Active centers on the surface of thermoactivated silica. Their reactivity toward organoaluminum compounds

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Interaction between organoaluminum compounds (triethylaluminum, ethoxydiethylaluminum, and diethoxyethylaluminum) and the surface of silica activated at various temperatures (200—800 °C) was studied by IR spectroscopy, mass spectrometry, and quantum chemistry. Formation of structural silanon defects on the surface of silica activated at 800 °C was considered. It was established that the fraction of terminal silanol groups involved in the interaction with organoaluminum compounds on the surface of silica thermoactivated above 600 °C is low, and siloxane bonds and structural surface defects play a determining role. The thermodynamic favorability of coordination of organoaluminum compounds on these active surface centers is shown. The structure and routes of decomposition of aluminum-containing surface intermediates were studied.

Key words: silica, surface, organoaluminum compounds, active surface centers, intermediates, clusters, silanon groups, terminal silanol groups.

The problem of formation of metal-containing catalytically active surface moieties during interaction between organometallic compounds (OMC) and active centers of the silica surface is of considerable recent interest. However, to perform a directed formation of metal-containing structures on the surface, it is necessary to reveal, if possible, all active centers of the silica surface at various temperatures of its activation and to evaluate their reactivity toward OMC molecules, in particular, molecules of organoaluminum compounds (OAC).

According to the literature data, terminal silanol groups are main reaction centers of the thermoactivated silica surface on which reactions of OMC occur. The fact that mechanical activation of silica[1] results in the formation of active structural surface defects of a radical type and silanon centers was proved by UV and ESR spectroscopy and quantum chemical calculations. It has been assumed in several works[2,3] that radical and ionic defects are formed on the surface of silica thermoactivated above 600 °C due to dehydration of geminal silanol groups, and =Si=O groups are formed due to dehydration of geminate silanol groups. However, experimental data confirming the existence of these defects on the thermoactivated silica surface are scarce.

The purpose of this work is to study the interaction of Et$_3$Al, (EtO)Et$_2$Al, and (EtO)$_2$EtAl used for preparing metallocomplex catalysts with the surface of silica activated within the 200 to 800 °C temperature range. In addition, the study of this interaction could determine the reactivity of various active centers of the silica surface toward OAC molecules.

Experimental

Aerosil (Degussa) with a specific surface of 175 m^2 g^{-1}, which was molded at 200 kg cm^{-2} into pellets at 6—8 and 12 mg cm^{-2} for spectral studying, was used as the adsorbent. Prior to letting in OAC vapor, the Aerosil was preliminarily calcinated in air (300 °C, 3 h) and then evacuated at 200, 400, 500, 600, 700, or 800 °C (3 h, 1.3·10^{-3} Pa). Samples were modified in a special high-vacuum cell described in a previously published work.[4] IR spectra were recorded on a Specord IR-75 spectrometer attached to an AKROS automated system of digital registration and mathematical treatment with sixfold storage, smoothing, and subsequent differentiation of the IR spectra. Mass spectra were obtained on an MI-1305 mass spectrometer with an energy of the ionizing electrons of 70 eV, emission current of 15 mA, and accelerating voltage of 2 kV. Gases were admitted in an ion source through a dosing valve from the admission system at 20 °C and 2.6—5.2·10^{-5} Pa in the region of the source. OAC were synthesized according to known procedures.[5]

Models of surface structures were calculated by the semiempirical MNDO-PM3 method (see Ref. 6) in the approximation of molecular cluster with complete optimization of geometry of an OAC molecule and partial optimization of the geometry of a cluster. Some calculations were duplicated by MNDO and AM1 methods (see Refs. 7 and 8, respectively).

