

Surface Rehydration of Variously Dehydrated Eta-Alumina

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The surface dehydration and rehydration of well-characterized eta-alumina have been investigated by means of gas adsorption microcalorimetry and infrared spectroscopy.

Dehydration shows a multiplicity of surface hydroxyl species, some of which are not reformed on water adsorption at room temperature. The creation of an undissociated water phase takes place from the earliest stages of rehydration.

Differential heats steeply decrease with surface coverage, while the adsorption energy distribution does not seem to depend on the dehydration degree.

INTRODUCTION

Transition aluminas are widely used as catalysts and their activity strongly depends on adsorbed water. It is also known that, when exposed to the atmosphere, aluminas are covered by molecularly adsorbed water (1-3) and chemisorbed water in the form of surface hydroxyls (4, 5). On thermal dehydration, increasing amounts of surface water are desorbed. A thorough investigation of the readsorption of water seemed of some interest in so far as it could provide information on the nature of adsorbed species and adsorption mechanisms.

In a previous paper (6), some of us were able to distinguish a water phase reversibly adsorbed at room temperature on surface hydroxyls from water that chemisorbs on the bare surface. All of the available data also seem to suggest that water chemisorption may occur in several forms, before a multilayer physical adsorption begins.

Special care has been devoted to the ad-

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sorption in the submonolayer region and infrared spectroscopy has been used together with calorimetry to understand which species are formed and what is the influence of hydroxyl concentration on the heats of adsorption.

EXPERIMENTAL METHODS

Eta-alumina was prepared following the method proposed by McIver, Tobin and Barth (1). The surface area was 220 m²/g and the *t*-plot method indicated the absence of microporosity. These and other characteristics have been described in a previous paper (6).

The calorimetric technique and apparatus have been previously described (6). Small doses of water vapor were volumetrically determined and allowed to adsorb onto the sample placed in a Tian-Calvet differential microcalorimeter. The experiments have been carried out using a number of very small doses (about 30 per run) and stopping the adsorption runs at $p/p_0 = \sim 0.2$ in order to prevent secondary effects due to the meso-porous structure of the adsorbent. Water pressures were read on a Pirani gauge calibrated for water vapor in the 1×10^{-4} - 1×10^{-1} Torr range and on an oil manometer at pressures up to ~ 5 Torr. All untreated samples were

hydrated at 500°C in the vacuum system and then dehydrated for ~ 12 hr at various temperatures, which will be hereafter indicated with a number following the greek letter η (e.g., η -740 means a sample of η -alumina that was rehydrated at 500°C and dehydrated at 740°C). The highest dehydration temperature used was 740°C in that it is still far enough from the η - θ transformation point to preserve the η -form and corresponds to an almost complete surface dehydroxylation.

Owing to the important role played by the data relative to the adsorption on the material pumped off at room temperature (shown below) data corresponding to η -25 were obtained on averaging the results of several runs.

The samples for the ir determinations were prepared by compressing into thin pellets under a pressure of 130–180 kg/cm² some 60–80 mg of alumina from the same batch as used for the microcalorimetric experiments. The pellets were placed in *in situ* cells, previously described (8), and underwent thermal treatments as similar as possible to the ones carried out in the calorimetric cells. The infrared spectra were recorded on a Beckman ir 12 double beam spectrometer, flushed with dry air to optimize the working conditions in the spectral regions of interest in which the presence of atmospheric humidity might cause poor reproducibility and background overlapping.

RESULTS AND DISCUSSION

Calorimetric Measurements

Figure 1 shows regular isotherms ($\mu\text{moles m}^{-2}$ vs p/p_0) and "calorimetric" isotherms (cal m^{-2} vs p/p_0) relative to the adsorption of water vapor on samples out-gassed at various temperatures. Whatever the pressure, adsorbed amounts N_a and evolved integral heats Q^{int} grow with increasing dehydration temperature owing to the removal of ever larger amounts of surface hydroxyls. All curves exhibit a constant shape and their final sections are fairly parallel. Two ranges are distin-

