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Quantum Chemical Modelling Protolytic Equilibrium on Surface Oxide Materials

Yuliya Danchenko*

Kharkiv National University of Civil Engineering and Architecture 61002, Sums kaya street, 40, Kharkiv, Ukraine

* Correspondence: u_danchenko@ukr.net

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ABSTRACT

The results of calculation of the acid and basic properties of a surface of the disperse oxide materials on the basis of SiO_2 , $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 by the method of quantum chemical modelling are presented in the article. The correspond models of the superficial active centres for this purpose are offered, the constants of their protolytic equilibrium pK_a and free Gibbs's energy deprotonation reactions are calculated. It is established, that acidity of all types of the superficial active centres increases among $\text{Al}^{3+} < \text{Fe}^{3+} < \text{Si}^{4+} < \text{Ti}^{4+}$ depending on the nature of the central element. The acidity of the isolated centres grows at increase of quantity of OH-groups. The vicinal superficial centres $\text{Si}_2\text{O}_5(\text{OH})_2$ and $\text{Ti}_2\text{O}_5(\text{OH})_2$ have the greatest acidity from all spectrum of the researched centres. It is established by the results of calculations that the acidity of the active centres grows at increase in quantity of the adsorbed water molecules at surfaces for all disperse oxide materials. This dependence is approximated by the linear equation of a kind $\text{pK}_a = \theta \cdot n \text{H}_2\text{O} + \text{pK}_{a0}$, and the free member pK_{a0} has real physical sense of an indicator of acidity of the waterless active centres.

Keywords: The Acid And Basic Properties; Quantum Chemical Modelling; The Active Centre; The Disperse Oxide Material

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QUANTUM CHEMICAL MODELLING PROTOLYTIC EQUILIBRIUM ON SURFACE OXIDE MATERIALS

Yuliya Danchenko*

Kharkiv National University of Civil Engineering and Architecture
61002, Sumskaya street, 40, Kharkiv, Ukraine

*u_danchenko@ukr.net

www.nzaar.com

Abstract

The results of calculation of the acid and basic properties of a surface of the disperse oxide materials on the basis of SiO_2 , $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 by the method of quantum chemical modelling are presented in the article. The correspond models of the superficial active centres for this purpose are offered, the constants of their protolytic equilibrium pK_a and free Gibbs's energy deprotonation reactions are calculated. It is established, that acidity of all types of the superficial active centres increases among $\text{Al}^{3+} < \text{Fe}^{3+} < \text{Si}^{4+} < \text{Ti}^{4+}$ depending on the nature of the central element. The acidity of the isolated centres grows at increase of quantity of OH-groups. The vicinal superficial centres $\text{Si}_2\text{O}_5(\text{OH})_2$ and $\text{Ti}_2\text{O}_5(\text{OH})_2$ have the greatest acidity from all spectrum of the researched centres. It is established by the results of calculations that the acidity of the active centres grows at increase in quantity of the adsorbed water molecules at surfaces for all disperse oxide materials. This dependence is approximated by the linear equation of a kind $pK_a = \theta \cdot n_{\text{H}_2\text{O}} + pK_a^0$, and the free member pK_a^0 has real physical sense of an indicator of acidity of the waterless active centres.

Keywords: The Acid And Basic Properties, Quantum Chemical Modelling, The Active Centre, The Disperse Oxide Material

1. Introduction

One of the major sections of modern polymeric materials technology is physic chemistry of the superficial phenomena in composite materials. The urgency of this direction is connected with creation of new building polymeric composites, many of which are heterogeneous systems with advanced interfaces of phases. The properties of a surface of the dispersible phase define the initial stage of adhesive interaction - adsorption, wetting, flowing property of polymeric binding on a surface of the filler, formation phases' partition border, imbibitions of the filled and reinforced systems by polymers. The disperse mineral oxide materials which advantages are connected with availability, cheapness, and also possibility to receive building materials with a complex of necessary properties are more often applied by working out of new polymeric composite materials for building like fillers. The chemical and mineralogical structure of these fillers and, accordingly, their

superficial properties are extremely unstable in connection with their natural origin. Besides, disperse particles of the oxide materials, having superfluous superficial energy, easily adsorb molecules of water from air, which form the hydroxyl and hydrated layer in the form of the active centres' wide spectrum and which acid and basis properties are studied insufficiently [1,2].

2. Literature Review

It is known, that the structure of adsorptive superficial layer of the oxide materials consists of chemically connected water molecules forming a layer OH-groups (Brensted's active centres) and the subsequent hydrated layers from the water molecules connected with hydroxyl layer by means of hydrogen communications. Besides, it is supposed, that the aprotic Lewis's acid and basic active centres which quantity on air-dry surfaces, apparently, is insignificant, can be presented on a surface. Definition of the acid and basic

characteristics of the active centres of a superficial layer of the disperse oxide materials is a difficult problem, but it is very important, from the technological point of view. The literature review testifies that the methods, allowing to define quantity and properties of the superficial active centres are basically experimental [1-3], and also are settlement based on quantum chemical models [4], they often lead to inconsistent results.

