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SURFACE CHARACTERIZATION OF VARIOUS SILICAS
A tentative correlation between the energies of adsorption sites and the different biological activities

*V. Bolis, B. Fubini** and *G. Venturello*

ISTITUTO DI CHIMICA GENERALE ED INORGANICA, FACOLTÀ DI FARMACIA,
UNIVERSITÀ DI TORINO, VIA PIETRO GIURIA, 9, 10125 TORINO, ITALY

In order to correlate the biological activity of silica to its surface properties, the analysis of surface sites on three kinds of silicas of different origins and textures has been performed by adsorption calorimetry.

Mechanically micronized quartz (5.2 m^2g^{-1}), an amorphous silica of low surface area ("Porasil F"; 16.1 m^2g^{-1}) and a high surface area silica obtained by ignition ("Aerosil"; 380 m^2g^{-1}) have been considered.

The heat and mechanism of interaction of water vapour on the surface of quartz reveal a few highly reactive sites not present in the amorphous specimens. The surface behaviour of the latter two specimens is the same, in spite of the large difference in surface area.

Radicals produced in quartz by mechanical grinding account for its reactivity and are correlated here to the fibrotic activity of quartz, as opposed to the non-fibrogenicity of amorphous silicas.

The heats of interaction of amorphous and crystalline forms with proline also point to a reactivity on quartz that is absent from amorphous silica.

Silica dusts are not biologically inert. They are able to disrupt the cell membrane (cytotoxic activity) and it is generally considered that this is the starting point of the silicotic process, after which fibrosis develops (fibrotic activity) [1]. Although the mechanism of action is not yet fully understood, it is clear that both activities are caused by certain characteristic properties of the silica surface. The understanding of silica toxicity thus relies on an accurate study of the physico-chemical properties of the exposed silica dust surface.

A great deal of work has already been performed on the surface chemistry of silica from the standpoint of its catalytic properties as a single component and as a support for compound catalysts, or in view of the use of silica in chromatographic columns. In both cases the general thrust relies on having samples with as large a surface area as possible; these are mainly obtained by preparing porous samples by precipitation from silicic acid solutions, and non-porous samples by the ignition of silicon compounds. Both kinds of samples are amorphous.

When dealing with biological properties, attention has to be focussed first of all on particle size: large particles (5.10^3 nm) do not cause silicosis, since these particles are retained before they reach the lung, nor do very small particles, as they can be released in the air by breathing. The ability to destroy the cell membrane also depends upon the particle size: the denaturing effect was found to increase with the increase in size of colloidal silica particles. The proposed mechanism was that large particles would stretch the protein molecule of the membrane by adsorption forces, whereas small particles (2–3 nm) would be too small to separate the protein coils [2].

Although much confusion has arisen regarding the different biological activities of various silicas, the earlier work clearly indicates that not all forms of silica causing damage to the membrane result in silicosis. Only a few polymorphs, mostly crystalline, are able to develop a factor which stimulates the fibroblasts to build up collagen ending up in the fibrotic nodule.

A complete understanding of these processes therefore calls for a thorough investigation of the surface chemistry of coarse silica powders of different origins, with particular attention to the crystallinity and to the way in which the surface has been created (mechanical grinding, precipitation, ignition).

The adsorption of water on these surfaces provides a useful tool for surface analysis. Water is in fact a constituent of a silica surface exposed to the atmosphere, for when equilibrated with water vapour the surface is mostly hydroxylated (surface silanols) and molecular water is bound to the silanols. Water can be released by heating under vacuum, and this process is reversible or irreversible depending on the outgassing temperature. Most authors agree that membrane damage is caused by the arrangement of the silanols, which interact with the protein or phospholipidic constituents of the membrane [3, 4]. Hypotheses on some characteristic arrangements of these groups templating the fibrogenic factor have also been put forward recently [5].

