

Application of Nuclear Magnetic Resonance to the Study of the Superficial Constitutive Water of Anatase

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The superficial constitutive water of anatase has been studied by NMR in "rigid-lattice" conditions. Spectral interpretation by shape function calculation leads to a distribution of protons between molecular water and OH groups and to characteristic distances between protons. OH groups cover all the available surface of the most hydrated sample and the water molecules are attached to the OH groups. Models of the coverage of the principal surface planes are studied by associating the NMR results with reasonable assumptions concerning the physicochemical properties of these planes. The (001) plane is the most prevalent. The OH groups occupy two different sites corresponding to overall charges of opposite sign. A description of the dehydration mechanism has been tested by considering the behaviour of the model in terms of the total equivalent concentration of water.

Introduction

The superficial constitutive water of solids of large specific area such as the oxides of silicon, aluminum and titanium, silicoaluminas, zeolites, etc., can have an important bearing upon their physicochemical behavior. In particular, it may be related to their catalytic activity.

¹H NMR constitutes a valuable method for studying the superficial constitutive water even when this method is limited to the "rigid-lattice" case. Then, the principal effect is dipolar interaction between spins, described in classical papers (1-6) concerned with crystals. However, since the first work on silica (7) and silica-alumina (8) few studies have been carried out on the constitutive water of solids of high specific area. Freude *et al.* (9) calculated the line

shape of ¹H spectra of OH groups diluted on solid surfaces. Moreover, there are two reports based on the measurement of the second moment M_2 of proton signals: Stevenson (10) calculated the Al-H distances in Y-zeolites, and one of us proposed a distribution of the H atoms in silica gels (11). The relative concentrations of hydrogen in different groups (OH, H₂O, etc.) can be determined quite well by this first approach, but a spatial distribution of these groups cannot be obtained. Recently we studied the superficial constitutive water of rutile, and calculated the shape functions of the spectra (12). We apply the same method here to the interpretation of the spectra of anatase. From the parameters retained for the calculated spectra we can propose for each dehydration temperature a probable H atom distribution between

OH groups and water molecules, as well as the corresponding proton-proton distances.

Independently, knowing the positions of the heavy atoms on each possible plane of the surface, we can make reasonable hypotheses for the location of the OH groups and the water molecules on this surface; these lead to coverage patterns and dehydration models which we adopt on condition that they agree with the NMR results. The interest of the information thus obtained is evident in that two of us have observed that the degree of anatase dehydration is related to the catalytic activity of this surface in the dehydration of formic acid (13).

Experimental

The anatase used was prepared from TiCl_4 in a flame reactor (14-16).¹ The mean diameter of the nonporous particles is about 6 nm. The specific area ($320 \text{ m}^2 \text{ g}^{-1}$) is the same for all the samples considered here, which were treated at 10^{-4} Torr at temperatures between 22 and 395°C . Each sample will be designated as A_x , where x represents the approximate water content expressed as the equivalent number of water molecules per square nanometer of the sample surface.

According to Primet *et al.* (17-19), all the H_2O and OH groups of anatase are accessible to D_2O vapor and are therefore located on the surface. The spectra were recorded at 100 K on a Bruker CXP apparatus at 95 MHz. The powder samples are contained in 10-mm tubes. Each spectrum corresponds to 1000 accumulations and the signal/noise ratio is between 100 and 20 depending on the extent of dehydration. The experimental spectra are symmetrized hand-drawn copies (about 140 points per curve).

¹ We thank the laboratory of Professor S. Teichner at the "Université Claude Bernard," Lyon for preparing the anatase.

Shape Function Calculation

For the more hydrated samples the superficial constitutive water of active solids is present usually in the form of OH groups and water molecules. We discussed previously why we proposed to use the magnetic configuration of three protons situated at the corners of an isosceles triangle (T configuration) to account for the magnetic interactions between protons of OH groups and of water molecules inside one configuration (20, 21). The equations for calculating the shape function are those given by Andrew and Finch (22); they have been recalculated and programmed (20, 23). The base of the triangle represents then the proton-proton distance in a water molecule; a hydrogen atom belonging to an OH group is assumed at the other corner. In the calculation we consider as many groups as possible, limited by the number of water molecules or of OH groups in the formula of the compound. The excess of water molecules or OH groups is usually described by a two-spin configuration, D, calculated by Pake (1); the complete system is denoted T + D.

