

21. Chausov, F. F. Linear organic–inorganic heterometallic copolymers  $[(\text{Fe}, \text{Zn})(\text{H}_2\text{O})_3\{\text{NH}(\text{CH}_2\text{PO}_3\text{H})_3\}]_n$  and  $[(\text{Fe}, \text{Cd})(\text{H}_2\text{O})_3\{\text{NH}(\text{CH}_2\text{PO}_3\text{H})_3\}]_n$ : The missing link in the mechanism of inhibiting local steel corrosion with phosphonates [Text] / F. F. Chausov, N. V. Somov, R. M. Zakirova, A. A. Alalykin, S. M. Reshetnikov, V. G. Petrov et. al. // Bulletin of the Russian Academy of Sciences: Physics. – 2017. – Vol. 81, Issue 3. – P. 365–367 doi: 10.3103/s106287381703008x

*Досліджено кислотно-основну рівновагу на поверхні оксидів CaO, MgO, FeO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>. З використанням квантово-хімічного моделювання запропоновані моделі безводних та гідратованих активних центрів на поверхні оксидів. Встановлені закономірності зміни кислотно-основних та енергетичних параметрів модельних поверхневих активних центрів в залежності від природи центрального елемента кристалічної решітки, кількості OH-груп та числа гідратації*

*Ключові слова: оксидний наповнювач, композиційний матеріал, поверхневий активний центр, кислотно-основна рівновага*

*Исследовано кислотно-основное равновесие на поверхности оксидов CaO, MgO, FeO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>. С использованием квантово-химического моделирования предложены модели безводных и гидратированных активных центров на поверхности оксидов. Установлены закономерности изменения кислотно-основных и энергетических параметров модельных поверхностных активных центров в зависимости от природы центрального элемента кристаллической решетки, количества OH-групп и числа гидратации*

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# INVESTIGATION INTO ACID-BASIC EQUILIBRIUM ON THE SURFACE OF OXIDES WITH VARIOUS CHEMICAL NATURE

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## 1. Introduction

Ukraine has virtually inexhaustible deposits of various mineral oxides, which can replace foreign ones in a manufacture of building polymer-based composites. The use of Ukrainian materials as fillers for building purposes is conditioned by affordability, low cost, and a capability of obtaining materials with a variety of necessary operational and technological properties. Interest in this area is primarily due to the study of the physicochemical properties of surface phenomena in composite materials [1–6]. The relevance of this trend arises in the process of creating new polymeric building composites which constitute heterogeneous systems with highly developed interphase boundaries. Properties of the dispersed phase surface determine the initial stage of adhesion interaction between the components: adsorption, wetting, spreading of the dispersion media over the filler surface, forming the interphase boundary, impregnation of filled and reinforced systems [3–5]. Of all existing theories of interphase interaction in polymeric composite materials, the acid-base one is the

least studied. Its existence is confirmed by studies over recent years [2, 7]. When choosing components for a composite material, it is important to predict interactions on the interphase surface which are simultaneously determined by the acid-base properties of the polymer and the acidic strength of the adsorption centers on the filler surface [2]. Therefore, investigation of the acid-base equilibrium on the surface of oxide fillers of various chemical natures is relevant both from theoretical and practical points of view.

## 2. Literature review and problem statement

In connection with the natural origin of mineral oxide fillers, chemical and mineralogical composition and, consequently, surface properties, are extremely unstable. Besides, mineral particles have a redundant surface energy which includes acid-base (polar) energy of surface centers [8, 9] and easily adsorb molecules of water from air [10–12]. The effect of chemically and physically adsorbed water on the acid-base

properties of oxide surface is confirmed experimentally. It was proved that amount and acid-base parameters of the active centers in the oxide material surface change in case of their burning [7] or mechanical treatment (milling) [4]. When water is adsorbed, a hydroxyl-hydrated layer is formed on the surface that is characterized by a wide spectrum of active adsorption centers, the acid-basic properties of which are of great scientific interest [13–15] although insufficiently studied.

The structure of the adsorption surface layer consists of chemically bound water molecules that form the first hydroxyl layer of OH groups (Brønsted centers) and subsequent hydrated layers from water molecules bound with the hydroxyl layer via hydrogen bonds [10, 13]. There may be aprotic acidic and basic Lewis centers in the oxide surface the number of which is small in the air-dry surfaces. Determination of the acid-base characteristics of the active centers in a surface layer of oxide materials is a complex but very important task. For this purpose, authors of works [10, 16–18] use methods that make it possible to determine number and acid-base parameters of the surface-active centers, mainly experimentally. For example, methods of IR spectroscopy [17], adsorption of gases in a gaseous medium [10, 12] or color indicators in liquids [13–15, 18] are used. The authors of papers [11, 16] applied method of potentiometric titration of suspensions. Experimental methods are informative but labor-intensive and do not permit determination of the chemical nature of active centers. The authors propose a method for quantum-chemical modeling to elucidate chemical nature of the active centers and investigate protolytic equilibrium on a silica surface [19] and in mixed oxides [20] which allows one to calculate the dissociation constant and the Gibbs energy of deprotonation processes of surface OH groups. But these studies do not take into account influence of adsorbed water molecules on the acid-base and energy parameters of active centers.

