

ELECTROSTATIC ASPECTS OF ADSORPTION ON SILICA AND TITANIA SURFACES

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Abstract

The influence of outer electric field of the ionic crystal surface layer on the structure of adsorption complexes is examined and their role in the run of physico-chemical processes at the solid-gas interface is studied. Taking into account of the subsurface electric field has been shown to allow to predict the structure of primary adsorption complexes, to estimate the energetics of the transformations of molecules at solid surfaces, and to determine properties of the surface compounds formed.

An *a priori* analysis on the reactivity and peculiarities of chemical behavior of molecules is a rather difficult but quit solvable task of theoretical chemistry. If molecules interact with solid surface, the complexity of its solution increases repeatedly. This is cause by the circumstances as follows: firstly, an interaction occurs between two systems of different nature – molecule and surface that can be considered to be endless at the scale of partner; secondly, it is difficult to simulate a surface adequately that is a macrodefect of the crystal periodic structure. Moreover, a definite grade of amorphization of surface layer is a characteristic of even typical crystals [1]. Taking into account probable relaxation and reconstruction of real surface as compared with ideal one, obtaining valid structural information on surface and subsurface layer of solids seems to be rather problematic. A cluster model of solid and its surface that is natural for chemists operating terms of local chemical bonds (despite it is not quite suitable for the systems with covalent bond) may be considered to be fit for the objects with ionic bonds that are objects of our investigation.

In the latter case we have a system of alternating charge densities what presses to take into account long-range electrostatic interactions caused by charges at dots of the crystalline lattice of support as well as by those of the atoms limiting its surface. Such a counting of electrostatic effects is not common used for description of the reactivity and chemical transformations of admolecules within subsurface layer what effects on the correctness of the results obtained.

From the concept aspect, a microscopic description of the reactions at solid surface with ionic bond type should include the following moments:

1. An analysis of electronic and nuclear subsystems of the molecule-reagent;
2. An examination of electronic and nuclear subsystems of solid what is possible provided subsurface layer is simulated at appropriate level;
3. A calculation of the interaction between them at the account of surface electrostatic field (orientation and polarization of admolecule, deformation of admolecule and local surrounding of reactive site of the surface;
4. The final stage is an act of chemical transformation at solid surface what assumes knowledge on multidimensional surface of potential energy.

This program can be realized, in principle, at two levels: the non-empirical one foresees calculations of admolecule and small cluster, i.e. badly simulates the surface itself, and the semiempirical one allows to examine, besides admolecule, a large clusters that performs the structure of the most characteristic surface parts in a proper way.

Nevertheless, the case of the system taking into account expanding process molecule reaction complicated and effective scheme example, let us of solid support

A fragment of β -cristobalite subsurface layer minimum ρ with atom, and constant silicon atom surface H_2O , HF) are atom. A region entrance into it small electron potential value potential barrier cavity. It should spatial distribution (silicagels and of β -cristobalite



Chemical properties of chemically non-connected nature functional groups substantially less than that of hydroxy as compared with hexagonal cavities ligands into co

Nevertheless, the approach described can not be realized practically in the pure form in case of the systems interesting for chemistry, and so a necessity arises of the adequate taking into account of electrostatic field and potential of solid object. A problem of expanding procedure of the calculation of electrostatic potential accepted in the theory of molecule reactivity [2] to the interaction of admolecules with solid surface is rather complicated and labor-consuming but we were a success in its solution and in developing effective scheme of calculation for the case of ionic crystals. Taking silica surface as an example, let us demonstrate the importance and fruitfulness of counting electrostatic field of solid support.

A fragment of hydroxylated SiO_2 surface is performed in the fig. 1 that has a structure of β -cristobalite (111) face, and the electrostatic potential distribution itself within subsurface layer is given in the fig. 2 [3]. It is seen from this figure that there is a local minimum ρ within the plane of silanol group at the distance of about 1 Å from its oxygen atom, and continuous regions of positive potential are characteristic of hydrogen and silicon atom surroundings. It allows to assume that small polar molecules (for example, H_2O , HF) are capable of penetration into coordination sphere of hydroxylated silicon atom. A region of high positive ρ value in the hexagonal cavity of surface layer and near entrance into it forming the most considerable adsorption potential for binding anions and small electron donor molecules is of particular interest. A region with little negative potential value stationed above entrance into the cavity seems to determine relatively low potential barrier for penetration of anions and small electron donor molecules into the cavity. It should be noted that the qualitative conclusions on the peculiarities of the ρ spatial distribution obtained for model systems are applicable also to disperse silicas (silicagels and aerosil) with the surface resembling structurally the crystallographic faces of β -cristobalite.

