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Reactivity towards water of silicon nitride: energy of interaction and hydration dehydration mechanism

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The heat of adsorption and adsorbed amounts of $H_2O_{(vap)}$ have been measured on an industrial crystalline Si_3N_4 outgassed at 400 and 800° C. A nearly uniform surface is present after the 400° C thermal treatment, where H_2O is adsorbed via hydrogen bonding to surface OH and NH groups with a heat of adsorption of $\cong 50\,kJ\,mol^{-1}$. After 800° C thermal treatment, which involves the dehydration and condensation of OH and NH groups, water is readily dissociated at the surface ($-\Delta H > 50\,kJ\,mol^{-1}$) and the pristine surface is formed on which water is hydrogen bonded again. No hydrophobic patches are detected. The results are discussed in comparison with SiO_2 behaviour in similar conditions.

1. Introduction

Silicon nitride is a very important material for various recent technological applications and particularly as new resistant ceramic material. In spite of its great engineering importance little is known of its chemistry. Chemical studies devoted to its electronic and crystallographic structure have been thoroughly reviewed by Jennings *et al.* [1]. Most of the other research work on this solid is devoted to its preparation [2–5] and to the phase transition [6–9].

The application of Si_3N_4 both as a refractory material and as a passivating agent in microelectronics would require a detailed knowledge of its surface chemistry, in order to predict the reactivity in different atmospheres and the behaviour upon sintering. Furthermore Si_3N_4 has been recently proposed as a possible heterogeneous catalyst [10], which obviously needs a detailed description of the surface of the solid, active sites etc. To our knowledge very few researches have been devoted to this field, with the notable exception of Lorenzelli and co-workers [11–13], who performed a detailed investigation by Fourier transform infrared spectroscopy (FTIR) on an amorphous sample of Si_3N_4. Three IR-active species have been found at the surface by Busca *et al.* [12] on their sample outgassed at 400° C: an OH characterized by a stretching frequency of $3742\,cm^{-1}$ not far from the one found for silanols on silica, an NH stretching frequency of $3355\,cm^{-1}$, and an SiH ($2290\,cm^{-1}$).

Whereas the presence of the SiH group may be due to the particular preparation route adopted by the authors, the other two groups (hydroxyl and imido) are likely to be present on any Si_3N_4 surface previously outgassed *in vacuo*. Furthermore, by the adsorption of several probe molecules, the presence of an Si_3N: exposed basic group has been hypothesized. The OH groups are slightly less acid than the corresponding ones on silica, and adsorb several molecules via weak hydrogen bonds. Upon adsorption of water, a broad band at $3600\,cm^{-1}$ (assigned to interacting OH groups) appears, which is eliminated by outgassing above 300° C. Physisorbed molecular water is eliminated by simple evacuation at room temperature.

Obviously quantitative data are needed for a complete description of the surface as far as the number and the strength of adsorption sites is concerned. Because of the crucial role of the water in ceramic production, sintering etc. and of the fact that any sample exposed to the atmosphere will react with $H_2O_{(vap)}$, the interaction with $H_2O_{(vap)}$ has to be studied prior to any other investigation by means of probe molecules. Our laboratory has been devoted for many years to the characterization of H_2O adsorption by measuring the variation of the heat of adsorption with coverage, which allows on the one hand the distinction of molecularly and dissociatively bonded water, and on the other the distinction of hydrophilic and hydrophobic patches at the surface [14–16]. This technique is doubly quantitative, as it gives adsorbed amounts and the related energies of interaction and matches quite satisfactorily with the IR results [17, 18]. Furthermore, comparison between adsorption performed on samples outgassed at different temperatures provides a picture of the modification produced by the thermal treatment at the surface [17].

We have therefore measured the heat of adsorption of H_2O at room temperature on an industrial sample of crystalline Si_3N_4, used as a ceramic refractory and with a fairly large surface area, outgassed at two different temperatures. The results obtained are compared with the corresponding ones on silica.

Work is still in progress on other Si_3N_4 materials and with other adsorbates in order to clarify both the surface properties of different Si_3N_4 samples and their differences with respect to silica.

