SURFACE HYDRATION OF CRYSTALLINE AND AMORPHOUS SILICAS

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The surface properties of three SiO_2 samples, one crystalline (quartz) and two amorphous, with a large difference in particle size, have been investigated by thermal analysis, adsorption calorimetry and infrared spectroscopy. The variation in the silanol group population upon thermal treatment has been followed via the evolution of the i.r. bands at 3745–3750 cm^{-1} (free hydroxyl groups) and 3650–3550 cm^{-1} (adjacent pairs of SiOH) and the evolution of the heat of adsorption of water with coverage on the outgassed samples.

The adsorption capacities increase in the sequence high surface area amorphous sample < low surface area amorphous sample < quartz. Dehydroxylation of the surface leads to an increasing hydrophobic character shape of the isotherm, heat of adsorption below the heat of liquefaction of water. The same thermal treatment ($T = 673$ K) brings about dehydroxylation leaving only isolated silanols on the high surface area amorphous silica, and partial dehydroxylation of the low surface area material. Quartz is totally hydrophilic, as its regular structure probably stabilizes the hydroxyl layers at the surface.

It is well known that any silica has hydroxyls (silanols) and siloxane bridges (Si—O—Si) at its surface. Their relative abundance depends upon both the thermal treatment and the morphology of the sample (crystallinity and particle size) and plays an important role in the surface properties of the material [1, 2].

In the present study, three silica samples with different structures (quartz and amorphous silicas) and different particle sizes (two amorphous silicas with different surfaces areas) were examined in order to evaluate the relative distribution of surface silanol and siloxane groups.

The thermal dehydration pathways of the samples were determined by means of differential scanning calorimetry; interacting and isolated surface hydroxyls were monitored by infrared spectroscopy. Finally, the affinity towards water—related to the population of silanol groups—was evaluated by means of water adsorption on samples outgassed at 673 K. Both adsorptive capacities and heats of interaction were measured as a function of coverage.

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Experimental

Materials

The silica samples, which were described in a previous paper [3], are:

i) a crystalline silica (quartz, Q), BET surface area 5.2 m^2g^{-1}; ii) a low surface area (l.s.a.) amorphous silica (Porasil, P), BET surface area 16.1 m^2g^{-1}; iii) a high surface area (h.s.a.) amorphous silica (Aerosil, A), BET surface area 380 m^2g^{-1}.

The water employed was distilled in high vacuum several times before use.

Methods

DSC. A DuPont differential scanning calorimeter was employed. The samples were heated from r.t. up to 873 K in flowing argon (first run), and the DSC curves were recorded. The baselines were obtained by reheating the samples with the same schedule in argon, without exposure to air.

Adsorption microcalorimetry. The adsorption of water and the related heat were measured at 303 K by means of a volumetric apparatus connected to a Calvet microcalorimeter [3, 4]. Small doses of water were successively admitted onto the sample in the calorimetric cell. The differential heat of adsorption of water as a function of coverage was obtained in this way.

Samples were pretreated in vacuo at 673 K following the procedure described earlier.

Thermogravimetry. The adsorption of water was also measured at 298 K with a Sartorius microbalance (sensitivity = 10^{-5} g) connected to a conventional high-vacuum system (10^{-4} Pa).

The samples were previously heated in situ up to the desired temperature (range r.t.—673 K) and subsequently saturated at r.t. with ~2.5 kPa of water vapour for 1 hour ($p/p_0 \simeq 0.8$). The weight gain was recorded. The system was next evacuated at r.t. to measure the content of removable water, and then outgassed at 413 K to evaluate the content of strongly held molecular water.

Infrared spectroscopy. The infrared spectra of self-supporting Aerosil and Porasil pellets were obtained with a Perkin–Elmer 580 B spectrophotometer in the region 4000–1200 cm^{-1}. The infrared cell allowed thermal treatment in situ and was connected permanently to a conventional high-vacuum system (10^{-4} Pa) [5]. In the case of quartz, the spectrum in the 2000–4000 cm^{-1} region could not be explored because of light scattering.