Results and Discussion

The IR spectra of Aerosil activated at 800 °C exhibit a weak absorption band (AB) at 1264 cm^{-1} against a background of the absorption in the range of vibrations of the silica skeleton. This band was assigned to vibrations of surface =Si=O groups (see Ref. 9). Taking into

account a high reactivity of this group toward H_2O and D_2O molecules, we performed hydrolysis of Aerosil activated at 800 °C. When H_2O (or D_2O) vapor is let in, the band at 1264 cm^{-1} disappears. After treatment of this Aerosil *in vacuo* at 400 °C to removing physically adsorbed H_2O (or D_2O) and bound Si—OH and Si—OD groups, two new bands appear in the spectrum: at 3743 and 3751 cm^{-1} (in the case of H_2O) and 2756 and 2763 cm^{-1} (in the case of D_2O), which can be assigned to geminal silanol groups[10]

$$\text{>Si}\Big\langle{}^{OH}_{OH} \quad \left(or \quad \text{>Si}\Big\langle{}^{OD}_{OD} \right).$$
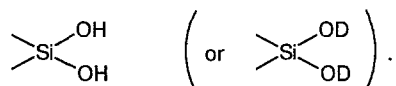
The band of terminal silanol groups at 3749 cm^{-1}, which is observed, as known, in the spectrum of initial Aerosil, remains in the spectrum, and treatment with D_2O vapor results in the appearance of the band of terminal $\geq$Si—OD groups at 2761 cm^{-1}.

It is noteworthy that there are no AB of =Si=O groups at 1264 cm^{-1} in the IR spectra of Aerosil activated at 600 °C.

Thus, an increase in the temperature of silica activation to 800 °C results in the formation of structural silanon defects on its surface. In addition, other active centers, terminal silanol groups and siloxane bonds, also exist on the thermoactivated silica. We assume that such active centers should differ in their reactivity toward organic derivatives of aluminum.

The majority of authors consider terminal silanol surface groups to be the main reaction centers for trimethylaluminum[11—16]:

$$\text{>Si—OH} + Me_3Al \longrightarrow$$

$$\longrightarrow \text{>Si—O—AlMe}_2 + MeH, \qquad (1)$$
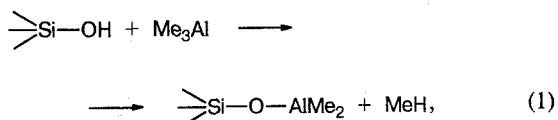
although other researchers[14—16] assume that Me_3Al also interacts with surface siloxane bonds:

$$\text{>Si}^{O}\text{Si}\langle + Me_3Al \longrightarrow$$

$$\longrightarrow \text{>Si—O—AlMe}_2 + \text{>Si—Me}. \qquad (2)$$

We have previously found that the fraction of terminal silanol groups involved in the interaction between triethylaluminum and Aerosil activated at 600 °C is low, and the determining role in formation of aluminum-containing surface structures belongs to surface siloxane bonds on which aluminum-containing intermediates are formed to be decomposed yielding carbene, unsaturated hydrocarbons, surface Si—H groups, and aluminum-containing structures.[17]

Since the activation temperature of silica exerts a substantial effect on the reactivity of various active

surface centers toward OAC, we studied the dependence of the degree of participation of terminal silanol groups of the Aerosil surface in the interaction with Et_3Al on the temperature of activation of Aerosil (Fig. 1). The degree of participation was characterized by the η value, which was determined from the IR spectra as the ratio between the difference in optical densities of the initial and remaining after interaction with Et_3Al absorption bands of terminal silanol groups and the optical density of the initial band.

It can be seen from Fig. 1 that terminal silanol groups of the surface are virtually not involved in the interaction with Et_3Al at temperatures of Aerosil activation above 600 °C. The intensity of the absorption band of Si—OH groups at 3749 cm^{-1} decreases insignificantly. However, the IR spectra of Aerosil activated at 800 °C and then treated with Et_3Al at 20 °C exhibit intense AB at 2800—3000, 1430, and 1390 cm^{-1} belonging to stretching and deformational vibrations of C—H bonds of organic ligands of adsorbed molecules and AB at 674, 711, and 824 cm^{-1} assigned to stretching vibrations of Si—C, Al—C, and Al—O bonds in metal-containing surface moieties.[16] Subsequent heating of this Aerosil to 400 °C results in β-hydride decomposition of the organoaluminum-containing surface moieties to form ethylene. In the IR spectrum, the intensity of AB of vibrations of C—H bonds decreases, and the bands of vibrations of surface Al—H (1756 cm^{-1}) and Si—H (2251 and 2263 cm^{-1}) bonds appear.

