

Surface and Adsorption Studies of High Surface Area Oxides

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Abstract. Modern FT-IR spectroscopy offers an ample potential for the study of adsorption and desorption processes on high surface area materials. Three examples will be presented here: (i) the thermal desorption of H₂O from SiO₂, (ii) the chemisorption and physisorption of H₂O on SiO₂, (iii) the interaction of NH₃ with OH groups on MgO surfaces.

Key words: FT-IR spectroscopy, surface, adsorption, SiO₂, MgO.

Intermolecular interactions [1] are not only relevant in the bulk of condensed matter, where they are intimately related to physical properties such as elasticity, viscosity, etc. Intermolecular interactions are also of significant importance at interfaces. This is particularly true for solid surfaces. Their characterization by IR spectroscopy requires a sufficiently large surface area of the substrate. In this respect single crystals cause major difficulties. Conversely, large surface areas are obtained by preparing the substrate in a highly dispersed form. Examples are SiO₂ and MgO powders. In addition to bulk absorption considerable losses of light intensity do, however, originate from light scattering. In order to cope with the inherently low signal level, a recourse has only recently been made to modern FT-IR technology [2] in combination with cryogenic detectors [3, 4]. As a consequence an improvement in resolving power and scan speed of two orders of magnitude was obtained over a wide spectral range (10000–10 cm⁻¹). This represents an ample potential for a further advancement of our understanding of surface structures. The spectral interval comprising the lattice vibrations of the bulk material is, of course, not available (e.g., SiO₂: 1300–300 cm⁻¹ [4], MgO: 950–300 [5]). If access to this region is required, surface specific techniques such as photoacoustic

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and diffuse reflectance spectroscopy [2] have to be applied. In spite of the progress in FT technology, they are still limited by comparatively low sensitivity.

The enormous sensitivity of modern FT-IR spectrometers used in the transmission mode will be demonstrated here by the study of adsorption and desorption processes of H_2O on SiO_2 [4] and of NH_3 on MgO [5]. There is a considerable interest in the use of these oxides as adsorbents, catalysts, catalyst supports, consistence modifiers, etc.

Experimental

The instrument used in the studies presented here is an evacuable FT-IR/FIR spectrometer model IFS-113 v (Bruker Analytische Meßtechnik, Karlsruhe, FRG) equipped with sets of properly selected light sources, filters, beam splitters, and detectors including the LN_2 -cooled mercury cadmium telluride detector for the mid IR range.

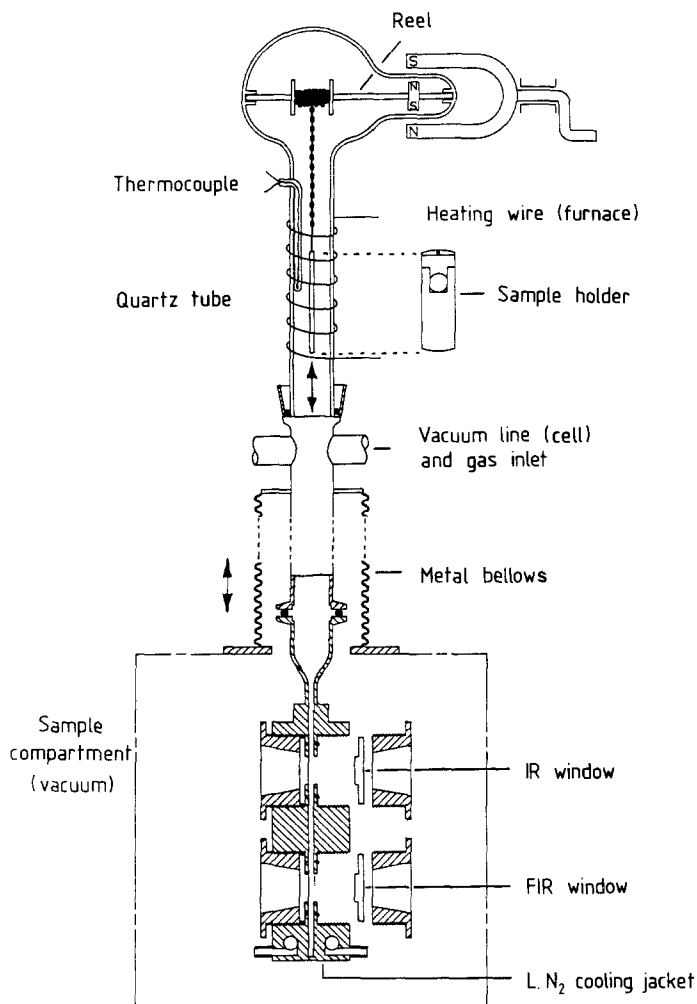


Fig. 1. Schematic representation of the adsorption cell (explanation see text). Used by permission, ref. [4]