Results and discussion

Thermal analysis

DSC curves are reported in Fig. 1. The crystalline quartz structure is confirmed (Fig. 1a) by the endothermic peak of $\alpha \rightarrow \beta$ quartz inversion at 848 K [6], which is totally absent for the amorphous samples (Fig. 1b and c). The latter instead show some vestiges of the cristobalite crystalline structure at 523 K ($\alpha \rightarrow \beta$ cristobalite inversion peak) [6], in agreement with the hypothesis suggested by Frondel that amorphous silica powders are formed by subcrystalline particles having the
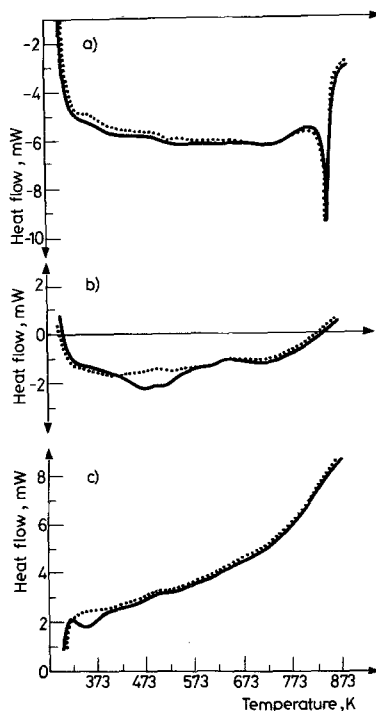

Fig. 1 DSC curves, solid line; base line, dotted line
a) Quartz b) Porasil (l.s.a.) c) Aerosil (h.s.a.)

cristobalite structure [7]. A deviation of the baseline, however, is also observed at this temperature in the quartz DSC curve (Fig. 1a).

From a surface chemistry aspect, the most interesting feature is the endothermic deviation from the baseline, occurring between 300 and 600 K, which appears in the first heating run and is totally absent in the successive runs (baseline), provided that

the sample is kept constantly under inert gas between successive runs. This is ascribed mainly to the endothermic loss of water, adsorbed at the surface or arising from condensation of adjacent surface OH. The DSC curves can thus be regarded as indicative of the dehydration pathways of the samples.

Marked differences between the three samples can be pointed out:

a) Amorphous samples show a defined peak, whereas quartz exhibits a deviation over a wider temperature range.

b) The peak maximum for the high surface area sample (Aerosil) lies at a lower temperature (~ 350 K) than that for the low surface area one Porasil (~ 470 K).

c) Quartz still loses water to an appreciable extent at 573 K, a temperature at which the phenomenon is already completed for the amorphous materials.

The elimination of water from the surface is clearly slower and more activated on quartz than on amorphous silicas. As concerns the differences found between the two samples of the latter, the higher the surface area, the easier the water can be removed from the surface. A rough evaluation of the endothermic heat indicates that this increases in the sequence $A < P < Q$, if expressed per unit surface area.

Adsorption of water vapour

The differential heats of adsorption of water ($q^{diff} = dQ^{int}/dn_a$) on the three silica samples examined, outgassed at 673 K, are shown in Fig. 2.
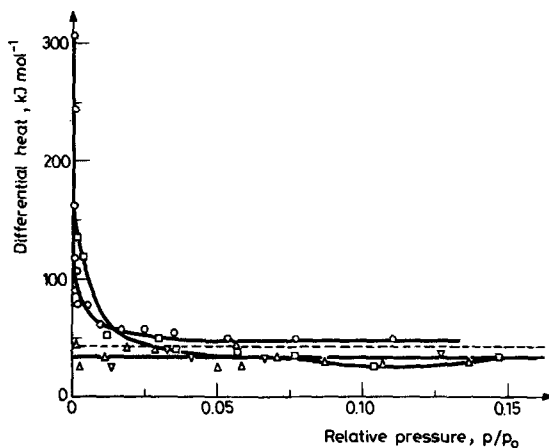

Fig. 2 Differential heat of adsorption of water vapour on silica surfaces outgassed at 673 K (4 h), as a function of relative pressure ($p_0 = 4.20$ kPa vapour pressure of water at 303 K).
○ Quartz, □ Porasil (l.s.a.), △ ▽, Aerosil (h.s.a.).
The two symbols in the Aerosil curve indicate separate experiments.
— — — Latent heat of liquefaction of water

Some peculiar differences in the curves may be noted:

1) The heat of adsorption of water on quartz is higher than 44 kJ mol^{-1}—the latent heat of liquefaction of water—in the whole range examined ($0 \leqslant p/p_0 \leqslant 0.15$).

