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Reduction of the Surface of Silica Gel by Hydrogen Spillover

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It is shown that when silica gel is treated in hydrogen at about 800°C in the presence of a metal but without physical contact with it, reduction of siloxane bridges into Si–H groups occurs. The metals investigated are Ni, Pt, Pt, Ta and W. Traces of metal are found on the silica surface as shown by ESCA measurements.

It is suggested that the metal is transported as an oxide in the vapor phase through the intervention of traces of water and that it invades the silica surface. Its further reduction on the silica surface provides the site for hydrogen spillover.

Among the investigated metals the order of activity was Ta > Ni > Pt > W.

INTRODUCTION

When silica gel is heated at increasing temperature in vacuum the initial broad OH stretching band observed in the ir region between 3700 and 3400 cm^{-1} decreases progressively in intensity and sharpens (*1*, *2*). Above 500°C a single band with a spectral width of the order of 10 cm^{-1} is obtained. At this stage the OH content is between 1 and 2 OH groups/100 $Å^2$. The silanol groups are isolated and rather stable since the narrow OH stretching band, though weaker, is still present after heating at 1000°C. The presence of H_2 at various pressures in the ir cell does not change these observations.

The reactivity of silanol groups towards methanol is well documented. It is known (*3*) that surface methoxylation proceeds by two competing mechanisms, namely, the opening of siloxane bridges and the esterification of silanols. Once the surface is methoxylated, Morterra and Low (*4*, *5*) have shown that the effect of increasing the temperature is very different from that described above. Above 700°C a band that may be assigned to a Si–H stretching is observed at about 2300 cm^{-1}. Above 800°C it disappears progressively. The reaction by-products include formaldehyde, acetylene and hydrogen.

The present contribution aims to show that the presence of certain metals in the reaction cell generates at about 800°C in presence of molecular hydrogen surface SiH groups identical to those obtained by Morterra and Low after pyrolysis of the methoxylated silica gel. The procedure that is described does not provoke the sintering of the gel since the N_2 BET surface before and after the treatment has not changed significantly. The presence of the metal is absolutely essential. It is our opinion that the chemisorption of molecular hydrogen on highly dehydrated silica as reported by Morterra and Low (*6*) may have been initiated by metal traces.

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EXPERIMENTAL METHODS

The silica gel used for this work was Degussa Aerosil, the BET surface area of which is 170 m^2/g.

The gel was agglomerated by gently compressing the powder at 25 kg/cm^2. In this way, wafers weighing 40 mg/cm^2 and suitable for the infrared study were obtained.

The wafer was attached to a fused silica holder in a classical ir cell in which the compartment used for the pretreatment at high temperature was made from fused silica. The silica gel wafer was pretreated by outgassing at 800°C for 15 hr. A few millimeters below the wafer holder and without any physical contact with it, small metal rods of about 10 mm/4 mm o.d. were introduced before the pretreatment, nickel, tantalum, platinum and tungsten were used. Since these metals have very low vapor pressure at 800°C ($<10^{-10}$ Torr) vaporization as such could not take place.

After the cell had been cooled to 20°C, dry and chemically pure H_2 (purity better than 99.9%) was introduced and the sample was heated for desired periods of time at 880°C. Infrared spectra were recorded from time to time at room temperature and the increase of the 2300 cm^{-1} Si–H stretching absorption was followed by measuring the optical density.

Some wafers were removed and used for ESCA measurements. It was observed in these cases that the Si–H bond was rather stable even when the sample was exposed to the air for several days. However, heating at 400°C in the air results in a fast disappearance of the 2300 cm^{-1} band.

In some cases H_2 adsorption isotherms were measured on samples treated exactly in the same manner as for the ir work. However, in this case, several wafers were

