Structure and coordination of organometallic groups on a chemically modified SiO_2 surface

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The structural, electronic, and energy parameters of the metal-containing clusters $(H_3SiO)_3Si{-}O{-}XMe_n$ (X = H, B, Al, or Zn; n = 0, 1, or 2), which model organometallic groups on a SiO_2 surface modified with B-, Al-, and Zn-containing alkyls, have been studied by quantum-chemical methods. Full geometry optimization for these clusters was carried out by the SCF MO LCAO method taking into account the electron correlation within the frameworks of the MP2 and B3LYP schemes using the 6-31G(d) (6-311G(d) for Zn) basis set. The effect of the crystal environment was taken into account in calculations of silicon-oxygen clusters containing 10 and 30 silicon atoms using the *ab initio* SCF/6-31G(d) and semiempirical MNDO-PM3 methods. Various modes of coordination and interactions of organometallic groups with oxygen atoms of surface groups were studied. For the organoaluminum group on the surface, two stable conformations were found, namely, the three-coordinate structure with the chain $-O-AlMe_2$ ligand and the four-coordinate (quasicyclic) structure with the Al atom that forms two nonequivalent bonds with the O atoms at the same Si atom. The four-coordinate structure is energetically more favorable. No stable structures were found for the organoboron and organozinc fragments.

Key words: silica, surface, organometallic active sites; quantum-chemical studies.

Studies of the structure and the state of the surface have attracted growing interest in recent years. These studies are of particular importance in the science of materials (nanotechnology), catalysis, photocatalysis, microelectronics, and advanced technologies. Quantum-chemical methods, molecular mechanics, dynamics, and the Monte Carlo method are the most informative approaches used in these studies. These methods adequately describe many properties of simple surface groups, for example, of metal clusters,[1] for which several simple theoretical models have been developed and confirmed by quantum-chemical calculations.[2] These models and calculations provide a reasonable explanation for the available experimental data on the spectral and ionization properties as well as on the energetics of chemisorption of small molecules (H_2, CH_4, CO, and C_2H_4) on simple crystals (graphite and metals).

Quantum-chemical calculations of adsorption on the surface of metal oxides and nonmetals are also abundant.[3-6] Recently, zeolites and interactions of admolecules with their Brönsted active centers have attracted considerable attention.[7-9] In connection with studies of catalytic cracking of petroleum products, many works have been devoted to activation of H_2O, CO, and simple organic molecules on catalysts of this type.[9] However, less attention has been given to organometallic surface groups with different organic ligands bonded to oxides. The structures of these groups, the characteristic features of coordination of the metal atom to the surface, and the effect of these groups on the catalytic activity are still poorly understood.

Silicon oxide with organic or organometallic groups bonded to the surface is of interest from the standpoint of applied problems as well as for understanding the processes that occur on the surface.[10] Presently, activation of C—O bonds in heterogeneous processes of binding of CO and CO_2 to form polycarbonate systems on a silica surface chemically modified with B-, Al-, and Zn-containing alkyls is considered a promising application of chemically modified silica.[11]

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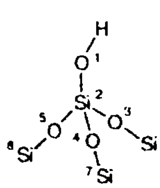
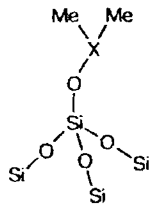
In the course of modification, the replacement of hydrogen atoms of terminal OH groups occurs on the surface to form surface alkoxy groups >Si—O—MAlk$_n$ (M = B, Al, or Zn; n = 1 or 2) followed, apparently, by their chemical transformations. The structure of surface alkoxy groups, modes of coordination of the metal atom in these groups, its possible catalytic activity, and the effect of the environment on the activity are still open questions.

Because B, Al, and Zn are strong complex-forming agents, the above-mentioned groups may belong both to the low-coordinate (chain) and high-coordinate types. In the latter case, the central atom forms hypervalent bonds with the adjacent groups on the surface. Although zeolites and aluminosilicates,[7,8] alkoxy derivatives,[12] organic radicals on the surface,[10,13,14] surface defects, and organometallic compounds that interact with surface defects[10,15,16] have been studied extensively, the data on structures of analogous organometallic groups are scarce in the literature. The modes of coordination, characteristics of coordination bonds of the B, Al, and Zn atoms with the surface, and their electronic states remain unknown.

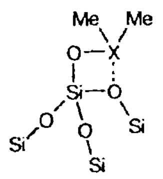
In this connection, it is essential to apply high-level theoretical methods to these systems with the aim of studying B-, Al-, and Zn-containing structures on the SiO_2 surface in detail and for developing a theoretical model of the surface active center that adequately describes the activation and catalytic properties of these systems. In this work, we studied the SiO_2 surface modified with $AlMe_3$, BMe_3, and $ZnMe_2$. The replacement of hydrogen atoms of terminal OH groups (structure *A*) resulted in organometallic groups bonded to the SiO_2 surface. The Al- and B-containing derivatives can have structure *B* or *C*, and the Zn-containing derivative can have structure *D* or *E* (the terminal atoms are omitted; in all the cases, the numbering schemes of the centers correspond to structure *A*):



A



B



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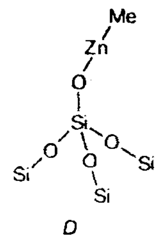

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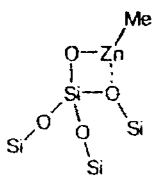

E

Calculation procedure

The molecular cluster $(H_3SiO)_3Si—OH$ (cluster **1**) and its organometallic derivatives $(H_3SiO)_3Si—O—XMe_n$ (X = H, B, Al, or Zn; n = 0, 1, or 2) were studied by high-level *ab initio* quantum-chemical methods followed by estimations of the effects of the cluster size and the crystal environment using calculations of clusters of different sizes by available methods. These clusters contain 4, 10, and 30 silicon atoms and serve as models of a fragment of the surface of the SiO_2 crystal with the β-cristobalite structure. Terminal O atoms were closed by H atoms. Therefore, the molecular clusters (Fig. 1), which represent surface fragments containing organometallic groups bonded to terminal OH groups of silicon-oxygen compounds with the stoichiometric formulas $Si_4O_4H_{10}$ (cluster **1**), $Si_{10}O_{28}H_{16}$ (cluster **2**), and $Si_{30}O_{77}H_{34}$ (cluster **3**), were used as models.

