Structure of alumina surfaces

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The structure of hydroxylated alumina surface is analysed by IR spectroscopy. The variety of OH groups differing in number and coordination of surrounding metal atoms, for the completely hydrated surface, either formed by ideal low-index planes, or complicated by crystal edges and corners or cation vacancies, is restricted to six, but grows dramatically upon dehydroxylation. The results account for the complex structure observed previously in the IR spectra of surface OH groups after high-temperature treatment, and enable us to explain specific properties of transition aluminas.

Although alumina is a very important material for industrial technology, electronics, catalysis *etc.*, even the bulk structure of some alumina and aluminium hydroxide modifications is still under discussion, to say nothing about the structure of their surfaces. In the present paper we review the existing models of alumina surfaces and using most known spectroscopic and structural data about the surface and bulk of the material try to explain the surface properties of transition aluminas, their resemblance and dissimilarity with those of corundum, and of the initial aluminium hydroxides, as well as of the oxides of other elements.

Our knowledge about alumina surfaces, as well as for most other disperse oxides, is based mainly on the results of spectral studies of their hydroxy group cover, the structure of which reflects that of the dehydroxylated active surface of the oxide. As a rule, IR spectra of surface hydroxy groups show a number of narrow bands, the positions of which are very sensitive to the local surroundings of a group; all the existing models of alumina surfaces are based to some degree upon IR spectroscopy data.

There are a great number of studies where the observed spectra of surface hydroxy groups are rationalized starting from various assumptions about factors which determine the number of bands in the stretching OH region. According to Hallam,[1] supplementary bands are due to combinations of the stretching OH vibration with low-frequency modes corresponding to hydrogen bonds between adjacent OH groups. Ref. 2–4 also consider hydrogen bonding to be the only reason for the appearance of additional bands, assigning only the most high-frequency band to isolated hydroxy groups. In ref. 5 and 6 it was assumed that OH groups are bonded to metal atoms in different coordination, and this affects their frequency. Some time ago, the most popular model of the γ-Al₂O₃ surface was that proposed by Peri,[7] who believed that the alumina surface is represented mainly by the (100) face, and that the ν(OH) frequency is determined by the number of surrounding oxygen ions. Despite further improvements *e.g.*, ref. 8, this model could not explain a number of experimental results obtained for alumina, and moreover, it could not be extended to oxides of other elements, or even other faces of spinel aluminas.

Tsyganenko and Filimonov[9⁻11] have proposed a general approach to the interpretation of IR spectra of surface OH groups for oxides with different crystal structures, that did not require the existence of preferential crystal faces and was based on the assumption that the frequency of an isolated OH group is determined primarily by the number and nature of metal atoms bound to it. This idea enabled one to consider together all the data on the OH frequencies of surface hydroxy groups, of bulk OH groups of different materials without hydrogen bonding, and even of gaseous inorganic acids.[12,13] It became possible to elucidate the difference between the IR spectra of hydroxides and surface hydroxy groups, and to follow the regularities in the frequency dependence on the nature of the element or the number of atoms bound to the oxygen atom of the OH group,[13] further supported by the results of quantum-mechanical calculations.[13,14]

According to ref. 10, the total number of OH group types, differing in the number of surrounding metal atoms, for every oxide should be one unit less than the coordination number of oxygen in the bulk crystal lattice. This means that on the surface of practically all the known crystallographic Al₂O₃ modifications, where every oxygen atom is bound to no more than four aluminium atoms, there are only three types of OH group, bound to one, two or three Al atoms. Appearance of additional bands in the spectrum of surface OH groups of alumina can be explained either by hydrogen bonding between adjacent hydroxy groups, if the temperature of preevacuation was not too high, or by different coordination of surface aluminium ions.[10,11]

This approach was successfully applied and developed for γ- and η-Al₂O₃ by Knözinger and Ratnasamy[15] who on the basis of Lippens' data[16] on the alumina surface structure, analysed the position of ions on (111), (110) and (100) faces of the spinel structure and found that there are five types of OH group, type I groups bond to a tetrahedrally (Al$_T$) or octahedrally (Al$_O$) coordinated aluminium atom, type II groups form a bridge between Al$_T$ and Al$_O$ or between two Al$_O$ atoms, and type III groups bond to three Al$_O$ atoms (here, as before[10,11] we refer to the groups bound to one, two and three metal atoms as type I, II and III groups, respectively). These five structures were associated with the five absorption bands observed earlier[17] in the region 3800–3700 cm⁻¹ of the spectrum of γ-Al₂O₃.

This interpretation,[15] although reasonable itself, contains, as we shall see below, certain drawbacks. To say nothing about the details of the surface structures and OH group concentration, later somewhat corrected in ref. 18 and 19, we should note the principal point that the types of OH group considered corresponded to the completely hydroxylated surface, while the IR spectra they were related to had been registered after high-temperature treatment, when the environment of surface hydroxy groups, in particular the coordination of aluminium atoms, was changed.

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Further studies of γ-[20,21], η-[22,23], χ-[24] and θ-[25] alumina modifications have shown that IR spectra of their surface OH groups are in reality even more complicated and contain no less than nine sufficiently well resolved absorption bands of non-associated surface hydroxy groups. The reasons for such a heterogeneity are discussed below, and principles of OH group classification and band assignment, put forward in our earlier paper,[26] are developed. The structure of the alumina surface and the hydroxy cover of the completely hydrated faces and crystal edges are considered based on the analysis of the bulk crystal lattice, IR spectroscopic data and quantum chemical calculations.

The removal of surface OH groups during high-temperature treatment is accompanied by the appearance of coordinatively unsaturated metal ions, that exhibit electron accepting properties, acting as surface Lewis-acid sites, and of coordinatively unsaturated oxygen ions, which act as Lewis-basic sites. As far as the properties of the site, produced by dehydroxylation, are determined by the same local arrangement of surface atoms that governed those of the desorbed OH group, the latter could be considered as one more test molecule for Lewis acidity and basicity, which is sensitive to the strength and geometry of the sites. However, analysis of this problem is beyond the scope of this paper.

Although this paper deals mainly with an alumina surface, the reasons for surface heterogeneity are thought to be the same for most solids, and we believe that the results presented here can be directly applied to other oxides.

Structure of an ideal completely hydroxylated surface of low-index planes

First, let us consider some general regularities resulting from the formal construction of the hydroxy cover model following the procedure described in ref. 9–11. The hydroxylated oxide surface is regarded to be the result of multiple cleavage of a single crystal, followed by saturation of dangling bonds with water molecule fragments, in such a way that oxygen atoms in the formed OH groups will occupy the positions of oxygen atoms in the infinite crystal lattice, and coordination of metal atoms on the hydroxylated surface will be the same as in the bulk crystal.