For the most part, natural polymineral fillers are oxide mixtures in which one component is the largest (more often  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ), and other components ( $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ) can be considered as impurities. There are rough approaches that allow one to pre-evaluate surface properties of oxides. Thus, virtually all polyminerals contain  $\text{SiO}_2$ , so the content of this oxide can serve as a rough criterion of acidity of their surface. It is known that if the filler contains less than 45 % of  $\text{SiO}_2$ , it is classified as ultrabasic, 45–52 % as basic, 52–65 % as medium, 65–70 % as acid, and more than 75 % as hyperacid. The above classification is limited to the mandatory presence of  $\text{SiO}_2$  in the filler composition and gives a rough estimate of the acid-base properties of the material surface. Another imperfect and approximate classification is one according to which the same materials can be referred to both solid acids and solid bases. At the same time, a great number of researchers have established experimentally that there are active centers with a spectrum of acidity function on the surface of mixed oxides such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  [14, 17, 18],  $\text{CaO}$ ,  $\text{MgO}$  [7].

A quantum-chemical theoretical approach was proposed in [21, 22] for the study of the acid-base parameters of active centers of disperse oxide materials. It is based on the chemical and mineralogical nature and takes into account up-to-date information on the surface structure of air-dry oxides. Acidity parameters of the active centers on the surface of crystalline oxides with central cations  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{Ti}^{4+}$  were investigated. Correlation of the obtained results of quantum-chem-

ical modeling and calculations with experimental data of potentiometric titration of aqueous suspensions of the studied dispersed materials containing oxides was shown. It has been established [21] that the quantum-chemical approach to modeling surface active centers and the algorithm for calculating acid-base parameters can be used for a preliminary estimation of surface properties of mineral oxide materials and determination of chemical nature of the centers prevailing on the surface. However, these works investigated a limited number of oxides of different chemical natures.

Thus, investigation of the acid-base equilibrium of the surface adsorption hydroxyl-hydrated oxide layer with different chemical properties remains unresolved. Also, regularity of variation of acid-base and energy parameters of the surface-active centers of a wide spectrum of oxides depending on the number of OH-groups and adsorbed water molecules has been insufficiently studied and remained no systematized.

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### 3. The study objective and tasks

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This work objective was to investigate the acid-base equilibrium on the surface of oxides of various chemical properties using the method of quantum-chemical simulation of surface active centers. This will make it possible to predict chemical structure of surface in the mineral oxides, which are used as fillers in composite materials. The idea of the surface properties of oxide fillers will ensure prediction of acid-base interactions on the phase boundary and adjust performance characteristics of the composites. To achieve this goal, the following tasks were formulated:

- determine the basic provisions for quantum-chemical modeling of active centers on the surface of oxides and offer acid-base equilibrium schemes;
- create chemical structural formulas (models) of surface active oxide centers and calculate acid-base and energy parameters;
- find out regularities of dependence of the acid-base and energy parameters of the active centers on the chemical nature and the number of OH-groups and adsorbed water molecules.

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### 4. Quantum-chemical modeling of active centers on the oxide surface and the scheme of acid-base equilibrium

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There are theoretical and experimental studies devoted to modeling oxide and mixture surfaces [16, 19, 20]. To calculate acid-base and energy parameters, the authors used models of the active centers that are likely to exist on the surface of oxides. Also, it is taken into account that the chemical structure and properties of the centers in large part depend on the chemical nature of the oxide, its aggregate state and the conditions of the course of surface equilibrium processes. For simulation of acid-base equilibrium on the surface of air-dry oxides, all of the above-mentioned factors were taken into account as well as well-known information on the structure of the hydroxyl-hydrate layer and the main types of the surface-active centers.

Among the main provisions and principles that can help to propose quantum-chemical models of surface active centers and acid-base equilibrium, the following should be highlighted:

– there are two main types of functional OH groups with different acidic forces on the surface of oxides: isolated and vicinal (hydroxyl layer chemically bound to the surface of water molecules);

– gaseous water is adsorbed in clusters of 2–4 molecules on hydroxyl groups of the surface at the expense of hydrogen bonds (hydration layer of the bound water molecules);

– the parameters of the surface-active centers are determined by the ratio of energy and dimensional characteristics of all components of the geometrically coordinated structure of the crystal lattice fragment as well as by the presence of adsorbed water molecules.

In accordance with the above-mentioned provisions, quantum-chemical models of active centers on the surface of oxides of various chemical nature were constructed. Central element  $E^{n+}$  of the crystal lattice with a coordination number  $N$ , oxygen atoms, OH groups and water molecules were included to the structural formulas of the modeled active centers. For example, Fig. 1 shows chemical structural formulas (models) of anhydrous active centers and centers with one adsorbed water molecule on the surface of silicon oxide with a central element  $Si^{4+}$ .

Anhydrous isolated centers contain one, two (a geminal center) or three OH groups and are associated with the central element. The vicinal centers contain two central elements and two OH groups which are interconnected by a hydrogen bond. Bridge groups which are centers with exchange protons and located in the surface cavities [10] were not investigated in the work. In addition to the three types of anhydrous centers, the subject of the study included hydrated centers containing one to five water molecules and attached to the anhydrous center in accordance with the known mechanism of hydration of surface OH groups [10, 19, 20]. Similarly, models of active centers on the surface of oxides with central elements  $Fe^{3+}$ ,  $Fe^{2+}$ ,  $Al^{3+}$ ,  $Ti^{4+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  were constructed.