The choice of the cluster was determined by the fact that the structure of activated aerosil used in experiments on modification of the surface is most similar to the structure of cristobalite with a large portion of isolated (not involved in hydrogen bonding) terminal OH groups. Therefore, the clusters shown in Fig. 1 allow one to model the most typical isolated organometallic active centers. The distance between the adjacent centers in the crystallographic section is 3—4 Å. A successive increase in the cluster size allowed us to estimate the effect of the surface on the structure of the surface group under study, which was calculated for a small cluster. In the case of the terminal OH group and organoaluminum centers, this effect is considered below.

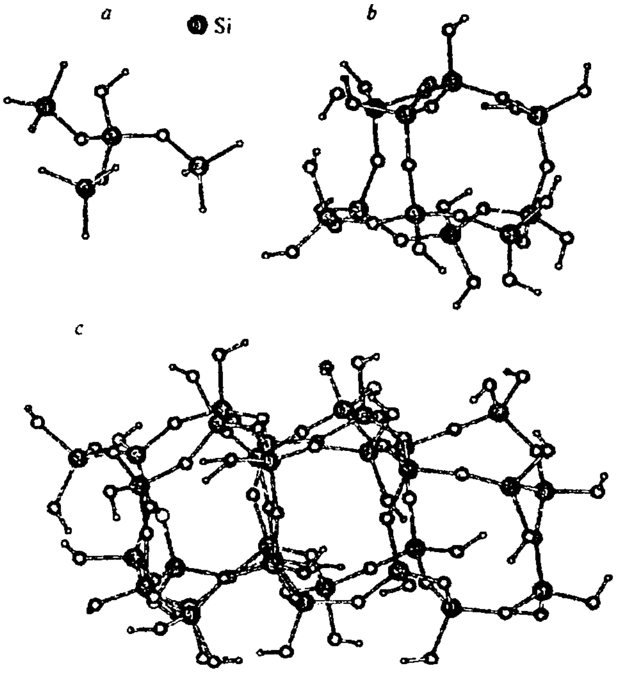

Fig. 1. Optimized structures of the clusters used as initial models of the SiO_2 surface: *a*, cluster **1** (MP2/6-31G(d) method); *b*, cluster **2** (HF/6-31G(d) method); and *c*, cluster **3** (MNDO-PM3 method).

The calculations were carried out by the SCF LCAO MO method with the 6-31G(d) (6-311G(d) for Zn) basis set and by the semiempirical MNDO-PM3 method. Cluster **1** was calculated taking into account the electron correlation using the second-order Möller—Plesset perturbation theory (MP2) as well as within the framework of the density functional theory (DFT) with the use of the B3LYP exchange-correlation functional.[17] The geometric parameters and energetics of the medium-sized structures (cluster **2**) were calculated by *ab initio* and semiempirical methods. The effect of the crystal environment in the large systems (cluster **3**) was estimated only by the semiempirical method. The *ab initio* calculations were carried out using the GAUSSIAN 94 [18] and GAMESS programs.[19] The semiempirical calculations were carried out using the MOPAC program.[20]

Results and Discussion

Geometrical structures. The calculations with full geometry optimization of cluster **1**, $(H_3SiO)_3Si{-}OH$, which models the free terminal OH group of the SiO_2 surface, and its analogs, $(H_3SiO)_3Si{-}O{-}BMe_2$, $(H_3SiO)_3Si{-}O{-}AlMe_2$, and $(H_3SiO)_3Si{-}O{-}ZnMe$ that contain organometallic fragments bonded to the surface, were carried out by the correlated *ab initio* method and within the framework of the density functional theory. The results of calculations indicate unambiguously that the active centers containing different metal atoms have different structures. Two stable conformations were found for the Al-containing active center, namely, the structure with the three-coordinate Al atom, *i.e.*, with the chain arrangement of the Si—O—Al atoms (structure **A**), and the structure with the four-coordinate Al atom, *i.e.*, the cyclic form with the Al atom that forms two nonequivalent bonds with O atoms of the support (structure **B**). For the B- and Zn-containing derivatives, we did not found stable conformations in which the central atom is additionally coordinated to the nearest O atoms.

The optimized structures of cluster **1** with different organometallic groups are shown in Fig. 2. The corresponding geometric parameters are given in Table 1. From the data in Table 1 it follows that virtually all bond lengths determined by the PM3 method differ substantially from those calculated by the *ab initio* method. The Si—O bond lengths calculated by the PM3 method are systematically overestimated, on the average, by 0.02—0.03 Å compared to the values calculated by the *ab initio* method. Almost all bond lengths increase monotonically in the series HF—DFT—MP2. In most cases, the differences in the bond angles are insignificant. The results of calculations by the DFT method are in substantially closer agreement with the results obtained by the MP2 method. The bond lengths differ generally by approximately 0.01 Å (see Table 1).