The procedure has, in general, nothing to do with the real process of the hydrated alumina formation, but is a thought experiment that leads finally to model surface structures, consistent with most of the up-to-date experimental results. The main supposition used here is that the crystal structure, or at least the mutual coordination of atoms, is kept unchanged up to the very surface of the oxide particles. This is enough, however, to draw the first important conclusion that not any number of different types of hydroxy group is possible for such a surface.

If the coordination number of oxygen in the bulk lattice is four, on both sides of the cleft crystal either the type II OH groups will only appear, or equal quantities of types I and III groups. In general, it can be shown[26] that to retain stoichiometry when saturating the surface of a crystal or amorphous oxide particle with certain coordination numbers of metal and oxygen by dissociative adsorption of neutral water molecules, the mean number of metal atoms bound to the oxygen of the surface OH group should be equal to half of the coordination number of the bulk oxygen ions.

In fact, consider the saturation of dangling bonds on the surface of an oxide particle, which contains N formula units of, e.g. Al_2O_3, by k water molecules in such a way that the coordination number of surface metal ions will be the same as in the bulk. If the coordination number of bulk oxygen is n, for aluminium it will be $1.5n$, to retain stoichiometry. Dissociative adsorption of water will give $2k$ OH groups, k of which will be formed from water protons and surface oxygen ions.

Instead of the initial $3N$ oxygen atoms we shall have now $3N - k$ non-protonated bulk oxygens. As a result of all the $2N \times 1.5n$ bonds formed by aluminium ions, $(3N - k)n$ bonds will bind them with the bulk oxygen ions, and the remainder $3nN - (3N - k)n = kn$ bonds will link the aluminium atoms with the $2K$ OH groups. Thus, the mean number of bonds per OH group will be $kn/2k = n/2$.

This rule is not strict for very disperse powders where the number of hydroxy groups arising on intersections of cleaving planes, i.e. on the edges and tops of microcrystals, will be comparable with that for the regular face, or for those oxides where the charge or coordination number of the cations or the concentration of vacancies in the lattice is not constant. The influence of these factors will be analysed separately below.

Thus, on the surface of stoichiometric oxides with a coordination number of oxygen higher than two, OH groups bound to several metal atoms not only can, but have to exist. For this reason, the model of the γ-alumina surface, represented by the (100) plane with type I OH groups only,[7,15] can scarcely be close to reality. Further details arise if we distinguish OH groups bound to different metal atoms. In the spinel lattice each oxygen atom is surrounded by three octahedrally and one tetrahedrally coordinated metal atoms.
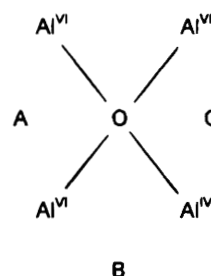
If we do not distinguish between oxygen atoms originated from oxide and those from water molecules, there are three non-equivalent ways of cracking this fragment: (i) removing one Al_O (e.g., plane AB), (ii) one Al_T (plane BC) atom or (iii) cleaving it into two pieces each containing two aluminium atoms, both Al_O or a pair of Al_O and Al_T (e.g., plane AC in our scheme). In each case, after saturating the dangling bonds with H and OH fragments, two different OH groups will appear. In all, each of the three types of OH group will be of two kinds: those that are in contact with Al_O atoms only, and those that have one Al_T in the coordination sphere of oxygen.[10,11] As a result, for a completely hydroxylated surface of alumina with a magnesium spinel structure, the following six kinds of OH group, differing in the number and coordination of metal atoms bonded to oxygen, should exist:
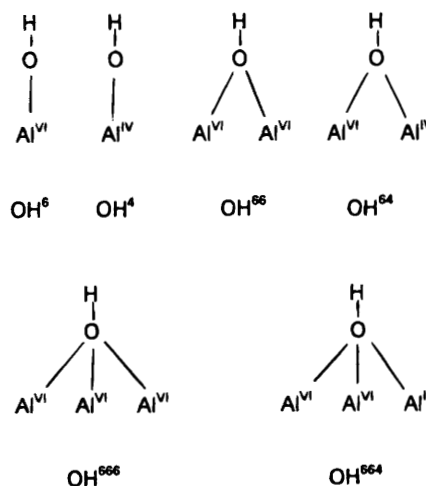
which are denoted as OH^6, OH^4, OH^{66}, OH^{64}, OH^{666} and OH^{664}, respectively. In the denotations used by Knözinger and Ratnasamy,[15] who have not considered the last configuration, these structures correspond to Ib, Ia, IIb, IIa, IIIb and IIIa hydroxy groups respectively.

After cleavage of a crystal and following hydration of the emerging surface, metal atoms, which form the coordination sphere of oxygen, will be divided between two OH groups on the opposite planes of the cleaved crystal. As a result, according to their coordination, these OH groups are somewhat complementary to each other. If there are type OH^6 groups on one side, an equal number of OH^{664} groups should be on the other, the OH^{66} groups correspond to OH^{64}, OH^{666} to OH^4. The surface model, described in ref. 15, when on one side of the hydrated (110) face there are OH^4 and OH^{66} groups (denoted as Ia and IIb, respectively) and only the OH^6 (Ib) groups on another, cannot be constructed by saturation of the cleaved crystal with water molecules and is not plausible.

The model of three main low-index faces for a crystal with a spinel structure, constructed in the above manner, is shown in Fig. 1–3, where both the mutual arrangement of metal–oxygen polyhedra as well as the disposition of OH groups and metal atoms bound to them, are presented. Two different surface structures, denoted following ref. 16 should exist for each of the (111), (110) and (100) faces. Each couple can be considered as two opposite sides of a cleft crystal and contain equal number of hydroxy groups.
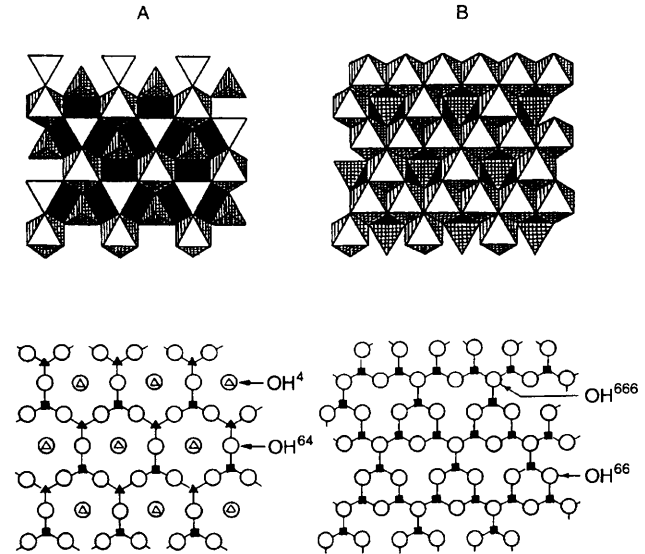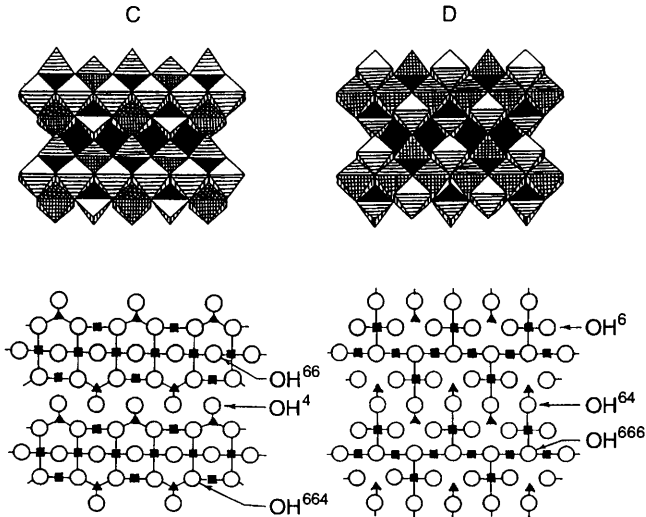