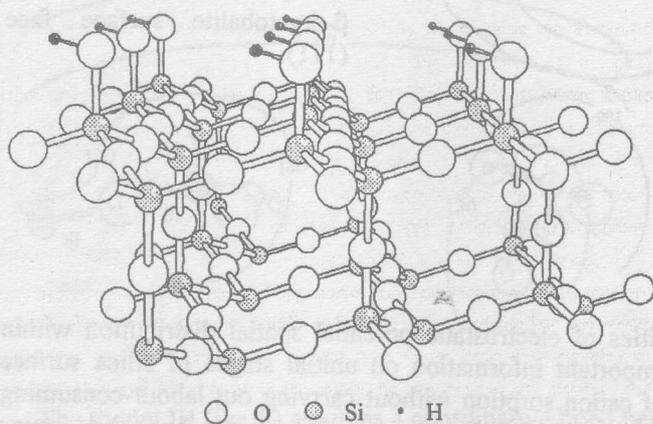


Fig. 1. A schematic representation of the structure of silica surface similar to the β -cristobalite face (111)

Chemical modification is known to be capable to change substantially sorptive properties of silica surface [4]. Due to identity of support for a hydroxylated and chemically modified silicas changes in sorptive properties of different samples are to be connected naturally with corresponding peculiarities of ρ within the surrounding of functional groups. Thus in case of chlorinated silica (fig. 3) it should be noticed that ρ has substantially lesser heterogeneity above surface near a functional group as compared with that of hydroxylated SiO_2 [5]. The smaller negative value of potential near chlorine atom as compared with that the oxygen atom of silanol group as well as negative values above hexagonal cavity indicate a considerable rise of potential barrier for embedding small ligands into coordination sphere of the chlorosilyl group silicon atom. Probably just this

fact can explain an initial hydrophobity and reduced speed of the primary stages of hydrolysis of the chlorinated SiO_2 surface. An analysis of the electrostatic potential profiles near the chlorinated, aminated (fig. 4), and hydrogenated (fig. 5) silica surface discovers a distinct dependence on the nature of functional groups and allows to describe clearly a comparative activity of these groups in the processes of polar compounds adsorption [6].

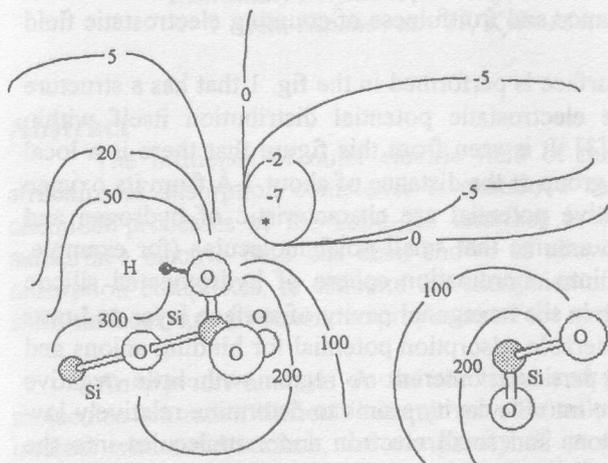


Fig. 2. The profile of electrostatic potential (in J/mol) in the surroundings of β -cristobalite face (111)

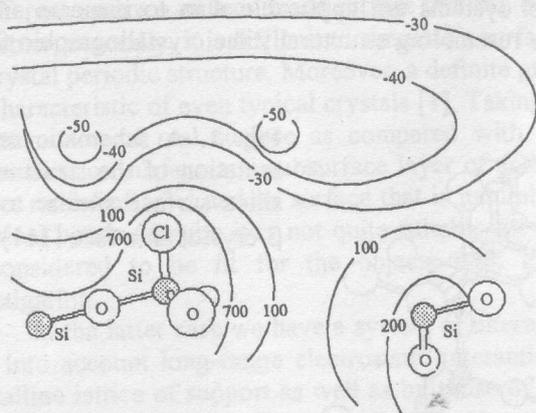


Fig. 3. The profile of electrostatic potential (in J/mol) in the surroundings of totally chlorinated β -cristobalite surface face (111).

An analysis of the peculiarities of electrostatic potential spatial distribution within subsurface layer can give an important information on unitial stages of silica surface hydration and on peculiarities of cation sorption without carrying out labour-consuming computations on potential energy surface [7]. It is known that besides hydroxyl groups almost always there are water molecules on silica surface bound to it in various way. According to the literature data the main features of hydrate cover in the regions of isolated hydroxyl groups can be described within frameworks of three models. A formation of hydrogen bonds between surface silanol group and H_2O molecule is a characteristic of the models I and II (fig. 6 and fig. 7). The first model has water molecule as proton donor whereas the second one has silanol group. Within model I (fig. 6) there are no regions of the ρ negative values near oxygen atom of silanol group. Such a region is present near oxygen atom of admmolecule, the minimum being rather considerable and equating to -260 kJ/mol. The access of cations into these regions from solution or vacuum is out of barrier, i.e. their trajectories completely pass through the regions of negative potential values. It is follows from this figure that when sorbing, the cations firstly are

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localized within the regions of minimal ρ values near the water molecule oxygen atom followed by exchange with the nearest proton that does not take part of hydrogen bond formation. Analogous conclusions are true also for the model II.

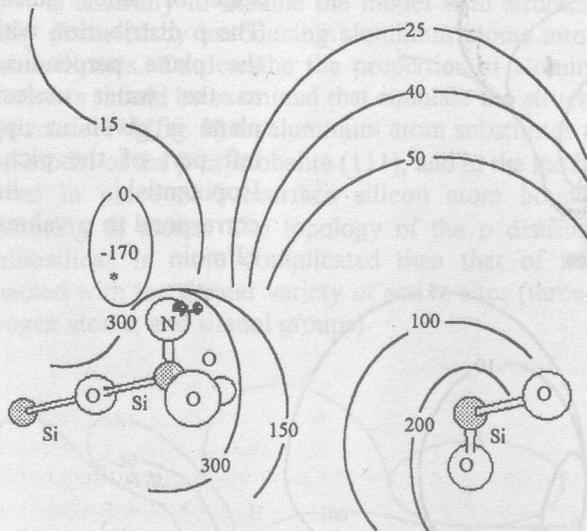


Fig. 4. The profile of electrostatic potential (in J/mol) in the surroundings of totally aminated β -cristobalite surface face (111)