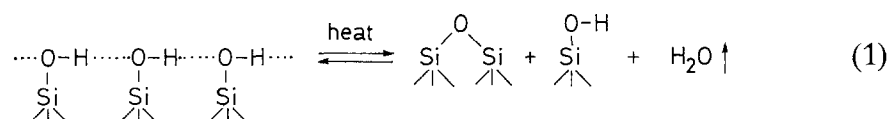
An appropriate cell [4] which enables IR and FIR studies to be performed on one and the same sample is shown schematically in Fig. 1. The five major components are: (a) the optical part where the sample is exposed to IR and FIR light, (b) the furnace, where the sample is thermally degassed at preselected temperatures, (c) the magnetically driven reel which allows to position the sample in the furnace or in the IR/FIR beam path, (d) the flexible metal bellows which make it possible to move the whole cell up and down in order to get the IR or FIR windows into the beam path, and (e) the high vacuum line and adsorbate gas inlet (not shown in Fig. 1). The whole system replaces the standard cover plate of the evacuated sample compartment of the interferometer and is tightly fixed after a careful optical alignment.

SiO₂ (Aerosil 300, Degussa) and MgO (Merck) are commercially available. The samples are, without any further preparation, pressed to pellets (20–50 mg) which are then subjected to an appropriate thermal treatment within the cell (see above). In the first step they are generally strongly degassed at 1000 to 1100°C. Then they are exposed to a certain H₂O vapour pressure, in order to establish a well defined initial surface state before starting the IR experiments. These were carried out at room temperature.

Results and Discussion

Thermal Desorption of SiO₂ Surfaces

On increasing the degassing temperature of SiO₂ to 600°C an extremely sharp band near 3750 cm⁻¹, which is assigned to the stretching vibration of isolated surface OH groups, gains intensity (Fig. 2 *a* and *b*). This may be understood in terms of two processes: (i) the surface is freed from physically adsorbed H₂O molecules and (ii) a surface reaction according to



takes place which produces progressively more and more isolated surface OH and siloxane groups. Finally, at temperatures above 600°C, an unspecified diffusion process brings originally isolated surface OH groups

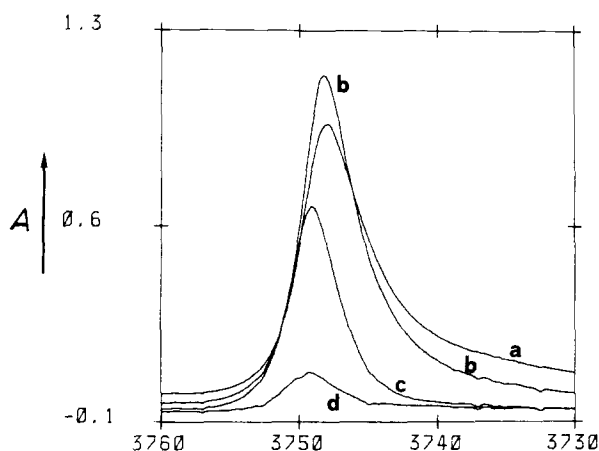
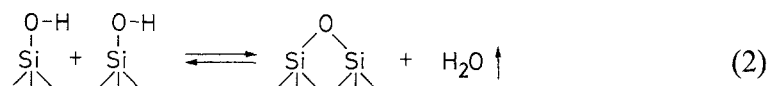


Fig. 2. Band contour of the stretching vibration of free surface OH groups on silica subjected previously to different degassing temperatures: *a*: 450°C, *b*: 600°C, *c*: 900°C, and *d*: 1100°C. Used by permission, ref. [4]

together which then react according to



and initiate a decrease of intensity of the respective band (Figs. 2 *c* and *d*).

The true shape of the OH stretching band of isolated OH groups on SiO₂ surfaces (Fig. 2) has been recorded only recently [4]. Earlier attempts suffered from both the influence of insufficient resolving power and erroneous intensity contributions [4, 6]. The relevant changes of position and shape of the band induced by the degassing procedure are likely to be related to the presence of both single and geminal free OH groups which give rise to slightly different OH stretching bands. They have been subject to very controversial discussions for the last two decades ([4] and refs. cited therein).

H₂O Adsorption on SiO₂ Surfaces

If SiO₂ samples, pretreated in the way described in the above subsection, are exposed to water vapour, time-resolved IR spectroscopy allows us to monitor chemisorption and physisorption processes on a time-scale of seconds or even fractions of a second [4].