Fig. 2 Model of a completely hydroxylated face (110)C and (110)D, shown as in Fig. 1

Table 1 summarises the calculated total surface concentrations of OH groups, obtained with crystal lattice parameters of γ-Al_2O_3, and the ratio of different types of OH groups for each variant of the faces in question.

Hydroxy groups of the (111) face are formed from the close packed layer of oxygen ions. They lie in one plane and have

Fig. 1 Model of completely hydroxylated faces (111)A and (111)B of a crystal with a spinel structure; above, surface arrangement of metal–oxygen octahedra and tetrahedra; below, the same face fragment with the shown metal–oxygen bonds and local environment of different kinds of OH groups. (▲) Al_T, (■) Al_O; (△) and (□) Al_T and Al_O situated under oxygen atoms; (○) OH groups.
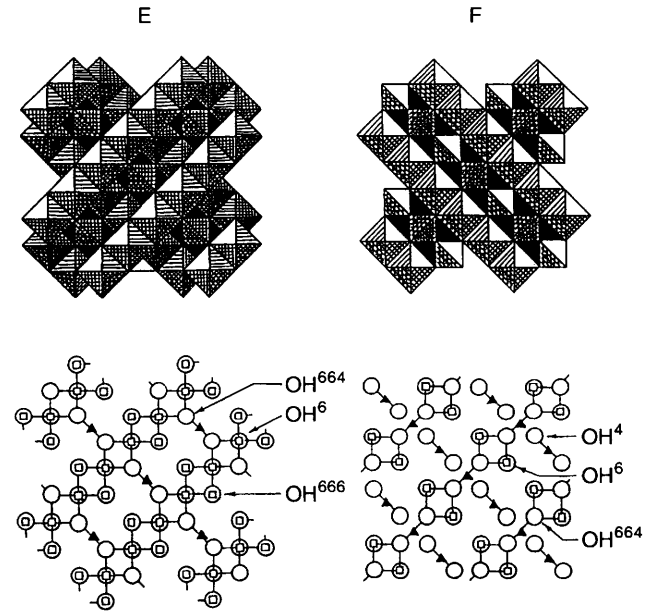
Fig. 3 Model of completely hydroxylated face (100)E and (100)F, shown as in Fig. 1

Table 1 Total coverage Θ and ratio of concentrations for different kinds of OH groups, as well as surface charge for the completely hydroxylated surfaces of γ-alumina and magnesium spinel

			charge per nm^{-2}	
face	Θ/nm^{-2}	concentration ratio	$MgAl_2O_4$ [a]	γ-Al_2O_3
(111)A	14.8	$OH^4 : OH^{64}$ 1 : 3	-1.85	$+1.85$
(111)B	14.8	$OH^{66} : OH^{666}$ 3 : 1	$+1.85$	$+1.85$
(110)C	18.1	$OH^4 : OH^{66} : OH^{664}$ 1 : 1 : 2	$+2.66$	$+5.66$
(110)D	18.1	$OH^6 : OH^{64} : OH^{666}$ 2 : 1 : 1	-2.66	-1.13
(110)neutral	18.1	$OH^6 : OH^4 : OH^{66} : OH^{64} : OH^{666} : OH^{664}$ = 2 : 1 : 1 : 1 : 1 : 2	0.00	$+2.26$
(100)E	19.3	$OH^6 : OH^{664} : OH^{666}$ 1 : 1 : 1	$+3.22$	$+4.82$
(100)F	19.3	$OH^4 : OH^6 : OH^{664}$ 1 : 1 : 1	-3.22	0.00
(100)neutral	19.3	$OH^6 : OH^4 : OH^{666} : OH^{664}$ 1 : 1 : 1 : 1	0.00	$+3.22$

[a] For $MgAl_2O_4$ the lattice parameter a here was taken to be equal to 7.89 Å, as for alumina.

the same surface OH concentration of 14.8 nm^{-2} for both the (111)A and (111)B layers. As can be seen from Fig. 1, type II groups predominate here. Their concentration is three times higher than that of OH^4 groups for the (111)A layer, or that of OH^{666} for (111)B.

Two layers of the (110) face (Fig. 2) contain all the six above mentioned OH groups, possible for the hydroxylated surface of γ-alumina. The presence of geminal OH group pairs is typical for the (110)D face. Rows of these groups protrude over the layer of OH^{64} and OH^{666}. Groups OH^4 and OH^{66} at the (110)C layer also protrude over the plane of the OH^{664} groups; the total OH coverage here is even higher than for the close packed oxygen layer.

Both the two variants of the (100) face have similar rows of OH^6 groups. In one case, as shown before,[10,18] namely (100)E, each aluminium atom bearing such a group is also bound to four type III groups, two OH^{666} and two OH^{664}. In another variant, (100)F, the OH^{666} groups are absent and the place of each pair of such groups is occupied by a tetrahedrally coordinated Al atom which bears a pair of geminal type OH^4 groups. The OH^6 and OH^4 groups form a dense layer under which type III groups are situated. In both the (100)E and F cases, due to the double-layer OH group arrangement at the surface, their concentration is 1.5 times higher than that of 12.8 nm^{-2}, corresponding to the model of Peri.[7] The high surface OH concentrations for the (100) and (110) faces (19.3 and 18.1 nm^{-2}, respectively) enable us to explain the experimental data of ref. 17 which reported the amount of water chemisorbed at 373 K to be as high as 18.2 nm^{-2}, if it is converted in the units of OH group concentration.

It should be noted that the mean number of metal atoms bound to one OH group for each of the above six layers is not equal to two. Some of them have an excess of type I hydroxy groups, while others have the excess of type III. The sum of the OH group formal charges, obtained as in ref. 15, and assigned to the unit of surface area, is negative for the (110)D layer, and positive for almost all the remainder. Values of this specific surface charge for γ-Al$_2$O$_3$ are also given in Table 1. We conclude then, that the layers are polar and each one, as a rule, cannot represent the whole surface of microcrystal.