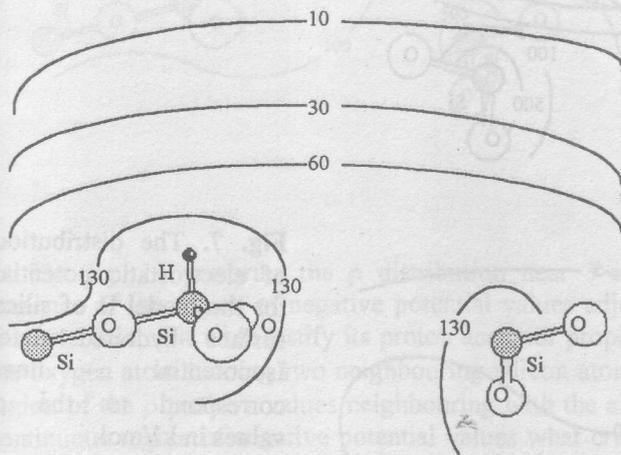


Fig. 5. The profile of electrostatic potential (in kJ/mol) in the surroundings of totally hydridesilylic β -cristobalite surface face (111)

The model III (fig. 8) assumes a coordinative bond between the H_2O molecule oxygen atom and surface hydroxylated silicon atom and is common used for an explanation of the firm keeping of water with disperse silica surfaces. The presence of one compact region of the negative potential values is a characteristic of it. Similar to the models I and II the ρ minima are near the water molecule oxygen atoms and corresponds to -240 kJ/mol. Nevertheless in this case the difference in the potential values near oxygen atoms between silanol group and coordinatively bonded water is not such considerable as in the models examined above but does not exclude an opportunity of the initial localization of the cations sorbed in these minima.

Thus the data on the ρ distribution confirm the initial stage of cation sorption with silica surface to occur accompanied by the molecules of sorbed water rather than by structural silanol groups.

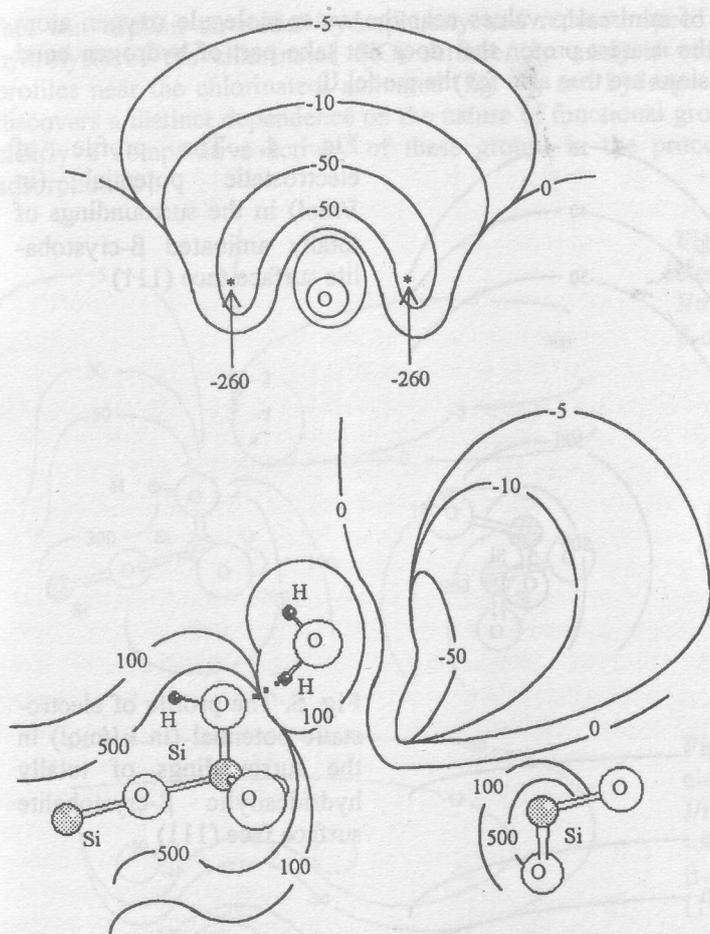


Fig. 6. The electrostatic potential distribution for the model I of hydrated state of silica surface. The ρ distribution within the plane perpendicular to the water molecule plane is given in upper left part of the picture. Isopotential lines correspond to ρ values in kJ/mol

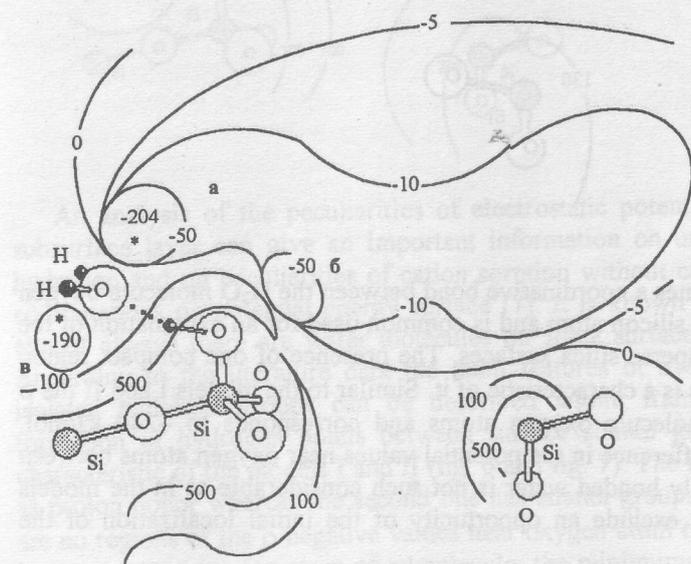


Fig. 7. The distribution of electrostatic potential for the model II of silica surface hydrated state. Isopotential lines correspond to the ρ values in kJ/mol

