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Modifying the Functional Cover of the γ-Al_2O_3 Surface Using Organic Salts of Aluminum

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Abstract—A method is suggested for modifying the surface properties of alumina without changing its chemical composition. The sorption of aluminum complexes with organic acid ligands on the γ-Al_2O_3 surface is reported. The thermal decomposition of the adsorbed oxalate complexes yields supported aluminum oxide compounds on the surface of the initial support. This modifies the functional cover of the γ-Al_2O_3 surface, altering the proportions of different types of surface hydroxyl groups, reducing their total number, and lowering the concentration of weak Lewis acid sites.

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One of the key problems of the synthesis of supported metal catalysts, including Pt/Al_2O_3, is that of producing active sites in which the metal has a preset chemical environment, electronic state, and particle size. Conventional approaches to this problem include variation of the nature of the precursor and/or chemical modification of the support [1–4]. For example, the introduction of a halogen not only increases the acidity of the support and leads to a more uniform distribution of the active component in the catalyst grain, but also stabilizes part of the supported platinum in the electron-deficient state [2, 3]. A similar effect can be attained by introducing a second or third metal. In this case, the "dilution" of the active metal in the polymetallic particle conserves its degree of dispersion and the shift of electron density from one metal to another produces the necessary electronic state [4]. For example, in the production of platinum/alumina reforming catalysts, high-dispersity platinum active in the desired reaction (paraffin dehydrocyclization) is obtained by chemical modification that includes chlorination of the support (alumina) and addition of a second metal (Re, Sn) to platinum [1, 4].

At the same time, it is unclear whether it is possible to impart the necessary adsorption and catalytic properties to the supported metal by optimizing the metal–support interaction, without introducing chemical admixtures (modifiers or promoters). This interaction commences while the metal complex precursor of the active component is being anchored to the support and depends considerably on the chemical composition and nature of the adsorption sites [2, 5]. It is believed that these sites on the alumina surface are Lewis acid sites [6] and hydroxyl groups [2, 7, 8]. Five to seven types of hydroxyl groups are distinguished on the alumina surface, which differ in their coordination number (terminal and bridging hydroxyls) and in the coordination number of aluminum ions [9–12]. The difference between the acid–base properties of surface OH groups may determine their interaction with anionic platinum(IV) complexes and, accordingly, the precursor binding strength and, subsequently, the properties of the supported platinum.

The purpose of this work was to change the ratio of different types of hydroxyl groups on the alumina surface at a constant chemical composition of the surface. This was done by modifying γ-Al_2O_3 with an organic salt of aluminum. The subsequent thermal decomposition of this salt in an oxidative atmosphere was expected to yield, on some areas of the support surface, supported aluminum oxide compounds possessing structural and adsorption properties other than those of the initial γ-Al_2O_3.

When introducing modifying ions, their binding on the support is generally left out of consideration and only the modifier content and the effect of the modifier on the properties of the support are controlled [1, 2]. We studied the speciation of aluminum oxalate and acetate in aqueous solution and their interaction with the surface groups of the support. We aimed at chemisorbing the modifier in such a way as to rule out the formation of a bulk aluminum oxide phase in the pore space of γ-Al_2O_3 and any significant changes in textural characteristics.

EXPERIMENTAL

γ-Al_2O_3 (Condea) had a particle size of 0.1–0.25 mm, a specific surface area of $S_{BET} = 202$ m^2/g, an adsorption pore volume of $V_{ads} = 0.55$ cm^3/g, and an effective pore diameter of $D_{eff} = 11.1$ nm. The sodium and iron content of the support was 0.003 and 0.021 wt %, respectively. γ-Al_2O_3 was modified with aluminum oxalate and acetate solutions containing preset salt concentrations. The aluminum oxalate solutions were prepared from the crystalline hydrate $Al_2(C_2O_4)_3 \cdot nH_2O$ (pure grade, Reakhim); the aluminum acetate solutions, from basic aluminum acetate $Al(OH)(CH_3COO)_2$ (analytical grade, Fluka).

