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Abstract

Full Text

PHYSICAL CHEMISTRY

M. M. EGOROV

ON THE NATURE OF THE SURFACE OF CATALYTICALLY ACTIVE ALUMINUM OXIDE

(Presented by Academician M. M. Dubinin, 5 IV 1961)

The surface of aluminum oxide and, in particular, of the catalytically active γ -form is hydrated. The degree of hydration of the surface largely determines its adsorption and, apparently, catalytic properties. Previously, in work (1), the content of structural water was determined in samples of aluminum oxide subjected to heat treatment over a wide temperature range, and the heats of wetting of these samples by water were determined. The data obtained made it possible to divide the total amount of structural water into water belonging to the bulk and to the surface hydrates of alumina. It is of interest to calculate the degree of hydration of the surface of various modifications of Al_2O_3 on the basis of the crystallography of the bulk phases, and to compare the results of the calculation with experiment.

Whereas crystallographic calculations for the surface of silica have been made by many authors (2-5), for aluminum oxide they have not been carried out. In the present communication we shall consider the surface of hydrargillite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), corundum ($\alpha\text{-Al}_2\text{O}_3$), and $\gamma\text{-Al}_2\text{O}_3$. The structures of the bulk phases of these modifications are described in (6-8).

The simplest calculation is that of the concentration of hydroxyls on the surface of hydrargillite corresponding to the plane of perfect cleavage (001), where each hydroxyl ion is bonded to two Al ions, and each Al ion is bonded to three overlying hydroxyls and three underlying hydroxyls

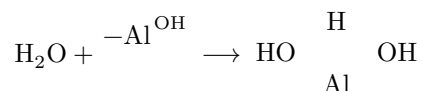
[[structural diagram: Al-OH network]] (1)

An elementary area $a_0 \times b_0$ contains 6 hydroxyls, which amounts to $11.4 \mu\text{M}/\text{m}^2 - \text{H}_2\text{O}$. Formation of the (100) face is accompanied by the rupture of coordination bonds* Al-OH and by disruption of the normal octahedral coordination of Al:

[[structural diagram showing rupture of Al-OH bonds and formation of surface Al-OH groups]] (2)

* For each coordination bond in the structures of aluminum oxide (except for the γ -form) there is a valence of 1/2. The concept of unsaturated valence is used by us as convenient working terminology. It is analogous to the “strength” of a coordination bond introduced by Pauling.

Upon contact of such a surface with water (hydration), the normal coordination is restored:



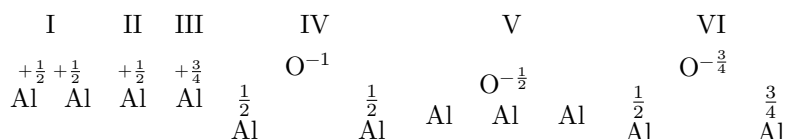
In this case states are formed in which the proton belongs to two anions. The degree of hydration of such a surface is about $10.2 \mu\text{M}/\text{m}^2\text{—H}_2\text{O}$.

The hydrated surface of corundum is structurally analogous to a layer of hydrargillite (scheme (1)). Per elementary hexagonal area ($a_0 = 4.76$) there are three anions, which corresponds to a degree of hydration of the (0001) surface equal to $12.7 \mu\text{M}/\text{m}^2\text{—H}_2\text{O}$. The processes of thermal dehydration and rehydration can be represented by the scheme:



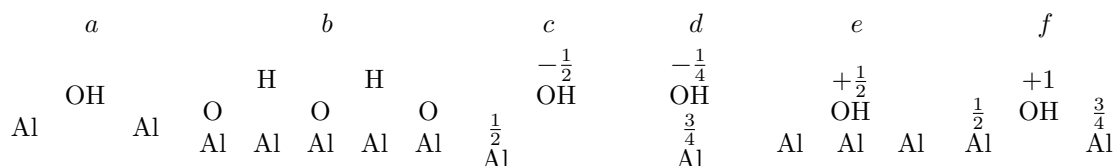
The dehydrated state of the surface is stabilized, by analogy with scheme (2), when the coordination number of some Al atoms decreases to 4 and of others to 5.

Turning to the cubic modification of aluminum oxide ($\gamma\text{-Al}_2\text{O}_3$), it should be noted that its structure is a defective spinel. The defectiveness of the structure consists in the fact that trivalent aluminum ions are located in a certain number of tetrahedral interstices of the close packing of oxygen ions, instead of the divalent cations in the case of an ordinary spinel. In a number of other interstices the cations are absent, i.e., there exists a local excess and deficiency of cations in the crystal structure. The cleavage surface of the structure (along the octahedron plane) will contain the following centers:



Mutual saturation of the broken bonds will disturb the coordination of the aluminum atoms, but will not lead to complete saturation of the valences. On

the surface, as in the bulk, local defects are partially retained. In the process of surface hydration one may expect the appearance of the following groups:



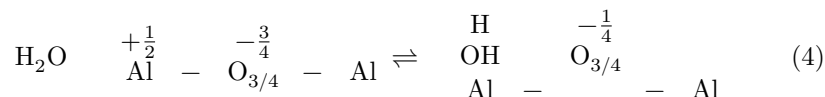
Mutual compensation of defects of different sign (*c, d, e, f*) in neighboring groups is possible only partially. It may also be assumed that the process of surface hydration is accompanied by the incorporation of hydrogen (H₂) into tetrahedral interstices beneath the surface layer of anions*, where, owing to the defectiveness of the spinel structure of $\gamma\text{-Al}_2\text{O}_3$, there is a local deficiency of cations. In this case a significant part of the surface defects is removed, but the stoichiometry is disturbed. Assuming that these two variants of hydration can be combined—

* This hydrogen could be called “buried.”