Surface charges calculated for the stoichiometric lattice of magnesium spinel MgAl$_2$O$_4$ with divalent cations in tetrahedral positions are also tabulated in Table 1. In the latter case the different sides of the cleft crystal have the same values, but opposite signs of surface charge. The result is quite natural for the two halves of the crystal before hydration, but it is also evident that after saturating each couple of dangling bonds at opposite sides by fragments of neutral water molecules we can only change the balance of charges between the two faces, while the total sum of charges for both will remain zero. More positive charge values for alumina faces arise because when replacing divalent magnesium ions by trivalent aluminium we do not yet take into account the presence of cation vacancies. This will be done in the next section.

We can however, build a model of a neutral (100) face if we replace in the (100)F layer one half of tetrahedral Al atoms bearing two geminal OH^4 groups by pairs of OH^{666} hydroxy groups. Such a face will have an equal number of type I and III OH groups complementary to each other, and can be considered as a hydrated surface of a crystal cleaved in a special way so that the Al$_T$ ions, occurring in the cleaving plane, would be equally shared between the two halves. Similarly, if we replace the row of Al$_O$ carrying pairs of geminal OH^6 groups for two OH^{664}, taking into account the changes in the coordination of the other OH groups, we obtain the model of a neutral (110) face and data for these neutral faces are given in Table 1. Although not so easy, it is also possible to build a neutral (111) face model, which can be considered as consisting of layer A and B domains, the borders of the latter bearing hydroxy groups not characteristic for both the pure layers.

On the (0001) face of α-Al$_2$O$_3$ (corundum), shown in Fig. 4, there are only OH^{66} type groups whose concentration amounts to 15.3 nm^{-2}. The face is not polar, since all the hydroxy groups are neutral. Another face typical for the corundum lattice, (11$\bar{2}$0), is also uncharged and contains equal numbers of OH^6, OH^{66} and OH^{666} groups.

Role of cation vacancies and structural OH groups

The γ-alumina surface differs from that of the spinel structure shown in Fig. 1–3 mainly due to the presence of cation vacancies. In fact, to fit the stoichiometry, one-ninth of metal atom positions in the alumina lattice should be vacant. There is controversy in the literature concerning the localisation of vacancies, but they are believed to occupy mainly either octahedral or tetrahedral positions.[27] According to ref. 28, the vacancy distribution is not the same for γ- and η-Al$_2$O$_3$, where both octahedral and tetrahedral positions can be vacant.

The absence of some surface aluminium ions will lead to the transformation of some type III OH groups into type II, the latter can be changed into type I, while some of the type I groups will disappear. However, the bulk oxygen atoms, adjacent to the vacant positions of surface Al atoms will become three-coordinate, and will take the opportunity to attach a proton to form type III OH groups. As a result, we always have the same six kinds of OH groups as above, the overall OH group concentration will not change greatly, but new types of hydroxy groups will arise for each layer. If both octahedral and tetrahedral vacancies are allowed, all the above six kinds of OH groups can exist on the surface of any of the three low-index faces.

In our consideration we assume that the concentration of vacancies in the bulk crystal and on the surface is the same and is determined by the stoichiometry. In the case of very finely dispersed powders such as transition aluminas, however, one can suppose that it is not so and that the charge of the bulk may be compensated by the excess of oppositely charged ions at the surface. Soled[29] has even proposed a model of γ-alumina, where there are no bulk vacancies at all, with aluminium cations occupying both Al and Mg positions, while the excess of positive charge in the bulk is compensated by a monolayer of surface OH$^-$ ions. This idea is consistent with our model of a completely hydrated surface, if we assume that all the surface is formed by the negatively charged (110)D face. This charge, although rather low, can balance the positive bulk charge of a given certain lattice volume without cation vacancies.
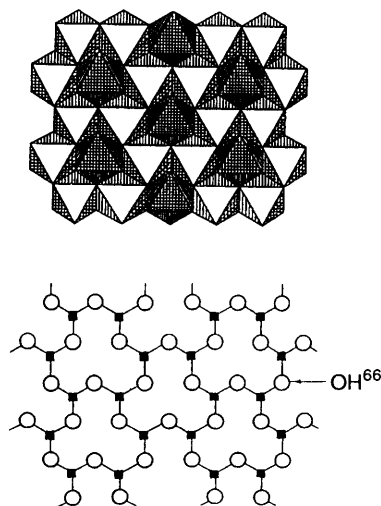

Fig. 4 Model of completely hydroxylated (0001) face of α-alumina, shown as in Fig. 1

An alumina surface can be presented by one of the above layer structures without surface vacancies and be neutral if the extra positive charge due do the substitution of Mg^{2+} by Al^{3+} is equal to the negative charge of the polar plane. As seen from Table 1, this is the case for the (100)F layer, where the type I groups predominate, but the negative charge of the $MgAl_2O_4$ surface is zero for alumina.

The hydrated material is further away from charge equilibrium. Some authors[30,31] have suggested that protons may be trapped in cation vacancies in the bulk. This was supported by X-ray diffraction data of Ushakov and Moroz,[27] who have shown that some of the O^{2-} ions in spinel aluminas are replaced by OH^- ions.

IR spectroscopic evidence for such structural hydroxy groups has recently been presented by us.[32] It was shown that absorption of structural and surface hydroxy groups can be separated if we replace surface protons by D_2O at room temperature. Then wide bands of structural OH groups remain at ca. 3500 and 3300 cm^{-1}. The corresponding OD bands were observed at 2590 and 2480 cm^{-1}, respectively. The location of these hydroxy groups in the bulk was established by the fact that their bands are not affected by absorption of CO, ammonia, pyridine or SO_2 when the bands of free surface hydroxy groups disappear.

It was proposed that protons strongly trapped in tetrahedral vacancies account for the low-frequency band at 3300 cm^{-1}, which reveals higher resistance to deuteriation, while another band at 3500 cm^{-1} is due to the hydrated octahedral vacancies.[32] Such an assignment was supported by IR data for the hexagonal tohdite alumina modification where the OH groups absorb at 3240 cm^{-1}, and are located exclusively in tetrahedral vacancies.[33] Structural OH groups can arise during the surface hydration of oxide or may be formed in the very process of hydroxide decomposition. The compound HAl_5O_8 with a spinel lattice, where all the cation vacancies are hydrated, should be the first product of boehmite dehydration. It can represent a further cubic modification of hydrated alumina with the same composition as hexagonal tohdite.

A simple estimation shows that due to the structural OH groups, the water content of transition aluminas may be twice as high as that estimated for the monolayer surface coverage by chemisorbed water.[32] Thus, we have one more explanation of the gravimetry results by Peri,[14] that the amount of water, irreversibly held by γ-alumina at 373 K can be much higher than a monolayer.

Protons trapped in the bulk cation vacancies and their migration between the bulk and the surface may account for different unusual properties of transition aluminas,[32] but their existence itself will not lead to any new structures on the hydroxylated surface. In our consideration we should distinguish between the absorption of bulk and surface hydroxy groups when interpreting the IR spectra of aluminas and have to take into account that proton mobility can lead to charge redistribution and affect the balance between the concentration of type I and type III surface hydroxy groups.