Adsorption isotherms for aluminum compounds on γ-Al_2O_3 (20 ± 1°C) were obtained by the discrete samples technique. The weight ratio of the support to the solution of the aluminum compound was 1 : 25. Preliminary experiments demonstrated that the establishment of the equilibrium in the adsorption of aluminum oxalate complexes on γ-Al_2O_3 takes at least 24 h. The pH of solutions was measured with a calibrated electrode on a SevenMulti pH meter (Mettler Toledo). The aluminum concentration in solutions before and after adsorption was determined by atomic absorption spectroscopy (AAS) on an AA-6300 spectrometer (Shimadzu).

The alumina samples to be examined were loaded with the amount of modifier that corresponded to the maximum possible amount of chemisorbed complexes. After drying at 120°C, the samples were calcined at 550°C for 3 h.

The ^{27}Al NMR spectra of aluminum oxalate and acetate solutions were recorded on an AC-200 spectrometer (Bruker) with a broadband multinuclear probe operating at a frequency of 52.15 MHz and $T =$ 25°C in the pulsed mode without a deuterium lock (pulse width of 5 μs, digitization delay time of 27.5 μs, pulse delay time of 0.5 s, 25 kHz spectral window, 16000 data points per spectrum, acquisition time of 8–24 h). A 1 M $Al(NO_3)_3$ solution was used as the external standard.

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of the aqueous $Al_2(C_2O_4)_3$–γ-Al_2O_3 system were recorded on a Nicolet 5700 spectrometer (Thermo Fisher Scientific) with a deuterated triglycine sulfate (DTGS) detector and a horizontal ATR attachment (Smart Specular ATR). The optical element was a ZnSe crystal. For obtaining a spectrum, 32 scans were coadded in the 400–4000 cm^{-1} range at 4 cm^{-1} resolution over 30 h and were compared to the background spectrum of water-wetted γ-Al_2O_3.

The acid properties of the surface of calcined samples of the initial and modified γ-Al_2O_3 were studied by IR spectroscopy using adsorbed probe molecules. The spectra were recorded in the transmission mode on an FTIR-8400S infrared spectrometer (Shimadzu) in the 700–7000 cm^{-1} range with 4 cm^{-1} resolution. The samples, pressed into pellets without a binder, had a density of 15–19 mg/cm^2. They were placed in an adsorption cell with NaCl windows and were held in a vacuum adsorption unit in air (500°C, 20 min) for removing organic impurities and then in vacuo (10^{-6} bar, 500°C, 1.5 h). The acid properties of the samples were studied by successive CO adsorption at 77 K. The concentration of Lewis acid sites was estimated as the integrated intensity of the ν(CO) absorption bands in the 2175–2240 cm^{-1} range; the concentration of OH groups, as the integrated intensity of the ν(OH) absorption bands in the 3650–3800 cm^{-1} range. The concentrations were calculated using the formula

$$C_s = \frac{A}{10^{-3}\rho A_0},$$

where C_s is the concentration of the surface group (μmol/g), A is the observed integrated intensity of the absorption band (cm^{-1}), ρ is the density of the pellet (mg/cm^2), and A_0 is the integrated absorption coefficient (cm/μmol). The concentration of surface OH groups was estimated using $A_0 = 5.3$ cm/μmol [13]. In the estimation of the concentration of Lewis acid sites, A_0 was taken to depend on the adsorption site type (strength) and the following A_0 values (cm/μmol) were used: 1.25 (2225 cm^{-1}), 1.0 (2200 cm^{-1}), and 0.9 (2190 and 2178–2180 cm^{-1}) [11]. Absorbances (A) were determined after the deconvolution of the observed spectrum into its components.

The thermal decomposition of $Al_2(C_2O_4)_3 \cdot nH_2O$ was studied by differential thermogravimetric (DTG) analysis with online mass spectrometric identification of volatile decomposition products. DTG measurements were carried out on an STA 449C Jupiter synchronous thermal analyzer (Netzsch) between 25 and 1000°C at a heating rate of 10 K/min in flowing argon (15 ml/min).