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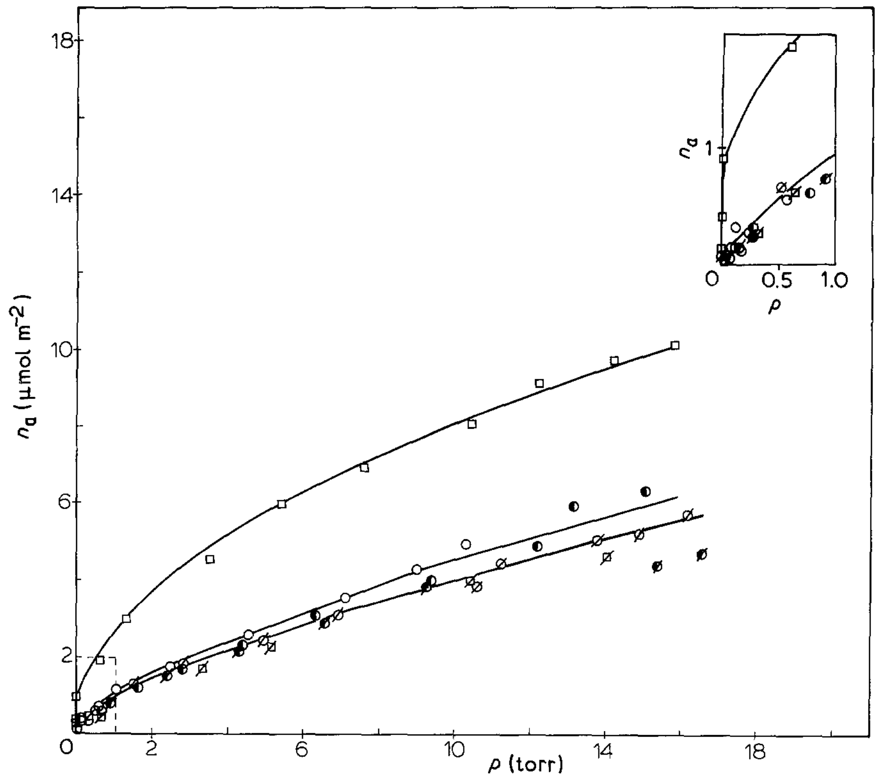

Figure 1 Adsorption of $H_2O_{(vap)}$ on Si_3N_4. Volumetric isotherms: (○, ◐) ads I on SN400; (ϕ, ◐) ads II on SN400; (□) ads I on SN800; (⌹) ads II on SN800.

2. Experimental procedure

2.1. Materials

Silicon nitride (LC-12, Starck, Berlin) was kindly supplied by Dr Babini from Istituto per la Ricerca e la Tecnologia Ceramica (IRTEC–CNR) in Faenza. It is an industrial crystalline specimen, mainly constituted by the α phase (90%) with 3% of the β phase. The chemical analysis produced by the firm itself reports the following impurities (wt %): free Si 0.1, Fe 0.03, Al 0.10, Ca 0.02, Na 0.005. The reported value for the BET surface area is $19\,m^2\,g^{-1}$. The water vapour employed in adsorption was obtained from the evaporation of gas-free H_2O, distilled several times *in vacuo*.

2.2. Methods

The adsorption of H_2O was measured on samples outgassed at 400 and 800° C. Samples will therefore be indicated as SN400 and SN800, respectively. The thermal treatment was performed within the calorimetric cells in a vacuum apparatus as follows: after evacuation at room temperature, the temperature was slowly raised up to the fixed value ($\cong$ 1 h) and then kept at the chosen temperature for 2 h. Particular care was taken to keep low the pressure of desorbed gases over the sample. However, a sudden rise in pressure was detected at 120° C, probably due to the desorption of molecular water, and also at 500 to 600° C during the preparation of SN800. The cell was then transferred into the calorimetric vessel without exposure to the atmosphere and submitted to water adsorption. The heat of adsorption and related adsorbed amounts were measured by means of a Tian–Calvet microcalorimeter connected to a volumetric apparatus, following a technique previously described [14, 19].

A stepwise adsorption run (ads I) was performed by subsequent admission of very small doses of H_2O vapour, in order to examine the variation of the heat of adsorption with coverage from the lowest coverage values possible. The experiment were stopped when the competitive adsorption on the glass walls was no longer negligible as the equilibrium pressure was approaching the saturating pressure value. The sample was then evacuated by direct outgassing until no deviation from the calorimetric baseline, due to further desorption of water, was detected. In this way an overall heat of desorption was measured, but it was not possible to measure the corresponding desorbed amounts. A second adsorption run (ads II) was then performed in the same way in order to evaluate, by comparison between data from ads I and ads II, the fraction of H_2O irreversibly held at the surface. The calorimeter was kept at a constant temperature of 30° C.