## Effect of the edges and corners

Assuming that microcrystals of a dispersed oxide powder are uniform in their shape and size, one can estimate the average particle size starting from BET surface area data or following[29] from gravimetric data on the quantity of adsorbed water. For cubic or octahedral spinel Al_2O_3 particles such an estimation gives an order of crystal dimensions of about 10 nm. For such particles the amount OH groups located on microcrystal edges is up to 7–10% of the total number of surface anions and they cannot be neglected when interpreting the spectral data. Moreover, the residual hydroxy groups of the partially dehydroxylated surface could be located prefer-

entially on the defects including the edges, then OH groups located on the edges may even predominate at the surface.
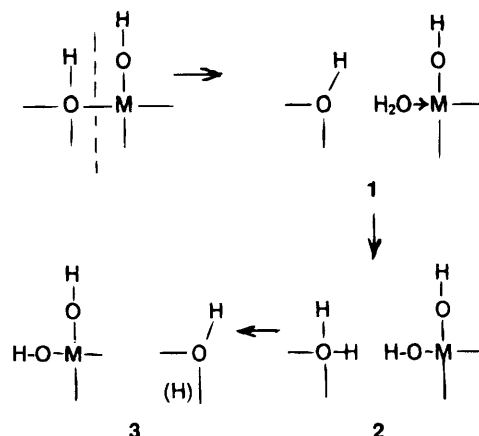
Edges of crystal solids could be regarded as intersections of two cleavage planes, and we can illustrate the peculiarities of edge hydroxy groups using the above scheme, where the already hydroxylated surface is cleaved, and the arising dangling bonds of the edge atoms are saturated by water. If water molecules complete aluminium coordination without dissociation we arrive at structure 1. Simple attachment of H and OH to the edge atoms of the opposite sides of a cleaved crystal as in structure 2, leads to a pair of geminal OH^6 groups on the metal atom and transforms the OH group, that had been attached to this form, to a coordinated water molecule. However, the proton affinity of such an OH type, type II in our scheme, would not be high, and if water dissociation is energetically favourable, the proton could preferentially be trapped in the cation vacancy, as shown in structure 3.

Thus, on the edges, OH groups should have a lowered number of surrounding metal ions, as compared with a regular face. The edge aluminium atoms should typically bear pairs of geminal type I OH groups, or could be saturated by coordinated water molecules.
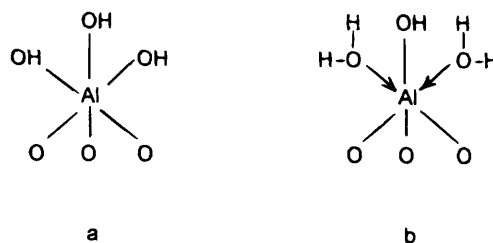
For the Al_O atoms on the corners of microcrystals, a formal consideration gives structure **a** with three OH^6 groups bound to one metal atom. Such a structure, however, has too high a negative charge. Most likely, one OH group will be sufficient, and the coordination sphere of the Al atom may be completed to an octahedron by two coordinated water molecules as in structure **b**.

In any case, if we do not distinguish between oxygen ions, OH groups or coordinated water molecules as ligands of Al atoms when determining the kind of OH group bound to it, on a completely hydroxylated surface of an alumina crystal with edges and tops, no other OH groups should exist, but the six varieties described above.

Taking in total, if the dangling bonds of the surface atoms are saturated with fragments of water or with coordinated water molecules, then for the completely hydroxylated spinel alumina surface, the types of OH group differing in the number and coordination of the metal atoms bound to them, are restricted to the six above mentioned kinds. This conclusion is valid not only if the surface is presented exclusively by the low-index crystal faces, but also if one takes into account

the presence of edges and corners of microcrystals and the effect of cation vacancies.

Effect of surface dehydroxylation

As a rule, narrow absorption bands in the spectra of dispersed oxides, due to the isolated OH groups of different types manifest themselves only after vacuum treatment at high temperature, when a considerable part of the hydroxy cover is removed and the coordination of metal ions, surrounding the residual OH groups, is changed. In this section we analyse the influence of dehydroxylation on the local environment of OH groups.

To follow the changes in the structure of hydroxy cover during the dehydroxylation process, we have to know the sequence of OH group desorption, and to have information about the mobility of different species at the surface. As in the earlier models,[7,15] we believe that at the first stage of dehydroxylation only pairs of adjacent groups will react, but not in a random way as in the model of Peri.[7] The first to be desorbed are the pairs, where the basic group has the highest negative charge, while another, which donates a proton, is the most acidic, *i.e.* it has the highest positive or lowest negative charge.

When estimating the net charge of hydroxy groups we follow the same procedure as in the work by Knözinger and Ratnasamy,[15] but take into account not only the number of surrounding metals and their coordination, but also the coordination changes during the dehydroxylation. The charge of the Al^{3+} ion is assumed to be equally shared between all the oxygen atoms of the AlO_m polyhedron. Then the charge on an OH group will be $3/m - 1$ for the OH^m group, $3/m + 3/n - 1$ for the OH^{mn} and $3/m + 3/n + 3/k - 1$ for OH^{mnk}. The obtained charge values are given in Table 3. Charges on the oxygen atoms are one unit less than those on the corresponding OH groups.

Although the obtained OH group charge values do not coincide with those calculated by quantum-chemical methods for cluster models,[34,35] the tendencies of charge changes with the number of surrounding atoms or their coordination are well reproduced, and preferable condensation of hydroxy groups with maximal difference of charges is consistent with the results of theoretical considerations.[18]

When all the pairs of adjacent OH groups are desorbed, further removal of isolated surface hydroxy groups is possible only as a result of surface ion diffusion. As in earlier work,[7,15] we assume here that the mobility is the highest for protons. Our data[32] show that at temperatures above 673 K practically all the bulk protons can be readily be exchanged with those at the surface. It is natural to expect that surface proton diffusion starts at even lower temperatures, and the OH groups can be desorbed even if they are distant from each other. If at the final stage of dehydroxylation only one kind of OH group with equal charges remains at a crystal face, their mutual condensation should also be possible.

If one layer has an excess of, say, type III groups, they can combine with the extra type I groups of another layer due to proton migration between different faces. This process, as well as proton migration from the bulk cation vacancies to the surface with subsequent desorption of water molecules, should lead to surface charge redistribution with an excess of positive charge at the surface. The charge increase has to be compensated by cation migration in the opposite direction. At even higher temperatures the sintering occurs, a process which also requires oxygen ion mobility. Although the mobility of protons as well as of Al^{3+} ions at high temperatures complicates the picture, *e.g.* leading to restoration of OH groups which have already been eliminated at lower temperatures,[15] the tendency for metal coordination number lowering on water desorption should result in new kinds of OH group.