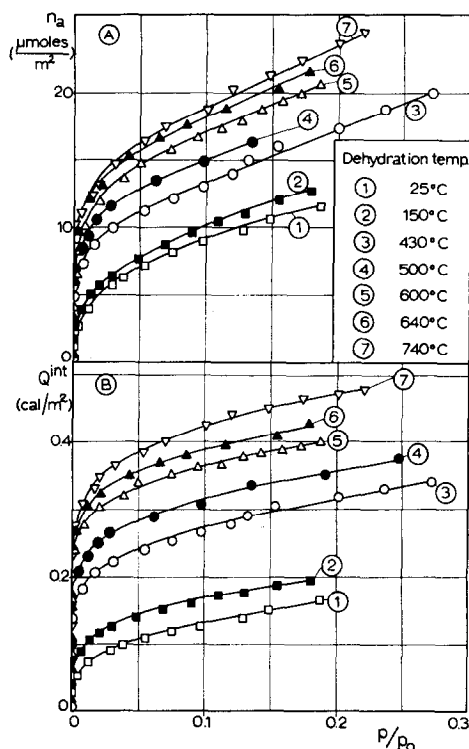


FIG. 1. Adsorption isotherms (A) and "calorimetric" adsorption isotherms (B) of water vapor on η -alumina dehydrated at various temperatures. (1, 2, 3 and 7) Taken from Ref. (6).

guishable. The first, characterized by non-detectable equilibrium pressures, probably corresponds to a chemisorption onto sites of surface unsaturation. The second, characterized by the appearance of an equilibrium pressure, mainly corresponds to the creation of a physically adsorbed layer, even though at the beginning of this second range, the two phenomena probably coexist. On passing from one range to the other a relevant change in the adsorption kinetics occurs, revealed by a different shape of heat evolution peaks: peaks due to chemisorption are typical of activated phenomena, while in the pressure-dependent range heat evolutions are practically instantaneous.

From the end of the chemisorption process and for every higher pressure, the isotherms relative to increasing dehydration temperatures exhibit displacements on the

TABLE 1
HEATS OF ADSORPTION OF WATER ON η -ALUMINA AT 25°C AND RELATED DATA^a

T_i (°C)	$Q_{(T_i)}$ (cal/m ²)	$N_{a(T_i)}$ (μ moles/ m ²)	$Q_{(T_i)} -$ $Q_{(25)}$ (cal/m ²)	$N_{a(T_i)} -$ $N_{a(25)}$ (μ moles/m ²)	$\bar{q}_{(T_i)} =$ $\frac{Q_{(T_i)} - Q_{(25)}}{N_{a(T_i)} - N_{a(25)}}$ (kcal/mole)	$\Delta Q_{(T_i)}$ $Q_{(T_i)} - Q_{(T_{i-1})}$ (cal/m ²)	$\Delta N_{a(T_i)}$ $N_{a(T_i)} -$ $N_{a(T_{i-1})}$ (μ moles/m ²)
740	0.423	19.3	0.291	10.2	27.4	—	—
640	0.392	18.5	0.260	9.4	31.2	0.031	0.8
600	0.368	17.3	0.236	8.2	31.7	0.024	1.2
500	0.314	14.8	0.182	5.7	28.8	0.054	2.5
430	0.264	13.3	0.132	4.2	27.7	0.050	1.5
150	0.169	10.4	0.037	1.4	28.6	0.095	2.9
25	0.132	9.1	—	—	—	0.037	1.4

^a T_i = dehydration temperature; $Q_{(T_i)}$ = integral heat evolved up to $p/p_0 = 0.1$; $N_{a(T_i)}$ = amounts adsorbed up to $p/p_0 = 0.1$; $\bar{q}_{(T_i)}$ = mean irreversible chemisorption heat.

ordinate scale proportional to the increment of chemisorbed amounts and heats evolved. These amounts, termed ΔN_a and ΔQ^{int} are reported in columns 7 and 8 in Table 1, which summarizes some of the aspects of the adsorption process.