The discrepancy between the results obtained by the HF and MP2 (DFT) methods indicates that the correlation effects must be taken into account in studies of such systems. Nevertheless, all geometric characteristics of the clusters under consideration determined by the HF method are in complete agreement with the data obtained taking into account the electron correlation. Therefore, it is hoped that the use of the *ab initio* method for extended clusters, to which the MP2 method cannot be applied, will allow one to adequately reproduce qualitative regularities of their structures.

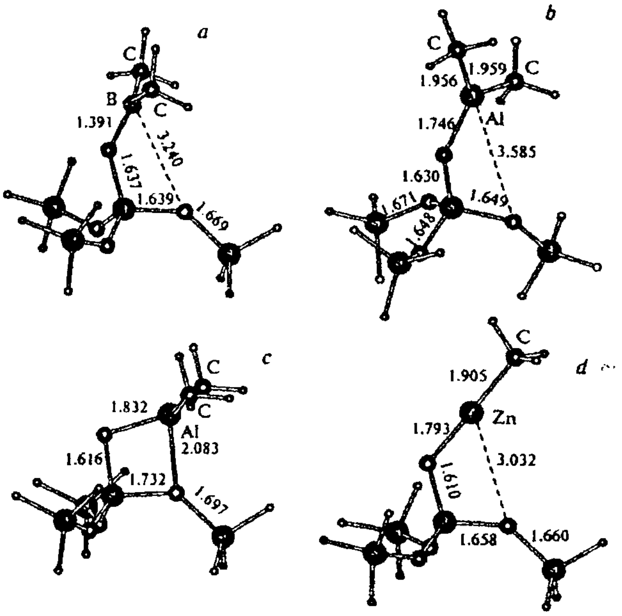

Fig. 2. Structures of the model clusters optimized by the MP2/6-31G(d) method: *a*, $(H_3SiO)_3Si{-}O{-}BMe_2$; *b*, $(H_3SiO)_3Si{-}O{-}AlMe_2$ (structure **A**); *c*, $(H_3SiO)_3Si{-}O{-}AlMe_2$ (structure **B**), and *d*, $(H_3SiO)_3Si{-}O{-}Zn{-}Me$.

The replacement of the terminal hydrogen atom of the initial cluster $(H_3SiO)_3SiOH$ by the organometallic group leads to a shortening of the Si(2)—O(1) bond by 0.02—0.04 Å and to a substantial change in the bond lengths in the first coordination sphere about the Si(2) atom. At the same time, the O—Si bond lengths in the second coordination sphere about this atom remain virtually unchanged, which indicates that the properties of organometallic surface structures are adequately modeled by small clusters. Therefore, the effect of the substituent is to a large extent localized and confined to the first coordination sphere about the Si(2) atom. This fact suggests that the positions of remote atoms can be fixed accurately in studies of organometallic groups.

The calculated (MP2/6-31G(d)) energies of the substitution reactions (E_r)

$$(H_3SiO)_3Si{-}OH + XMe_n \rightarrow$$

$$\rightarrow (H_3SiO)_3Si{-}OXMe_{n-1} + CH_4 \qquad (1)$$

are given in Table 2 (X = B, Al, or Zn; n = 1 or 2) without taking into account the zero-point energy (which may be sensitive to the cluster size and is differently

Table 1. Geometric parameters of the model structures $(H_3Si-O)_3Si-O-XMe_n$, (X = H, B, Al, or Zn; *n* = 0, 1, or 2) optimized by different methods

Geometric parameter	PM3	RHF/ 6-31G(d)	B3LYP/ 6-31G(d)	MP2/ 6-31G(d)
$(H_3SiO)_3SiOH$				
r/Å				
O(1)—H	0.945	0.946	0.967	0.970
H—O(3)	2.676	2.666	2.650	2.656
Si(2)—O(1)	1.694	1.631	1.650	1.657
Si(2)—O(3)	1.666	1.617	1.637	1.643
Si(2)—O(4),O(5)	1.665	1.612	1.632	1.639
O(3)—Si(6)	1.675	1.639	1.659	1.671
O(4)—Si(7),Si(8)	1.673	1.636	1.657	1.670
Angle/deg				
Si(2)—O(1)—X	115.7	117.5	114.9	114.7
O(1)—Si(2)—O(3)	106.2	108.2	108.0	107.9
$(H_3SiO)_3SiOBMe_2$				
r/Å				
O(1)—B	—	1.355	1.364	1.392
B—C	—	1.589	1.584	1.575
B—O(3)	—	3.668	3.734	3.241
Si(2)—O(1)	—	1.604	1.621	1.638
Si(2)—O(3)	—	1.611	1.628	1.640
Si(2)—O(4),O(5)	—	1.612	1.630	1.641
O(3)—Si(6)	—	1.635	1.655	1.670
O(4)—Si(7),Si(8)	—	1.632	1.652	1.669
Angle/deg				
Si(2)—O(1)—Al	—	168.3	172.4	138.0
O(1)—Si(2)—O(3)	—	108.7	107.9	108.0
$(H_3SiO)_3SiOAlMe_2$ (structure A)				
r/Å				
O(1)—Al	1.709	1.710	1.731	1.746
Al—C)	1.904	1.966	1.959	1.956
Al—O(3)	4.100	3.852	3.764	3.559
Si(2)—O(1)	1.663	1.601	1.621	1.633
Si(2)—O(3)	1.668	1.620	1.639	1.647
Si(2)—O(4),O(5)	1.670	1.621	1.640	1.650
O(3)—Si(6))	1.674	1.635	1.657	1.670
O(4)—Si(7),Si(8)	1.672	1.633	1.655	1.667
Angle/deg				
Si(2)—O(1)—Al	171.9	155.5	149.9	134.7
O(1)—Si(2)—O(3)	107.3	109.8	110.1	109.5
$(H_3SiO)_3SiOAlMe_2$ (structure B)				
r/Å				
O(1)—Al	1.775	1.788	1.815	1.833
Al—C	1.947	1.973	1.966	1.965
Al—O(3)	1.889	2.145	2.137	2.084
Si(2)—O(1)	1.639	1.589	1.610	1.617
Si(2)—O(3)	1.731	1.700	1.722	1.732
Si(2)—O(4),O(5)	1.666	1.605	1.627	1.633
O(3)—Si(6)	1.703	1.671	1.689	1.698
O(4)—Si(7),Si(8)	1.676	1.642	1.663	1.676
Angle/deg				
Si(2)—O(1)—Al	102.8	103.1	101.2	100.0
O(1)—Si(2)—O(3)	85.9	95.1	95.3	94.9
$(H_3SiO)_3SiOZnMe$				
r/Å				
O(1)—Zn	1.768	1.792	1.793	1.785
Zn—C	1.943	1.946	1.905	1.885
Zn—O(3)	3.708	3.407	3.128	3.032
Si(2)—O(1)	1.666	1.586	1.611	1.617
Si(2)—O(3)	1.671	1.637	1.658	1.667
Si(2)—O(4),O(5)	1.673	1.629	1.646	1.653
O(3)—Si(6)	1.675	1.639	1.660	1.672
O(4)—Si(7),Si(8)	1.673	1.633	1.655	1.667
Angle/deg				
Si(2)—O(1)—Zn	141.9	135.0	123.6	121.0
O(1)—Si(2)—O(3)	111.8	109.4	108.3	107.3