In fact, on dehydroxylation without proton or cation diffusion, the number of aluminium atoms surrounding the residual OH groups cannot change, and we always have the same type of I, II and III groups at the surface. However, considering the coordination of cations, we have to take into account that desorption of the first coordinated water molecules or removal of any surface OH group after attaching a proton leads to a decrease of the coordination number of surface aluminium atom. If this atom is involved in the coordination sphere of another OH group, the properties of the latter will be altered and another kind of hydroxy group is generated. To see the results, let us analyse certain crystal faces.

The (111)A is the only layer where dehydroxylation can start without formation of new kinds of hydroxy groups, because the basic OH^4 groups are bound to aluminium ions that have no other hydroxy groups in the coordination sphere. Their condensation with the protons of the neighbouring OH^{64} groups will occur until only the OH^{64} groups remain on the surface at total coverage of 50%. Then, coupling of the remaining OH^{64} groups should result in the appearance of either OH^{54} or OH^{63} groups. If the process is well organised, so that at 50% coverage we have the ideal rows of OH^{64} groups, total dehydroxylation can theoretically be achieved with the formation of the OH^{54} groups only. In a more realistic random process of desorption we have to assume the appearance of the OH^{53} and OH^{44} as well, and even OH^{43}, although the probability for the latter to arise will be extremely low. The completely dehydroxylated ordered surface will have chains of O^{2-} ions bridging three- and five-coordinated aluminium ions. The last proton on such a surface will evidently be held as the OH^{53} type hydroxy group.

On the hydroxylated (111)B layer each proton of the OH^{666} structure can join to one of the six surrounding equivalent OH^{66} groups. Desorption of the first such couple will change the coordination of two Al_O cations, initially bound to the latter group and result in the appearance of two OH^{56}, one OH^{566} group and one three-coordinate oxygen in the position of the former group OH^{666}. After reaching 50% coverage, all the OH^{666} groups will be removed, and for an ordered surface all the remainder of the groups are OH^{56}. A random process can also give OH^{556} and OH^{55} groups. On the ordered dehydroxylated surface rows of oxygen ions bound to three or two Al^{3+} ions with lowered coordination will remain. The last proton on such a surface will evidently be bound to the most negatively charged bridged oxygen ion giving a OH^{55} group.

Analysis of the (111) face performed in ref. 15 is consistent with our results, although the authors did not consider changes in the cation coordination. The results of the (110) and (100) face consideration are, however, quite different.

Desorption of the first OH^4 with a proton of the most acidic OH^{664} group on the (110)C face results in transformation of the latter type to even more acidic OH^{663}. Up to the complete removal of all the OH^4 and complete transformation of the OH^{664} at 50% coverage no other groups will appear. Further dehydroxylation will occur *via* desorption of OH^{66} with the protons of OH^{663} groups, and both will change their environment. The former will turn first into OH^{65}, then OH^{55}, the latter into OH^{653} and then OH^{643}. The last to be desorbed will be the OH^{55} and OH^{643} groups.

After removal of one of the geminal OH^6 groups from the (110)D face, a terminal OH^5 group bound to a five-coordinate aluminium atom will appear. Two other groups bound to the same Al atom will transform from OH^{64} and OH^{666} into OH^{54} and OH^{665}, respectively. For the ordered procedure the type III groups will disappear at 50% coverage when one group of each geminal OH^6 pair will be removed. Then OH^5 will be desorbed with the protons of the OH^{54} groups. In a more random process two geminal OH^6 groups may disap-

pear before the protons of the adjacent type II or III groups, then the types OH^{664} and OH^{44} should arise at medium coverages. At the completely dehydroxylated surface all the type I groups will be removed leaving the rows of Al_T atoms formed from Al_O. The last protons will be attached to the most basic oxygen ions bridging two four-coordinate Al as OH^{44}, or will remain as isolated OH^5 groups.

Dehydroxylation of the neutral (110) face will start in the same way, but due to the balance between the concentration of type I and III groups they will disappear simultaneously. The last to be desorbed will be the OH^{55} and OH^{44} groups. No additional kinds of hydroxy groups will appear at intermediate coverages, except those of the polar (110)C and D layers.

At the (100)E layer the OH^6 groups will associate with protons of the OH^{664}, until all the hydroxy groups of both kinds will be used. Meanwhile, new varieties such as OH^{654}, OH^{665}, OH^{554} and OH^{655} should arise. After 2/3 of the initial coverage is removed, only the latter will remain at the surface. Their mutual condensation, although energetically unfavourable, should lead to the formation of the OH^{644} groups.

Desorption of OH^6 with the protons of OH^{664} on the (100)F layer will lead to the formation of the OH^{654} and then OH^{554} until all the type III groups disappear, and only the rows of geminal OH^4 hydroxy groups remain at the surface. Their desorption should result in the appearance of OH^3 groups linked to one three-coordinate aluminium, and very basic ($q_{eff} = -1.25e$) mono-coordinated oxygen ions. Quantum-chemical analysis of a cluster model of an alumina surface fragment with a pair of geminal OH^4 groups was performed in ref. 36 where the arising acid–base pairs of OH^3 and three-coordinate Al^{3+} ions were regarded as sites of dissociative hydrogen adsorption. On the completely dehydroxylated surface, rows of basic oxygen ions should remain, the last to be desorbed will be the OH^3 groups.

The energetically unfavourable processes of mutual type I or type III hydroxy condensation can be avoided if the surface is formed by the neutral (100) layer where the number of type I and III OH groups is balanced. Here, however, removal of both the geminal OH^4 groups with the protons of neighbouring type III groups should lead to two-coordinate Al^{3+} ions, which are not stable and at high temperature would migrate to the bulk and occupy the cation vacancies.

There is no problem of surface charge for the (0001) and ($11\bar{2}0$) corundum α-Al_2O_3 faces. Desorption of the first OH^{66} from the (0001) face changes the coordination of two surrounding Al atoms and results in four OH^{65} groups and one surface oxygen. Then the OH^{55}, OH^{64} and OH^{54} groups should appear. The latter face is also not too complicated. While OH^6 groups will be desorbed with the protons of OH^{666} hydroxy groups, the only new kind to arise will be the OH^{665} groups. When all the type I and type III OH groups are removed, the chains of OH^{66} will start to condense giving OH^{65} and, finally, OH^{55} groups.

The results of the above analysis of dehydroxylation process for the six considered layers of the (111), (110) and (100) faces of spinel structure are summarized in Table 3. To follow the dynamics of the OH type changes, we distinguish here four stages of dehydroxylation: before, *viz.*, prior to desorption; initial desorption, that is after removal of the first isolated couples of OH groups when new kinds of OH groups coexist with those of the completely hydroxylated surface; a medium stage when the less abundant groups of the initial surface are removed, and a variety of the new kinds appear; and, finally, the final stage when the last protons remain on the most basic oxygen ions of completely dehydroxylated surface.