3. Results

The volumetric isotherms (n_a against p) are reported in Fig. 1. Two separate experiments, with different amounts of the sample from the same batch, were performed on SN400 in order to check the reproducibility of the results. The corresponding calorimetric isotherms (Q^{int} against p) are reported in Fig. 2. Symbols on the ordinate axis indicate the value of heat evolved during adsorption and not absorbed during desorption, thus measuring the heat related to the irreversible adsorption of H_2O. In fact these values are close to the difference between ads I and ads II for the same sample. Three main facts can be deduced from Fig. 1:

(i) For SN800 the adsorption involves nearly twice the amount of $H_2O_{(vap)}$ compared with SN400 at the same equilibrium pressure;

(ii) the adsorption on SN400 (ads I) is characterized by the presence of an appreciable equilibrium pressure

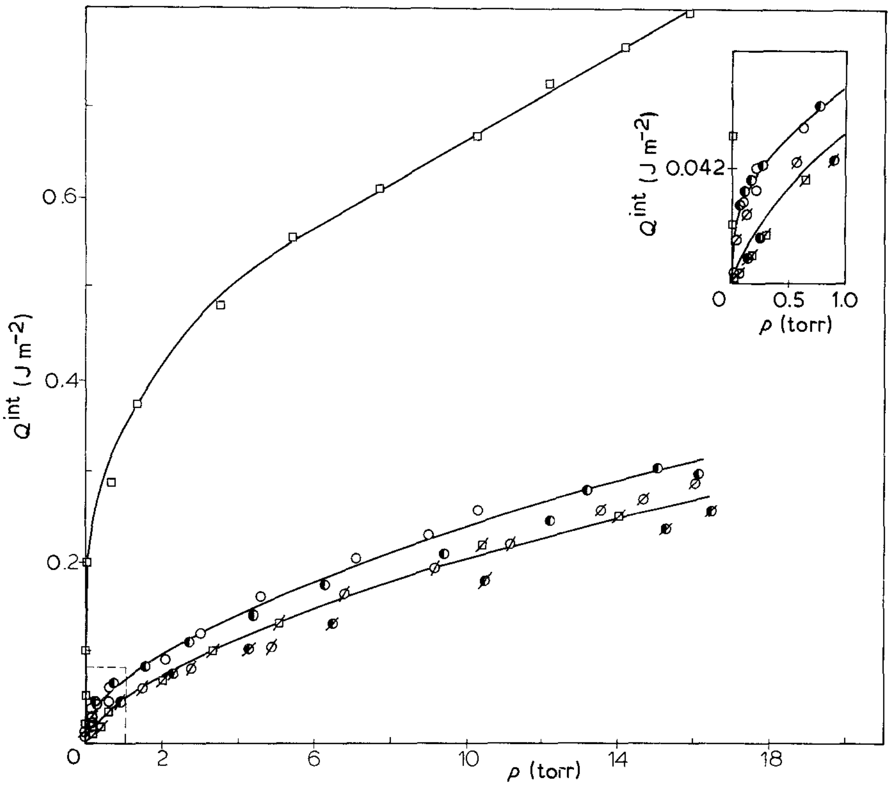

Figure 2 Adsorption of $H_2O_{(vap)}$ on Si_3N_4. Calorimetric isotherms. Symbols are the same as in Fig. 1.

from the very beginning, whereas on SN800 (ads I) the first four doses (up to an uptake of 1 μmol m^{-2}) are adsorbed without the appearance of a detectable equilibrium pressure;

(iii) the water adsorbed on SN400 is mainly reversible, but only for some 0.5 μmol m^{-2} (10% of the whole adsorption at 15 torr equilibrium pressure) measured from the difference between ads I and ads II, whereas on SN800 half of the water adsorbed is irreversibly held at the surface.

The fact that the experimental points from SN800 ads II fall nearly on the same curve as the ones from SN400 suggests that the main difference between SN400 and SN800 is due to the irreversible adsorption of H_2O which would occur to a very large extent on SN800 and in a very small amount on SN400. An overall estimate of the molar enthalpy measured at the equilibrium pressure of 15 torr is given in Table I. The reversible adsorption has a value of 50 kJ mol^{-1}, as expected for a very weak adsorption of molecular water, whereas the irreversible process occurs with an average value of 92 kJ mol^{-1} to a very small extent on SN400 and with 113 kJ mol^{-1} in larger amount on SN800. The higher value for SN800 is likely to be due to the presence of more energetic sites created only after prolonged outgassing at high temperature.