In addition, at 20 °C Et_3Al interacts with Aerosil activated at 800 °C almost without formation of unsaturated hydrocarbons (ethylene, propene, and butene), which are formed in considerable amounts during adsorption of Et_3Al at 20 °C on Aerosil activated at 600 °C
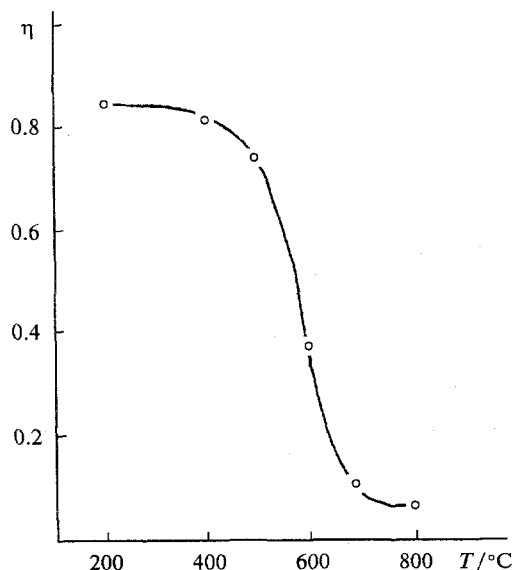
Fig. 1. Dependence of the η ratio of the number of terminal silanol groups on the surface of Aerosil, which entered the reaction with triethylaluminum, to their initial number, on the temperature of silica activation.

(see Ref. 17). There are no AB of surface Si—H groups in the IR spectrum of this Aerosil, and the intensity of the band of terminal Si—OH groups decreases insignificantly. All this testifies that the fraction of siloxane bonds and terminal silanol groups involved in the interaction with Et_3Al on the surface of Aerosil activated at 800 °C is considerably lower than that on the surface of Aerosil activated at 600 °C.

We assume that organometallic surface structures, whose AB are observed in IR spectra, can be formed with participation of silanon surface groups, which appear simultaneously with radical or ionic defect centers due to depolymerization of the silica skeleton according to the general scheme:
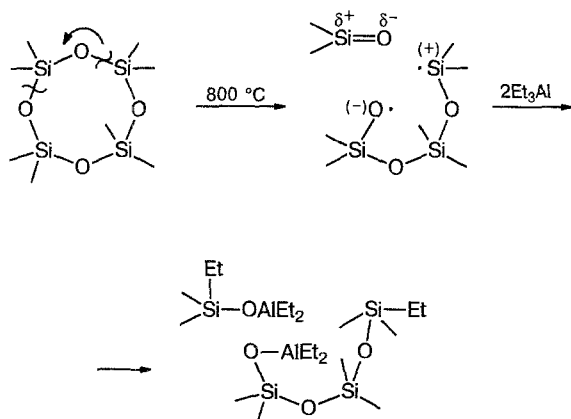
Not only alkoxide derivatives $(EtO)_2EtAl$ and $(EtO)Et_2Al$, but also Et_3Al interact with Aerosil activated at 800 °C in a different way than with Aerosil

activated at 600 °C. It has been shown previously[17] that OAC $((RO)_3Al$, $(RO)_2RAl$, and $(RO)R_2Al$, where R = Et, Bu^t) interact with Aerosil activated at 600 °C and below via terminal silanol groups to form aluminum-containing structures on the surface evolving alcohols (ROH) to the gas phase.