Use of idea on the role of electrostatic potential in oxide surface chemistry allows also to simulate the change in surface properties in clear way when various admixture ions are introduced into oxide matrix [9]. For example, modifying silicas is probable via

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isomorphous substitution of aluminum atoms for some quantity of silicon atoms. A rather considerable part of disperse silica surfaces, in particular those of aerosil and silica gels, being characterized by the structural elements that are typical of the β -cristobalite (111) face, it is naturally to assume the model with structural parameters of this face that is slightly distorted by introducing aluminum atoms into silicate matrix to be suitable for aluminosilicates. To describe the properties of aluminosilica surface more completely, two models should be examined that simulate the structure of its most important sections. In the model IV (fig. 9) an aluminum atom substitutes a hydroxylated silicon atom in the initial model of the β -cristobalite (111), and in the model V (fig. 10) an aluminum atom is inserted in place of subsurface silicon atom bound with four siloxane bounds to neighboring Si atoms. The topology of the ρ distribution within subsurface region of aluminosilicas is more complicated than that of initial hydroxylated silica what is connected with the greater variety of active sites (three-coordinated silicon atoms, bridge hydrogen atoms, and silanol groups).

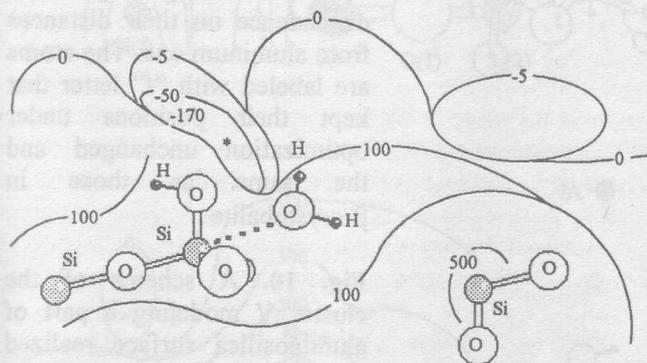


Fig. 8. The distribution of electrostatic potential for the model III of silica surface hydrated state. Isopotential lines correspond to the ρ values in kJ/mol

The fig. 11 performs the ρ distribution near 3-coordinated aluminum atom. The presence of the region of negative potential values adjoining the bridge oxygen atom is characteristic of it what testify its proton acceptor properties. Such regions are absent for the oxygen atom binding two neighbouring silicon atoms in β -cristobalite. The compact region of the ρ positive values neighbouring with the aluminum atom is surrounded with continuous region of negative potential values what creates a rather perceptible potential barrier for the penetration of electron donor molecules to the Lewis acidic site that is 3-coordinated aluminum atom in the case given. For the cluster V the potential near 4-atomic fragment of $\equiv\text{Al-OH-Si}\equiv$ has only positive values (fig. 12), i.e. the access of proton acceptor molecules or anions to the Brönsted acidic site is practically out of barrier [10].

The examination of the local state densities (LSD) of the systems under consideration can serve as one more example of obtaining useful information on the properties of concrete atoms in surface structures [11]. The fig. 13 performs these state densities of silicon and aluminum atoms calculated for the cluster IV. Thus, the one of the maxima of LSD of aluminum atom is stationed within the energy region from -1 to $+1$ eV, and the energy of the highest occupied orbital is of -8.4 eV. The $3p_z$ aluminum atom orbital pays the main contribution to this maximum what gives grounds to assume a localization of the surface electronic state at this atom displaying as an electron donor site. The principal maximum of a hydroxylated surface silicon atom is localized within energy region corresponding to the highest occupied orbitals, and there is a maximum within -1 to $+1$

eV testifying the electron acceptor properties of this atom. A coordinative bond of electron donor molecules with hydroxylated surface silicon atom seems to be realized due to the presence of the LSD maximum within the region of vacant levels. For a subsurface silicon atom, all the maxima are within the region of lower energies. Analogous features of the mutual stationing the LSD maxima of various type silicon atoms are characteristics of the β -cristobalite.

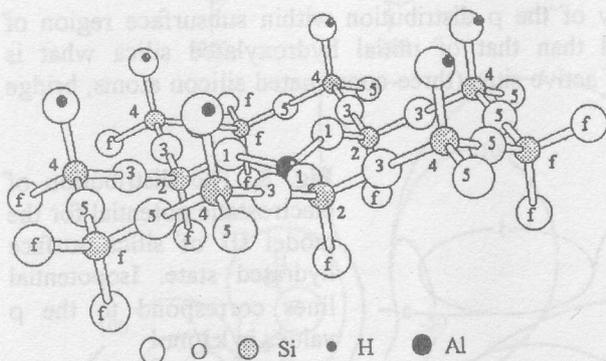


Fig. 9. A scheme of the cluster IV modeling a part of aluminosilica surface realized due to the change of hydroxylated silicon atom by aluminum one within surface layer of β -cristobalite. The atoms numbering is given in dependence on their distances from aluminum one. The atoms are labeled with "f" letter that kept their positions under optimization unchanged and the same as those in β -cristobalite