As to the presence of an appreciable equilibrium pressure, it has to be pointed out that this appears long before the accomplishment of the irreversible adsorption. In fact it appears from the first dose on SN400, and at a coverage of about 1 μmol m^{-2} on SN800, whereas the total irreversible adsorption is more or less five times greater. This suggests that irreversible adsorption, probably slow and activated, occurs in parallel with reversible adsorption over a large coverage interval.

A more detailed description of the variation of the energy of interaction with coverage is given by the evolution of the differential heat of adsorption with coverage. In order to give an idea of the variation dose by dose, we have shown in Figs 3, 4 and 5 the partial molar enthalpies of adsorption ($\bar{q} = Q^{int}/n_a$) for each dose as a function of the adsorbed amount.

Fig. 3 reports the values obtained from the two separate experiments on SN400 ads I, Fig. 4 reports data from SN800 ads I and Fig. 5 reports all the ads II values, two from SN400 (Fig. 5a) and one from SN800 (Fig. 5b). The heats of adsorption of the water reversibly uptaken (Fig. 5) are the same for SN400 and SN800 and show a very narrow range of variation of the interaction enthalpy, which is around 63 kJ mol^{-1} at the lowest coverage but after few doses reaches the constant value of $\cong$ 50 kJ mol^{-1}, in agreement with the value reported in Table I. Also for SN400 ads I the variation of the energy of interaction with coverage is very narrow, with the notable exception of the very first dose which exhibits a very high

TABLE I Calorimetric data for p = 15 torr

	SN400			SN800		
	ads I	ads II	irrev.	ads I	ads II	irrev.
n_a(μmol m^{-2})	6.0	5.5	0.5	10.2	5.5	4.7
Q^{int}(J m^{-2})	30.1	25.5	4.6	78.7	25.5	53.1
$-\Delta H$(kJ mol^{-1})	47	46	92	77	46	113

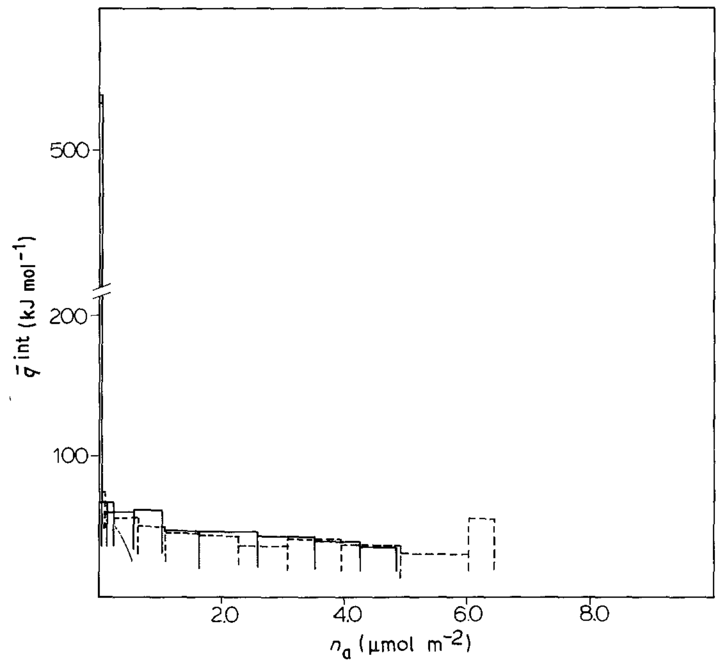

Figure 3 Partial molar enthalpy of interaction of water vapour with silicon nitride: full and dashed lines are two separate experiments on SN400.

value ($-\Delta H > 50\,\mathrm{kJ\,mol^{-1}}$), probably due to irreversible chemisorption. Then the enthalpy decreases from 63 down to 46 to $50\,\mathrm{kJ\,mol^{-1}}$ as in ads II. The fact that at low coverage the amount of $H_2O_{(vap)}$ adsorbed with $63\,\mathrm{kJ\,mol^{-1}} < -\Delta H < 46\,\mathrm{kJ\,mol^{-1}}$ is somewhat larger in ads I than in ads II may be due to the contribution of the irreversible adsorption, which in that region is likely to occur alongside reversible adsorption. However, the main result arising from Figs 3 and 5 is the *constancy of the heat of interaction*, around $50\,\mathrm{kJ\,mol^{-1}}$, very little above the latent heat of liquefaction ($44\,\mathrm{kJ\,mol^{-1}}$). This indicates the presence of mainly one process. Furthermore the absence of a consistent variation of site energy with coverage indicates that very little heterogeneity is present at the surface of Si_3N_4, when outgassed below or at 400° C (Fig. 4). It is noteworthy that the constancy of the heat of adsorption is attained after the adsorption of $4.60\,\mu\mathrm{mol\,m^{-2}}$, which is very near to the value calculated in Table I for irreversible adsorption. Therefore, superposition of the two processes occurs to a rather small extent, as the heat of adsorption below $4.60\,\mu\mathrm{mol\,m^{-2}}$ clearly indicates the prevalence of irreversible processes, and the value of the constant part at high coverages is near to that found for reversible adsorption.