To take into account interactions between configurations, Gaussian broadening (parameter β) is superposed on the absorption of each configuration assumed to be isolated.

The parameters defining the two-spin configuration, D, are:

$$\alpha_D = 3\mu/2 R_D^3 \quad \text{and} \quad \beta_D = 3\mu/2 X_D^3,$$

μ is the magnetic moment of the proton;
 R_D is the distance between two protons in the configuration;

X_D is a distance whose value is near that of the shortest distance between a H atom of the configuration and a H atom outside it.

The parameters defining the three-spin configuration, T, are:

$$\alpha_T = 3\mu/2 R_T^3, \quad \beta_T = 3\mu/2 X_T^3, \\ \lambda = R'_T/R_T$$

R_T and R'_T are the lengths of the base and of the two other sides, respectively, X_T is a distance whose value is near that of the shortest distance between a H atom belonging to the T configuration and a H atom outside it.

For the less-hydrated samples most of the constitutive water is best described by a Lorentzian absorption curve characterized by ΔL , its half width at half-maximum amplitude. According to the literature, curves of this form in "rigid-lattice" condition account for the random distribution of spins in magnetically diluted systems (9, 24).

A weighting coefficient, w_i , is associated with the contribution of each configuration i so that $\sum w_i = 1$. A least-squares minimization procedure using the Newton coefficients method adjusts the parameters to fit the calculated spectra to the experimental ones.

A model is acceptable only if the parameters conserve geometrical and physical significance relative to the chosen con-

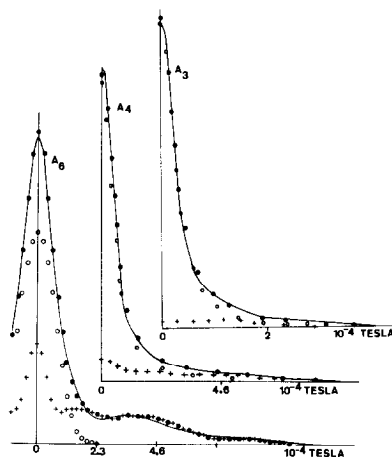


FIG. 2. Half-absorption curves for some anatase samples: (—) experimental spectrum, (●●●) computed curve. The other signs represent partial computed contribution of: for A_6 , (+ + +) T, (○ ○ ○) D; for A_4 , (+ + +) T, (○ ○ ○) D; for A_3 , (+ + +) D, (○ ○ ○) Lorentzian absorption curve.

figurations, for example $R \leq X$. The precision relative to each of the T + D model independent parameters is as follows, w_T : ± 0.01 , R_T : ± 0.002 nm, X_T : ± 0.005 nm, $\lambda = \pm 0.05$, R_D : ± 0.003 nm, X_D : ± 0.005 nm.

NMR Results

Since the experimental spectra were identical at 130 and 100 K we assume that the lattice is "rigid." For each degree of hydration of anatase we calculated an acceptable spectrum simulating the experimental one (Figs. 1 and 2). The values of the NMR parameters for the models are presented in Table I.

Table I is self-explanatory, and will not be discussed in detail. Consider for example the case of A_6 : 71% of the protons are distributed as isosceles triangles, the length of whose base, 0.158 nm, characterizes the protons belonging to water molecules. The equal sides of the triangle, 0.252 nm, correspond to a distance such that the apical proton is that of an OH group. The protons which do not take part in the triangular

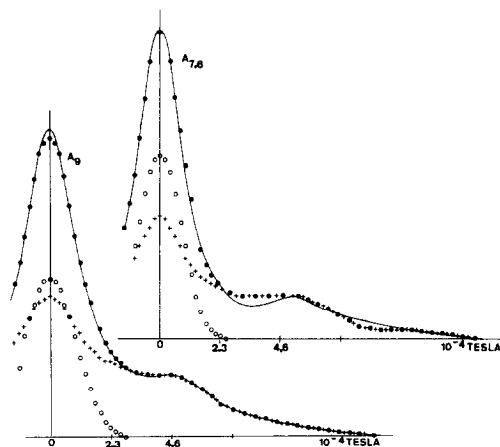


FIG. 1. Half-absorption curves for some anatase samples: (—) experimental spectrum, (●●●) computed curve, (+ + +) weighted computed contribution of configuration T, (○ ○ ○) weighted computed contribution of configuration D.