The most widespread disperse fillers for building polymeric materials are materials on a basis of oxides Si, Al, Fe, Ti and some other elements which maintenance it is possible to consider as extrinsic minerals. Research of the acid and basic properties of oxides' surface by various methods leads to inconsistent conclusions that is connected not only with their unstable chemical and mineralogical structure, but also substantially depend on technology of preparation of samples, dispersion, conditions of storage and many other factors which define the degree of a surface's saturation by water molecules. It is obvious, that presence of the adsorbed water molecules and their quantity essentially influences acid force of functional hydroxyl groups of oxides' surface [1].

The data about laws of change of acidity of the active centres from the degree of oxides' hydration for the various chemical nature will help to interpret existing experimental data, and also to predict the superficial acid and basic properties of the superficial active centres in mixed oxide materials.

The work purpose is application of quantum chemical modelling for an estimation of acid force of the active centres on a surface of the mineral disperse oxide materials.

3. Research Methods

The approach based on the chemical and mineralogical nature of acid force of the superficial active centres of disperse oxide materials is applied in work. This approach takes into attention the modern information about structure of the surface air-dry oxides. The applied approach is based on some representations:

1) Two types of functional hydroxyl groups with various acid force – the isolated and vicinal active centres (a layer of water molecules chemically connected with a surface) is present on the oxide materials' surface;

2) The gaseous water by the means of hydrogen communications (layers of physically connected water molecules), forming a wide spectrum of the active centres is adsorbed on the hydroxyl surface groups in the form of clusters, consisting of 2-4 molecules;

3) The acid and basic parameters of the superficial active centre are defined by a parity of power and dimensional characteristics of all components of geometrically co-ordinated structure of a fragment of the crystal lattice, and also by presence of the adsorbed water molecules.

Authors [2] offer the formula for calculation of acid force of differently charged ions existing in water solutions or on a surface of the firm bodies:

$$pK_a = pK_w - \frac{r_{E^{n+}}(cn)}{r_{OH^-} \cdot N(cn)} (I_3^{n+} + m \cdot A_{O^{-2}} + k \cdot I_{H^+}), \quad (1)$$

where – pK_w – ion product of water; $r_{E^{n+}}(cn)$ – radius of the central element with coordination number N , nm; $r_{OH^-} = 0,153$ nm – radius of the functional hydroxyl group; $I_{E^{n+}}$ – the energy of the central element ionisation, eV; $A_{O^{-2}} = -6,76$ eV – the energy of affinity of ion to electron O^{-2} ; $I_{H^+} = 13,59$ eV – the energy of proton ionisation; k and m – stoichiometrical coefficients.

Those circumstance, that calculation is conducted only for the hydrated ions existing in the water environment, limits application of the given formula for definition of acid force of the air-dry disperse materials' superficial centres.

4. Analysis & Results

The indicators of acidity of the superficial active centres of oxides with central elements Si^{4+} , Al^{3+} , Fe^{3+} , Ti^{4+} have been calculated using the formula (1).

The models of the superficial active centres of oxide material, in which structure the following atoms directly connected with the active centre are included: the central element with coordination number N , oxygen atoms, OH-group atoms, and also water molecules, have been used for calculation of acid force of the active centres of a surface. These active centres are the isolated ones containing one, two and three OH-group, connected with the central element E^{n+} , and also vicinal ones, containing two elements E^{n+} and two OH-groups, united by hydrogen communication. The bridging groups, which are the centres with exchange protons, are situated in cavities of a surface and were not considered in research. The calculations were made for the hydrated active centres containing from one to five water molecules, which are adsorbed according to the known mechanism of superficial OH-groups hydration [2,4].

The power and dimensional parameters of the superficial active centres used for calculation of their acid force are presented in tab. 1.

Tab. 1. Power and dimensional parameters of the superficial active centres

Central element (E^{n+})	N	$r_{\text{E}^{n+}}$, nm	$I_{\text{E}^{n+}}$, eV
Al^{3+}	6	0,061	28,44
Fe^{3+}	6	0,067	30,65
Si^{4+}	4	0,042	45,13
Ti^{4+}	4	0,056	43,24

Free Gibbs's energy of deprotonation reaction of the active centres at $T = 298\text{K}$ is calculated under the formula $\Delta G = pK_a \cdot 2,303 \cdot R \cdot T$ [4]. Tab. 2 contains the received dependences of an indicator of acidity of the active centres by the nature of central element and number of the adsorbed water molecules (hydration number $n_{\text{H}_2\text{O}}$).