## 5. Calculation of acid-base and energy parameters of the active centers

The most informative characteristics of the acid-base equilibrium include two parameters: the equilibrium constant of the deprotonation reaction of a certain surface-active center  $K_a$  and the decimal logarithm with a negative sign  $pK_a$ :

$$AC-H \leftrightarrow AC^- + H^+, \quad (1)$$

$$K_a = [AC^-] \cdot [H^+] / [AC-H], \quad (2)$$

$$pK_a = -\lg K_a, \quad (3)$$

as well as the energy characteristic of the reaction, i. e. the Gibbs free energy  $\Delta G$  (isobaric-isothermal potential).

Table 1 shows models of active centers of the hydroxyl layer of oxides and formulas for calculation of the acid strength.

Calculation of  $pK_a$  active centers was carried out in accordance with the algorithm developed by authors of work [16]. The proposed algorithm used to determine  $pK_a$  hydrated hydroxocomplexes of aluminum which were obtained as a result of interaction of the aluminum oxide surface with water molecules in an aqueous solution:

$$pK_a = pK_w - r_E^{n+}(cn) / r_{OH} \cdot N(cn) \times \\ \times (l \cdot I_E^{n+} + m \cdot A_0^{-2} + k \cdot I_H^+), \quad (4)$$

where  $pK_w$  is an ionic product of water;  $r_E^{n+}(cn)$  is radius of the central element with the coordinating number  $N$ , nm;  $r_{OH} = 0.153$  nm is radius of the functional hydroxyl group;  $I_E^{n+}$  is the energy of ionization of the central element, eV;  $A_0^{-2} = -6.76$  eV is the energy of affinity to the electron of ion  $O^{-2}$ ;  $I_H^+ = 13.59$  eV is proton ionization energy;  $l$ ,  $m$  and  $k$  are stoichiometric coefficients.

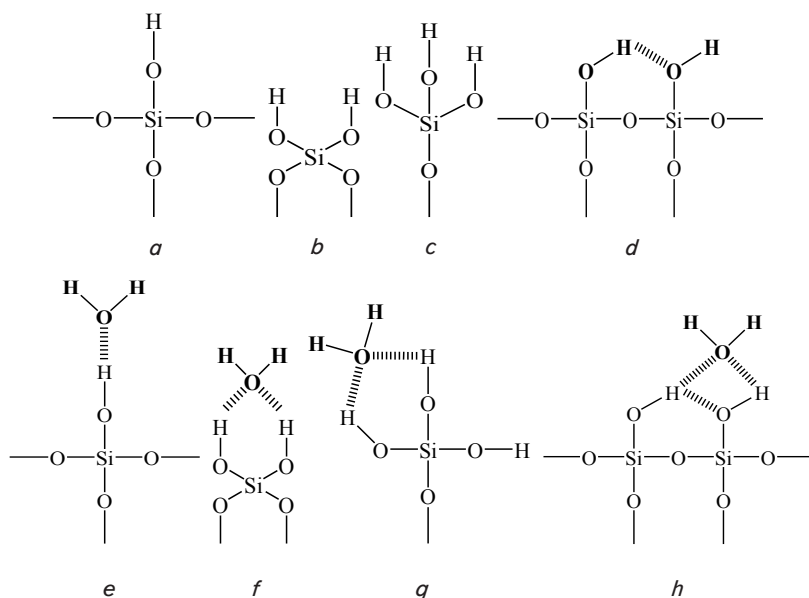


Fig. 1. Models of anhydrous and hydrated active centers on the surface of silicon oxide with a central element of a crystalline lattice  $Si^{4+}$ : *a* – a center with one OH group; *b* – a center with two OH groups (geminal); *c* – a center with three OH groups; *d* – a center with one OH group and one  $H_2O$  molecule; *e* – a geminal center with one  $H_2O$  molecule; *f* – a center with three OH groups and one  $H_2O$  molecule; *g* – a vicinal center with one  $H_2O$  molecule

Table 1

Models of active centers of the hydroxyl surface layer and schemes of deprotonation reactions

Scheme of deprotonation reaction of active centers	Formulas for calculation of the deprotonation constant
Isolated center with one OH group $\equiv E-OH \leftrightarrow \equiv E-O^- + H^+$	$K_a = [H^+][\equiv E-O^-] / [\equiv E-OH]$ $pK_a = pH - \lg([\equiv E-O^-] / [\equiv E-OH])$
Isolated center with two OH groups (geminal) $=E-(OH)_2 \leftrightarrow =E-(OH)O^- + H^+$	$K_a = [H^+][=E-(OH)O^-] / [=E-(OH)_2]$ $pK_a = pH - \lg([=E-(OH)O^-] / [=E-(OH)_2])$
Isolated center with three OH groups $-E-(OH)_3 \leftrightarrow -E-(OH)_2O^- + H^+$	$K_a = [H^+][-E-(OH)_2O^-] / [-E-(OH)_3]$ $pK_a = pH - \lg([-E-(OH)_2O^-] / [-E-(OH)_3])$
Vicinal center with two OH groups connected with hydrogen bond $-E_2O(OH)_2 \leftrightarrow -E_2O(OH)O^- + H^+$	$K_a = [H^+][-E_2O(OH)O^-] / [-E_2O(OH)_2]$ $pK_a = pH - \lg([-E_2O(OH)O^-] / [-E_2O(OH)_2])$

The Gibbs free energy (isobaric isothermal potential) of reactions of deprotonation of active centers at T=298 K was calculated by the formula:

$$\Delta G = pK_a \cdot 2,303 \cdot R \cdot T \tag{5}$$

Table 2 shows the energy and dimensional parameters of the selected central elements used for calculation.