reproduced by various theoretical methods) and temperature corrections. The basis set superposition error was also not included in the E_r value. However, the above-considered results allow qualitative conclusions that the formation of $-O-AlMe_2$ groups on the surface is the most exothermic reaction. It should be taken into account that in the gaseous phase, $AlMe_3$ exists as the dimer Al_2Me_6. The corresponding energy of dimerization is 84 kJ per mole of Al_2Me_6.[20] The value E_r (82.1 kJ mol^{-1})[21] calculated by the MP2/6-31G(d) method is in perfect agreement with the experimental value, which indicates that the geometrical structure and energetics not only of Al_2Me_6 but also of organometallic groups coordinated to the surface are adequately described by correlated *ab initio* methods. It should be noted that the PM3 approximation for the Zn-containing system gave a positive value of E_r, which is inconsistent with the chemical concept of the exothermic character of reaction (1), whereas the *ab initio* calculations gave a chemically reasonable negative value of approximately -20 kcal mol^{-1}.

Modes of coordination of the central atom to the surface. As follows from the above-mentioned data, the B and Zn atoms in clusters **1** that contain organometallic groups bonded to the surface are three- and two-coordinated, respectively, whereas the Al atom tends to be additionally coordinated to surface oxygen atoms. This is evidenced by the Al—O(3) distance (2.08 Å), which is substantially smaller than the analogous distance in other systems (larger than 3 Å) as well as by the Si(2)—O(3) bond, which is noticeably longer in the Al-containing cluster (1.73 Å) than in the initial cluster $(H_3SiO)_3SiOH$ (1.64 Å) and in other organometallic structures (1.64—1.67 Å). The elongation of the Al—O(1) bond is most pronounced in going from structure **A** (1.746 Å) to **B** (1.833 Å).

The bonds between the Al atom and the two O atoms are nonequivalent: the Al—O(1) bond is a slightly elon-

Table 2. Calculated total energies of the model clusters (E) and energies of the substitution reactions (E_r) $(H_3SiO)_3Si{-}OH + XMe_n \rightarrow (H_3SiO)_3Si{-}OXMe_{n-1} + CH_4$ (X = B, Al, or Zn; n = 1 or 2)

Model cluster	E/au				E_r/kcal mol^{-1}			
	PM3[a]	RHF/ 6-31G(d)	B3LYP/ 6-31G(d)	MP2/ 6-31G(d)	PM3[a]	RHF/ 6-31G(d)	B3LYP/ 6-31G(d)	MP2/ 6-31G(d)
$(H_3SiO)_3SiOH$	−362.85	−1461.2726416	−1465.1795715	−1462.2903913				
$(H_3SiO)_3SiOBMe_2$	—	−1564.6799707	−1569.3300347	−1566.0278368	—	−37.8	−37.5	−37.5
$(H_3SiO)_3SiOAlMe_2$	−383.73	−1781.9106049	−1786.9266980	−1783.2427634	−28.2	−49.2	−47.9	−50.8
(structure **A**)					(−22.3)[b]	(−47.0)[b]		(−31.6)[b]
$(H_3SiO)_3SiOAlMe_2$	−403.85	−1781.9086690	−1786.9278496	−1783.2505020	−48.3	−48.0	−48.6	−54.2
(structure **B**)					(−42.4)[b]	(−45.8)[b]		(−35.0)[b]
$(H_3SiO)_3SiOZnMe$	−320.72	−3277.9929849	−3283.8213315	−3279.5174392	+20.9	−28.6	−19.9	−23.9

[a] For the PM3 method, the enthalpies of formation ($\Delta H_f°$/kcal mol^{-1}) are given. [b] The energies relative to Al_2Me_6 are given in parentheses.

gated covalent bond (1.83 Å), whereas the Al—O(3) bond has a pronounced donor-acceptor character (2.08 Å). This is determined by the fact that, unlike the O(1) atom, the O(3) atom can form only a coordination bond with the Al atom.