The IR spectrum of adsorption and desorption of $(EtO)_2EtAl$ on Aerosil activated at 800 °C is presented in Fig. 2. When $(EtO)_2EtAl$ vapor is let into the cell, the intensity of the AB at 3749 cm^{-1} of terminal silanol groups does not decrease and even increases (see Fig. 2, spectrum 2). Intense AB at 2800—3000, 1446, and 1386 cm^{-1} appear in the IR spectrum. They are assigned to stretching and deformational vibrations of C—H bonds of organic ligands of adsorbed molecules. There are also a band at 1726 cm^{-1} of vibrations of Al—H bonds and bands at 3450 and 3680 cm^{-1} of disturbed silanol groups.[4] The formation of OAC complexes with silanol groups on the surface can be assumed:
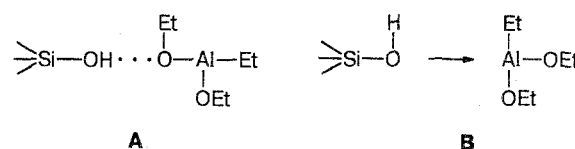
Complex **A** is less active, which is evidenced by disappearing the AB at 3680 cm^{-1} from the spectrum, when a sample of modified Aerosil was treated *in vacuo* at 20 °C (see Fig. 2, spectrum 3). Complex **B** is stable on the surface below 100 °C, and an increase in the temperature of desorption results in the upfield shift of the band from 3450 cm^{-1} to 3580 cm^{-1}. The AB of
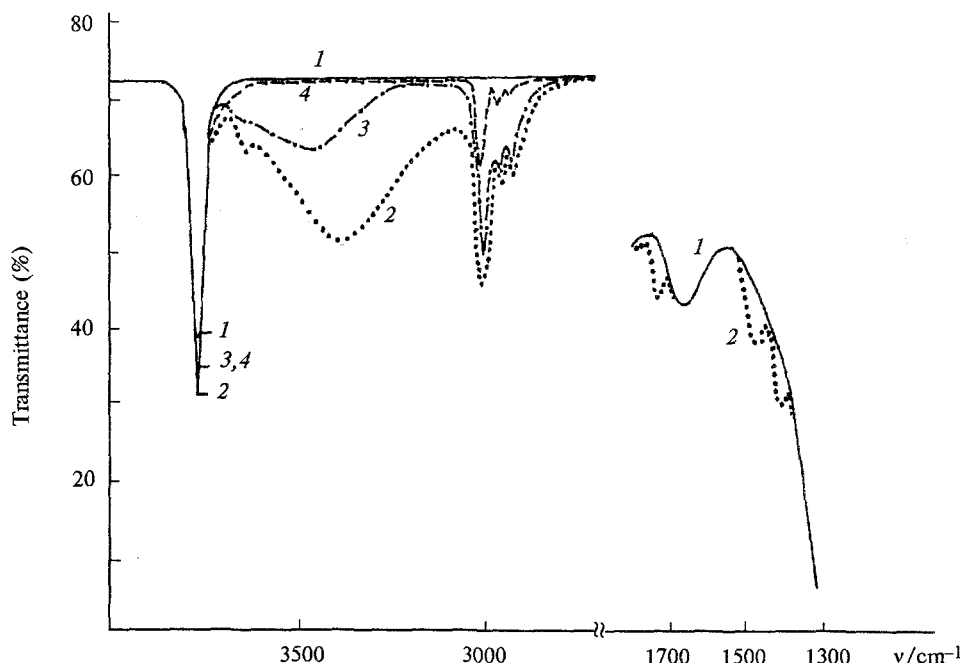
Fig. 2. IR spectra of Aerosil activated *in vacuo* at 800 °C (*1*), then treated with diethoxyethylaluminum at 20 °C for 60 min (*2*), and evacuated at 20 °C for 30 min (*3*) and at 400 °C for 30 min (*4*).

vibrations of C—H bonds of an organic ligand remain in the spectrum when modified Aerosil is thermally decomposed below 400 °C (see Fig. 2, spectrum *4*).