Some aspects of the kinetics of H_2O adsorption are illustrated in Fig. 6, where the thermokinetics are shown by the shape of the heat emission peaks (heat against time curves). Fig. 6a shows the peak related to the adsorption of the very tiny first dose ($0.05\,\mu\mathrm{mol\,m^{-2}}$) on SN400 (ads I and II) and on SN800 (ads I and II). Both the ads II peaks exhibit the same typical trend for fast processes: the peaks are very

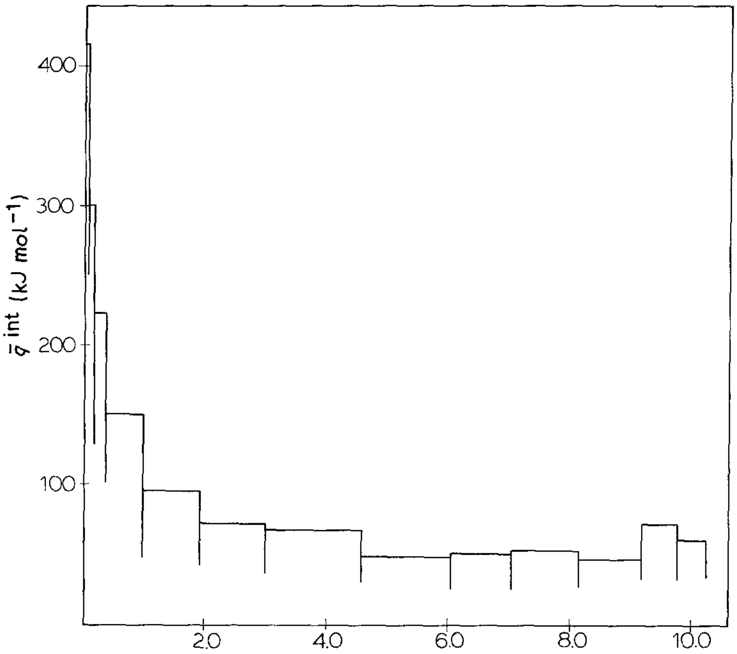

Figure 4 Partial molar enthalpy of interaction of water vapour with silicon nitride: adsorption on SN800, ads I.

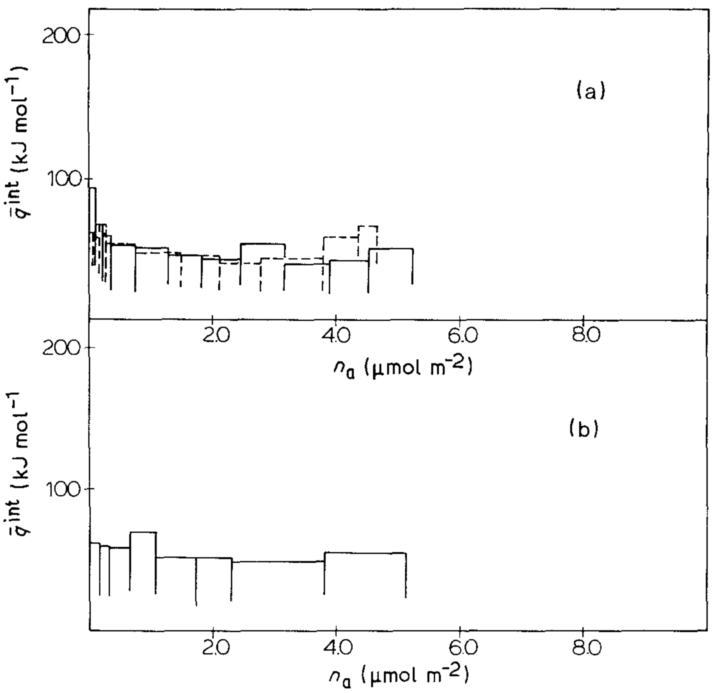

Figure 5 Partial molar enthalpy of interaction of water vapour with silicon nitride: (a) full and dashed lines, two separate experiments on SN400 ads II; (b) adsorption on SN800, ads II.