All the data have been calculated at $p/p_0 = 0.1$, i.e., at a pressure at which the first physically adsorbed layer is likely to be complete (3) and chemisorption processes are largely over as revealed by the absence of any slow kinetic mechanism. In columns 2 and 3 integral values are reported, while in columns 4 and 5 the reversible fractions [i.e., $N_{a(25)}$ and $Q_{(25)}^{int}$] have been subtracted, in order to isolate real chemisorptive contributions. A difference between re-adsorbed amounts (column 5) and desorbed quantities measured by other authors (1) can be observed. This difference decreases with increasing dehydration temperature and cancels out on samples dehydrated at 740°C where the adsorbed quantity nearly corresponds to the total rehydroxylation of the (111) face of the spinel structure. Mean chemisorption heats (column 6) do not show any particular dependence on dehydration temperature and range between 27 and 33 kcal/mole. This result agrees with the linearity of heats of immersion against water content (over a wide range of dehydration temperatures) found by McIver, Tobin and Barth (1) on eta-alumina. The mean heat on the η -150 sample seems very

high: errors connected with evaluation of adsorbed amounts, which in the particular case of η -150 are likely to be quite high, could possibly account for this. However, it must be noticed that experiments carried out at different adsorption temperatures[‡] confirm that the adsorbed species reversible at 150°C involve exceptionally high heat values.

While these data indicate a relative independence of the whole process on dehydration temperature, the trends of integral and differential heats with coverage on each sample (Fig. 2) show a strong heterogeneity as regards water adsorption sites. Differential heats steeply decrease at low coverages and approach the water vapor condensation heat around the completion of the first physically adsorbed layer. In particular they all show an exponential dependence on coverage made up of two exponential branches characterized by different slopes, as discussed elsewhere (9).

As higher dehydration temperatures cause higher amounts to be chemisorbed, differential heats attain their constant value (condensation heat) at different coverages. They all show the same trend and extrapolated initial values reported in Table 2, are fairly similar except for

[‡] Experiments are being carried out in our respective institutes dealing with the adsorption of several other molecules at various temperatures on eta and other aluminas.