In order to acquire a picture of the surface sites, we have therefore started a comparative study of the heats of adsorption of water on various silica samples. As no detailed calorimetric work on the H_2O/SiO_2 system at low coverage has yet been carried out to our knowledge, high surface area samples have also been considered. This paper reports results obtained on mechanically ground quartz, coarse amorphous silica (surface area of the same order of magnitude as that of quartz), and high surface area amorphous silica obtained by ignition.

The presence of surface radicals on the mechanically created surface was monitored by esr. The reactivities of same samples with proline, an amino acid particularly relevant to the silicotic process [6, 7], were also tested.

Experimental

Materials

– Micronized crystalline quartz ($SiO_2 > 99\%$) from SIC (Soc. Ital. Chimici), BET surface area (krypton) 5.2 m^2g^{-1}.

– "Porasil F", totally amorphous silica, from Alltech Europe (Belgium), BET surface area (krypton) 16.1 m^2g^{-1}.

– "Aerosil", totally amorphous silica, from Degussa (Germany), BET surface area (nitrogen) 380 m^2g^{-1}.

The crystalline and amorphous structures of all samples were confirmed by XRD analysis.

Pretreatments

Samples for water adsorption were outgassed in the calorimetric cell and then transferred in vacuo into the calorimetric vessel (Calvet microcalorimeter). The three silica specimens were all pretreated at 413 K for 2 h. Quartz was also pretreated at 673 and 1073 K (4 h). One quartz sample, after a first adsorption run, was outgassed in the calorimeter at the adsorption temperature (303 K) for 12 h.

Samples for heat of immersion experiments were previously outgassed in vacuum at 413 K, then briefly exposed to the atmosphere and sealed in a glass tube.

Samples employed in esr measurements were also outgassed in vacuo at 413 K in a suitably designed esr cell.

Method

The heats of adsorption and amounts of adsorbed water vapour were measured at 303 K by means of a Tian Calvet calorimeter connected to a volumetric apparatus described previously [8, 9]. Water was distilled in high vacuum several times before use. Adsorption was investigated at very low coverage by admitting small consecutive doses of water onto the adsorbent in the calorimetric cell.

The heats of immersion in amino acid solutions were measured at 310 K by means of a C.R.M.T. (Setaram) calorimeter. The sample (sealed in a glass tube) and the solution were placed in the calorimetric cell. By simple rotation of the calorimetric body, a pestle broke the glass tube, thereby admitting the solid into the solution. Sodium citrate/citric acid buffer solutions (pH = 5) were employed for the measurements with proline. A blank with the buffer solution was recorded in each experiment.

Esr spectra were taken on a Varian E 109 spectrometer operating in the X band mode (9.4 GHz).

Results and discussion

The differential heats of adsorption of water as a function of the equilibrium pressure are reported in Figs 1a, 1b and 1c for quartz, Porasil and Aerosil previously outgassed at 413 K. The differential heat values (q^{diff}) have been calculated as $q^{\text{diff}} = dQ^{\text{int}}/dn_a$, where Q^{int} is the integral heat of adsorption and n_a the corresponding uptake [9]. In all cases adsorption was carried out up to the same equilibrium pressure of water ($p/p_0 = \sim 0.15$), far beyond the point at which the latent heat of liquefaction of water was attained (44 kJ mol^{-1}), so that nothing more than physical adsorption in multilayers, with the same heat, could be expected if the experiments were continued.

The main differences between Figs 1a, 1b and 1c depend on what happens in the earlier stages of hydration. The heat released by the first dose on quartz (~ 200 kJ mol^{-1}) is far larger than the corresponding values on Porasil and Aerosil (100–120 kJ mol^{-1}).

From ~ 100 kJ mol^{-1}, the three samples exhibit similar behaviour: the differential heat of adsorption decreases progressively until it attains a value very near the latent heat of liquefaction of water, and subsequently remains constant around it.

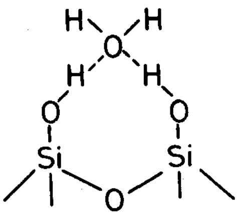
The adsorption of water thus indicated three kinds of sites:

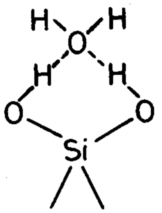
(i) Sites interacting with water vapour with a heat of interaction above 120 kJ mol^{-1}, present only on quartz.