The $(H_3SiO)_3Si{-}O{-}AlMe_2$ system with the four-membered Si—O—Al—O ring is more stable than the structure with the chain arrangement of the ligand. This is confirmed by the semiempirical (PM3) and *ab initio* (MP2/6-31G(d) and B3LYP/6-31G(d)) calculations. However, the estimates of the relative energies of the two structures (**A** relative to **B**) are substantially different. According to the PM3 calculations, this value is 20.2 kcal mol^{-1}, whereas the value calculated by the B3LYP and MP2 methods are as small as 0.8 and 4.8 kcal mol^{-1}, respectively. It should be noted that the two last-mentioned values do not include the zero-point energy and temperature corrections. In addition, this value may depend on the model of the crystal surface used. This effect is discussed below. According to the PM3 method, the energy barrier to transition between structure **A** and more stable structure **B** is *ca.* 5 kcal mol^{-1}.

The formal increase in the coordination number of the Al atom leads to only insignificant changes in the electronic structure of the $-O-Al(CH_3)_2$ group (Table 3). The charges on the surface Si(2) and O(3) atoms change most noticeably. These changes correlate with the concept of the purely electrostatic (polarization) interaction, while the donor-acceptor transfer of the electron density from the surface (the O(3) atom) to the Al atom is absent. This suggests that the additional interaction between the Al and O(3) atoms is purely electrostatic.

Table 3. Mulliken atomic charges in the model clusters $(H_3Si{-}O)_3Si{-}O{-}XMe_n$ (X = H, B, Al, or Zn; n = 0, 1, or 2) calculated by the RHF/6-31G(d) method

X	q/au					
	X	O(1)	C	Si(2)	O(3)	O(4),O(5)
H	0.476	−0.859	—	1.609	−0.849	−0.839
B	0.732	−0.676	−0.726	1.607	−0.832	−0.834
Al (**A**)	1.104	−0.898	−0.821	1.671	−0.852	−0.853
Al (**B**)	1.115	−0.885	−0.823	1.717	−0.982	−0.844
Zn	1.359	−1.126	−1.121	1.722	−0.907	−0.894

The diagrams of the one-electron energy levels calculated by the HF method for the systems under consideration are shown in Fig. 3. At the left of Fig. 3, the diagram of MOs of the terminal OH group is shown. The highest occupied molecular orbital (HOMO) of this structure is localized primarily on the Si(2)—O(1)—H fragment. The HOMO of metal-containing compounds is formed by orbitals of the O(1) atom and of the MMe_n fragment ("the residue" of the σ-system of the M—C bonds of the alkyl group). In this case, LUMO is a virtually pure unoccupied p-orbital of the B, Al, or Zn atom. Therefore, the organometallic group bonded to the surface is a Lewis center on the surface. The metal atom makes the major contribution to the acidity of this center, and the basic properties are determined by the M—C moiety and by the O(1) atom. As follows from Fig. 3, an additional coordination of the Al atom causes an increase in the energy of HOMO by ~0.5 eV. Therefore, the main properties (the ability toward hydrolysis and insertion into M—C bonds) are higher in the case of the four-coordinate Al atom.

The activation and catalytic characteristics of the aluminum-containing surface center are affected by the presence of the O(1) atom in the strongly distorted Si(2)—O(1)—Al fragment (the Si—O—Al angle is 100—103°, whereas in structure **A**, this angle is 150—170°). This distortion may affect the acid-basic properties of the O(1) atom. In addition, in going from form **A** to **B**, the Al—O(1) bond is substantially lengthened, and its polarity increases noticeably due mainly to an increase in the positive charge on the Al atom in structure **B**.

Unlike the system $(H_3SiO)_3Si{-}O{-}AlMe_2$, the boron- and zinc-containing system are not prone to additional coordination of the central atom by O atoms of the support. This is attributable to the fact that the B atom carries a substantially lower charge (the Coulomb

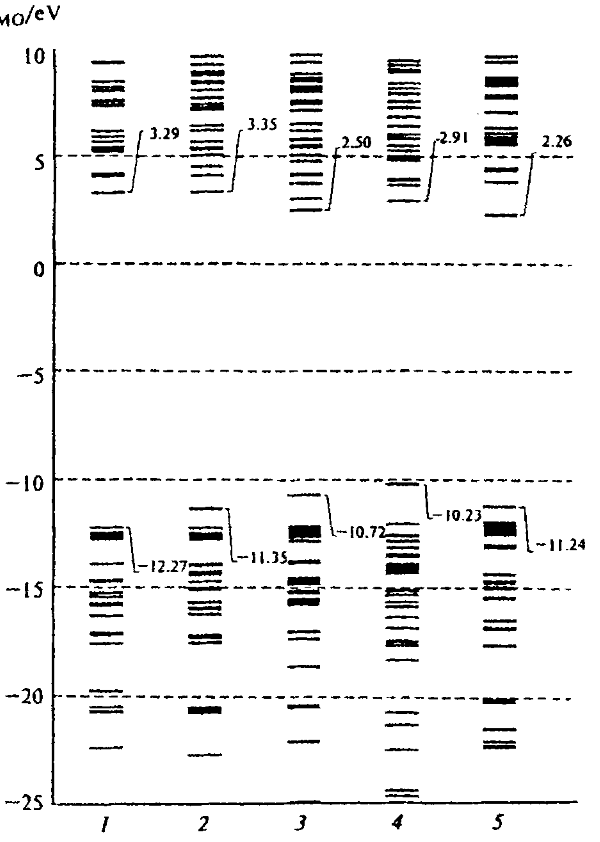

Fig. 3. One-electron energy levels (calculated by the HF/6-31G(d) method) of cluster **1** that contains organometallic groups: *1*, $(H_3SiO)_3Si—OH$; *2*, $(H_3SiO)_3Si—O—BMe_2$; *3*, $(H_3SiO)_3Si—O—AlMe_2$ (structure A); *4*, $(H_3SiO)_3Si—O—AlMe_2$ (structure B); and *5*, $(H_3SiO)_3Si—O—Zn—Me$.

attraction to the O(3) atom is substantially weaker than that to the Al atom) and has a smaller atomic radius (0.8 Å) compared to Al (1.4 Å). Therefore, an additional coordination requires substantial strain of the Si—O—B bond angle and the corresponding bonds of the surface group. Moreover, the Al atom in alkyl derivatives forms four-coordinate structures with the tetrahedral arrangement of the Al—C bonds substantially much more readily than the B atom.

