Water on silica and silicate surfaces
IV. Silane treated silicas

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With 18 figures and 5 tables

(Received December 9, 1975)

A number of studies of silica surfaces have emanated from this Laboratory. Assessment of surface areas by both argon and nitrogen adsorption has been examined (1); ice nucleation by partially hydrophobed silicas has been studied (2); water adsorption (3) and near infrared reflectance (NIR) spectroscopy have also been employed to study these silicas (4) which have some of the surface hydroxyls removed by thermal treatment (2). In these investigations the parent material was HiSil 233, a wet-precipitated silica, described further in table 1. Partially hydrophobed products were compared to a Cab-o-Sil, a flame hydrolyzed aerosil type, possessing a lower surface concentration of hydroxyls. The apparent too high density of OH's on the HiSil (table 1) strongly suggests the presence of micropores, a contention already put forward by Sing (5). The ice nucleation work had already suggested that the residual OH's on Cab-o-Sil are widely separated. This conclusion is supported by the work reported here.

Table 1. Silica samples

<table>
<thead>
<tr>
<th>Silica</th>
<th>Surface Area</th>
<th>OH Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>HiSil 233</td>
<td>123 m²/g</td>
<td>1 OH/7 Å²</td>
</tr>
<tr>
<td>Wet precipitated</td>
<td>Ar: 16.0 Å²</td>
<td>1 OH/7 Å²</td>
</tr>
<tr>
<td>Cab-o-Sil M-5</td>
<td>178 m²/g</td>
<td>1 OH/40 Å²</td>
</tr>
<tr>
<td>Aerosil; SiCl₄</td>
<td>178 m²/g</td>
<td>1 OH/40 Å²</td>
</tr>
</tbody>
</table>

We have pioneered the use of the NIR technique (4) to study water adsorption on silicas. Fig. 1 displays a sketch of the apparatus. Since a loose bed of the powder is used, the problem of adherent particles and distorted surfaces as in pressed discs is minimized. Further, the temperature control is far better (within 0.2 °C) than in transmission infrared where the temperature rise can be over 50 °C. In addition, we scan with monochromatic light to reduce the heating effect. The addition of water vapor is made through the obvious port provided for the purpose. Fig. 2 shows the NIR spectra obtained for one of the thermally treated HiSils. This overtone region is rich in interesting bands while lacking in background from the silica. At about 7300 cm⁻¹, the SiOH stretch overtone band (2ν) occurs. The addition of water diminishes this band while increasing the neighboring H-bonded OH band at 7150 cm⁻¹. The band at 5300 cm⁻¹ is a combination band (ν + δ) which develops as the water molecules are added to the surface.

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Fig. 2. The spectra obtained as water is adsorbed on partially dehydrated HiSil. The No. 1 spectrum shows the absence of absorption at 5300 cm⁻¹ because this case represents the absence of physically adsorbed water. This band develops as water is adsorbed, while the broad band at about 7150 cm⁻¹ grows at the expense of the sharp peak at 7300 cm⁻¹.

It was a natural consequence of our earlier work to attach organic ligands to the silicas and to study, by isotherms and by the NIR technique, the interaction of water with these treated silicas. The organosilanes employed in this study are depicted in table 2, along with the shorthand notation used hereafter. It turns out to be fortunate that both the HiSil and the Cab-o-Sil were employed; the two treated surfaces in each case behave quite differently toward water and the alkoxylated surfaces are quite different. The HMDS breaks up upon reaction with the silica surface and the question has never been addressed in the past as to whether the resulting NH₃ interacts with the surface. Besides HMDS, only the unsaturated C=C compound is reacted from the vapor phase albeit at elevated temperatures. The other three compounds are reacted from solution as we shall see below. The vinyl compound and the three alkoxysilane compounds are used in the surface treatment of glass fibers used in polymer composites; therefore, there is great interest in water interaction with these treated surfaces. Furthermore, it was thought that organic ligands fixed to a tractable surface such as silica would provide a more viable path to the study of their interaction with water than would cell membranes, water dispersions of the organics and the like.

No previous workers have examined water interaction with silane-treated silica. The interaction of HMDS was reported in 1968 by Stark et al. (5) and the kinetics of the reaction with an undefined silica by Hertl and Hair (6) in 1971. Kiselev and his co-workers (7) in 1961 and 1964 examined the reaction of trimethylchlorosilane with silica, as did Snyder and Ward (8) in 1966, and Hair and Hertl (9) for all the methyl chlorosilanes. Stark et al. (5) in 1968 also examined the reaction of trimethylhydroxysilane, trimethylchlorosilane and HMDS with silica. Lee (10) in 1968 examined the product of hydroxysilane treatment of glass slides by contact angle measurements in an attempt to learn the configurations of the ligands on the surface. In 1970, Kharilonov et al. (11) also reported on their studies of hydroxysilane reactions with silicas.

**HMDS-treated silicas.** An advantage of HMDS is that it reacts with the Si₇–OH’s (Si₇ is a surface silicon atom) from the vapor state even at room temperature. The surface OH’s are titrated by the HMDS according to:

$$\text{HMDS} + 2 \rightarrow \text{Si}₇\text{–OH} \rightarrow \text{Si}₇\text{–O} – \text{Si(CH₃)}₃ + \text{NH₃}. \quad [1]$$

The question as to whether the NH₃ also reacts with the surface hydroxyls had not been discussed heretofore. The cross-sectional area of the trimethyl ligand is about 40 Å²; therefore on Cab-o-Sil, if the sparse OH’s are equispaced,