TABLE I
DISTRIBUTION OF PROTONS BETWEEN THE DIFFERENT MAGNETIC CONFIGURATIONS AND CHARACTERISTICS OF THESE CONFIGURATIONS FROM THE INTERPRETATION OF NMR SPECTRA

Symbol	w_T	R_T (nm)	R'_T (nm)	X_T (nm)	λ_T	w_D	R_D (nm)	X_D (nm)	β_T/α_T	β_D/α_D	w_L	ΔL (10^{-4} Tesla)
A_9	0.71	0.158	0.252	0.285	1.6	0.29	0.306	0.307	0.169	0.99		
$A_{7,6}$	0.64	0.156	0.257	0.315	1.65	0.36	0.320	0.340	0.121	0.83		
A_6	0.53	0.164	0.263	0.392	1.6	0.47	0.348	0.350	0.073	0.99		
A_4	0.2	0.164	0.262	0.385	1.6				0.08		0.8	0.5
A_3						0.1	0.240	0.40		0.22	0.9	0.3
$A_{1,6}$						0.55	0.22	0.30		0.39	0.45	0.4

configurations, that is 29%, are about 0.306 nm away. The shortest distances outside the configurations considered, X_T and X_D , measure 0.285 and 0.307 nm, respectively: the difference between them is small. In short, two out of three protons in each T configuration, that is 48%, belong to water molecules; all the others are in the form of OH groups. The number of OH groups per square nanometer of the surface of A_9 is thus 9.34. Assuming that only the OH groups occupy the anatase surface to the exclusion of water molecules, the mean size of each OH group is 0.107 nm². Now the theoretical size of an OH group situated on the surface of a solid has been estimated as 0.127 nm² (25). Given the hypothesis regarding the coverage of A_9 which we have made, we find therefore a value which is about the same even slightly smaller. Consequently the OH groups cover all the available surface and the water molecules must be considered as attached to the OH groups.

For several degrees of hydration, by means of an analysis analogous to that above, the relative proton distribution between water molecules and OH groups can be determined and the latter can be counted according to their distances. For example, from A_9 to A_6 the distances between OH groups increase regularly with the degree of dehydration and on the surface of A_4 13% of the protons remain as molecular water.

In A_4 the protons of OH groups not supporting water molecules are described by a spectrum of Lorentzian form which, as we have already said characterizes diluted spins. Equations have been proposed in the literature to relate the width of such a signal to the superficial spin density (7, 9). The width of the Lorentzian signal decreases from A_4 to A_3 (Table I) as can be expected from an increase in the dilution, but we have not been able to relate these values quantitatively. From A_3 to $A_{1,6}$, on the other hand, the width of the Lorentzian signal increases. The reason for this in-

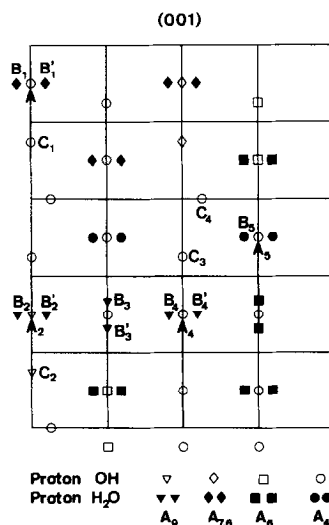


FIG. 3. Protons located on the (001) plane of the anatase surface (extended to 20 unit cells).

crease is the presence of paramagnetic Ti^{3+} sites which have been detected by EPR (13). It can be foreseen that the effect of these sites upon nearby protons will be to broaden considerably the corresponding part of the NMR signal. The same reason is probably responsible for the presence in the $A_{1.6}$ spectrum of a contribution of configuration D with a value R_D of 0.22 nm, probably not significant, smaller than that found in the more hydrated compounds (0.306 nm). This contribution corresponds to 55% of the protons. Ten percent of the A_3 protons are described by a configuration of the same type with an R_D of 0.24 nm, which we assume to be also nonsignificant.