There are several consequences which follow from the data presented in Table 2. First, the number of different kinds of hydroxy groups grows enormously on dehydroxylation, the total number being more than 20. As the surface OH concen-

Table 2 Different kinds of OH groups, arising at certain stages of dehydroxylation on the surface of oxides with spinel-type structure

OH group type	stage of dehydroxylation			
	before	initial	medium	final
I	OH^6	OH^6		
		OH^5	OH^5	OH^5
	OH^4	OH^4	OH^4	
			OH^3	OH^3
II	OH^{66}	OH^{66}		
		OH^{65}	OH^{65}	
	OH^{64}	OH^{64}	OH^{64}	
			OH^{63}	
			OH^{55}	OH^{55}
		OH^{54}	OH^{54}	
				OH^{53}
			OH^{44}	OH^{44}
III	OH^{666}	OH^{666}		
		OH^{665}	OH^{665}	
	OH^{664}	OH^{664}	OH^{664}	
		OH^{663}	OH^{663}	
			OH^{655}	
	OH^{654}			
			OH^{653}	
			OH^{644}	OH^{644}
			OH^{643}	OH^{643}
			OH^{554}	

tration decreases some hydroxy groups disappear until at the final stage of dehydroxylation the variety of hydroxy groups is reduced to few possible kinds, which remain on the almost completely dehydroxylated surface.

Secondly, and the most remarkable result is that the last hydroxy groups to be removed are not related to those which were present on the initial hydroxylated surface. Most of the above six kinds of OH groups should disappear after removal of 50–75% of the initial amount of hydroxy groups.

Thirdly, surface dehydroxylation causes a constant decrease in the coordination number of cations surrounding the OH group. This tendency, illustrated in Table 2, results in the growth of positive charge of the hydroxy groups and hence an increase of their acidity, accompanied by the appearance of negatively charged basic oxygen atoms. If the first to be desorbed are the most basic and the most acidic OH groups; the trends of acidity increase on water desorption means that the new type I hydroxy groups (OH^5 and OH^3) should be more stable than the initial OH^6 and OH^4. The new type III hydroxy groups are even more acidic than the initial OH^{666} and OH^{664} and should be, in contrast, less stable, and the last hydroxy groups, such as OH^{644} and OH^{643} would scarcely survive the high temperature treatment; their protons would rather migrate to find more basic oxygen atoms.

The same general tendencies are also true for α-alumina; however, here the number of different structures is much less as compared with spinel aluminas. All the OH groups, oxygen or Al^{3+} sites we can realize for the corundum structure are those considered above for γ-alumina. At the same time, the most unsaturated sites, which should exist on γ-alumina, such as OH^3, three-coordinate Al^{3+} or mono-coordinated oxygen bound to it, are not typical for the corundum surface. Moreover, the main faces are not polar here and there are no complications due to the presence of cation vacancies.

The above conclusions, obtained here for an ideal model of infinite crystal faces, do not change if we take into account the influence of cation vacancies, edges and corners. In fact, the tendency of edge hydroxy groups to have lower coordination and of aluminium ions to retain molecular water will lead to the same kinds of hydroxy groups as listed in Table 2, the only difference is that the new varieties of hydroxy groups could appear at an earlier stage of surface dehydration.
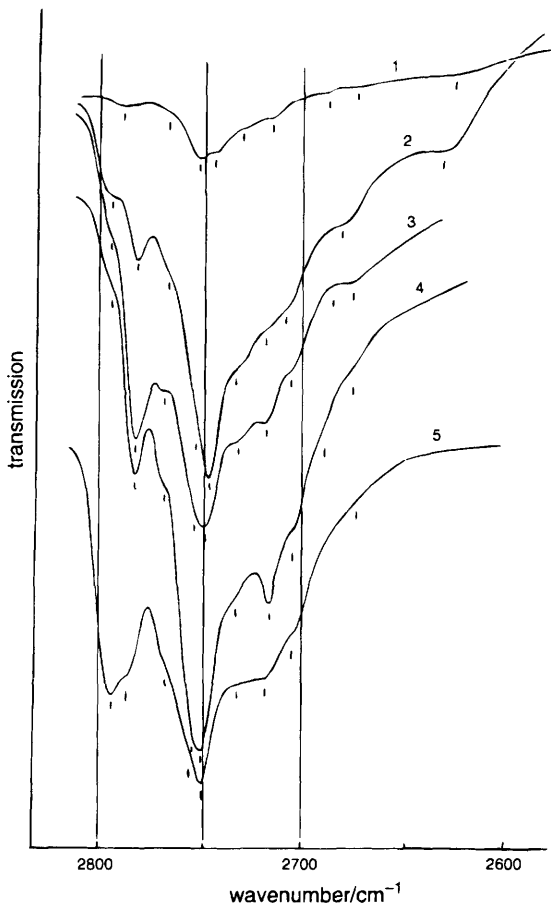
Fig. 5 IR spectra of α- (1), Θ- (2), η- (3), γ- (4) and χ-Al_2O_3 (5) after evacuation at 873 K

Band assignment

There are many experimental data on the IR spectra of surface OH groups of alumina. Most of the early studies reviewed in ref. 10, 11 and 26 as well as more recent publications[20–26] deal with three bands or groups of bands at *ca.* 3780, 3730 and 3700 cm^{-1} that can be attributed to the type I, II and III OH groups, respectively.[10–12,15,25,26]

Typical IR spectra of the hydroxy cover of six different alumina modifications treated under the same conditions are shown in Fig. 5. To avoid the influence of atmospheric water absorption, spectra of deuteriated samples were run in the stretching OD region with a high signal to noise ratio. Analysis of these spectra reveals up to ten bands, that have practically the same positions but different intensities. Using the second derivative spectra[37] one could resolve even more fine structure of the central band, which consists of four maxima at 2765, 2761, 2756 and 2752 cm^{-1} that correspond to the OH peaks at 3749, 3744, 3737 and 3732 cm^{-1}. The different intensities of distinct maxima in the spectra of different alumina modifications, as well as their individual behaviour on thermoevacuation or hydrogen–deuterium exchange,[26] suggest that these maxima belong to certain surface structures, and not to the combination modes with low-frequency vibrations, as supposed in ref. 1.

Recent results of computer modelling[38] show that a fine structure in the IR spectra of ordered or random adsorbed layers can be strongly influenced or even removed by the effect of dynamic interaction between the vibrating dipoles. This effect, however, is strongly dependent on coverage and the intensity of absorption. In our opinion this could be important at early stages of dehydroxylation, when besides shorter distances between the interacting dipoles, the intensities of OH bands are enhanced due to hydrogen bonding between adjacent OH groups. After high-temperature treatment the influence of dipole coupling on the spectra of surface OH groups should be negligible and was not detected in the experiments with isotopic mixtures. Nevertheless, if the experimental bandwidth could be lowered due to better crystallinity or low temperatures, and the instrument resolution is high enough, this effect can represent a limit for drawing more detailed information from the fine structure of the IR band.