(ii) Sites with a heat of interaction decreasing with coverage from 120 to 44 kJ mol^{-1}, present, although with different abundances, on all three samples.

(iii) Sites for the adsorption of water with a heat of about 44 kJ mol^{-1}, on all samples from a certain coverage onwards.

The behaviour common to the three samples is what is to be expected for a vapour adsorbed on a heterogeneous surface and ending up with multilayer adsorption. In the present case, as the outgassing temperature is very low (413 K), only molecular water is expected to be removed from the surface during the pretreatment. The surface should thus be left with all its surface hydroxyls, and subsequent adsorption of water would replace the molecular water removed. The decrease in the heat of adsorption is caused by intrinsic heterogeneity in the distribution of surface hydroxyls on the various crystallographic planes exposed in powdered samples. In fact, it has been reported by several authors that, depending on the distance between silicon atoms in a particular plane, vicinal, geminal or non-interacting silanol can be found [10]. Adsorption of one water molecule on top of a pair of silanols, vicinal or geminal, as in the following scheme, probably occurs on all three samples:





These processes are consistent with a heat of adsorption in the range 120–60 kJ mol^{-1}, as both mechanisms involve multiple hydrogen-bonding. At higher coverage, when water is adsorbed on adsorbed water itself, building up a sort of water cluster [11, 12], the heat of adsorption tends to the heat of liquefaction. The aspects of the energetics of the H_2O–SiO_2 interaction, which seem to be fairly general and not correlated to a particular kind of silica, will be discussed in more detail elsewhere. From the standpoint of the biological activity, attention has to be focussed mainly on the differences in reactivity between the various samples, and particularly on the very high initial heat of interaction on quartz.

It has already been reported that the heat of immersion of quartz in water is higher than the corresponding values for amorphous specimens [13]. The heat of immersion reported, however, including in one value the total energy of interaction, cannot distinguish between an increase in the number of adsorption sites or in their energy of interaction. At the same equilibrium pressure in our case, the adsorption values are higher on quartz than on Porasil and Aerosil; however, the most striking difference in surface properties consists in the initial heat of adsorption.

A clear-cut interpretation of the nature of the sites on quartz yielding such a high heat of interaction is not straightforward. The heat values are not consistent with the adsorption of undissociated water. Even on more ionic solids, such as aluminas, the coordination of water on surface-unsaturated cations gives a heat of interaction lower than 180 kJ mol^{-1} [14]. Heats of adsorption of water above this value on various solids [15–17] have always been assigned to the dissociation of water itself on the surface sites, giving rise to a pair of surface hydroxyls. Following the reaction

$$O^{2-} + H_2O \rightarrow 2\,OH^-$$

these processes are known to occur much more easily on ionic oxides than on covalent ones, where the covalent bonds between oxygen and the other component have to be broken. A partial rehydroxylation of the silica surface at some strained siloxane bridges, created upon thermal outgassing in vacuum, has been reported. These processes, however, are very slow and need substantial water vapour pressure to occur even to a limited extent [18, 19].

A possible role of some impurities always present on quartz samples and exhibiting a high reactivity towards water is unlikely, as the results in Fig. 1a are fairly reproducible with samples of different origins and impurities [20]. Moreover, these sites evolve with the pretreatment temperature. The variation in the initial heat of adsorption of water on quartz at 303 K as a function of the outgassing temperature is reported in Fig. 2. These high-energy sites present at 413 K attain a maximum at 673 K and disappear at 1073 K.