A surprisingly high initial heat of interaction with water was found at very low coverage ($\sim 6.10^{-2}$ molecules H_2O/nm^2, $p/p_0 \simeq 10^{-3}$). This can be assigned to a specific interaction of water with sites other than silanols also present on the quartz outgassed at lower temperature (413 K), as previously reported [3]; this will be discussed in a future paper in the context of the biological properties of quartz [8].

2) In contrast with the behaviour of quartz, the heat of adsorption of water on amorphous silicas is below 44 kJ mol^{-1}.

The heat of adsorption of water on Aerosil (h.s.a.) is ~ 35 kJ mol^{-1}; this value is nearly constant with varying coverage and is lower than the latent heat of liquefaction. The heat of adsorption of water on Porasil (l.s.a.) at low coverage (~ 0.7 molecules H_2O/nm^2, $p/p_0 \simeq 0.03$) is higher than the latent heat of liquefaction of water, but at $p/p_0 > 0.03$ (~ 1.2 molecules H_2O/nm^2) the energy of interaction decreases below 44 kJ mol^{-1}.

The heat of interaction of water with a solid can be used to define the degree hydrophilicity of the surface, and in our case is directly related to the degree of hydroxylation. If the heat of adsorption of water is higher than 44 kJ mol^{-1}, the surface can be defined as hydrophilic, and if lower, as hydrophobic [8–10]. Heat of adsorption values of 150–60 Kj mol^{-1} have been assigned to the interaction of water molecules with vicinal silanols via two H-bonds [3], whereas heat values approaching 44 kJ mol^{-1} correspond to the progressive build-up of multilayers of adsorbed water. The heat of adsorption of a water molecule on single (isolated) silanols via only one H-bond has been reported to be ~ 25 kJ mol^{-1} [11].

On the basis of these facts, the following conclusions can be drawn:

1) The hydrophilic character of quartz outgassed at 673 K indicates that its surface is still highly hydroxylated.

2) Porasil outgassed at the same temperature is partially dehydroxylated. In fact, at $p/p_0 \simeq 0.02$ ($q^{diff} > 60$ kJ mol^{-1}), the number of water molecules adsorbed on quartz is ~ 2/nm^2, whereas on Porasil it is ~ 0.9/nm^2. This indicates that the hydrophilic patches are more extended on the surface of quartz than on Porasil.

3) On Aerosil—where the heat of interaction of water is lower than 44 kJ mol^{-1} in the whole range examined—vicinal silanols able to absorb water via two H-bonds are practically absent.

Outgassing at 673 K leads to the progressive removal of surface silanols by condensation into siloxane bridges and elimination of water molecules [12]; the effect of the thermal treatment, however, differs markedly for the three samples examined.

6*

On the quartz surface, only mild dehydroxylation was produced. Major effects were produced on amorphous silica, particularly on the finely divided form. Their hydrophobic character—indicated by both the heat of adsorption values and the shape of the adsorption isotherm (not reported for the sake of brevity)—suggests that thermal treatment at 673 K involves much more dehydroxylation than on quartz.

On Aerosil (h.s.a.), the constancy of the heat of adsorption below 44 kJ mol^{-1} indicates that the large majority of the silanols are isolated, i.e. the distance between the OH groups is sufficiently high to prevent the adsorption of water via two H-bonds.

Porasil (l.s.a.) exhibits behaviour intermediate between those of quartz and Aerosil (h.s.a.). Initially, the heat of adsorption is higher than 44 kJ mol^{-1}, but when the coverage is increased, it falls below this value. This suggests that some patches of hydrophilic sites (vicinal silanols) are still present on its surface, together with large patches of isolated silanols. On this low surface area amorphous silica, thermal treatment at 673 K produced partial dehydroxylation.

The adsorption capacities of the three silica samples were evaluated via thermogravimetric measurements, at a relative pressure $p/p_0 \simeq 0.8$.

The results are given in Table 1. The data are reported as mg of water gained or lost by the samples per square metre. The percentage of water adsorbed, removed upon outgassing at r.t., is also reported.