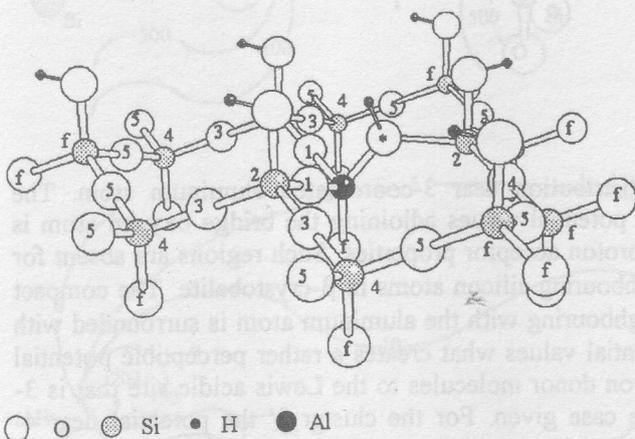
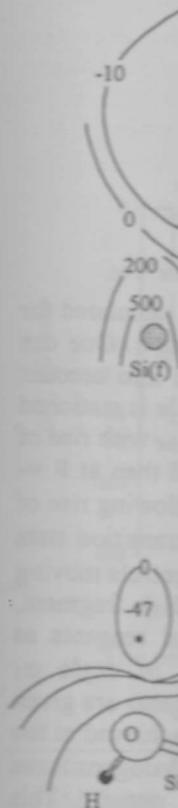


Fig. 10. A scheme of the cluster V modeling a part of aluminosilica surface realized due to the change of bulk subsurface silicon atom by aluminum one within surface layer of β -cristobalite. The atoms numbering is given in dependence on their distances from aluminum one. The atoms are labeled with "f" letter that kept their positions under optimization unchanged and the same as those in β -cristobalite

Basing on ideas on the importance of taking the electrostatic potential within subsurface layer of oxides into account, let us examine the peculiarities of the elementary acts of the chemical transformation at the surface. Both a modifier molecule and the surface reactive site with neighboring atoms undergo to deformation changes in the processes of the chemical modifying of surface. It was shown in the literature [4] that the main contribution to the activation energy of the reaction of electrophilic substitution of the silanol group proton



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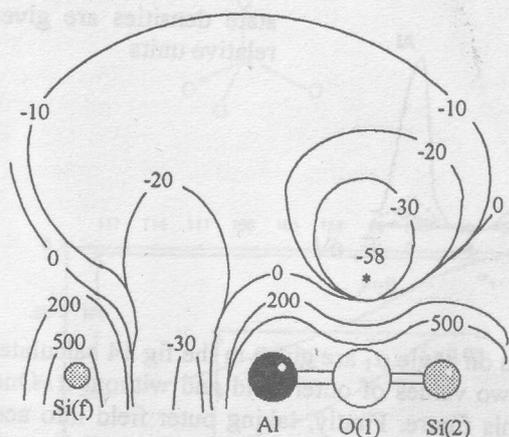


Fig. 11. The distribution of electrostatic potential for the cluster IV within the plane perpendicular to the plane of the $\text{Al}[\text{O}(1)\text{Si}(2)]_3$ fragment and crossing the Si(2), O(1), Al, and Si(f) atoms. The potential values are given in kJ/mol

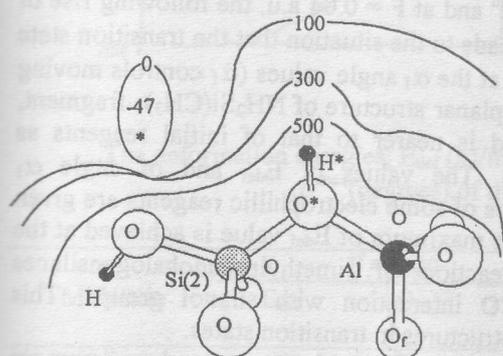


Fig. 12. The distribution of electrostatic potential for the cluster V within the plane of $(\text{HO})\text{Si}(2)\text{O}^*\text{AlO}(f)$. The potential values are given in kJ/mol

To estimate this difference, generally speaking, two approaches can be used. According to the first one the results should be compared of quantum chemical calculations of isolated molecule with analogous data for the same molecule near surface, the configuration of transition state being applied. The second approach makes it possible to change the study of molecule near surface with its examination within some effective electrostatic field [12, 13]. Of course the total calculation on the effect of the field of complicated distribution is impossible practically, but general conformities to natural laws of the influence of surface on admolecule can be elucidated within the approximation of homogenous electric field.

The second approach being applied, let us examine what is the role of subsurface electrostatic field in the reactions of electrophilic substitution of the proton of isolated silanol group with trimethylsilylic radicals $-\text{SiR}_1\text{R}_2\text{R}_3$. These reactions run *via* four-centered transition states [4] (see fig. 14). A deformation is essential for such transition states of the admolecule silicon atom tetrahedral surrounding up to planarity of the XR_1R_2 atomic group as well as a trigonal-bipyramidal configuration of the system: modifier molecule + silanol group oxygen atom. A degree of distortion of the central silicon atom tetrahedral surroundings is controlled by angles α_1 and α_2 that are equal to 90° for a planar conformation of the group mentioned.