The Zn atom exhibits substantially lower electron-withdrawing ability, and it is more strongly coordinated to the O(3) atom compared to the B atom, which is evidenced by the smaller Si(2)—O(1)—Zn bond angle, the shortened Zn—O(3) bond (r(Zn—O(3)) = 3.03 Å, r(B—O(3)) = 3.24 Å)), and the substantially elongated Si(1)—O(3) bond (1.658 Å compared to 1.639 Å in the organoboron system). At the same time, the Zn—O(3) bond is very weak, which is evidenced also by the virtually undistorted O(1)—Zn—C angle. The —O—Zn—Me fragment is very flexible and labile due to the two-coordinate state and the large atomic radius of the zinc atom, which is favorable for interactions with adjacent surface groups.

Effect of the surface on the structure of the active center. The effect of the surface can be estimated from changes in the geometric and electronic characteristics of the clusters under study as their sizes are increased. Full geometry optimization of the successively increased structures $(H_3SiO)_3Si—OH$ (cluster **1**), $Si_{10}O_{28}H_{16}$ $[(SiO_2)_{10} \cdot 8H_2O)]$ (cluster **2**), and $Si_{30}O_{77}H_{34}$ $[(SiO_2)_{30} \cdot 17H_2O]$ (cluster **3**) was carried out. The results of calculations are given in Table 4 from which it follows that, on the whole, clusters **2** and **3** describe reeasonably well the experimental cristobalite structure. In particular, the Si—O bond lengths are 1.61—1.62 Å (HF/6-31G(d)) and 1.65—1.67 Å (PM3) (the corresponding experimental value for quartz is 1.61 Å).[20] The Si—O—Si angles are 160—170° (the experimental value is 147°).[20] The O atoms deviate randomly from the planes through the Si atoms.

The results of calculations demonstrate that the bond lengths change only slightly in going from the smallest clusters to the medium-sized and large clusters. The optimized geometric parameters of clusters **2** and **3** are inconsistent with the geometry of the ideal crystal as a

Table 4. Bond lengths and atomic charges in the model clusters (**1**—**3**) representing the terminal OH group on the SiO_2 surface

Parameter	RHF/6-31G*		PM3		
	1	**2**	**1**	**2**	**3**
r/Å					
O(1)—H	0.946	0.948±0.001 (4)	0.945	0.944±0.001 (3)	0.947±0.003 (18)
Si(2)—O(1)	1.631	1.620±0.004 (4)	1.694	1.697±0.002 (3)	1.701±0.003 (18)
Si(2)—O(3)	1.614±0.003 (3)	1.618±0.005 (12)	1.665±0.001 (3)	1.655±0.003 (12)	1.651±0.006 (86)
O(3)—Si(6)	1.637±0.002 (3)	1.615±0.008 (12)	1.674±0.001 (3)	1.651±0.002 (12)	1.651±0.006 (86)
q/au					
H	0.476	(0.487±0.010) (4)	0.198	(0.191±0.003) (4)	(0.201±0.010)(18)
O(1)	−0.859	−(0.800±0.004) (4)	−0.509	−(0.545±0.007) (4)	−(0.597±0.011)(18)
Si(2)	1.609	(1.480±0.018) (4)	1.200	(1.340±0.004) (4)	(1.465±0.021)(18)
O(3)	−(0.842±0.006) (3)	−(0.766±0.017) (12)	−(0.575±0.008) (3)	−(0.644±0.022) (12)	−(0.713±0.027)(36)
Si(6)	(0.918±0.004) (3)	(1.425±0.014) (6)	(0.709±0.008) (3)	(1.320±0.006) (12)	(1.469±0.049)(36)

Note: the sign "±" denotes the standard deviation (the number of parameters in the selection).