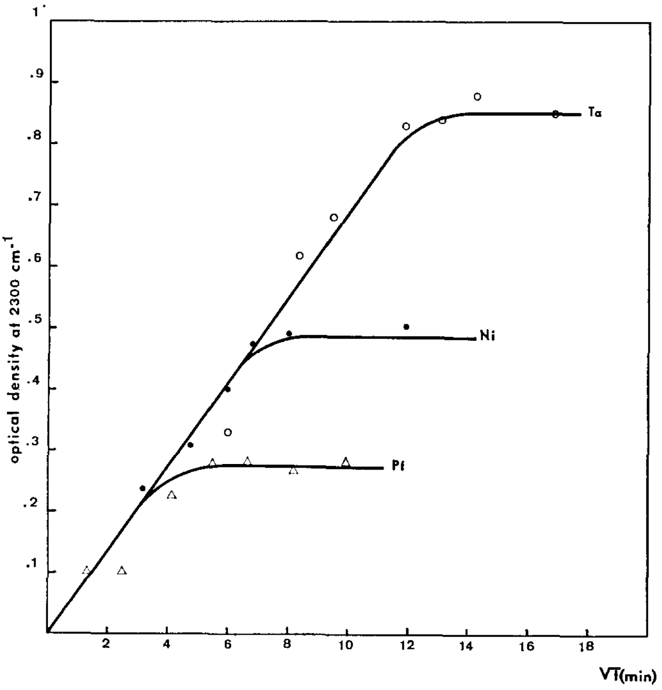


FIG. 1. Variation of the optical density of the 2300 cm^{-1} Si–H stretching band with respect to the square root of the reaction time (min) at 880°C in 60 Torr H_2 and in the presence of Ni, Pt and Ta. The weight of the Aerosil wafer was 40 mg/cm^2 in all cases.

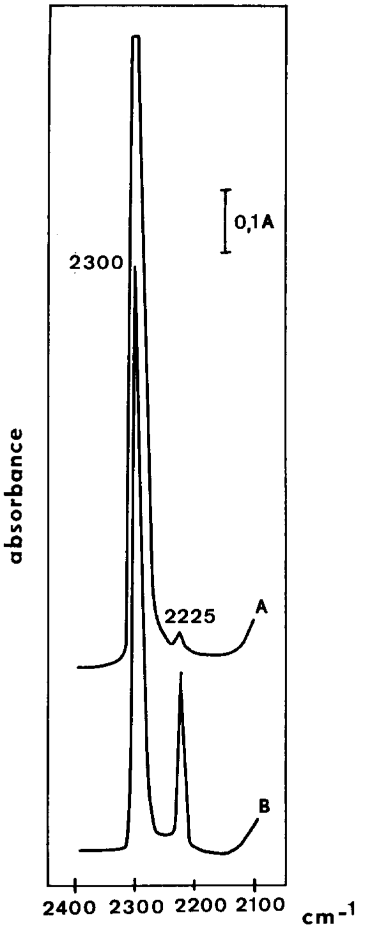


FIG. 2. Infrared spectra observed for the Aerosil: (A) treated at 900°C in 60 Torr H_2 for 3 hr; (B) after outgassing at 830°C for 40 hr and then brought into contact at 350°C with 80 Torr H_2 for 13 hr. The metal was tantalum.

used in order to increase the accuracy of the volumetric determinations and they were in physical contact with the metal rods.

In order to appreciate the influence of this contact a wafer holder made from tantalum was also used in order to observe the eventual difference in intensity of the Si–H band.

ESCA measurements were made with a Vacuum Generators instrument with the following settings: source Al *K*α, 10 kV, 50 mA; signal averager, 256 memories; energy of the analyzer, 180 eV.

RESULTS

At 880°C in the presence of 60 Torr H_2, the variation of the optical density of the Si–H stretching band with respect to the square root of the time is shown in Fig. 1. These results have been obtained for similar wafers weighing 40 mg/cm^2 and they are thus comparable. With tungsten the extent of the reaction was very limited and the 2300 cm^{-1} band was hardly visible. It should be emphasized that no reaction occurs in the absence of metal but traces are sufficient to initiate the silica gel reduction process. For instance, the traces left by a tungsten rod used to open a hole in the fused silica tube may be sufficient!