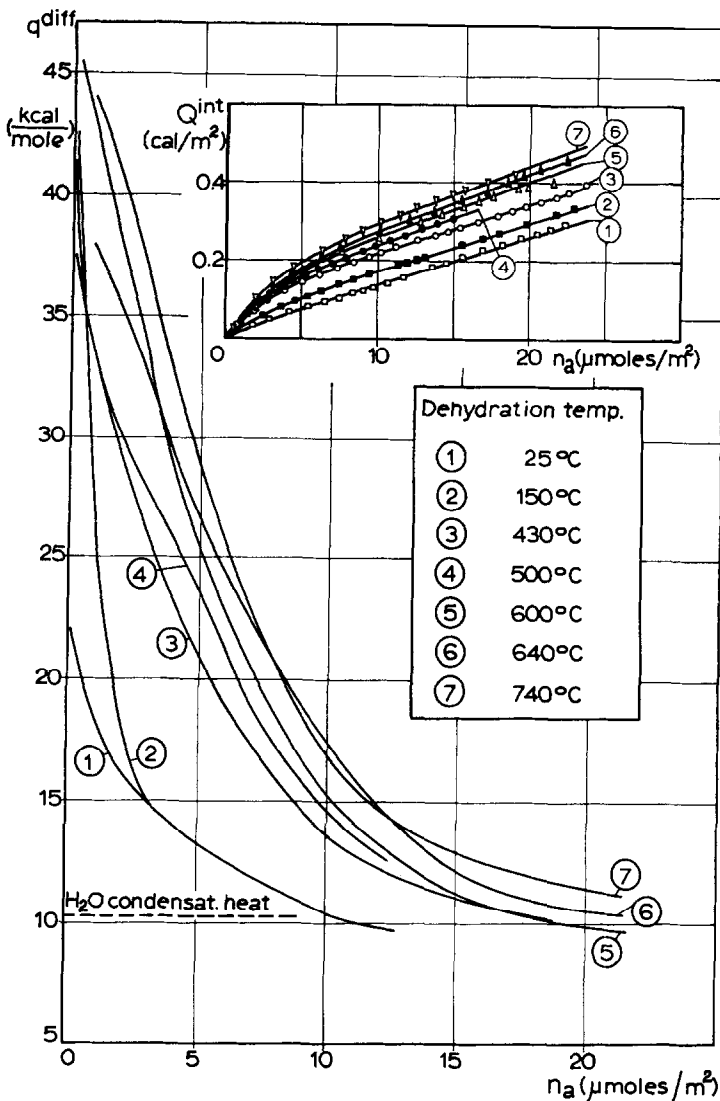


FIG. 2. Integral and differential heats of adsorption of water vapor on η -alumina dehydrated at various temperatures. Differential heats are represented as continuous lines as they were obtained by computer derivation of the whole integral heat curves (9). (1, 2, 3 and 7) Taken from Ref. (6).

TABLE 2
INITIAL DIFFERENTIAL HEATS

Dehydration temp (°C)	Extrapolated differential heat (kcal/mole)
150	42
430	38
500	43
600	48
640	45
740	51

η -25,** even though a slight increase with dehydration temperature can be observed.

Although they are of the same order of magnitude as experimental errors, the differences could be meaningful and suggest that small fractions of higher energy sites

** Differential heat curves of η -25, representing just the physical adsorption, have been discussed elsewhere (3, 6). Initial values are lower, but the trend is still exponential and almost entirely consist of the second branch.

may be produced with increasing dehydration temperatures. Whether this change of initial heats is real or fortuitous, the most relevant feature is that the site energy distribution is basically the same for adsorption on differently treated samples, in agreement with the mean values of Table 1.

The experimental data described above confirm that the degree of surface dehydroxylation is dependent on outgassing temperature, as already observed (1, 6).

As every outgassing run lasted long enough to reach equilibrium it may be inferred that, as the hydroxyl concentration decreases, larger and larger energies are required to remove the hydroxyls still present on the surface. On adsorption, on the contrary, such energies are not given back: from heat data analysis it is deduced that for every outgassing temperature, the surface situation is the same from a qualitative point of view (i.e., the site energy distribution is much the same), while the number of sites is different. It is most probable that adsorption and desorption follow different pathways. At the later dehydration stages the surface has isolated hydroxyls, whose migration is needed to evolve water: the outgassing temperature must therefore be increased to obtain higher surface clearing. Adsorption, on the other hand, occurs through hydroxyl couples. A surface model should be considered to account for the fact that higher dehydration temperatures only create more

sites, and not more energetic configurations.

From the data of Table 1 one may obtain an integral heat curve of "virtual" adsorption, i.e., the curve that would be obtained, if the sites were occupied in an exactly reverse order to that in which they were produced. The graph reported in Fig. 3 (full round points) was drawn plotting points whose coordinates are: $N_{a(740)} - N_{a(T_i)}$, i.e., the difference between adsorbed quantities on η -740 and on samples dehydrated at the various temperatures employed, and $Q_{(740)}^{int} - Q_{(T_i)}^{int}$, i.e., the difference of relative heats. The plot passes through the origin and is fairly linear, with a slope of about 28 kcal/mole in good agreement with mean adsorption heats of Table 1. Such linearity is probably the most striking evidence of the constant site energy distribution with varying dehydration temperature. In Fig. 3 the integral heat plot on η -740 has been reported in order to emphasize how, within a single chemisorption run, site heterogeneity is indeed revealed. In fact it can be noted that up to a certain coverage the η -740 curve lies above the curve of "virtual" adsorption and that the two plots cross at a coverage of about $10 \mu\text{moles}/\text{m}^2$, in good agreement with the quantity needed to rebuild the surface hydroxyls layer. This means that, even if there is a site distribution that is much the same on every sample, the first water molecules adsorb onto more energetic sites so that, for any