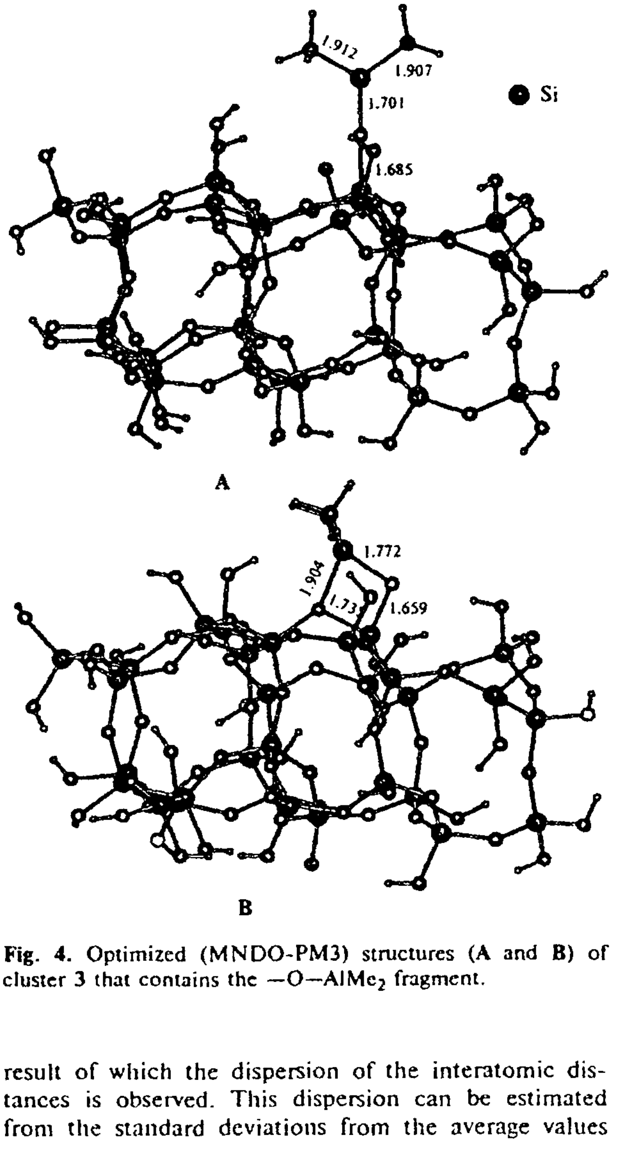

Fig. 4. Optimized (MNDO-PM3) structures (**A** and **B**) of cluster **3** that contains the —O—AlMe$_2$ fragment.

result of which the dispersion of the interatomic distances is observed. This dispersion can be estimated from the standard deviations from the average values given in Table 4. From Table 4 it follows that all geometric parameters calculated by the PM3 method for clusters **2** and **3** are virtually identical and differ within the dispersion of these values in cluster **3**. However, the semiempirical and *ab initio* approaches gave substantially different geometric parameters for clusters **1** and **2**. As mentioned above, the *ab initio* methods used reproduce substantially more adequately the experimental values of the Si—O bond lengths. When the *ab initio* method was used, the Si(2)—O(1) bond length tends to the normal value observed in the crystal in going from cluster **1** to **2**, *i.e.*, this bond is substantially shortened as the cluster is extended.

The effect of the surface on the structures of organometallic fragments can be considered analogously. The geometry of the successively increasing systems, $(H_3SiO)_3Si—OAlMe_2$, $[Si_{10}O_{28}H_{15}]—AlMe_2$, and $[Si_{30}O_{77}H_{33}]—AlMe_2$, was optimized. The results of calculations are given in Table 5 from which it follows that the geometry of the fragment in the coordination sphere of the three-coordinate metal atom changes only slightly under the effect of the surface. Most of the bond lengths change by 0.001—0.005 Å as the cluster size increases. In the coordination sphere of the metal atom, the Al—O(3) bond is most substantially lengthened in structures **A** (by ~0.05 Å) and **B** (by ~0.02 Å). In the former case, the elongation is attributable to the effect of the crystal, which repels the —O—AlMe$_2$ group. In the latter case, this elongation is attributable to the drawbacks of cluster **2** as a model of the surface: the adjacent unit cells do not affect the surface Si(6)—Si(8) atoms, which leads to "contraction" of cluster **2** and to an increase in the distance between the O(3) and Al atoms. Analogously, the crystal strongly affects the Si(2)—O(1) bond, which is lengthened by 0.01—0.02 Å in going to large cluster systems. In all cases, the difference in the energies of structures **A** and **B** is also reproduced. The energies of clusters **1** and **3** are virtually identical.

In connection with the problem of the choice of an adequate model of the surface center, it was of interest

Table 5. Calculated (PM3) energy and geometric parameters of the model clusters (**1**—**3**) representing the surface group Si—O—AlMe$_2$

Parameter	$(H_3SiO)_3Si—O—AlMe_2$ (**1**)		$[Si_{10}O_{28}H_{15}]—AlMe_2$ (**2**)		$[Si_{30}O_{77}H_{33}]—AlMe_2$ (**3**)	
	A	**B**	**A**	**B**	**A**	**B**
$E_A—E_B$*/kcal mol^{-1}	20.1		16.1		20.4	
r/Å						
O(1)—Al	1.709	1.775	1.706	1.772	1.703	1.772
Al—O(3)	4.100	1.889	4.104	1.915	4.155	1.905
Al—C	1.904	1.947	1.908	1.952	1.911	1.961
Si(2)—O(1)	1.663	1.639	1.671	1.647	1.684	1.660
Si(2)—O(3)	1.668	1.731	1.653	1.742	1.654	1.735
Si(2)—O(4),O(5)	1.670	1.666	1.648	1.649	1.644	1.639
Angle/deg						
Si(2)—O(1)—Al	171.9	102.2	172.7	101.1	177.5	100.5
O(1)—Si(2)—O(3)	107.3	85.8	107.9	87.3	106.0	87.4

* The difference in the energies of structures **A** and **B**.

to consider the advantages and drawbacks of structure **1** as a model of the surface fragment. From the above-mentioned it follows that the calculated parameters of cluster **1** are quite stable to a substantial increase in its size and reflect rather adequately all characteristic features of the local environment of the active center typical of structure **2**. In particular, one of the siloxane bridges (Si(1)—O(3)—Si(6)) in cluster **2** is bent outward, while the two other bridges are bent inward. Cluster **1** has a similar structure. In both cases, the terminal OH group is directed toward the O(3) atom, apparently as a result of formation of a weak additional hydrogen bond. The validity of the choice of cluster **1** as a model of the surface is also evidenced by small changes in the geometry of the organoaluminum surface structure as the size of the cluster increases.