Table 2

Energy and dimensional parameters of the central elements

Central element (E <sup>n+</sup> )	N	r <sub>E<sup>n+</sup></sub> , nm	I <sub>E<sup>n+</sup></sub> , eV
Al <sup>3+</sup>	6	0.061	28.44
Al <sup>3+</sup>	5	0.056	28.44
Al <sup>3+</sup>	4	0,047	28,44
Fe <sup>3+</sup>	6	0,067	30,65
Fe <sup>2+</sup>	6	0.080	16,18
Si <sup>4+</sup>	4	0.042	45.13
Si <sup>4+</sup>	6	0.054	45.13
Ti <sup>4+</sup>	4	0,056	43,24
Ti <sup>4+</sup>	6	0.065	43.24
Ca <sup>2+</sup>	6	0.114	11.87
Mg <sup>2+</sup>	4	0.074	15.03

Using the energy and dimensional parameters of the central elements of the crystalline lattice of oxides of various chemical natures, pK<sub>a</sub> of active centers were calculated by formula (4). The number of central elements, OH groups and water molecules corresponded to the chemical structural formula of a certain active center (Fig. 1). The Gibbs free energy of ΔG centers was calculated by formula (5). Based on the calculations, the graphs of the dependence pK<sub>a</sub>=f(n<sub>H<sub>2</sub>O</sub>) were plotted.

Fig. 2–6 and Tables 3–7 present results of calculation of the acidity index of the active centers pK<sub>a</sub> and ΔG depending on the nature of the central element, the number of OH groups and the number of adsorbed water molecules (hydration numbers n<sub>H<sub>2</sub>O</sub>).

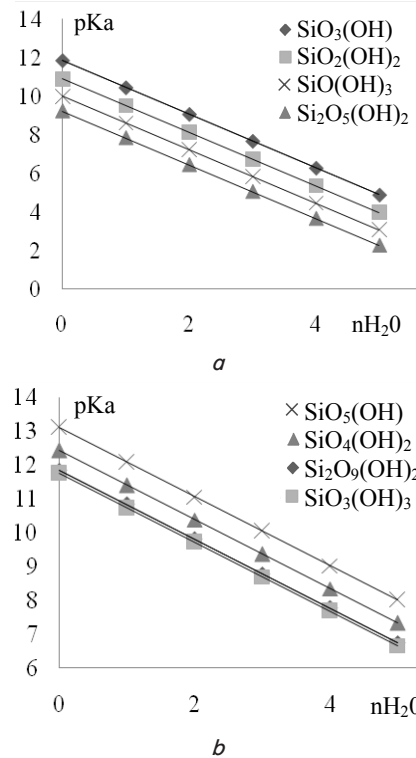


Fig. 2. Dependences of the change of pK<sub>a</sub> of the active centers on n<sub>H<sub>2</sub>O</sub> on the SiO<sub>2</sub> surface with central element Si<sup>4+</sup> and coordination number: a – 4; b – 6

Table 3

Results of calculation of acid-base and energy parameters of active centers on the surface of SiO<sub>2</sub>

Active center	Central element	Coordination number N	θ	pK <sub>a</sub> <sup>0</sup>	ΔG, kJ/mole
SiO <sub>3</sub> OH	Si <sup>4+</sup>	4	-1,39	11.85	67.58
SiO <sub>2</sub> (OH) <sub>2</sub>				10.92	62,28
SiO(OH) <sub>3</sub>				10.00	57.03
Si <sub>2</sub> O <sub>5</sub> (OH) <sub>2</sub>				9.23	52.64
SiO <sub>5</sub> OH	Si <sup>4+</sup>	6	-1,02	13.10	74.71
SiO <sub>4</sub> (OH) <sub>2</sub>				12.42	70.83
SiO <sub>3</sub> (OH) <sub>3</sub>				11.74	66.95
Si <sub>2</sub> O <sub>9</sub> (OH) <sub>2</sub>				11.85	67.58