Tab. 2. The results of calculation of parameters of acidity of the active centres of oxides' surface

Active centre	θ	pK_a^0	ΔG , kilo joule/mole
SiO_3OH	-1,39	11,85	67,58
$\text{SiO}_2(\text{OH})_2$		10,92	62,28
$\text{SiO}(\text{OH})_3$		10,00	57,03
$\text{Si}_2\text{O}_5(\text{OH})_2$		9,23	52,64
TiO_3OH	-1,85	11,29	64,39
$\text{TiO}_2(\text{OH})_2$		10,05	57,32
$\text{TiO}(\text{OH})_3$		8,82	50,30
$\text{Ti}_2\text{O}_5(\text{OH})_2$		7,96	45,40
AlO_5OH	-1,35	13,90	79,27
$\text{AlO}_4(\text{OH})_2$		13,01	74,20
$\text{AlO}_3(\text{OH})_3$		12,11	69,09
$\text{Al}_2\text{O}_9(\text{OH})_2$		13,36	76,19
FeO_5OH	-1,48	13,74	78,36
$\text{FeO}_4(\text{OH})_2$		12,75	72,71
$\text{FeO}_3(\text{OH})_3$		11,78	67,18
$\text{Fe}_2\text{O}_9(\text{OH})_2$		12,98	73,94

Approximation of the received dependences has led to the following linear equations: $pK_a = \theta \cdot n_{\text{H}_2\text{O}} + pK_a^0$. It has appeared, that the free member pK_a^0 has real physical sense of an indicator of acidity of the waterless active centres at $n_{\text{H}_2\text{O}}=0$. The calculated tangent of a corner of an inclination of direct dependence $pK_a = f(n_{\text{H}_2\text{O}})$ to an axis of abscises θ is the value for which the acidity indicator pK_a decreases at adsorption of one water molecule on the active centre. It is possible to confirm, that value θ characterises the degree of increase in acidity of the active centre in process of growth of hydration

number, and it increases among Al^{3+} (-1,35) $< \text{Si}^{4+}$ (-1,39) $< \text{Fe}^{3+}$ (-1,48) $< \text{Ti}^{4+}$ (-1,85).

The linear dependences $\text{pK}_a = f(n_{\text{H}_2\text{O}})$ for superficial active centres TiO_2 are resulted for example on fig. 1.

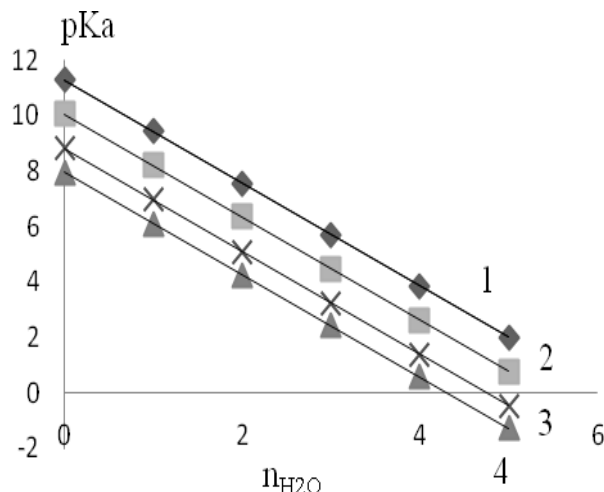


Fig.1. The dependences of change of pK_a active centres: 1- $\text{TiO}_3(\text{OH})$; 2- $\text{TiO}_2(\text{OH})_2$; 3- $\text{TiO}(\text{OH})_3$; $\text{Ti}_2\text{O}_5(\text{OH})_2$ on hydration number $n_{\text{H}_2\text{O}}$.

5. Discussion & Conclusion

The received values of the constant and free Gibbs's energy by the reactions of deprotonation of the waterless active centres show, that acidity of all types of the active centres increases among $\text{Al}^{3+} < \text{Fe}^{3+} < \text{Si}^{4+} < \text{Ti}^{4+}$ depending on the nature of the central element. The acidity of the isolated centres grows at increase of quantity of OH-groups from one to three, forming the active centre. The vicinal superficial centres $\text{Si}_2\text{O}_5(\text{OH})_2$ and $\text{Ti}_2\text{O}_5(\text{OH})_2$ have the greatest acidity from all spectrum of the researched centres. At the same time the vicinal centres $\text{Al}_2\text{O}_9(\text{OH})_2$ and $\text{Fe}_2\text{O}_9(\text{OH})_2$ are characterised more likely by the basic character and also by values of free Gibbs's energy deprotonation of reaction, which are in 1,5 times greater.

The calculated data show, that the acidity of the active centres grows at increase in quantity of the adsorbed water

molecules at surfaces for all oxide disperse materials, and it will be co-ordinated with conclusions of authors [2,5].

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