Surface Chemistry*. Dekker, New York 1967.
3. Peri J. B., Hensley A. L., jr: *J. Phys. Chem.* 72, 2926 (1968).
4. Davydov V. Ya., Kiselev A. V., Zhuravlev L. T.: *Trans. Faraday Soc.* 60, 2254 (1964).
5. Hambleton F. H., Hockey J. A., Taylor A. J. G.: *Trans. Faraday Soc.* 62, 801 (1966).
6. Armistead C. G., Tyler A. J., Hambleton F. H., Mitchell S. A., Hockey J. A.: *J. Phys. Chem.* 73, 3947 (1969).
7. Tyler A. J., Hambleton F. H., Hockey J. A.: *J. Catal.* 13, 35 (1969).
8. Schürer P., Kubelková L.: *Chem. listy* 65, 208 (1971).
9. Kubelková L., Jirů P.: Unpublished results.
10. Nakamoto K.: *Infrared Spectra of Inorganic and Coordination Compounds*. Wiley, New York 1963.
11. Parry E. P.: *J. Catal.* 2, 371 (1963).
12. Hertl W., Hair M. L.: *J. Phys. Chem.* 72, 4676 (1968).

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