The SiO₂ surface degassed at 1100°C exclusively contains traces of free surface OH groups. The curves in Fig. 3 a demonstrate that the water molecules react with the siloxane centers of the surface according to the back reaction of Eq. (2) [4, 7]. Two bands at 3715 and 3510 cm⁻¹ grow at the same rate and have to be assigned to pairs of hydrogen bonded vicinal OH groups (3715 cm⁻¹: proton acceptor, 3510 cm⁻¹: proton donor). This necessarily implies—at least at the stage of adsorption presented here—that mainly pairs of hydrogen bonded OH groups and nearly no larger chains ((OH)₃, (OH)₄, etc.) are formed. A similar situation arises in the experiment based on an SiO₂ sample degassed at 900°C (Fig. 3 b). The only difference refers to the position and the shape of the broad band centered around 3500 cm⁻¹. During the process of H₂O adsorption it is shifted to lower wave numbers and is deformed by a shoulder of increasing intensity around 3400 cm⁻¹. Obviously the formation of pairs of hydrogen bonded OH groups takes place more rapidly than in the previous experiment (Fig. 3 a) in such a way that a physisorption of H₂O molecules onto the OH pairs starts to compete with the chemisorption within the time interval of observation. The hydrogen bonded H₂O molecules give rise to a broad and unspecific absorption below 3500 cm⁻¹. The trend observed in Figs. 3 a and b continues for SiO₂ samples degassed at still lower temperatures. Fig. 3 c (450°C) and Fig. 3 d (300°C) already exhibit absorption of hydrogen bonded surface OH groups (unspecific absorption above 3400 cm⁻¹) before the water vapour has access to the SiO₂ sample (*t* = 0 s). Without any doubt the absorption assigned to physisorbed water now essentially dominates most of the spectral interval under consideration (Figs. 3 c and d). However,

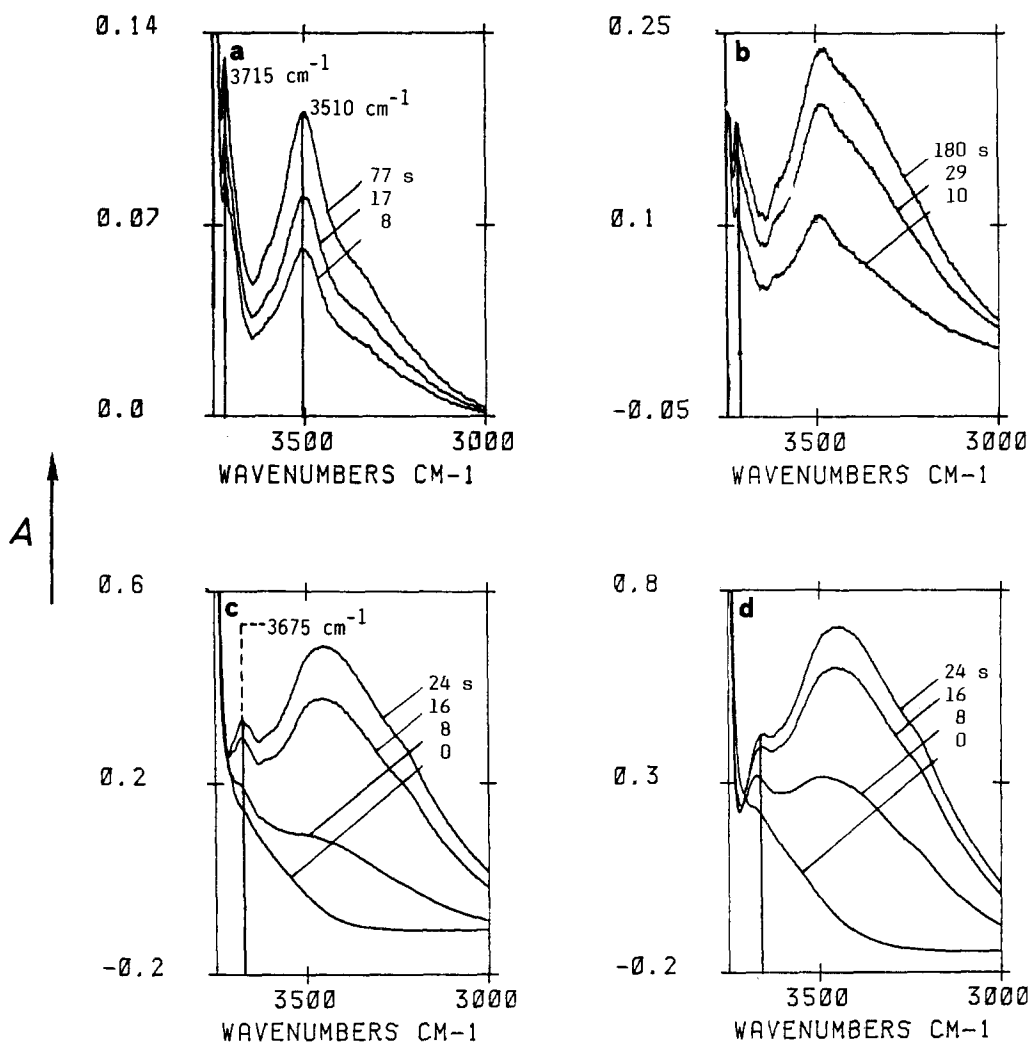


Fig. 3. Time-resolved IR spectra (OH stretching region) after the access of approximately $50 \mu\text{mol H}_2\text{O}$ to SiO_2 degassed at 1100°C (a), 900°C (b), 450°C (c), and 300°C (d). The time which passed since the addition of water vapour is indicated for each diagram. Used by permission, ref. [4]