While the admission that the increasing number of metal atoms bound to the oxygen atom of hydroxy groups lowers the OH stretching frequency is now supported by much experimental work[9–12,15,25,26] and quantum-chemical calculations,[14,39] the dependence of ν(OH) on the coordination of the surrounding metal atoms is still under discussion. Different authors assign the most high-frequency OH band of alumina observed at 3800 cm^{-1}, either[15,25] to OH^6 or[40] to OH^4 groups. The former assume that the dependence of OH frequency on the charge or on the electrostatic field of surrounding ions is monotonic. In this case the highest frequency should correspond to the OH$^-$ ion. The frequency of a free OH$^-$ ion, measured recently by means of laser spectroscopy[41]

Table 3 Charge and band assignment for different hydroxy groups of alumina

type of OH group	kind of OH group	q_{eff}/e	q_{calc}/e ref. 34	q_{calc}/e ref. 35	ν(OH)/cm^{-1}	ν(OD)/cm^{-1}
I	OH^6	−0.5	−0.597	−0.49, −0.54		
	OH^5	−0.4	−0.525	—	3780	2785
	OH^4	−0.25	−0.487	−0.50		
	OH^3	0	−0.419	—	3800	2800
II	OH^{66}	0	−0.403	−0.37, −0.40, −0.43		
	OH^{65}	+0.1	—			
	OH^{55}	+0.2	—			
	OH^{64}	+0.25	−0.338	−0.35	3750–3700	2765–2730
	OH^{54}	+0.35	—			
	OH^{44}	+0.5	—			
	OH^{63}	+0.5	−0.310			
	OH^{53}	+0.6	—			
III	OH^{666}	+0.5	—	−0.34		
	OH^{665}	+0.6	—			
	OH^{655}	+0.7	—			
	OH^{664}	+0.75	−0.276	−0.32, −0.31	3700–3635	2730–2680
	OH^{654}	+0.85	—			
	OH^{553}	+0.95	—			
	OH^{663}	+1.0	—			
	OH^{653}	+1.1	—			

is, however, as low as 3555.6 cm^{-1} ($\omega_e = 3738.44$ cm^{-1} with $\omega_\chi = 91.42$ cm^{-1}).

We believe that the dependence of the OH$^-$ ion frequency on the electric field is not monotonic, and is represented by a curve with a maximum. This was supported by a semi-empirical quantum-chemical calculation,[13] where a curve with a maximum exactly for aluminium was obtained for the type I OH groups bound to tetrahedrally coordinated atoms of different elements. A more recent calculation of ν(OH) values by semi-empirical MINDO/3 methods[42] for the five OH groups considered in ref. 15, has shown that for the type II and III OH groups the frequency increases with metal coordination number, while for the type I it decreases on transition from OH^4 to OH^6, despite the continuous increase of negative charge on the OH group. Non-empirical quantum-chemical calculations with 3-21G and 6-21G bases[34] support this result, showing an OH frequency decrease in the sequence OH^3 > OH^4 > OH^5. Thus, for basic type I OH groups an inverse frequency dependence on charge takes place, and the most high-frequency band corresponds to the lowest Al^{3+} coordination. This is in accord with the assignment of the 3800 cm^{-1} band in the spectrum of dispersed AlPO$_4$ to the OH^4 groups bound to aluminium.[43]

Correlation of the observed spectra with the results presented in Table 2 leads to the somewhat unexpected conclusion that the two high-frequency bands observed at *ca.* 3800 and 3780 cm^{-1} in the spectra of different alumina modifications after vacuum treatment at highest temperatures should be attributed to the OH^3 and OH^5 groups of the almost dehydroxylated surface. OH^4 absorption could contribute to the same 3800 cm^{-1} band, especially if the temperature of pretreatment was not too high. OH^6 groups that should disappear at an even earlier stage of dehydroxylation, could account for the absorption at 3760–3750 cm^{-1}, which still exists as a weak band in the spectra presented in Fig. 5.

We cannot present a detailed interpretation attributing each band observed in the IR to certain kinds of OH group from those listed in Table 2, restricting ourselves to the statement in Table 3 that the envelope of maxima in the indicated spectral region corresponds to the set of type II or type III hydroxy groups.

Conclusions

A model of a hydroxylated surface formed by (111), (110) and (100) cleavage planes for oxides with a spinel lattice has been elaborated. Two parts of the cleaved crystal, saturated by water fragments, represent two different layers with opposite charge and equal OH concentration. Surface OH groups for spinel or corundum structures are always of three types, *i.e.* bound to one, two or three metal atoms. Taking into account the coordination of aluminium atoms, one could distinguish for the completely hydrated spinel structure two sorts of every type of hydroxy group, six kinds altogether, which are unevenly distributed between the considered surface layers.

The surface concentration of OH groups determined from the proposed model for (110) and (100) faces is rather high, exceeding 19 OH nm^{-1}, in agreement with the observed high absorption capacity of transition aluminas towards water. Some part of the water could be retained by the absorbent in the form of protonated cation vacancies. The ability of protons to be trapped in the vacancies and to migrate between the bulk and surface is the main factor that accounts for unusual adsorption and catalytic properties of transition aluminas with respect to corundum.

The presence of cation vacancies, as well as the edges and corners of crystals, does not lead to new kinds of OH group on the completely hydrated surface. Visualisation of the hydrated alumina surface could be used to elucidate the etching of aluminas by aqueous solutions of acids and bases,[44]

or other processes at the Al$_2$O$_3$/water interface,[45] but cannot be directly applied for interpretation of the IR spectra of materials treated at high temperatures or for the analysis of catalysis mechanisms.

Removal of surface OH groups leads to the appearance of coordinatively unsaturated surface ions that play the role of Lewis acid and basic sites, and could be characterised by IR spectra of different adsorbed test molecules. The properties of these sites, not discussed here, are determined by the structure of the initial hydroxylated surface. The existence of five-coordinate Al ions on the surface of transition aluminas, which follows from the analysis of the crystal structure,[25,26] was recently proved by direct MAS NMR observations using the sophisticated technique of rotational echo double resonance (^{1}H–^{27}Al REDOR) with one pulse and cross-polarization.[46,47] The authors have found as well that a certain number of four-coordinate cations is produced at the alumina surface in the course of dehydroxylation.[47]

Even a partial dehydroxylation of the surface causes a dramatic increase in the number of OH group varieties, bound to the coordinately unsaturated surface cations. This explains the observed complex structure of the OH bands in the IR spectra. Detailed analysis of the dehydroxylation process enables us to determine the coordination of the last OH groups to remain on the surface of the almost dehydrated alumina after thermoevacuation. These hydroxy groups, which are completely different from those of the hydroxylated surface, could be correlated with the distinct peaks in the IR spectra of oxides after high temperature treatment.

The approach to the hydroxylated surface analysis, illustrated here for spinel aluminas, could easily be applied for any other oxide, including those not complicated by different metal coordination or by the presence of cation vacancies.

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