sharp and the heat emission terminates in 30 min; adsorption is in such a case quasi-instantaneous and the peak shape is determined by the inertia of the calorimeter itself. The first peaks on SN400 and SN800 are quite different: heat emission is very slow, the baseline is attained only after a long period of time (> 5 h) indicating the slow activated dissociation of H_2O at the surface. This is only for the first peak. If we consider the situation at $p \cong 0.3$ torr, both ads II and ads I on SN400 exhibit fast kinetics and only for SN800 is the slow dissociative process still going on. The peaks for SN800 exhibit the same trend up to an equilibrium pressure of $\cong 10$ torr where the kinetics become faster. Some kinds of slow process, however, are still detectable at high coverages, as a small shift from the baseline after most of the heat has been released is detectable.

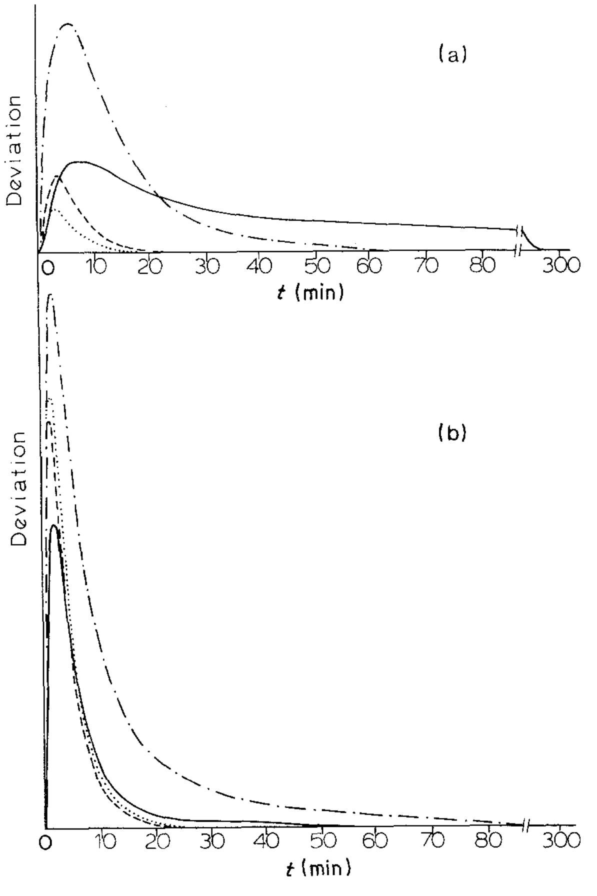

Figure 6 (a) Heat emission peaks for the first dose at $p \cong 0.1$ torr; (b) heat emission peaks for the sixth dose at $p \cong 3$ torr. Arbitrary units for deviations. (——) SN400 ads I; (–·–·–) SN800 ads I; (···) SN400 ads II; (– – –) SN800 ads II.

4. Discussion

The main result arising from the present data is that in spite of the marked covalency of Si_3N_4 its surface exhibits a typical hydrophilic behaviour.

4.1. Thermal treatment

Outgassing at 400 and 800° C produces very different surface arrangements. Outgassing at 400° C yields only the elimination of weakly bonded molecular water, leaving surface groups such as silanols and imido unaffected, but only for the small fraction of sites reacting irreversibly with water. Whereas the latter process probably involves the dissociation of water, the remaining groups (OH and NH) constitute a quasi-uniform distribution of sites where water can be coordinated. Outgassing at 800° C, on the other hand, involves the elimination of water (probably condensed from OH and NH groups) with subsequent formation of Si–N bridges which are not very stable and thus constitute reactive sites for the dissociation of H_2O. This latter process in turn will yield the pristine situation.

A possible scheme is reported in Fig. 7a. The above data qualitatively fit those reported by Busca and co-workers [12, 13] who found that upon adsorption of water a broad band at 3660 cm^{-1} appears, which was assigned by the authors to OH groups mutually interacting via hydrogen bonds. This band disappears upon thermal treatment, because of condensation to