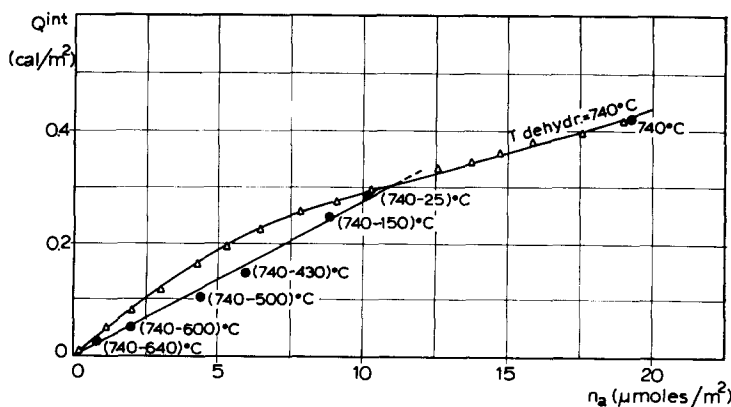


FIG. 3. Integral heats of adsorption on η -740 (Δ) (curve 7, Fig. 2) compared with integral heats of "virtual" adsorption (\bullet).

coverage before the two curves cross, the total heat evolved on η -740 is larger than the corresponding virtual heat. As a consequence, differential heats decrease at increasing coverages.

Figure 3 summarizes the two main aspects evidenced by the calorimetric data, i.e., the homogeneity in site distribution on different parts of surface freed from surface hydroxyls at different temperatures, and the heterogeneity of the adsorption process onto every single part. As a matter of fact, this homogeneity is rather puzzling, and a satisfactory explanation is not easily found. On one hand a surface structural modification could be the cause; occurring during thermal dehydration, it would produce at any temperature the same site distribution, no matter how many surface hydroxyls had been removed. On the other hand one could suggest some sort of "blindness" of water in revealing different site configurations, owing perhaps to the high number of hydrogen bonds likely to be created on adsorption. Nevertheless, within any part of the surface the adsorption process is heterogeneous, as revealed by the decrease of differential heats with coverage; this could be tentatively ascribed to repulsion effects among surface species. Lateral repulsions are usually associated with linear heat decreases (as in the Temkin isotherm) and in fact linear falls in differential heats have been found for systems like water-amorphous silica (10) in the reversible adsorption range. Our differential heat curves have steeper slopes (in fact they are exponential curves instead of straight lines both in the chemisorption and physical adsorption ranges). A possible explanation is that, compared with amorphous silica, stronger repulsions among both hydroxyls and water molecules are present here, because of their higher surface concentration on eta-alumina.

Infrared Spectra

Figure 4A shows the spectra in the 3850–3250 cm^{-1} region of a sample rehydrated at 500°C, and further dehydrated

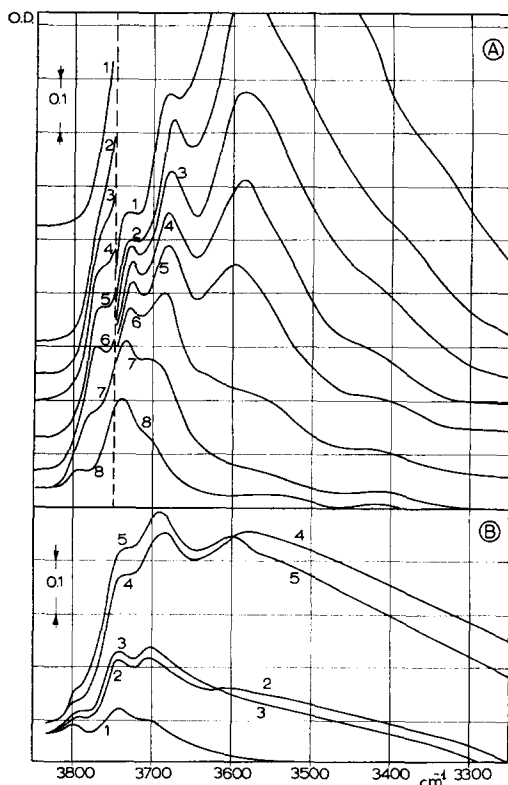


FIG. 4. Infrared spectra of eta-alumina in the OH stretching region. (A) Dehydration: (1–8) after dehydration at the following temperatures (°C): 25, 100, 200, 300, 400, 500, 600, 740; (B) rehydration: (1) sample dehydrated at 740°C; (2) after the first addition of water ($1 \mu\text{mole}/\text{m}^2$); (3) after evacuation at 180°C; (4) after the second addition of water ($3.5 \mu\text{moles}/\text{m}^2$); (5) after evacuation at 180°C.

at various temperatures, up to 740°C, while Fig. 5A shows the 1800–1350 cm^{-1} region spectra of the same sample in equilibrium with 14 Torr of water and dehydrated at 25, 100, 200 and 400°C.