Theoretical Study of the Surface Structure of Anatase and Discussion

In order to represent the geometry of each plane, we have considered it successively:

(i) In an ideal state, without water coverage, but with the stability which would be provided by this coverage. We assume that in the vicinity of each plane there are not only its Ti and O atoms but also bidentate oxygen atoms, that is, bonded to two Ti atoms of the plane and located slightly above it. Further, we assume charge localization such as results from the discontinu-

ity of the crystal at the surface; values are expressed as if the bonds were purely ionic.

(ii) In the real state in the presence of water, the above-described unsaturation of the surface atoms having been compensated by the formation of OH groups within the limit of the crowding allowed: all the possible sites will not necessarily be occupied.

We assume that the coverage obeys the following criteria: electrical neutrality of the surface thus obtained, normal bonds lengths and angles. We have also taken into account the surroundings of each OH group and the orientation of the O-H bonds due to the distribution and the nature of the superficial point charges.

According to the literature (17-19, 26) the external surface of anatase consists essentially of the (001) plane. We have therefore considered this plane but also the (010) and (100) planes, which have the same structure and a high ionic density. In these three planes, the Ti atoms are pentacoordinated to oxygen atoms; they bear therefore a charge of $(+\frac{2}{3})$ with the conventions given above. The O atoms of these three planes, each situated between two Ti atoms, are of two types: (i) One out of two is coordinated only to the two neighboring Ti atoms; it carries a charge of $(-\frac{2}{3})$ and in the case of the (001) plane, is 0.041 nm above the lat-

TABLE II
NUMBER OF WATER MOLECULES AND OH GROUPS PER UNIT CELL (0.143 nm^2) OF THE PLANE (001) OF ANATASE (ASSUMING THAT THIS PLANE CONSTITUTES THE WHOLE SURFACE).

Symbol	Total equivalent water (number of molecules)	Molecular water (number of molecules)	Number of OH groups	Number of OH groups in terms of the smallest proton-proton distances (nm)		
				<0.32	0.34-0.38	≥ 0.38
A_9	1.275	0.603	1.343	1.343	0	0
$A_{7.6}$	1.095	0.467	1.256	1.256	0	0
A_6	0.88	0.311	1.138	0.311	0.827	0
A_4	0.56	0.075	0.97	0.075	0	0.895
A_3	0.45	0	0.9	0.09	0	0.81
$A_{1.6}$	0.23	0	0.46	0.205	0.102	0.153

ter. (ii) The other O atoms are tricoordinated to Ti atoms and are neutral; they are located 0.041 nm below the (001) plane. For the (010) and (100) planes all the surface O atoms lie in the plane.

1. Study of the (001) Plane

Figure 3 shows a possible distribution of the protons by locating the elements of the dissociation of water (OH^- and H^+) on a certain number of unsaturated sites of 20 units of the (001) plane. The number of OH groups is what is found by NMR for A_0 , assuming that the anatase surface consists entirely of the (001) plane (Table II). In this way two types of OH group appear: those fixed on a Ti atom (denoted C_i) carrying an overall charge of $(-\frac{1}{2})$ and those based on an O of the lattice (denoted A_i) carrying an overall charge of $(+\frac{1}{2})$. The water molecules are attached to the OH groups by hydrogen bonds since, as we saw previously, the OH groups found by NMR occupy the surface completely. Moreover, NMR shows that the number of water molecules is about half that of OH. We therefore place a water molecule (whose protons are denoted B_i) preferentially on each positively charged OH of type A_i . Table III and IV include the coordinates of the different protons, relative to a Ti atom considered as the center of four unit cells, and the distances between these protons.