Table 1 Adsorption capacity towards water of silica samples

Pretreatment Temp., K	Sample	mg H$_2$O/m^2		%, Water reversibly adsorbed
		Weight gain at $p/p_0 = 0.8$*	Weight loss upon outgassing at r.t.	
413	Q	0.24	0.17	71%
673	Q	0.20	0.11	55%
413	P (l.s.a.)	0.19	0.16	84%
673	P (l.s.a.)	0.20	0.14	70%
413	A (h.s.a.)	0.09	0.09	100%
673	A (h.s.a.)	0.09	0.09	100%

* $p_0 = 3.20$ kPa vapour pressure of water at 298 K

The weight gain at $p/p_0 \simeq 0.8$ is due to the water molecules strongly adsorbed via two H-bonds (150–60 kJ mol^{-1}) and the multilayers adsorbed on top of them ($60 < q^{diff} < 44$ kJ mol^{-1}). At this high value of p/p_0, quartz exhibits an adsorption capacity only slightly higher than that of Porasil, but dramatically higher than that of Aerosil.

The r.t. outgassing of Aerosil saturated with water vapour after pretreatment at either 413 or 673 K produces complete elimination ($\sim 100\%$) of the adsorbed water molecules, showing no appreciable amount of water held strongly *via* two H-bonds. Parallel experiments demonstrate that at $p/p_0 \simeq 0.8$ there are no great differences in adsorption capacity between quartz and Porasil. However, the amount of water eliminated from the Porasil surface upon outgassing at r.t. is larger than that from quartz. On the quartz surface, at both pretreatment temperatures there is a more extensive distribution of vicinal silanols, interacting strongly with water molecules.

Upon subsequent outgassing at 413 K of the samples previously saturated with water vapour (data not reported in Table 1), very small amounts of water are retained on quartz and Porasil pretreated at 673 K, which may be ascribed to a partial, very limited, rehydroxylation of the surface.

Infrared spectroscopy

Figure 3 shows the i.r. spectra of Aerosil and Porasil pellets outgassed at 413 K and 673 K. The assignment of the bands in the relevant, 3900–3000 cm^{-1} region has been thoroughly discussed [8, 12]. It is generally accepted that the narrow band
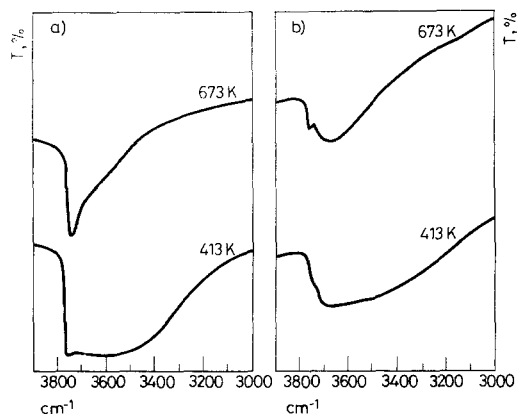

Fig. 3 Infrared spectra of Aerosil (h.s.a.) a) and Porasil b) (l.s.a.) after outgassing at 413 K and 673 K. The curves have been shifted to avoid overlapping

at 3745–50 cm^{-1} is attributable to the fundamental stretching vibration of isolated "free" hydroxyls on the surface, the broader bands and shoulders at 3650–3550 cm^{-1} to adjacent silanols mutually interacting via H-bonding, and the 3400–3500 cm^{-1} band to water molecules adsorbed on the OH groups mentioned

above. In most cases the contribution of "internal" hydroxyls is limited or absent. In the present report we are primarily interested in a comparison of the behaviours of different silicas upon outgassing. Though the i.r. spectrum of the crystalline sample is not available because of the high light scattering in the ν_{OH} region, the data in Fig. 3 relative to the high and low surface area amorphous materials are quite instructive. Besides the higher overall intensities of the bands in the case of Aerosil, due to the larger surface area, it should be noticed that:

1) The "free" OH band, as compared with the broad absorption due to the hydrogen-bonded hydroxyls, is more prominent in the case of Aerosil than in Porasil. A separate band at 3750 cm^{-1} is observed in the spectrum of Aerosil after outgassing at a temperature as low as 413 K, and even at r.t. (not shown in the Figure).

2) The H-bonded OH groups in Aerosil h.s.a. are definitely less resistant to outgassing than those in Porasil (l.s.a.). In the former, the band at 3650–3550 cm^{-1} decreases readily as the outgassing temperature is increased up to 673 K. Indeed, the i.r. evidence is that interacting hydroxyls are fairly stable on Porasil with outgassing up to 673 K.

3) Vestiges of the absorption due to adsorbed molecular water are still observed as a broad shoulder at wavenumbers lower than 3500 cm^{-1} in the spectrum of Porasil outgassed at 413 K, but are absent from the parallel spectrum of Aerosil.