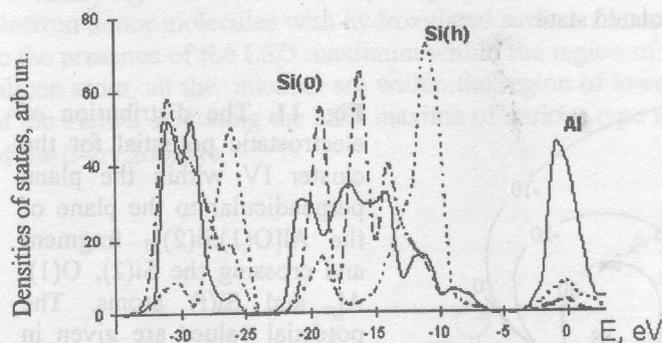


Fig. 13. The local state densities of the Si(o), Si(h) and Al atoms calculated for the cluster IV. The values of state densities are given in relative units

The plots of the heat of formation on angle α_1 are given in the fig 14 calculated for the isolated $\text{NH}_2\text{Si}(\text{CH}_3)_3$ molecule at two values of outer field and without it. One can make two important conclusion from this figure. Firstly, taking outer field into account created by lattice and surface atoms in the region where modifier molecule is stationed for the transition state structure results in decrease of deformation energy E_{def} with rise of field. Secondly, if the E_{def} maximum is achieved at $\alpha_1 = 90^\circ$ for zero field then at $F = -0.02$ a.u. this maximum corresponds to $\alpha_1 = 92^\circ$ and at $F = 0.04$ a.u. the following rise of α_1 to 95° occurs. Calculating subsurface field leads to the situation that the transition state of exothermic reactions considered is achieved at the α_1 angle values (α_1 controls moving on along reaction coordinate) that precede the planar structure of $\text{NH}_2\text{Si}(\text{CH}_3)_3$ fragment, i.e. the transition state structure at zero field is nearer to that of initial reagents as compared with the situation for zero field. The values of E_{def} and of angle α_1 corresponding to its maximum for the molecules of some electrophilic reagents are given in the table. It is seen from it first of all that the maximum of E_{def} value is achieved at the α_1 angle values $< 90^\circ$ for the endothermic reactions of trimethylpseudohalogenasilanes $(\text{CH}_3)_3\text{SiN}_3$, $(\text{CH}_3)_3\text{SiNCS}$, and $(\text{CH}_3)_3\text{SiNCO}$ interaction with silanol groups. This testifies a considerable distortion of molecule structures in transition states.

Thus, applying idea on subsurface electrostatic field allows to describe more correctly these reactions within the framework of the deformation model for activation barriers of the reactions of electrophilic substitution of silanol group protons and to elucidate factors determining a degree of distortion of the spatial structure of modifier molecules near adsorbent surface.

The advantages of this approach consist in simplicity (there is no necessity to examine interaction of admolecules with solid surface that appears only as effective electrostatic field created by it and lattice), in refusal from standard supermolecular description within the frameworks of usual approaches of zero differential overlap that in principle fail in description of potential barriers. Also an opportunity arises to compare reactivity of molecules in the reactions of proton electrophilic substitution not only in the row of related compounds (for example methylchlorosilanes) but of those containing various functional groups.

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Molecule	ΔH_f , kJ/mol
$(\text{CH}_3)_3\text{SiN}_3$	~ -100
$(\text{CH}_3)_3\text{SiNCS}$	~ -120
$(\text{CH}_3)_3\text{SiNCO}$	~ -140
$(\text{CH}_3)_3\text{SiCl}$	~ -160
$(\text{CH}_3)_3\text{SiBr}$	~ -180
$(\text{CH}_3)_3\text{SiJ}$	~ -200

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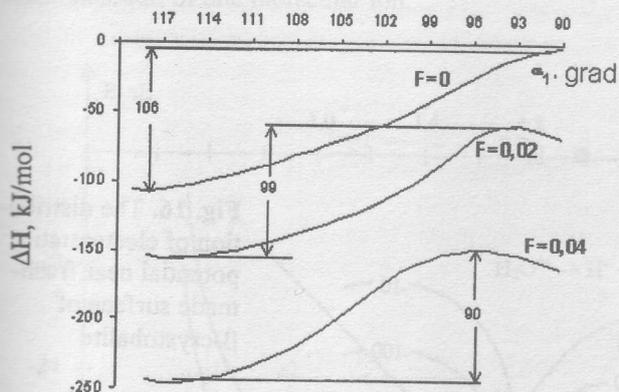
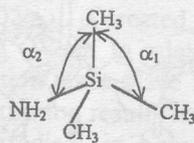
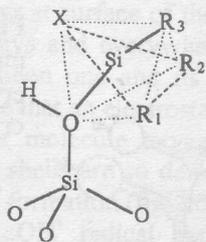


Fig. 14. The deformation energies of trimethylamino-silane molecule in zero field and those in the fields of $F=0.02$ and 0.04 a.u.