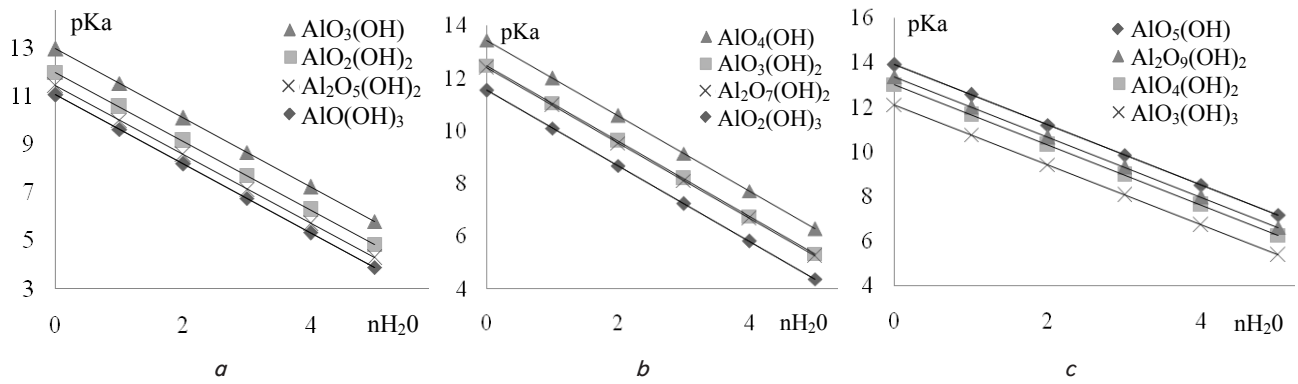


Fig. 3. Dependences of the change of  $pK_a$  of the active centers on  $n_{H_2O}$  on the  $Al_2O_3$  surface with central element  $Al^{3+}$  and coordination number:  $a - 4$ ;  $b - 5$ ;  $c - 6$

Table 4

Results of calculation of acid-base and energy parameters of active centers on the surface of  $Al_2O_3$

Active center	Central element	Coordination number N	$\theta$	$pK_a^0$	$\Delta G$ , kJ/mol
$AlO_3OH$ $AlO_2(OH)_2$ $AlO(OH)_3$ $Al_2O_5(OH)_2$	$Al^{3+}$	4	-1.43	12.96 12.00 11.05 11.43	73.91 68.43 63.02 65.19
$AlO_4OH$ $AlO_3(OH)_2$ $AlO_2(OH)_3$ $Al_2O_7(OH)_2$	$Al^{3+}$	5	-1.43	13.43 12.48 11.53 12.38	76.59 71.17 65.76 70.60
$AlO_5OH$ $AlO_4(OH)_2$ $AlO_3(OH)_3$ $Al_2O_9(OH)_2$	$Al^{3+}$	6	-1.35	13.90 13.01 12.11 13.36	79.27 74.20 69.09 76.19

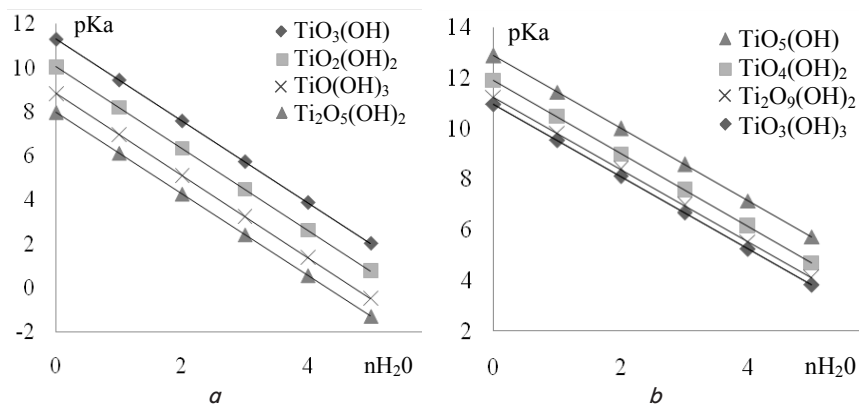


Fig. 4. Dependences of the change of  $pK_a$  of the active centers on  $n_{H_2O}$  on the  $TiO_2$  surface with central element  $Ti^{4+}$  and coordination number:  $a - 4$ ;  $b - 6$

Table 5

Results of calculation of acid-base and energy parameters of active centers on the surface of  $TiO_2$

Active center	Central element	Coordination number N	$\theta$	$pK_a^0$	$\Delta G$ , kJ/mole
$TiO_3OH$ $TiO_2(OH)_2$ $TiO(OH)_3$ $Ti_2O_5(OH)_2$	$Ti^{4+}$	4	-1.85	11.29 10.05 8.82 7.96	64.39 57.32 50.30 45.40
$TiO_5OH$ $TiO_4(OH)_2$ $TiO_3(OH)_3$ $Ti_2O_9(OH)_2$	$Ti^{4+}$	6	-1.43	12.87 11.91 10.96 11.25	73.40 67.92 62.51 64.16