We favour an interpretation based on the peculiarity of the formation of the surface by mechanical grinding. When covalent solids are crushed, covalent bonds are broken, giving rise to radicals at the created surface. The presence of radicals during quartz milling has already been pointed out and evidenced by some reactions [21]. Radicals

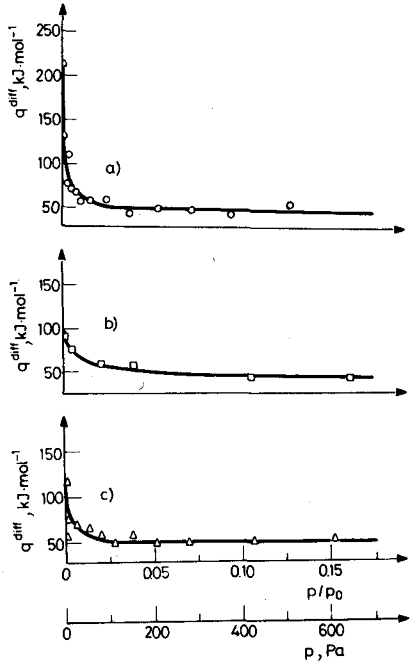


Fig. 1 Differential heat of adsorption of water vapour micronized quartz (a); Porasil (b) and Aerosil (c) as a function of equilibrium pressure

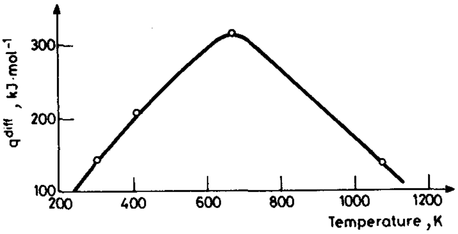


Fig. 2 Initial heat of adsorption of water vapour on micronized quartz as a function of outgassing temperature

such as Si• and SiO• on quartz crushed in high vacuum have been detected by esr [22, 23].

As to the fate of these radicals when the solids are exposed to the atmosphere or crushed in air, i.e. under the same conditions in which silica exhibits its toxicity, no hypothesis has no far been advanced.

It is very likely, however, that on surfaces created by crushing, unsaturated valencies such as Si$^\bullet$ and SiO$^\bullet$ can be saturated, yielding a strained siloxane bridge if the distance between the two radical groups is appropriate. On the other hand, these radicals, if isolated, may react with various atmospheric components. On the basis of various studies on the reactivities of cleaned crushed surfaces towards simple molecules such as O_2, CO and CO_2 [24, 25], we can assume that unsaturated valencies (Si$^\bullet$, SiO$^\bullet$) give rise to other radical species, such as $(\equiv SiOCO)^\bullet$, $(\equiv SiOO)^\bullet$, etc. The esr spectrum of micronized quartz, recorded in vacuum after outgassing at 313 K, is reported in Fig. 3. A structural signal near the free electron value reveals the presence of more than one radical species, produced during the micronization process. A signal is still present after outgassing at 673 K, but above this temperature the signal intensity decreases dramatically. Details on the interpretation and stability of this signal will be reported elsewhere; however, it does confirm that, even a long time after crushing, some radicals are still present on mechanically ground quartz. Water vapour may react with both very strained siloxane bridges and surface radicals and be dissociated. The heat of reaction in these cases would probably be rather high. The low number of sites (0.2 μ moles) having a heat of interaction with water higher than 120 kJ mol^{-1} is consistent with this interpretation. Reactions with other test molecules are required to confirm our hypothesis.