The deformation energies, E_{def} (kJ/mol), heat effects, Q (kJ/mol), and angles α_1^{max} (degrees) of the reaction of silylation

Molecule	F = 0.00			F = 0.02		F = 0.04	
	E_{def}	Q	α_1^{max}	E_{def}	α_1^{max}	E_{def}	α_1^{max}
$(\text{CH}_3)_3\text{SiN}_3$	151	98	90	141	88	130	85
$(\text{CH}_3)_3\text{SiNCS}$	175	120	90	163	86	148	83
$(\text{CH}_3)_3\text{SiNCO}$	172	168	90	164	85	153	80
$(\text{CH}_3)_3\text{SiCl}$	162	—	90	151	88	148	86
$(\text{CH}_3)_3\text{SiBr}$	140	—	90	128	98	114	102
$(\text{CH}_3)_3\text{SiI}$	126	—	90	108	100	86	105

In conclusion let us consider problems on the formation of hydroxylic cover on fresh-made surfaces. The electrostatic fields created by lattice ions near surface limiting crystal play the most important and determining role in its formation. Depending on oxide chemical composition, definite factors are promoted to the foreground, but general conformities to natural laws of hydroxylic cover formation can be observed using some simplest models. Thus, the fig. 15 demonstrates a fresh-made surface of β -cristobalite obtained by rupture of crystalline lattice according to the (111) incline plane. Three-coordinated silicon atoms are stationed in plane of this face, rows of single-coordinated oxygen atoms being risen above them. As the valencies of surface silicon and oxygen atoms are totally unsaturated, strongly heterogeneous electrostatic fields of high stress are created within their surroundings. Gradients of these fields can be judged from fig. 18.

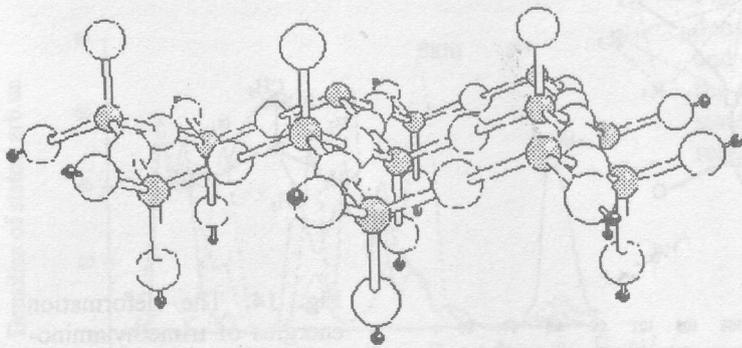


Fig. 15. A fresh-made surface of crystalline β -cristobalite

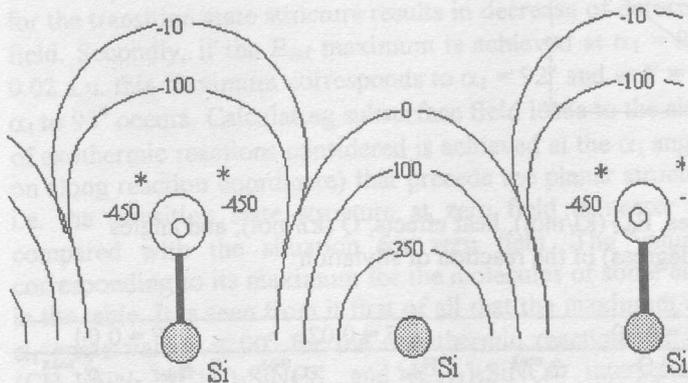


Fig. 16. The distribution of electrostatic potential near fresh-made surface of β -cristobalite

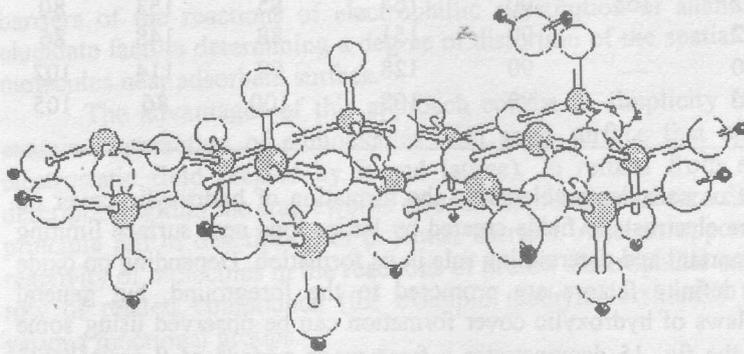


Fig. 17. Water molecule near fresh-made surface of β -cristobalite



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When hitting hollows at surface of the face discussed (fig. 19) a water molecule (there is an excess of it always and everywhere) takes its bearings such that its oxygen atom is stationed near a silicon one and its hydrogen atoms are stationed near oxygen ones. Calculations indicate that an electrostatic field of about 0.02 a.u. is created [12] within the region of the water molecule oxygen atom localization. When in such fields, water molecule electronic shells are so deformed that its ionization takes place following by a molecular ion H_2O^{+*} formation (fig. 20). Effect of field on this ion results in its consequent decomposition into OH^{\bullet} radical and H^+ . A hydroxyl radical is bound with three-coordinated silicon atom and proton migrates into nearest minimum of negative potential near oxygen atom. As a result two surface hydroxyl groups are formed due to decomposition of one molecular ion.