Nitrogen adsorption and desorption isotherms were recorded at 77 K on a Micromeritics ASAP-2020 volumetric vacuum surface area and porosity analyzer. The BET specific surface area (S_{BET}) was derived from the nitrogen adsorption isotherm at equilibrium relative nitrogen pressures of $P/P_0 = 0.05$–0.25. In the calculation of S_{BET}, we assumed that the area occupied by a nitrogen molecule in the filled monolayer is 0.162 nm^2. The adsorption pore volume (V_{ads}) was determined from nitrogen adsorption data for $P/P_0 =$ 0.990 under the assumption that the adsorbate density is equal to the density of the normal liquid and is 0.02887 mol/cm^3. Differential pore size distribution curves were obtained by the Barrett–Joyner–Halenda method [14].

The acid–base properties of aluminum oxide samples were studied using 1-hexene double-bond isomerization as the test reaction at 90, 100, and 110°C. The reaction conditions were similar to the conditions chosen for 1-pentene isomerization by MacIver et al. [15]. In order to prevent the deactivation of the catalyst and

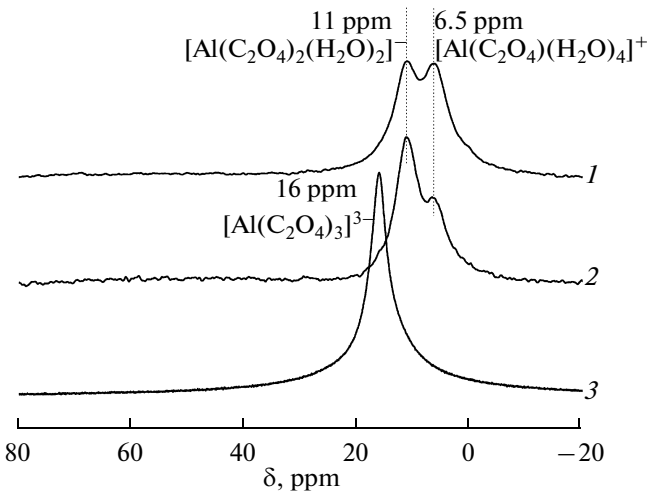


Fig. 1. ^{27}Al NMR spectra of aluminum oxalate solutions with α = (*1*) 1.5, (*2*) 2, and (*3*) 6.

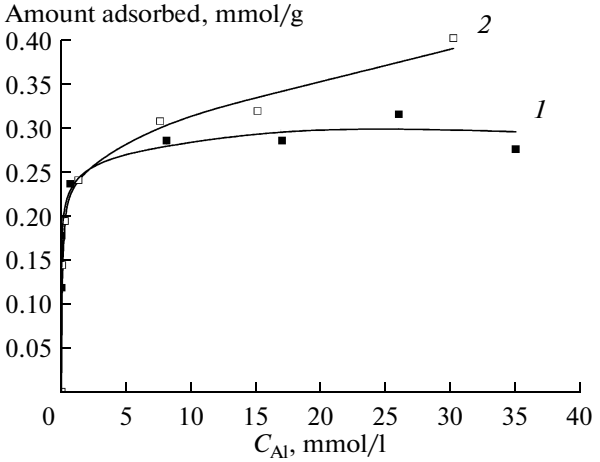


Fig. 2. Adsorption isotherms of aluminum oxalate on γ-Al_2O_3: (*1*) α = 1.5, pH 4.0–4.6; (*2*) α = 2, pH 4.8–5.6.

obtain reproducible results, all measurements were taken in the pulse mode. The reaction mixture was prepared by saturating helium with 1-hexene in a saturator at 24°C. Catalysts were tested at a constant He/C_6H_{12} molar ratio of 11 and a contact time of τ = 26 s. The catalyst sample (0.500 g) was placed in a U-shaped glass reactor and was conditioned before measurements in flowing helium at 200°C for 2 h. The initial reactant and the reaction products were analyzed online by gas–liquid chromatography on a Carlo Erba Instruments chromatograph (25 m × 0.2 mm capillary column, SE-54 stationary liquid phase, flame ionization detector).