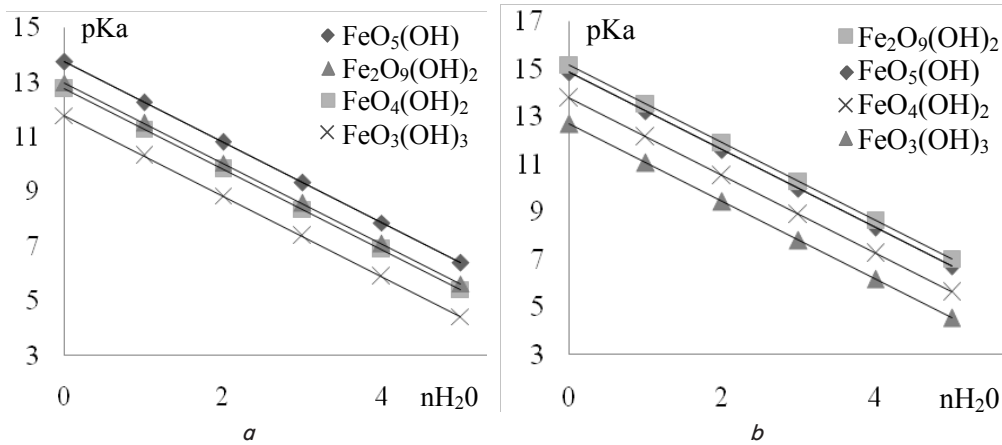


Fig. 5. Dependences of the change of  $pK_a$  of active centers on  $n_{H_2O}$  on the surface:  $a - Fe_2O_3$ ;  $b - FeO$

Table 6

Results of calculation of acid-base and energy parameters of active centers on  $Fe_2O_3$  and  $FeO$  surfaces

Active center	Central element	Coordination center N	$\theta$	$pK_a^0$	$\Delta G$ , kJ/mole
FeO <sub>5</sub> OH FeO <sub>4</sub> (OH) <sub>2</sub> FeO <sub>3</sub> (OH) <sub>3</sub> Fe <sub>2</sub> O <sub>9</sub> (OH) <sub>2</sub>	Fe <sup>3+</sup>	6	-1.48	13.74 12.75 11.78 12.98	78.36 72.71 67.18 73.94
FeO <sub>5</sub> OH FeO <sub>4</sub> (OH) <sub>2</sub> FeO <sub>3</sub> (OH) <sub>3</sub> Fe <sub>2</sub> O <sub>9</sub> (OH) <sub>2</sub>	Fe <sup>2+</sup>	6	-1.63	14.86 13.78 12.69 15.18	84.75 78.59 72.37 86.57

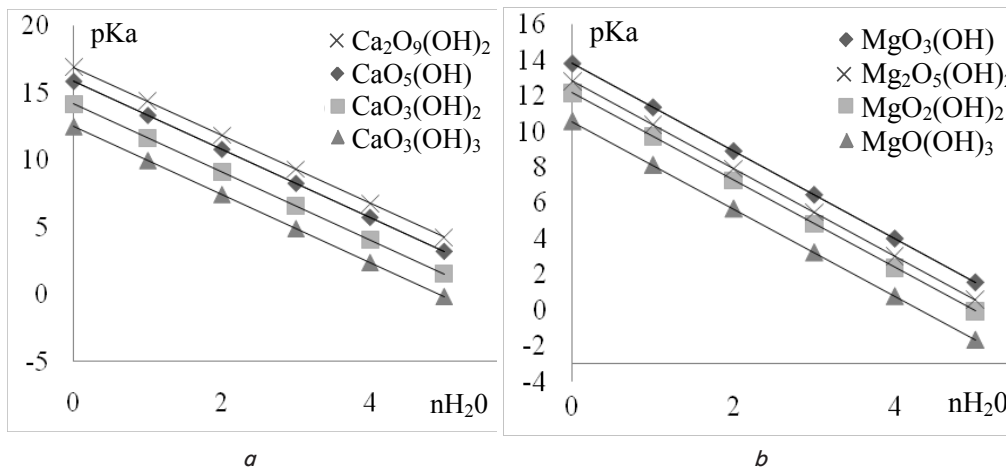


Fig. 6. Dependences of the change of  $pK_a$  of the active centers on  $n_{H_2O}$  on the surface of:  $a - CaO$ ;  $b - MgO$

Table 7

Results of calculation of acid-base and energy parameters of active centers on the surface of  $CaO$  and  $MgO$

Active center	Central element	Coordination number N	$\theta$	$pK_a^0$	$\Delta G$ , kJ/mol
CaO <sub>5</sub> OH CaO <sub>4</sub> (OH) <sub>2</sub> CaO <sub>3</sub> (OH) <sub>3</sub> Ca <sub>2</sub> O <sub>9</sub> (OH) <sub>2</sub>	Ca <sup>2+</sup>	6	-2.53	15.87 14.18 12.51 16.90	90.51 80.87 71.35 96.38
MgO <sub>3</sub> OH MgO <sub>2</sub> (OH) <sub>2</sub> MgO(OH) <sub>3</sub> Mg <sub>2</sub> O <sub>5</sub> (OH) <sub>2</sub>	Mg <sup>2+</sup>	4	-2.45	13.81 12.18 10.55 12.81	78.76 69.46 60.17 73.06



Calculated values of pK<sub>a</sub> and ΔG of deprotonation reactions of anhydrous and hydrated active centers indicate that acidity of all centers is directly proportional to the number of OH groups and the number of hydration  $n_{H_2O}$ . It was established that the higher the coordination number of the central element with the same charge, the higher pK<sub>a</sub> of anhydrous centers and the value of ΔG.

## 6. Discussion of the results and revealing regularities of dependence parameters of active centers on the chemical nature

The obtained regularities were compared with the indices of electrical affinity of cations and basicity of oxide surface (Table 8) according to data from paper [23].