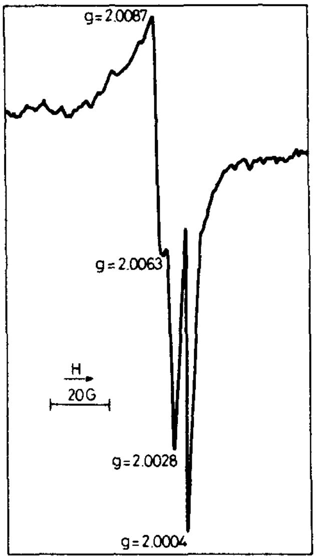


Fig. 3 Esr spectrum of micronized quartz outgassed at 413 K

Amino acids and proteins can be adsorbed on the surface of quartz [26, 27]. Most work, however, has been performed in non-aqueous solution, which is obviously different from the biological surroundings of the inhaled silica particle. We have measured the heats of immersion of our silicas in buffer solutions containing proteins or amino action of the protein or the amino acid with silica, the prevailing phenomenon being action of the protein or the aminoacid with silica, the prevailing phenomenon being the interaction with the water and buffer. Proline is an exception to this behaviour: a substantial net exothermic effect, lasting many hours, was detected when the quartz was contacted with the proline solution. No similar effects could be found with amorphous silicas. The exothermic process can probably be ascribed to the oxidation of proline to hydroxyproline, which has been reported to occur in the presence of quartz [7]. The quartz surface here may act as a catalyst or even an oxidizing agent itself: surface peroxo groups have indeed been detected recently on the surface of crushed quartz [28].

Conclusions

The analysis by adsorption calorimetry of the surface properties of SiO_2 compounds of different origins reveals some characteristics of crushed quartz dust which can be related to its biological toxicity. Radicals produced by grinding may act as very active sites for the dissociation of water and the oxidation of proline. Possibly the same sites may react within the cell with some more complex molecule whereby, in cascade reactions, the fibrogenic factor could be formed. From this respect, attention must be paid not only to the crystallinity of the material, but also to the way the exposed surface has been created.

The similarity of the rehydration processes on the two amorphous specimens, in spite of the large difference in surface area, also deserves comment. Small and large silica particles have different cytotoxic activities, which can be explained either by the mentioned mechanical model, small particles adapting to the large biomolecule, or by a chemical one, where the surface arrangements of silanols are actually different on particles of different sizes and origins. Our data would favour the former interpretation.

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Zusammenfassung — An drei Siliciumdioxidproben verschiedener Herkunft und Textur wurden Oberflächenzentren adsorptionskalorimetrisch mit dem Ziel untersucht, die biologische Aktivität von Siliciumdioxid mit dessen Oberflächeneigenschaften in Beziehung zu setzen. In die Untersuchung wurden mechanisch zerkleinerter Quarz (5.2 m^2 g—1), ein amorphes SiO_2 mit kleiner Oberfläche ("Porasil F"; 16.1 m^2 g^{-1}) und ein auf dem Verbrennungsweg erhaltenes Siliciumdioxid mit grosser Oberfläche ("Aerosil"; 380 m^2 g^{-1}) einbezogen. Wärme und Mechanismus der Wechselwirkung zwischen Wasser und der Quarzoberfläche weisen auf das Vorliegen einiger hochaktiver Zentren hin, die in den amorphen Proben nicht nachzuweisen sind. Das Oberflächenverhalten der amorphen Proben ist trotz des grossen Unterschiedes in der Oberflächengrösse gleich. Die in Quarz durch Zerkleinerung gebildeten Radikale bedingen dessen Reaktivität und werden mit der fibrotischen Aktivität des Quarzes in Beziehung gebracht, der sich darin von den keine fibrotische Aktivität aufweisenden amorphen Siliciumdioxidproben unterscheidet.

Резюме — С целью нахождения корелляции между биологической активностью двуокиси кремния и его поверхностными свойствами, проведен адсорбционный калориметрический анализ поверхностных участков трех типов двуокиси кремния различного происхождения и текстуры. Были рассмотрены механически микронизированный кварц (5,2 $m^2 g^{-1}$), аморфная двуокись кремния с низкой площадью поверхности ("Порасил Ф"; 16,1 $m^2 g^{-1}$) и прокаленная двуокись кремния с высокой площадью поверхности ("Аэросил"; 380 $m^2 g^{-1}$). Теплота и механизм взаимодействий паров воды на поверхности кварца показывают несколько высокореакционных участков, не представленных в аморфных образцах. Свойства поверхностей двух других образцов одинаковые, несмотря на большое различие их площадей поверхности. Радикалы, получаемые при механическом размалывании кварца, обусловливают его реакционную способность и коррелируются с фиброидной активностью кварца, в противоположность аморфной двуокиси кремния, не обладающей такой активностью. Теплоты взаимодействия кристаллической и аморфной форм двуокиси кремния с пропиленом также указывают на реакционную способность кварца.