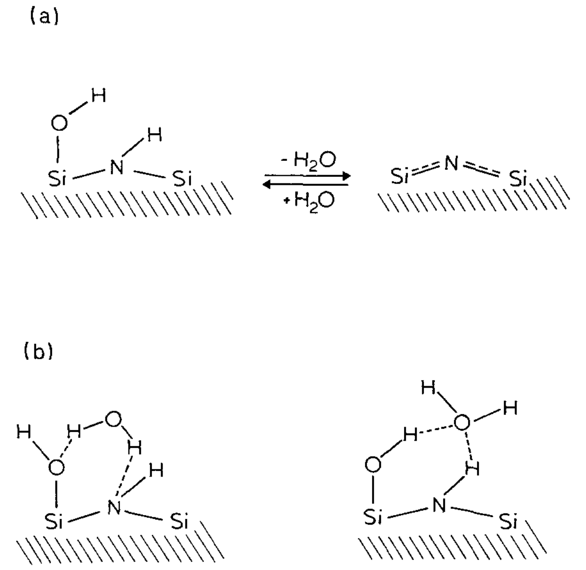

Figure 7 (a) Scheme for dehydration–rehydration of the Si_3N_4 surface; (b) two possible arrangements for hydrogen-bonded water.

give H_2O molecules. It is rather intriguing that in their case this occurs on a 400° C outgassed sample and that the $3600\,cm^{-1}$ band disappears upon heating at 300° C. This would imply that on their sample, dissociative adsorption would be a substantial phenomenon even after outgassing at 400° C. This can be due to the different nature of the two samples, one crystalline and the other amorphous. In fact great differences between crystalline and amorphous compounds may show up upon thermal treatment: it has been shown by some of us [18, 20] that at the same outgassing temperature (400° C) crystalline SiO_2 (α-quartz) retains most of its surface hydroxyls, whereas an amorphous silica does not. It is thus very likely that differences similar to those found on silica between crystalline and amorphous forms might occur also on Si_3N_4: in other words, more OH and NH would be present on our SN400 than on the amorphous sample investigated by Busca and co-workers.

4.2. Characteristics of water adsorption

The adsorption of molecular water occurs with a rather low heat of interaction (46 to $50\,kJ\,mol^{-1}$) on a nearly homogeneous surface. According to what was previously reported by Busca *et al.* [13] this process is totally reversible at room temperature. The heat of interaction is consistent with a molecular adsorption occurring via two hydrogen bonds onto surface silanols and imido groups, following one of the two possible schemes shown in Fig. 7b. It is also possible that two silanols or two imido groups may coordinate water, although separate couples of two OH or two NH groups, formed by contact with atmospheric water on the original sample, are not likely to be present. This is also in agreement with the substantial homogeneity of the surface, and with the absence of lateral interaction between admolecules.

It is noteworthy that in the spectrum reported by Busca *et al.* [12] on their sample outgassed at 400° C the OH band ($3742\,cm^{-1}$) is very narrow, characteristic of non-interacting OH. A substantial population of isolated silanols on silica brings about hydrophobicity [16, 18, 21]; as this is not the case on our silicon nitride, either the low surface area crystalline form behaves in a different way from the amorphous one or the presence of the N–H as well as Si–N bonds would play a crucial role in keeping the surface hydrophilic. An impressive reactivity towards water develops upon dehydration at 800° C and a remarkable heterogeneity in surface sites shows up. On the dehydroxylated surface water vapour readily reacts with dissociation of the molecule, following the reverse reaction schematized in Fig. 7a. This reaction, however, leaves a uniform hydrated surface because upon outgassing at room temperature and subsequent adsorption of water (SN800 ads II) the same situation as after adsorption at 400° C is found, both in adsorbed amounts (Fig. 1) and energy of interaction (Fig. 5). This reactivity indicates that silicon–nitrogen bridges at the surface, created by dehydration, are very reactive, being likely to be strained and chemically unstable. A different situation among the single bridges formed upon random dehydration of the surface (as created by thermal treatment) may account for the heterogeneity on SN800.

The presence also of strongly bonded molecular water, adsorbing alongside with dissociation, may not be ruled out; a detailed IR investigation on stepwise adsorption would be needed to confirm the proposed models. A reaction between H_2O and Si_3N surface groups, yielding *inter alia* silanols and ammonia, has been found when silicon nitride was heated at 500° C in water vapour by Lorenzelli *et al.* [11]. It is unlikely that the same reaction would occur in much milder conditions as in the present work; however, because of the enhanced reactivity upon outgassing at 800° C, this process might occur and contribute to the overall heat, although to a small extent. In any case the heats involved in the irreversible process are only consistent with the dissociation of the H_2O molecule, being similar (at the lowest coverages even greater) to the values found for the dissociation of H_2O on highly outgassed aluminas [14, 15, 17].