Thus, complexes of aluminum alkoxy compounds, in which a metal can be coordinated with four ligands (complex **B**), are easily formed on terminal silanol groups of Aerosil. Desorption at 100 °C results in the decomposition of the complexes to form initial OAC and Si—OH groups. No surface aluminum-containing active centers are formed during dissociation of these complexes.

It can be unambiguously concluded on the basis of the results obtained that terminal silanol groups on the surface of silica activated above 600 °C are not those main reaction centers toward OAC with both alkyl and alkoxyl radicals, which are responsible for the formation of metal-containing surface structures.

To determine the most energetically favorable methods of coordination of OAC molecules on silica, we calculated the enthalpies of complex formation of Me_3Al and Et_3Al with clusters modelling various active centers of the silica surface by the semiempirical quantum chemical MNDO-PM3 method. The structures $Si_4O_6(OH)_4$ (**1**), $Si_4O_6(OH)_2O$ (**2**), and $Si_4O_6(OH)_2$ (**3**) were chosen as the clusters (Fig. 3). Cluster **1** models the fragment of the surface of β-christobalite with a terminal silanol group. This cluster was also used for modelling the coordination of OAC on a siloxane group. Clusters **2** and **3** model the silanol active center on the silica surface. Although the structure of these clusters is not an exact fragment of the β-christobalite structure, they are rather representative in terms of this work. Similar model structures have been used previously[18] for studying reactions of Me_2Zn on Aerosil.

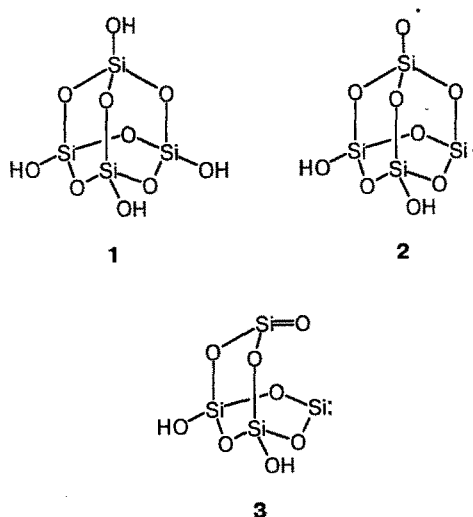The calculation shows that coordination on all active centers is also possible and thermodynamically favorable

Table 1. Enthalpies of complex formation $(-\Delta_f H°)$ between aluminum alkyls and surface active centers of silica

Cluster (active center)	$-\Delta_f H°$/kJ mol^{-1}	
	Me_3Al	Et_3Al
$Si_4O_6(OH)_3$—OH (silanol groups)	100.6	89.3
$Si_4O_6(OH)_4$ (siloxane bonds)	48.6	37.3
$Si_4O_6(OH)_2$—O	240.5	207.4
$Si_4O_6(OH)_2$ (silanon groups)	183.9	152.1

in the case of Me_3Al and Et_3Al (Table 1). Calculated geometric parameters for coordinated Me_3Al molecules are presented in Fig. 4.

As follows from the data presented, the coordination with a $=Si=O$ group is the most favorable. The enthalpy