...we obtained the following data on the composition of the surface:

1. “Buried” hydrogen (H₂) . . . $1 \mu\text{M}/\text{m}^2$
2. Isolated hydroxyls (*a*) . . . $7.7 \mu\text{M}/\text{m}^2$
3. Protons bound equally to two anions (in groups (*b*)) . . . $3.1 \mu\text{M}/\text{m}^2$
4. Protons bound $\frac{3}{4}$ to one anion and $\frac{1}{4}$ to others, or even more complexly. Protons in groups with incomplete saturation of valences. Hydroxyls bound not only to Al atoms, but also to “buried” hydrogen . . . $11.7 \mu\text{M}/\text{m}^2$

With complete dehydration, from a unit of surface there may be removed: water $11.7 \mu\text{M}/\text{m}^2$ and hydrogen (H₂) $0.5 \mu\text{M}/\text{m}^2$. If on the (0001) surface of corundum each hydroxyl is bound to two underlying aluminum atoms, then on the hydrated surface of $\gamma\text{-Al}_2\text{O}_3$ a considerable portion of the anions is bound to the bulk by a single bond (schemes). Such anions will be detached from the surface first of all. The dehydration—rehydration process may proceed, for example, according to the following scheme*:



The defectiveness of the surface structure and the diversity of its composition in the dehydrated and hydrated states, as well as the possible presence

Table 1

Phase composition, degree of surface hydration, heats of wetting, and irreversible adsorption for alumina samples*

No.	Calcination temperature, °C	Phase composition of the surface layer	Heat of wetting by water, erg/cm ²	Heat of wetting by ethanol, erg/cm ²	Degree of hydration of the surface of calcined samples, μM -H ₂ O per 1 m ²	Degree of hydration of the surface of rehydrated samples, μM -H ₂ O per 1 m ²	Calculated values of the degree of hydration	Irreversible adsorption of ethanol
1	200**	Distorted γ -form	342		9.4		11.7	
2	300	Distorted γ -form	384	330	7.75		11.7	3.0
3	400	Same	420		6.32		11.7	
4	500	Same	495	407	4.8	9.35	11.7	3.1
5	600	Same	520		4.43	9.7	11.7	
6	700***	Intermediate phases and corundum	500	500	4.3		11.7	
7	900	Corundum	670	555	1.4	11.1	12.7	3.6

* Data on the degree of hydration, heat of wetting by water, and phase composition of the samples are taken from (1).

** Beginning at 200°, the samples contain no bulk hydrate (1).

*** Beginning at a temperature of about 700°, recrystallization occurs in the surface layer with formation of corundum (1).

of superstoichiometric hydrogen may probably be connected with the known

catalytic properties of γ -Al₂O₃ (for example, the hydrogenation reaction ⁽⁹⁾). Defects apparently may move, “creep” over the surface within small regions, i.e., they may be localized on

* The interaction of the dehydrated surface with alcohol molecules can apparently be represented by an analogous scheme with the formation not only of OH groups, but also of OR groups, where R is the corresponding radical.

different atoms of the surface. By adsorbing one molecule or another, the surface of γ -Al₂O₃ can, as it were, “adapt” itself to its size by changing the distance between two of its defects of different sign. The development of such ideas may be of interest from the standpoint of the multiplet theory of catalysis.

Turning to comparison with experiment, it is necessary to emphasize that the crystallographic calculations carried out are of an approximate character. The real surface of a solid may differ from an ideal section ⁽¹⁰⁾. Table 1 presents experimental data on the degree of hydration of the surface of alumina samples and the heats of wetting by water ⁽¹⁾, as well as irreversible adsorption and the heats of wetting by ethanol.

The maximum values of the degree of hydration of the surfaces of corundum and of the γ -form, found from experiment, agree satisfactorily with the theoretical estimate. This shows that in the preceding work ⁽¹⁾ the separation of the water contained in bulk hydrates and of surface water was made correctly. Data on the rehydration of calcined samples indicate that the processes described by schemes (3) and (4) are completely reversible.

The heat of wetting of alumina by water increases as the surface is dehydrated. Consequently, the energy of rehydration predominates over the energy of interaction of water molecules with the hydrated surface. The heat of wetting by water of corundum is greater than that for the γ -form at approximately equal values of the degree of hydration. This is consistent with our view that surface hydroxyls on corundum are bound to the bulk more strongly than on the surface of γ -Al₂O₃. In work ⁽¹¹⁾ an increase was also found in the heat of wetting by water with increasing treatment temperature and decreasing water content in alumina samples.

Irreversible adsorption of ethanol vapor increases as the surface of Al₂O₃ is dehydrated. Probably, alcohol molecules interact not only with surface hydroxyls ⁽¹²⁾, but also with dehydrated regions according to schemes analogous to (3) and (4). The energy of interaction of alcohol with dehydrated regions is greater than for hydrated regions, since the heat of wetting of alumina by alcohol, as in the case of water, increases with decreasing degree of hydration of the surface.

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