It can be immediately observed that:

1. The existence of a thick layer of physically adsorbed water is clearly evidenced, in spectrum 1 of Fig. 5A, by the strong broad band centered at $\sim 1640 \text{ cm}^{-1}$ (hereafter termed the 1640 cm^{-1} band, although its real position is slightly variable, due to broadness) easily assignable to the "scissors" bending mode of molecular water. It is noteworthy that, in spite of the high water pressure ($p/p_0 \cong 0.5$), a shoulder is clearly seen at $\sim 3700 \text{ cm}^{-1}$

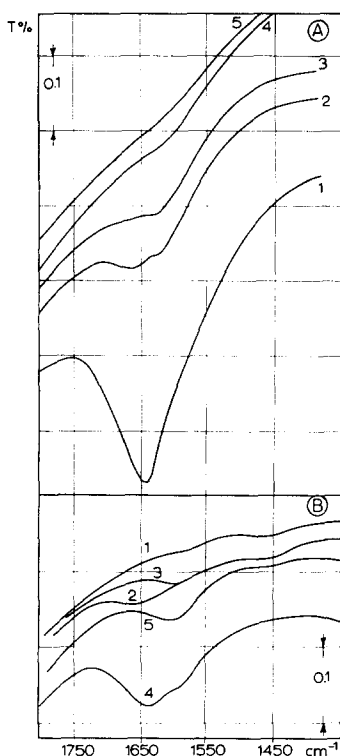


Fig. 5. Infrared spectra of eta-alumina in the water bending region. (A) Dehydration: (1) in equilibrium with 14 Torr of water; (2-5) after dehydration at the following temperatures ($^{\circ}\text{C}$): 25, 100, 200, 500; (B) rehydration: (1) sample dehydrated at 740°C ; (2) after the first addition of water ($1\ \mu\text{mole}/\text{m}^2$); (3) after evacuation at 180°C ; (4) after the second addition of water ($3.5\ \mu\text{moles}/\text{m}^2$); (5) after evacuation at 180°C .

(the relevant curve is not reported in Fig. 4A), i.e., in a spectral position typical of nonhydrogen-bonded hydroxyls.

2. Degassing temperatures of 25 and 100°C are not high enough to destroy the $1640\ \text{cm}^{-1}$ band completely, while no molecular water is left after dehydrating at 200°C (separate experiments showed that at 150°C the $1640\ \text{cm}^{-1}$ band is eliminated in a few hours). The dehydration at 25°C has already provided evidence of at least two bands probably ascribable to nonhydrogen-bonded hydroxyls, at 3690 and $3730\ \text{cm}^{-1}$, respectively.

3. A dehydration at 740°C does not cause the complete destruction of the layer of surface hydroxyls, even though both

their residual spectral intensity and quantitative data from other sources (1, 5) suggest a residual concentration not higher than 5-10%.

4. Dehydration stages between 25 and 740°C show that surface hydroxyls are strongly heterogeneous, unlike the situation observed in the case of other oxides like silica gel and magnesium oxide. This heterogeneity can be summarized through the identification of O-H stretching frequencies and temperature ranges of existence as follows:

a. A band, broad and unresolved with no apparent maximum and probably complex in structure, ranging down to $3000\ \text{cm}^{-1}$ is clearly assignable to the stretching modes of hydrogen-bonded hydroxyls. (Note that, as usual, it is impossible to distinguish between perturbed individual hydroxyls and hydrogen-bonded undissociated water.) This absorption is eliminated between 400 and 500°C , no discrete components being apparent at any dehydration stage.