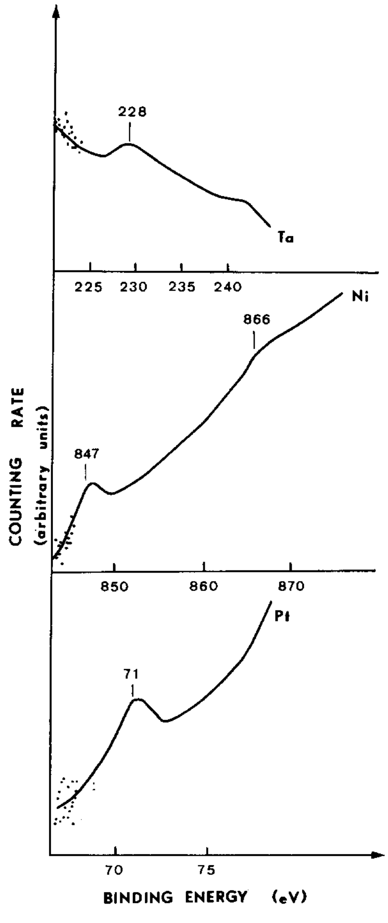


FIG. 3. ESCA spectra obtained for Aerosil wafers treated under the same conditions as in Fig. 1 for 2 hr.

The reaction is evidently diffusion controlled. The diffusion rate, as indicated by the slope of the linear function in Fig. 1, seems to be independent of the nature of the metal. On the other hand, the extent of the reaction depends strongly on the nature of the metal.

In Fig. 2 are shown two examples of infrared spectra. Two Si–H stretchings are observed at 2300 and 2225 cm^{-1}, respectively. The stronger band is always observed at 2300 cm^{-1}: it decreases in intensity after a long outgassing at 830°C. A weak band at 2225 cm^{-1} is reinforced when the outgassed sample is reexposed to H_2 at 350°C. The same bands were observed after pyrolyzing and outgassing a methoxylated silica by Morterra and Low (*5*). These authors have assigned the 2300 cm^{-1} band to surface Si–H and the 2225 cm^{-1} stretching to chemisorbed hydrogen.

It may be assumed that outgassing at 830°C produces exposed silicon atoms and that these atoms dissociatively chemisorb molecular H_2 at 350°C. The reason why the frequency of this Si–H band is different from that obtained by direct reaction is, however, not clear.

The ESCA spectra for wafers treated under the same conditions for 2 hr are shown in Fig. 3. For the three "active" metals the signal obtained after accumulating 256 × 200 sec scans in the region where the most intense peaks of the metal are expected to show up has given positive results. Table 1 indicates the assignments of these lines. No correction for the charging effect has been carried out since we were interested only in detecting the presence of the metal: indeed we deal with traces.

TABLE 1

Assignment of the ESCA Spectra Observed for Aerosil Wafers after Reduction at 880°C in Presence of Metals

Metal	Electronic Level	Binding energy (eV)	
		Observed	Theoretical
Ni	2*p* 3/2	847	855
	2*p* 1/2	866	872
Ta	4*d* 5/2	228	230
	4*d* 3/2	~245	242
Pt	4*f* 7/2	71	70
	4*f* 5/2	—	74

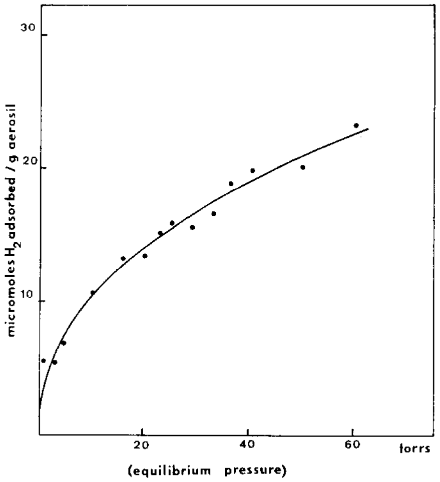


FIG. 4. H_2 adsorption isotherm at 820°C (in presence of Ta).

The Si_{2p} and O_{1s} peaks were not modified either in intensity or in position by the treatment. It was observed also that the Ta 4*d* $\frac{5}{2}$ peak intensity divided by the Si 2*p* peak intensity was about the same for the wafer as for the powder obtained by grinding the wafer. This is an indication that the dispersion of the metal within the wafer was homogeneous, at least to a first approximation. Irrespective of the amount of Si–H bonds present in the sample, outgassing in vacuum for a few hours at a temperature higher than 900°C results in the removal of the 2300 cm^{-1} band.