It is also necessary to consider the effect of boundary atoms of the cluster on the properties of the active center under consideration. In this work, we studied the possibility of closure of terminal Si atoms through hydroxyl groups with the fully optimized geometry. The results of calculations of the cluster $Si_4O_{13}H_{10}$, whose terminal bonds are closed through OH groups, demonstrated that when this model is used, the OH groups act as surface hydroxyl groups to form hydrogen bonds with the central (terminal) OH group. As a result, the optimized structure $Si_4O_{13}H_{13}$ does not reflect the properties of the terminal OH group on the surface of cristobalite and serves as a model of nearby (vicinal) hydroxyl groups bonded to the surface. When the boundary bonds of the cluster are saturated with hydroxyl groups, the model is improved if O atoms of the OH groups are fixed in specified positions, for example, in positions corresponding to the ideal crystal lattice.

The above-considered results suggest that the cluster **1** adequately describes the isolated active center on the surface of β-cristobalite, reproduces its structural parameters and chemical properties, and reflects the characteristic features of large cluster systems. This cluster adequately reproduces the geometry of the O_3Si—OH group, which is affected by the extended fragment of the surface. The studies of the effect of the crystal on the structure of the active center in the calculations of systems containing up to 149 atoms demonstrated that cluster **1** has all structural features typical of large clusters. The typical distortion of the Si—O—Si fragment, the weak coordination of the OH group to the nearest O atom, the geometric and electronic parameters, and the energetics of interactions between organometallic groups bonded to the surface and the surface are adequately described.

The surface group —O—$AlMe_2$ is characterized by the occurrence of two stable conformations with the four- and three-coordinate Al atom. Structure **B** with the Al atom that forms two nonequivalent bonds with the O atoms at the same Si atom is more stable. In going from form **A** to **B**, the energy of the HOMO of the system increases and the capacity for hydrolysis and insertion into M—C bonds increases. The positive charge on the Al atom and the polarity of the Al—O bond increase. As a result, insertion into this bond occurs easier. In addition, the catalytic and activation properties of this center are affected by the presence of the O(1) atom in the strained conformation with the substantially smaller bond angle and the elongated O(1)—Al bond.

For the B and Zn atoms of organometallic groups bonded to the surface, we did not observe the tendency to additional coordination to oxygen atoms of the nearest environment. The —O—BMe_2 and —O—Zn—Me fragments remain free and are flexible and labile, which is favorable for coordination to the nearby OH groups on fragments of the surface where possible.

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References

1. *Sovremennye problemy kvantovoi khimii: Metody kvantovoi khimii v teorii mezhmolekulyarnykh vzaimodeistvii i tverdykh tel* [*Modern Problems of Quantum Chemistry: Methods of Quantum Chemistry in the Theory of Intermolecular Interactions and Solids*], Nauka, Leningrad, 1987, 285 (in Russian).
2. *Theory of Chemisorption*, Ed. J. R. Smith, Springer-Verlag, Berlin—Heidelberg—New York, 1980.
3. A. Fahmi and R. A. van Santen, *J. Phys. Chem.*, 1996, **100**, 5676.
4. H. Nakatsuji, M. Yoshimoto, Y. Umemura, S. Takagi, and M. Hada, *J. Phys. Chem.*, 1996, **100**, 694.
5. K. J. Farnworth and P. J. O. O'Malley, *J. Phys. Chem.*, 1996, **100**, 1814.
6. M. A. Nygren and L. G. M. Pettersson, *J. Phys. Chem.*, 1996, **100**, 1874.
7. S. A. Zygmunt, L. A. Curtiss, L. E. Iton, and M. K. Erhardt, *J. Phys. Chem.*, 1996, **100**, 6663.
8. A. L. Yakovlev, K. M. Neyman, G. M. Zhidomirov, and N. Rösch, *J. Phys. Chem.*, 1996, **100**, 3482.
9. S. R. Blaszkowski, M. A. C. Nascimento, and R. A. van Santen, *J. Phys. Chem.*, 1996, **100**, 3463.
10. V. A. Radtsig, *Khim. Fiz*, 1995, **14**, No.8, 125 [*Russ. Chem. Phys.*, 1995, **14**, No.8 (Engl. Transl.)].
11. V. A. Dodonov and Yu. N. Krasnov, *Zh. Org. Khim.*, 1988, **15**, 52 [*J. Org. Chem. USSR*, 1988, **15** (Engl. Transl.)].
12. N. V. Alekseev, I. A. Abronin, N. N. Korneev, and E. A. Chernyshev, *Khim. Fiz*, 1996, **15**, No. 2, 69 [*Russ. Chem. Phys.*, 1996, **15**, No. 2 (Engl. Transl.)].
13. L. Yu. Ustynyuk, V. A. Radtsig, and N. N. Senchenya, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2409 [*Russ. Chem. Bull.*, 1995, **44**, 2303 (Engl. Transl.)].

14. L. Yu. Ustynyuk and V. A. Radtsig, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 497 [*Russ. Chem. Bull.*, 1996, **45**, 477 (Engl. Transl.)].
15. S. K. Ignatov, A. G. Razuvaev, and M. B. Molotovshchikova, *Khim. Fiz*, 1996, **15**, 150 [*Russ. Chem. Phys.*, 1996, **15** (Engl. Transl.)].
16. M. B. Molotovshchikova, V. A. Dodonov, G. N. Lysenko, S. K. Ignatov, and A. G. Razuvaev, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1906 [*Russ. Chem. Bull.*, 1995, **44**, 1827 (Engl. Transl.)].
17. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
18. *GAUSSIAN 94, Revision D.1*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
19. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
20. A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, 1986.
21. S. K. Ignatov, A. A. Bagatur'yants, A. G. Razuvaev, and O. Gropen, *Chem. Phys. Lett.*, 1998, in press.

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