b. A band of medium broadness ($\Delta\tilde{\nu}_{1/2} \cong 80-100\ \text{cm}^{-1}$) is visible at $3590\ \text{cm}^{-1}$ after dehydration at room temperature, despite its strong intensity, and following a gradual shift to $3600\ \text{cm}^{-1}$ is eliminated upon degassing at 500°C .

c. An absorption, already visible as a shoulder at $\sim 3700\ \text{cm}^{-1}$ in the presence of high water vapor pressures, is evident on evacuation as a discrete band centered at $3690\ \text{cm}^{-1}$ ($\Delta\tilde{\nu}_{1/2} \cong 50\ \text{cm}^{-1}$). It either grows somewhat or remains constant on dehydration up to 300°C , and then declines, disappearing above 700°C .

d. A sharper band ($\Delta\tilde{\nu}_{1/2} \cong 40\ \text{cm}^{-1}$) is first revealed at about $3730\ \text{cm}^{-1}$ upon evacuation at room temperature. It remains fairly weak and, in spite of the strong overlapping of adjoining bands, does not seem to decrease much in intensity on dehydration at higher temperatures. In practice it is the only species appreciably present after degassing above 700°C .

e. A sharp peak, centered at $3775-3780\ \text{cm}^{-1}$, exhibits a fairly variable intensity from sample to sample and from one experiment to another. When present, it

grows on dehydration between 100 and 500°C and disappears above 600°C.

f. A band is present at 3800 cm^{-1} , with a steady weak intensity, for dehydration temperatures from 500°C upwards. Not even a shoulder is visible at 3800 cm^{-1} for degassing temperatures lower than 400–500°C. If the curves 1–6 of Fig. 4A were not shifted upwards, as they are in the 3750–3850 cm^{-1} range, they would “cut” the 3800 cm^{-1} band of curve 8, showing that no contribution of this band exists for dehydration temperatures lower than 500°C.

Several experiments have also been carried out, in which variously dehydrated samples were rehydrated at room temperature. Among them, the rehydration run of an almost completely dehydroxylated pellet has seemed to us particularly meaningful. Some data, relative to the first water adsorption stages are reported in Figs. 4B and 5B. The most remarkable results are:

1. When the first small doses of water have been adsorbed, i.e., at the very beginning of the rehydration process, some undissociated water is already present, as revealed by the 1640 cm^{-1} band; this is not eliminated on evacuation at room temperature but readily desorbs between 100 and 200°C. Note that, even after the complete removal of the 1640 cm^{-1} band, the spectrum does not coincide with the base line relative to the dehydrated sample, as the increased surface hydroxylation brings about a background lowering all over the spectrum.

2. The reconstruction of the surface hydroxyl layer does not follow the same course as the dehydration. In fact the 4000–3000 cm^{-1} region spectra of Fig. 4B exhibit a poorer variety of components, than do the spectra of Fig. 4A. In particular it can be noted that:

- a. The broad and unresolved band below 3600 cm^{-1} starts growing in the earliest rehydration stages.

- b. The band at 3690 cm^{-1} is the only high frequency hydroxyl species clearly caused to increase by the first water doses.

- c. The other hydroxyl species, still present after degassing, are differently affected

by the beginning of the rehydration process. In fact the 3800 cm^{-1} band is scarcely perturbed, the 3730 cm^{-1} band is either slightly increased or unchanged and the 3780 cm^{-1} band, when present on samples dehydrated at lower temperatures (see footnote **), is immediately perturbed and displaced.

- d. After each water addition, a degassing at 150–180°C, whose major effect is the removal of undissociated water, brings about a decrease of the broad absorption below 3600 cm^{-1} . (Note that also in this case no discrete components of the band are evident.) Meanwhile, a general increase of intensity is observed in the “free” hydroxyl region, above 3600 cm^{-1} .

- e. As larger and larger amounts of water are adsorbed, all hydroxyl species are involved in hydrogen bonding, leading to a spectrum practically indistinguishable from that of the starting material, both in the 4000–3000 cm^{-1} region and around 1600 cm^{-1} . Nevertheless a further dehydration at increasing temperatures of the rehydrated sample does not retrace all the steps already outlined when discussing Fig. 4A (see footnote **).