Table 8

Electrical affinity of cations and basicity of oxides [23]

Oxide	Basicity, kJ	Cation	Electrical affinity, kJ
CaO	88.62	Ca <sup>2+</sup>	681.34
MgO	57.27	Mg <sup>2+</sup>	902.88
FeO	28.01	Fe <sup>2+</sup>	994.84
Al <sub>2</sub> O <sub>3</sub>	13.79	Al <sup>3+</sup>	1617.66
Fe <sub>2</sub> O <sub>3</sub>	-3.76	Fe <sup>3+</sup>	1646.92
SiO <sub>2</sub>	-7.52	Si <sup>4+</sup>	2403.50
TiO <sub>2</sub>	-19.65	Ti <sup>4+</sup>	2135.98

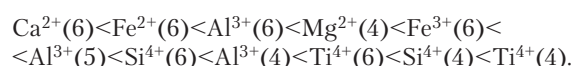
According to these data, electrical affinity of cations correlates with the basicity of the oxide surface. Exceptions are cations Si<sup>4+</sup> and Ti<sup>4+</sup>. Thus, at electrical affinity of Ti<sup>4+</sup> (2135.98 kJ) lower than that of Si<sup>4+</sup> (2403.50 kJ), basicity of SiO<sub>2</sub> (-7.52 kJ) is greater than basicity of TiO<sub>2</sub> (-19.65 kJ). A similar correlation is also characteristic for the results obtained. It should be noted that the revealed regularities coincide only with oxides in which crystalline lattice includes central elements with the same coordination number. The regularities do not correlate when the coordination number changes.

From the results presented in Fig. 2 and Table 3, it follows that vicinal anhydrous centers of Si<sub>2</sub>O<sub>5</sub> (OH)<sub>2</sub> and Si<sub>2</sub>O<sub>9</sub> (OH)<sub>2</sub> on the surface of SiO<sub>2</sub> are characterized by the lowest parameters pK<sub>a</sub> and consequently the highest acidic properties irrespective the coordination number of Si<sup>4+</sup>. Centers with the coordination number of the central element 6 exhibit lower acidity than the centers with the coordination number 4. Fig. 3 and Table 4 show that the acid-base parameters of the active centers on the Al<sub>2</sub>O<sub>3</sub> surface depend on the coordination number of the central element Al<sup>3+</sup> and the number of hydration. Anhydrous isolated active centers with three OH groups (AlO(OH)<sub>3</sub>, AlO<sub>2</sub>(OH)<sub>3</sub> and AlO<sub>3</sub>(OH)<sub>3</sub>) are characterized by the highest acidity. Isolated active centers with one OH group (SiO<sub>3</sub>OH, SiO<sub>5</sub>OH, AlO<sub>3</sub>OH, AlO<sub>4</sub>OH and AlO<sub>5</sub>OH) are characterized by the highest basicity. The active centers on the TiO<sub>2</sub> feature the highest acidity from all the oxides considered (Fig. 4 and Table 5). The surface of Fe<sub>2</sub>O<sub>3</sub> is more basic than the surface of FeO (Fig. 5 and Table 6) and this fact can be explained by a larger charge of the central element of Fe<sup>3+</sup>. Anhydrous FeO<sub>3</sub>(OH)<sub>3</sub> centers are characterized by the highest acidity,

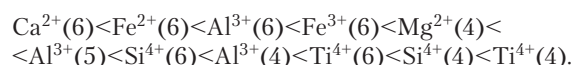
and FeO<sub>5</sub>OH and vicinal Fe<sub>2</sub>O<sub>9</sub> (OH)<sub>2</sub> centers are the most isolated. The surface of CaO is characterized by the highest basicity of all oxides considered (Fig. 6 and Table 7). Centers with the most basicity among all considered (isolated CaO<sub>5</sub>OH with pK<sub>a</sub>=15.87 and vicinal Ca<sub>2</sub>O<sub>9</sub>(OH)<sub>2</sub> with pK<sub>a</sub>=16.9) were found on the surface of CaO.

Summarizing the foregoing, it can be claimed that the coordination number and the charge of the central element are the determining factors for the acid-basic properties of the active centers. Acidic properties grow with decrease of the coordination number and increase of charge. It is obvious that radius of the central element ion increases and there is a "blurring" of its electron-acceptor ability which explains weakening of acid properties of the centers.

Analyzing all the results obtained, it is necessary to separate the isolated and vicinal active centers. Thus, according to the nature of the central element and the coordination number E<sup>n+</sup> (N), acidity of isolated centers increases in the following order:



According to the nature of the central element and the coordination number E<sup>n+</sup>(N), acidity of vicinal centers increases in the following order:



The comparative characteristic of the found regularities of change in the acidity index of isolated and vicinal centers depending on the nature of the central element indicates an identical nature and practically does not depend on the type of the active center.