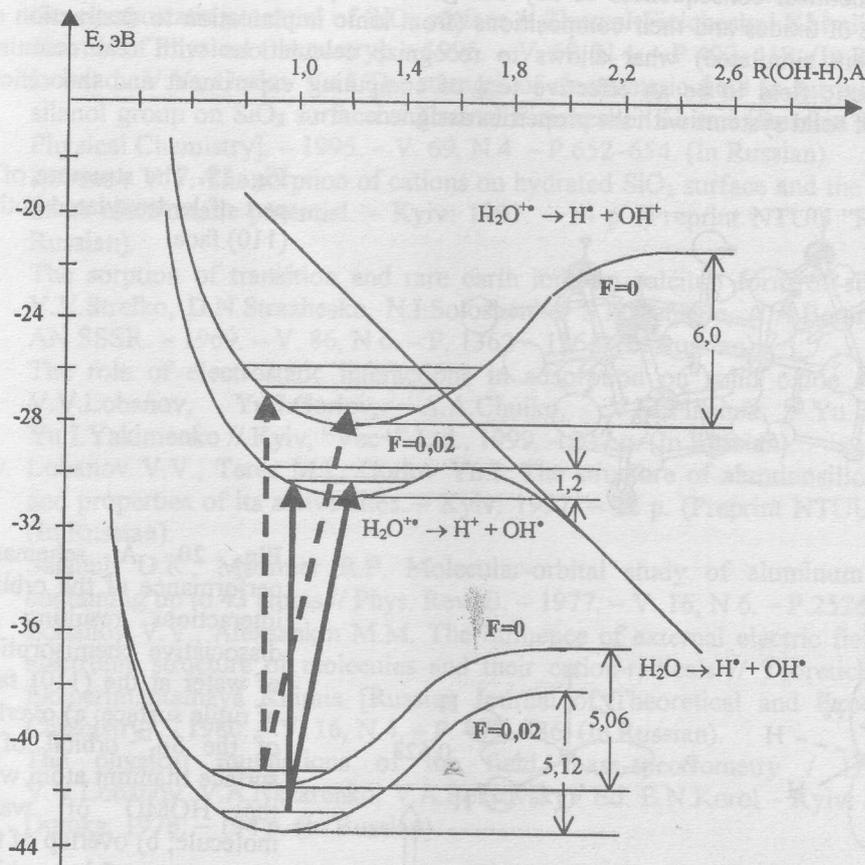


Fig. 18. A schematic performance of the processes of ionizing and decomposition of water molecule as well as of its molecular ion in zero field and in the field of 0.02 a.u.

Nevertheless such a mechanism of the formation of hydroxylic cover on fresh-made β -cristobalite (111) face is not universal one. Thus, in case of rutile (crystalline modification of titania) surface (110) face besides electrostatic field a mutual exchange of electron density between admolecule and surface (fig. 21) plays important role; as a result decomposition of water molecule and hydroxyl cover formation occur.

Some conclusion can be made from the data presented, in particular:

1. There is a clear and synonymous concretizing sites of polar molecule primary adsorption.

2. A heterolytic character of chemical reactions on SiO_2 surface follows from electrostatic potential distribution near silica surface with polar functional groups. An existence of potential regions with considerable values of opposite sign near these groups at the distances of about chemical bond length indicated strong polarization of the reactive site of reacting molecule as well as increase in bond polarity.
3. Change in nature of functional groups, hydration of silanol groups, inserting admixture atoms into silica matrix result in essential redistribution of electrostatic field and in respective varying adsorbent surface properties.

It should be noted that the information examined on active sites nature was obtained without carrying out complicated quantum chemical calculations within supermolecular approach. It is important that a clear analysis is probable on this basis of the chemical consequences of any change in composition and surface and bulk structure of oxides and their compositions (from ionic implantation to destruction of the system simulated) what allows to recognize calculations with real counting electrostatic field to be an effective tool of computing experiment and theoretical design of solid systems with the properties assigned.

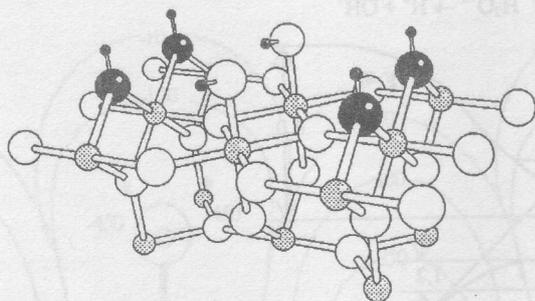


Fig. 19. The structure of a part of hydroxylated rutile (110) face

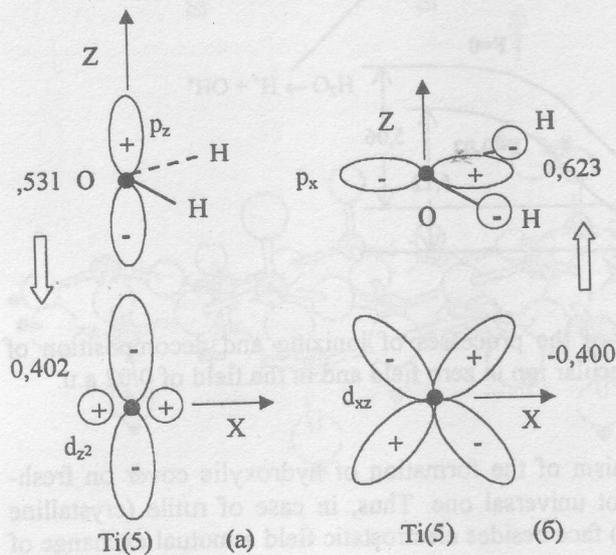


Fig. 20. A schematic performance of the orbital interactions resulting in dissociative chemisorption of water at the (110) face of rutile surface: a) overlap of the $3d_z^2$ orbital of a surface titanium atom with the HOMO of water molecule; b) overlap of the same atom $3d_{xz}$ orbital with the LUMO of water molecule. The direction of an electron density transfer is depicted with arrows

References

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