The reactions occurring on SN800 upon contact with water are thus the following:

(i) dissociation of H_2O to give surface OH and NH (Fig. 7a), $-\Delta H > 50\,kJ\,mol^{-1}$, and to a small extent to give NH_3 [12];*

(ii) reversible adsorption of molecular H_2O on to surface silanols and imido groups via two hydrogen bonds, with a nearly constant heat of interaction as on SN400 ($-\Delta H \cong 50\,kJ\,mol^{-1}$).

The kinetics of adsorption, as can be deduced both from the decrease of the pressure over the adsorbent and from the shape of the calorimetric peaks, are in

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*Evidence of the formation of ammonia by the hydrolysis of a freshly created silicon nitride surface has been recently found in our laboratory.

good agreement with the model proposed. The process occurring during ads II is very fast, consistent with the non-activated coordination of water via hydrogen bonds. On SN400 ads I, the first dose is adsorbed extremely slowly, even more slowly than on SN800: this is due to the dissociation of water, probably occurring either on a few Si_3N_4 dissociative sites created by the thermal treatment at 400° C or on to CaO impurities which are also present in the sample. The conversion of CaO into $Ca(OH)_2$ will occur also in the inner part of a CaO particle [22] but at a much slower rate than at the surface. The enthalpy values involved would be consistent with our values for irreversible adsorption.

After adsorption of the first dose only coordination takes place on SN400 and in fact the thermokinetics are identical to those from ads II. The case of SN800 is quite different: the slow process is present for a large part of the experiment although to a different extent, in agreement with the hypothesis that a substantial part of the adsorbed water is dissociated. The fact that the very first dose is adsorbed somewhat faster on SN800 than on SN400 may be due to the fact that at 800° C CaO impurities might have been converted into $CaSiO_3$, and thus no more conversion into hydroxide would occur. Dissociative adsorption occurs first (slow activated process) and then is followed by coordination of H_2O (fast process). The small deviation from the baseline persisting throughout most of the experiments confirms that to a small extent the two processes occur simultaneously.

4.3. Comparison between Si_3N_4 and SiO_2 reactivity towards H_2O

Because of the differences in crystallinity and surface structure a correct comparison between Si_3N_4 and SiO_2 surface reactivity is not easily made. A few facts, however, are rather striking and deserve to be pointed out, as they are probably linked to the particular technological properties of silicon nitride which constitute the basis for its wide industrial use. Bearing in mind that even among silicas considerable differences can be found in the surface properties depending upon the crystallinity, particle size and origin of the sample [16, 18, 20, 23] we outline here the major differences in surface properties found between most SiO_2 specimens and the Si_3N_4 investigated here. A future paper will be devoted to a comparison between silicon nitrides of different origins and crystallinities and various silicas.

The main differences between SiO_2 and Si_3N_4 upon thermal treatment in a vacuum and adsorption of H_2O are the following:

(a) On SiO_2 the affinity for water decreases with increasing the temperature of the thermal treatment: consequently the higher the temperature, the lower the amount of water adsorbed. In some cases also hydrophobicity develops [22]. This is due to the high stability of the siloxane (Si–O–Si) bridges where the bond is strengthened by π(d–p) bonding. On silicon nitride the trend is the opposite, as the adsorption of water increases in energy of interaction and extent on increasing the temperature of the thermal treatment. No hydrophobicity develops, at least before 800° C. The Si–N–Si bridges are less stable than Si–O–Si. Consequently H_2O is readily dissociated at room temperature on an Si_3N_4 outgassed surface, whereas the similar process occurs on silica only very slowly, under high H_2O pressures and to a very limited extent [24].

(b) In contrast with the previous point, the number of sites per unit surface area adsorbing molecular H_2O on silicon nitride is lower than on any SiO_2 examined, and their heat of interaction too is slightly lower than is found for crystalline quartz [20, 25]. This can be ascribed to the lower acidity of the OH groups reported by Busca *et al.* [13]. Accordingly all physisorbed water is desorbed at room temperature.

(c) Silicas exhibit much more heterogeneity towards the adsorption of water than silicon nitride, which in the absence of dissociative processes behaves more or less as an homogeneous surface.

5. Conclusions

Silicon nitride clearly exhibits peculiar surface properties upon dehydration and adsorption of water, different from those of any other covalent solid such as silica. This may account for its application in different industrial fields where the traditional ceramic oxides or silica cannot be used. The great changes in reactivity with water upon outgassing reveal that the thermal history of the sample may determine many of its properties and particularly its sinterability.

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