In Table II we give the NMR results for

TABLE III
COORDINATES (IN nm) OF
PROTONS RELATIVE TO A Ti
ATOM BELONGING TO FOUR
CELLS: (001) PLANE OF
ANATASE

A_4	(0.000; 0.189; 0.137)
A_5	(-0.378; -0.189; 0.137)
B_4	(0.075; 0.189; 0.384)
B_5	(-0.303; -0.189; 0.384)
C_3	(0.000; -0.075; 0.255)
C_4	(-0.075; -0.378; 0.255)

TABLE IV
THEORETICAL DISTANCES (IN nm) BETWEEN
PROTONS LOCATED ON THE (001) PLANE OF
ANATASE

C_3-C_4	C_3-C_5	C_3-A_5	C_3-A_4	C_3-B_4	C_4-B_5	C_4-A_5
0.320	0.349	0.410	0.289	0.304	0.324	0.377

the different samples A, relative to a unit cell of the (001) plane, assuming that the anatase surface consists only of this plane. The OH groups there are counted with respect to their distances. Dehydration can then be followed on Fig. 3 up to sample A_4 by using the NMR results. Between A_0 and $A_{7.6}$ about three water molecules of the 20 unit cells represented are eliminated, corresponding for example to the protons BB' labeled 2, 3, and 4 (black triangles). About two OH groups, which we assumed a priori to be neighbors and of opposite charge, are eliminated by condensation, A_2 and C_2 , for example (white triangles). From $A_{7.6}$ to A_6 three water molecules are eliminated (black diamonds) and two OH groups condensed (white diamonds). Between A_6 and A_4 four preexisting water molecules and five OH groups leave the surface (black and white squares, respectively). The loss of OH groups appears to occur always by reaction between neighboring groups of opposite charge. About 20 OH groups and one to two water molecules remain therefore on the 20 schematic unit cells of A_4 .

Beyond A_4 we felt that it was pointless to attempt to continue the representation of the dehydration in the (001) plane because of spectral broadening, mentioned above, first partial then total, probably related to the creation of Ti^{3+} ions.

2. Study of (010) and (100) planes

The (010) and (100) planes which can a priori also make up the anatase surface are dense but not so dense as the (001) plane. Considered as carriers of possible OH

group sites, they appear to consist of zones of the same layout as (001) alternating with zones which are empty of sites. It is therefore difficult, given the same area, to place on them the same number of OH groups as on the (001) plane of A_9 , whose surface was seen to be completely covered by these groups. In fact no theoretical distribution of the OH groups on the (010) and (100) planes seems to agree with that obtained experimentally by NMR. Consideration of these planes was not taken any further.

Conclusion

The method for interpreting the ^1H NMR spectra in a "rigid lattice" by calculating the shape functions, as applied by us to the superficial constitutive water of anatase, gives the distribution of the protons between water molecules and OH groups and also the spread of the latter in terms of the distances between them. The number of OH groups found by NMR for sample A_9 , the most hydrated, shows that they occupy the totality of its surface. The water molecules, half as numerous as the OH groups, are attached to these groups by hydrogen bonds. Comparison of the NMR results with the structure of the possible surface planes shows that the (001) plane is the most prevalent. Maximum packing of the surface at this plane by the OH groups does not permit one OH group to be attached to each possible site; 33% of the latter remain unoccupied. We consider that there are two types of OH group at the surface in equal numbers: those which are bound to Ti atoms bearing a negative overall residual charge; those whose O atoms belong to the lattice—bicoordinated to Ti atoms—have a positive residual charge. We assume that each "positive" OH group in A_9 hydrogen bonds a water molecule.

From the onset of dehydration, preexist-

ing water molecules are eliminated as well as water formed by condensation of OH groups. We suppose that this occurs between neighboring groups of opposite residual charge, thus maintaining the charge equilibrium. There is still molecular water in a sample dehydrated at 190°C and 10^{-4} Torr (A_4).

When dehydration is continued a new event is observed in the NMR spectra, in the form of the broadening of a part of them; we propose that this phenomenon is related to the appearance of Ti^{3+} centers, detected by EPR at a sufficiently high desorption temperature.

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