Figure 4 shows the hydrogen adsorption isotherm obtained in the presence of Ta at 820°C. Note that for 24.10^{-6} mole H_2 adsorbed per gram, 0.17 Si–H groups are present per 100 Å^2 on the surface. This is between 10 and 20% of the surface concentration in residual OH at this temperature.

Up to 900°C the optical density of the 2300 cm^{-1} band observed by using a Ta wafer holder or that made from fused silica without physical contact with the Ta rod were the same within the experimental errors. A chemical analysis carried out by the activation technique has shown that 38 ppm Ta were present in the gel for 23×10^{-6} mole H adsorbed/g SiO_2, e.g., at the last point in the isotherm shown in Fig. 4. After a treatment at 650°C in the presence of 60 Torr H_2, the amount of Ta measured in the gel was only 3.8 ppm at the "equilibrium," e.g., the leveling of optical activity of the Si–H band.

DISCUSSION

The problem of the metal carrier is most intriguing. A metal hydride should not be stable at the temperature used for reducing the silica surface and thus the transport as an oxide may be the favored way. It is known (*7*) that the mobility of an oxide on an oxide surface is higher than that of a metal and thus the rate limiting step could be the diffusion of the metal oxide on the silica gel surface. Skaupy (*8*) reported that the transport of tungsten from a hot metal wire toward a glass surface may be catalyzed by traces of water. The oxide is formed by the decomposition of water and the water is regenerated by the reduction of the oxide once it is deposited. Water is thus continuously recycled.

A somewhat similar mechanism could be proposed here. Traces of water could be present either as an impurity or resulting from some secondary process. Let *M* be a metal atom:

$$M + H_2O \rightarrow MO + H_2,$$

$$(MO)_s \rightarrow (MO)_g \rightarrow (MO) \text{ on silica gel,}$$

$$-\underset{|}{\overset{|}{Si}}-O-\underset{|}{\overset{|}{Si}}- + MO + \tfrac{3}{2}H_2 \rightarrow H_2O + MO-\underset{|}{\overset{|}{Si}}- + -\underset{|}{\overset{|}{Si}}-H,$$

$$\text{(eventually) } \tfrac{3}{2}H_2 + MO-\underset{|}{\overset{|}{Si}}- \rightarrow M + H_2O + -\underset{|}{\overset{|}{Si}}-H.$$

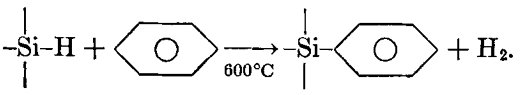
Traces of CO could provide an alternative mechanism whereby the metal is transferred to the silica surface.

In any event, since the number of metal atoms found on the silica surface is a small fraction of the number of H_2 molecules adsorbed, each metal atom contributes to the formation of more than one (or more than two) –Si–H groups.

Hydrogen spillover (*9, 10*) from the metal onto its supporting silica surface could explain the reason why, for instance in the case of tantalum, 0.2×10^{-6} g atom Ta/g SiO_2 were measured, whereas the number of H_2 molecules adsorbed at this stage of the reaction is more than 100 times larger (see Fig. 4). Spillover implies that each supported metal atom works as a source of nascent hydrogen atoms invading the surface and reacting with the siloxane bridges.

Of course, when each metal atom is surrounded by a domain where the Si–H concentration becomes high enough, the diffusion barrier stops the surface reduction process. This could explain the sudden change in the slope of the diffusion law observed in Fig. 1. The levels of reduction observed for the three metals Pt < Ni < Ta should depend either on the amount of metal transported in the gas phase or on its efficiency for initiating spillover. It is interesting to point out that the efficiency of the investigated metals for forming Si–H bonds decreases in the same order as their capacity for solubilizing H_2, namely Ta > Ni > Pt > W (*11*). It would be most interesting to know the concentration in Pt and Ni but accurate chemical analysis is difficult because of the small amounts involved.

Morterra and Low (*5*) already emphasized the reactivity of a reduced silica surface. To illustrate this, the Si–H containing silica gel was exposed to benzene vapor (~10 Torr) at 700°C. The ir spectra study showed the  band at 1435 cm^{-1} and the  accompanying stretch at 3070 cm^{-1}, whereas the Si–H stretch decreased strongly, suggesting the following reaction:



This is, of course, a very useful way for preparing organic coating bound to a silica surface by Si–C bonds.

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