These results agree well with the calorimetric data, which show that the high surface area amorphous silica develops a hydrophobic character upon outgassing at temperatures lower than those needed in the case of the low surface area amorphous material. In fact, the proportion of isolated silanols is larger on the surface of Aerosil than on Porasil, and consequently there is a larger proportion of water molecules adsorbed via a single H-bond with a heat of adsorption below the latent heat of liquefaction. The i.r. spectra show that on Porasil interacting hydroxyls are more stable and abundant, even after outgassing at 673 K. In this case water molecules may be stabilized by two H-bonds with a heat of adsorption higher than 44 kJ mol^{-1}, confirming the existence of large patches of hydrophilic sites, as shown by the calorimetric curves.

As mentioned in other sections of this report, such differences in the behaviour of Aerosil and Porasil must be related to the particle sizes. It is unfortunate that good quality i.r. spectra could not be obtained for the crystalline sample, but it is reasonable to infer that the trend observed on passing from the high to the low surface area amorphous material would have been confirmed in the case of quartz.

Conclusions

The comparison of the surface properties of crystalline and amorphous silicas shows intrinsic differences which cannot be ascribed only to particle size or creation of the surface, but are also related to the ordered or disordered lattice.

With the same thermal pretreatment, quartz more strongly retains both surface hydroxyls and strongly bonded molecular water.

A possible model for the stabilization of silanols on the quartz surface relies on the more ordered array and on the closer packing of the silicon atoms. These factors would favour the possibility of a regular hydrogen interaction between adjacent hydroxyls in large patches, whereas on amorphous silicas the random distribution restricts the extent and hence the stability of similar patches.

Some differences are also found between high surface area and low surface area amorphous samples in that the smaller particles are more easily dehydroxylated than the larger ones. Here too, a stabilization due to larger patches in bigger particles can be invoked.

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Zusammenfassung — Die Oberflächeneigenschaften von einer kristallinen (Quarz) und zwei amorphen SiO$_2$-Proben mit großen Unterschieden in der Partikelgröße wurden durch thermische Analyse, Adsorptionskalorimetrie und Infrarotspektroskopie untersucht. Bei thermischer Behandlung eintretende Veränderungen in der Silanolgruppenpopulation wurden durch Messung der IR-Banden bei 3745–3750 cm^{-1} (freie Hydroxylgruppen) und 3650–3550 cm^{-1} (benachbarte SiOH-Paare) und der Adsorptionswärme von Wasser an ausgeheizten Proben untersucht. Die Adsorptionskapazitäten nehmen in folgender Reihenfolge ab: amorphe Probe mit großer Oberfläche > amorphe Probe mit geringer Oberfläche > Quarz. Dehydroxylierung der Oberfläche hat zunehmenden hydrophoben Charakter (Gestalt der Isothermen, Adsorptionswärme kleiner als Kondensationswärme von Wasser) zur Folge. Bei der gleichen thermischen Behandlung (673 K) werden bei amorphen Siliciumdioxid mit großer Oberfläche eine nur isolierte Hydroxylgruppen zurücklassende Dehydroxylierung und bei Material mit kleiner Oberfläche eine teilweise Dehydroxylierung beobachtet. Quarz ist vollkommen hydrophyl, da die reguläre Struktur wahrscheinlich die Hydroxylschichten an der Oberfläche stabilisiert.

Резюме — Методом термического анализа, адсорбционной калориметрии и инфракрасной спектроскопии исследованы поверхностные свойства трех образцов двуокиси кремния, из которых один был кристаллическим (кварц), а остальные два — аморфными с различным размером частиц. За изменением плотности силанольных групп при термической обработке образцов следили по ИК полосам при 3745–3750 см$^{-1}$ (свободные гидроксильные группы) и при 3650–3550 см$^{-1}$ (смежные пары групп SiOH), а также по выделению теплот адсорбции воды дегазированными образцами. Адсорбционные способности увеличиваются в ряду аморфный образец с большой площадью поверхности < аморфный образец с малой площадью поверхности < кварц. Степень дегидроксилирования вызывает увеличение гидрофобного характера образцов (вид изотермы, теплота адсорбции ниже теплоты сжижения воды). Термическая обработка (Т = 673 К) вызывает дегидроксилирование только изолированных силанольных групп в аморфном образце с большой площадью поверхности и частичное дегидроксилирование в образце с малой площадью поверхности. Кварц является полностью гидрофильным, так его упорядоченная структура, вероятно, стабилизирует гидроксильные слои на поверхности.