The most remarkable result to be shown by the dehydration–rehydration experiments is that, in spite of the very different temperatures at which surface species are eliminated upon degassing, the rehydration at room temperature already involves in the earliest stages the formation of both hydroxyls and undissociated water. This phenomenon has been already observed, for example during the rehydration of titania (11, 12) but in that case the undissociated species exhibited a much higher stability than in the present case. Even though it is difficult to run good infrared spectra of highly hydrated materials, the above result has been confirmed for samples dehydrated at any temperature from 150°C upwards. We therefore conclude that rehydration always proceeds through a dissociative mechanism and a “coordinative” mechanism acting simultaneously and independently, and that the higher the dehydration temperature, the lower the percentage importance of the latter mech-

anism. In fact the nonreversible fraction (at room temperature) of the 1640 cm^{-1} band is largely independent of dehydration temperature. On the other hand, calorimetric data reported in the previous chapter showed that the mean integral heats of rehydration are fairly constant on varying the thermal dehydration conditions. These results seem to lead to a rather unexpected conclusion, namely that the two rehydration mechanisms do not involve highly different energies. All we can add at this point is that the heats of a dissociative chemisorption and of a nondissociative coordination, though individually quite different, could be somehow "balanced" by the secondary formation of strong lateral interactions of the hydrogen-bonding type.

However, the major difference between the two experimental techniques employed is quite evident in this case: while ir spectroscopy tends to emphasize even the smallest heterogeneity (see, for example, the variety of species and spectral shifts in the graphs of Fig. 4A), an "averaged" information is normally obtained from the calorimetric approach.

In view of the high sensitivity of the spectroscopic technique to heterogeneity, we think that the decreased complexity of rehydration spectra, in comparison with the dehydration pattern, lends some support to the hypothesis of a surface rearrangement taking place during thermal removal of surface water.

CONCLUSION

Infrared data clearly show that in the rehydration process at room temperature the creation of an undissociated water phase is already involved in the earliest stages. Parallel to it, there occurs a dissociative mechanism, which is heterogeneous in nature and leads to the simultaneous formation of various hydroxyl species. Calorimetric data are therefore made up of contributions coming from all the processes. The strong heterogeneity revealed by the fast decrease of differential heats must therefore be ascribed to coverage related effects and not to a separation

of the various processes contributing to the reconstruction of the surface layer.

The two mechanisms (dissociative and "coordinative") spectroscopically reveal a variable percentage importance with varying dehydration temperature, but do not lead to a change of mean rehydration heats. On the other hand, the differential heat plots seem to confirm that the two mechanisms do not involve greatly different energies and that the "coordinative" adsorption heats fall well within the spectrum of dissociative chemisorption heats.

A fairly good constancy has been deduced for the site energies distribution on varying the dehydration temperature. In this respect several factors that may contribute to such a result should be considered, particularly:

a. The dehydroxylation process involves, from a certain dehydration stage onwards, hydroxyls originally far apart and possibly located in different configurations, while the rehydroxylation process always proceeds through the creation of a pair of mutually perturbing hydroxyls.

b. Proceeding dehydration probably causes a gradual surface rearrangement, minimizing multiplicity and degree of uncoordination of sites, as can also be proved by the use of other adsorbed molecules (see footnote **).

c. The energy of dissociative chemisorption is not merely due to the interaction of a water molecule with a surface anion-cation couple, but also includes contributions from the formation of hydrogen bonds and other lateral interactions which can balance energy differences among sites. Note that, after a dehydration at the higher temperatures, when a production of high energy sites is to be expected, the formation of hydrogen bonds between newly formed and pre-existing hydroxyls becomes less probable.

The advantage of combining the two techniques is quite obvious. Calorimetric data reveal a striking independence of surface heterogeneity with respect to dehydration temperature and infrared data both confirm this and are of vital importance to distinguish various surface mechanisms.

Finally, we would like to emphasize the peculiar character of water as an adsorbate which, through the formation of many different species and of strong lateral interactions, at any coverage involves practically the whole surface. Therefore, the independence of surface heterogeneity on dehydration conditions observed here is unlikely to manifest itself with other molecules.

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