As a result of calculations, it was established that acidity of isolated centers increases in direct proportion with the increase in the number of OH groups. Fig. 7 shows graphs of decreasing the pK<sub>a</sub> index, i. e. increasing acidity of isolated centers depending on the nature of the central element and the number of OH groups. The tangent of the angle of inclination of the direct dependence pK<sub>a</sub>=f(nOH-groups) to the abscissa is the value at which the pK<sub>a</sub> of the active center decreases with an increase by one OH group. The values of these quantities are given in Table 9

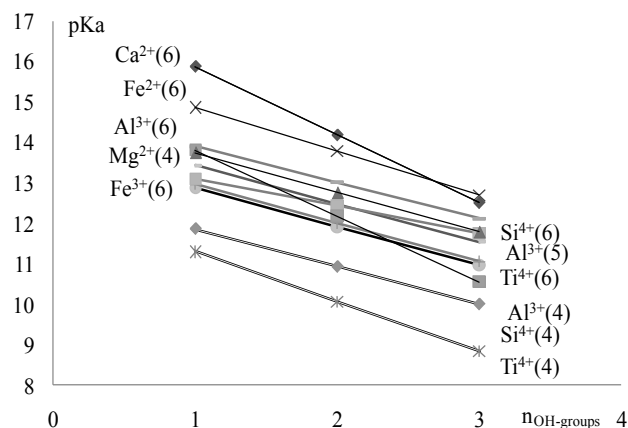
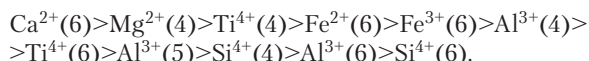


Fig. 7. Dependence of the change of pK<sub>a</sub> of isolated centers with the central element and the coordination number E<sup>n+</sup>(N) on the number of OH groups

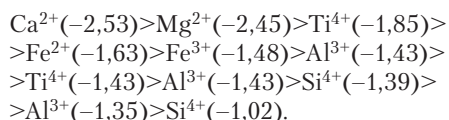
**Table 9**  
Tangent of the angle of inclination of the direct dependence  $pK_a=f(n_{OH\text{-groups}})$  of isolated active centers

$E^{n+}$	$Ca^{2+}$	$Fe^{2+}$	$Al^{3+}$	$Mg^{2+}$	$Fe^{3+}$	$Al^{3+}$	$Si^{4+}$	$Al^{3+}$	$Ti^{4+}$	$Si^{4+}$	$Ti^{4+}$
N	6	6	6	4	6	5	6	4	6	4	4
	1.69	1.08	0.90	1.63	0.98	0.95	0.68	0.96	0.96	0.93	1.23

Thus, the tendency to the growth of acidity of the active center with increase of OH groups in decreases in the following order:



It was established that when the amount of adsorbed water molecules increases, the acidity of the active centers of all types increases. This conclusion coincides with the results of work [10]. Approximation of the obtained dependences  $pK_a=f(n_{H_2O})$  (Fig. 2–6) has led to linear equations of the form  $pK_a = \theta \cdot n_{H_2O} + pK_a^0$ . It turned out that the free member  $pK_a^0$  has a real physical meaning of the acidity index of anhydrous active centers at  $n_{H_2O} = 0$ . Tangent of the angle of inclination of the direct dependence  $pK_a=f(n_{H_2O})$  to the abscissa axis  $n_{H_2O}$   $\theta$  is the value by which the acidity index  $pK_a$  of the active centers decreases with adsorption on them of one molecule of water (Tables 3–7). Thus, the value  $\theta$  characterizes the degree of growth of the active center acid properties as the number of hydration  $n_{H_2O}$  increases. The degree of growth of the active center acidity with increase in the amount of adsorbed water molecules decreases in the following order:



Comparison of the revealed regularity demonstrates a complete analogy. This fact may indicate an identical character of growth of acidity of the surface-active centers of

oxides of various chemical natures with increasing thickness of both hydroxyl and hydration surface layers.

### 7. Conclusions

1. The acid-base equilibrium on the surface of CaO, MgO, FeO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub> oxides was studied by simulating surface active centers. It was shown that the oxide surface constitutes a hydroxyl-hydrated layer with a wide spectrum of active centers. It was established that active centers in reactions of deprotonation are characterized by certain acid-base and energy parameters and can enter the acid-basic interactions.

2. With the use of quantum-chemical modeling, models of anhydrous and hydrated active centers on the surface of oxides were proposed. The created chemical structural formulas of the centers take into account the chemical nature and the crystalline structure of air-dry oxides, the aggregate state and the conditions for the course of surface equilibrium processes. Acid-base ( $pK_a$ ) and energy ( $\Delta G$ ) equilibrium parameters in reactions of deprotonation of active centers were calculated. It was found that the acidity indices  $pK_a$  of all anhydrous centers have high values from 7.96 to 16.9, that is, they feature weakly basic, strongly basic or alkaline nature. Accordingly, the Gibbs free energy values of deprotonation of centers are positive and vary from 45.40 to 96.38 kJ/mol.

3. Regularities of changes in the acid-base and energy parameters of model surface active centers depending on the nature of the central element of the crystal lattice of oxide, the number of OH-groups and the number of hydration (the number of adsorbed water molecules) have been established. It was found that the focal factors for the acid-base properties of the centers are the coordination number and the charge of the central element. Acidic properties increase with a decrease in the coordination number and with increase in the charge. It was shown that acidity of isolated and vicinal centers is directly proportional with the increase in number of OH groups and adsorbed water molecules. The identical character of growth of acidity of surface active centers in oxides of various chemical nature with an increase in thickness of both hydroxyl and hydration layers of the surface was revealed.

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