Fig. 3. Cluster modelling fragments of the silica surface with surface active centers: **1**, $Si_4O_6(OH)_4$; **2**, $Si_4O_6(OH)_2$—O; **3**, $Si_4O_6(OH)_2$.
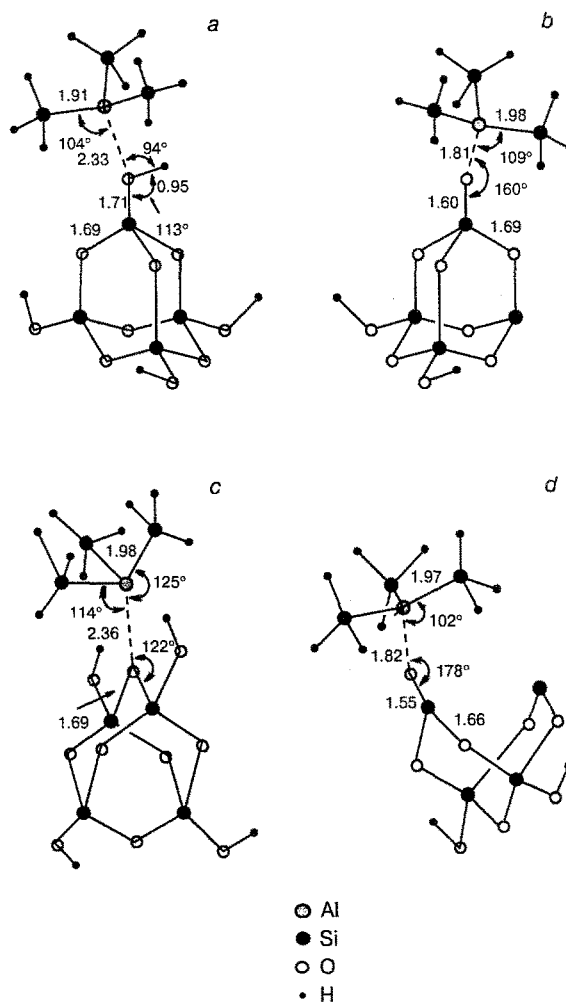

⊘ Al
● Si
○ O
• H

Fig. 4. Coordination of a Me_3Al molecule on different surface centers of silica: *a*, terminal silanol group; *b*, defect center of Si—O · type; *c*, siloxane surface bond; *d*, defect of Si=O type.

of this reaction, even taking account of its possible overestimation by the semiempirical method, can be sufficient for considerable activation of one or several Al—C bonds. This is confirmed by a considerable increase in the lengths of these bonds in the complex (1.98 Å) compared to that in a free Me_3Al molecule (1.89 Å) (Fig. 4, *d*). A similar conclusion can be made comparing the bond order of Al—C in the complex (0.885) and in the free molecule (0.975). The reason for this destabilization is the considerable (0.3 ē) charge transfer from the oxygen atom to the vacant p-orbital of aluminum. In the case of deformation of the geometry of Me_3Al, this orbital is strongly mixed with antibonding σ^*-MOs of Al—C bonds, which results in destabilization of the latter.

A lower energy effect takes place in the case of coordination of Me_3Al and Et_3Al molecules with the oxygen atom of the terminal silanol group. However, the calculation in this case also testifies that a strong complex with considerably lengthened (to 1.97 Å) Al—C bonds is formed (see Fig. 4, *a*). Although an intermediate position of a proton of the OH group between directions of Al—C bonds is the optimum conformation, the barrier of rotation around the Al—O bond is low, which can favor the further occurrence of reaction (1), depending on the conditions of the process.

The energy effect of the complex formation between R_3Al (where R = Me, or Et) and the oxygen atom of the of Si—O—Si siloxane group is the lowest. However, in this case, a strong deformation of an OAC molecule caused by steric hindrances also results in noticeable destabilization of Al—C bonds (see Fig. 4, *c*). The formation of this type complex creates a strong strain of the Si—O—Si group. The calculation was performed for the usual Si—O—Si moiety, which differs from the siloxane moiety formed by dehydration of two silanol surface groups. Coordination with the siloxane surface group can considerably destabilize the latter, decreasing the population density of the bonding σ^*-MO of the Si—O bond and thus favor the occurrence of reaction (2) on the surface.

The obtained results of quantum chemical calculations cannot yet unambiguously explain the observed effect of deactivation of terminal silanol groups relative to OAC at the temperatures of silica activation above 600 °C. However, in the case of this silica, defect active centers =Si=O (or $\geq$Si—O-·) appearing on the surface begin to play a predominant role in reactions with OAC. This is caused by the facts that coordination of OAC on

these centers is preferable to that of Si—OH and Si—O—Si groups and OAC molecules are more reactive.

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