there is an additional process which becomes effective only for SiO_2 samples degassed at temperatures below 900°C . It is related to the growth of the band at 3675 cm^{-1} , observed in Figs. 3 c and d and completely absent in Figs. 3 a and b. Obviously the related surface complexes are irreversibly destroyed at temperatures considerably above 450°C . They may only be restored, at least partially, after admitting large amounts of water.

NH_3 Adsorption on MgO Surfaces

As already discussed for SiO_2 (see first subsection) thermal treatment under vacuum characteristically influences the population of oxide surfaces with different types of OH groups. After degassing at ca. 180°C MgO exhibits

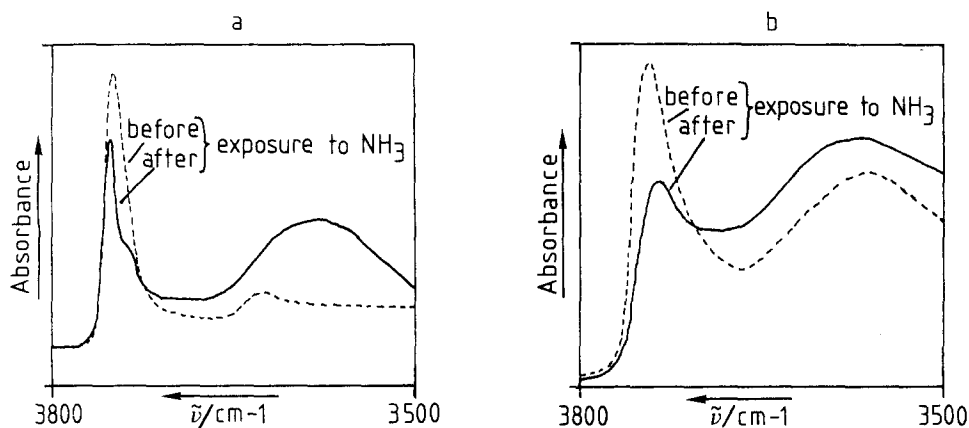
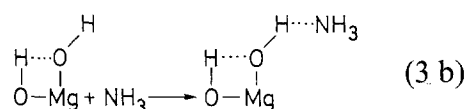
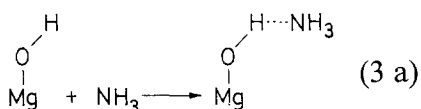


Fig. 4. Band contour of the stretching vibrations of isolated (a) and free (b) OH groups on MgO surfaces before and after the addition of NH_3 as probe molecules. The experiments in a and b were performed after degassing the MgO sample at 450 and ca. 180°C, respectively

two OH stretching bands [5, 8]: (i) a comparatively sharp one around 3750 cm^{-1} assigned to free surface OH groups and (ii) a broad one centered around 3550 cm^{-1} (Fig. 4 b, broken line) assigned to OH groups acting as proton donor in H bonded surface OH complexes. Degassing at 450°C , on the other hand, creates exclusively isolated surface OH groups. They give rise to only one absorption band of significant intensity. Its position is essentially the same as that of the aforementioned free OH groups (3750 cm^{-1} , Fig. 4 a, broken line).

The free and the isolated OH groups may be discriminated on the basis of their different reactivity towards NH_3 [5]. The band assigned to free OH groups in H bonded complexes (Fig. 4 b, broken line) exhibits a symmetric depletion after the access of NH_3 (Fig. 4 b, solid line). If the reacting surface sites are isolated OH groups (Fig. 4 a, broken line), a strongly asymmetric depletion is observed (Fig. 4 a, solid line). There is spectroscopic evidence [5] that NH_3 acts as proton acceptor in the surface complexes with isolated (3 a) and free (3 b) OH groups,



Obviously two different types of isolated surface OH groups are present exhibiting a different reactivity towards NH_3 . This clearly shows that, in principle, an effective surface analysis requires (i) different reactant molecules for probing different (e.g., acidic and basic) surface sites and (ii) a highly sensitive FT-IR spectrometer for the detection of minute spectral changes originating from the interaction with the probe molecules.

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