RESULTS AND DISCUSSION

Aluminum Oxalate: Speciation in Aqueous Solution and Adsorption on the γ-Al_2O_3 Surface

The composition of the solutions of aluminum oxalate complexes at different α = $C_2O_4^{2-}/Al$ molar ratios was studied by ^{27}Al NMR spectroscopy. The value of α was varied by introducing a certain amount of ammonium oxalate into the solution. The ^{27}Al NMR spectrum of the $Al_2(C_2O_4)_3$ solution at C_{Al} = 0.04 mol/l, pH 4.2, and α = 1.5 shows two resonances with chemical shifts of δ = 6.5 and 11 ppm (Fig. 1, curve *1*), which are assigned to the cationic complex $[Al(C_2O_4)(H_2O)_4]^+$ and the anionic complex $[Al(C_2O_4)_2(H_2O)_2]^-$, respectively [16–18].

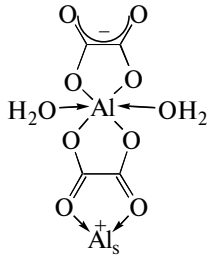
The broadening of the NMR lines is due to the quadrupole moment of the aluminum nuclei and is determined by the symmetry of the complexes. The deconvolution and integration of the spectral contours made it possible to quantitatively estimate the ratio of the complex species $[Al(C_2O_4)(H_2O)_4]^+$ and $[Al(C_2O_4)_2(H_2O)_2]^-$. At α = 1.5, these complexes are present in approximately equal proportions of 52 and 48%, respectively. The percentage of the anionic complex can be increased by introducing and additional amount of the oxalate ligand. At α = 2, the proportion of the $[Al(C_2O_4)_2(H_2O)_2]^-$ anion is 60% (Fig. 1, curve *2*). When the ligand in the solution is in large excess (α = 6), the NMR spectrum shows a single signal at δ = 16 ppm (Fig. 1, curve *3*), which is due to the triply charged anion $[Al(C_2O_4)_3]^{3-}$ [16, 18]. The domination of anionic oxalate complexes in the solution may be favorable for their chemisorption on the alumina surface, which is positively charged under the given experimental conditions (pH < 9) [19].

In order to determine the maximum possible amount of aluminum oxalate complexes chemisorbed on the γ-Al_2O_3 surface, we studied their adsorption at α = 1.5 and 2.0. It was found that, at α = 1.5, the adsorption isotherm is satisfactorily described by the Langmuir equation (Fig. 2). The maximum amount of adsorbed complexes is 0.29 mmol/g, which is equivalent to 0.78 wt % Al adsorbed (2.9% Al_2O_3). The adsorption equilibrium constant derived from the Langmuir equation in linear form is 1.57×10^4 l/mol. This large value is evidence that the chemisorbed metal complex is strongly bound [20]. The buildup of the anionic species in the solution on passing from α = 1.5 to α = 2 allows the amount of chemisorbed aluminum oxalate complexes to be increased by more than 30%.

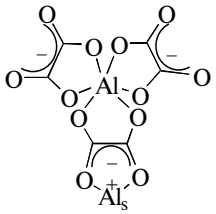
In order to determine the composition of the aluminum oxalate complexes bound to the γ-Al_2O_3 surface, we studied their interaction with the oxide surface by in situ ATR-FTIR spectroscopy. A solution with C_{Al} = 0.01 mol/l and α = 2 was used in these experiments. The observed absorption bands and their assignments are listed in Table 1. The ATR-FTIR spectra (Fig. 3) indicate that, as the adsorption time is extended, the absorption bands strengthen and some of them shift.

For short contact times between the aluminum oxalate solution and the Al_2O_3 surface, the ATR-FTIR spectrum (Fig. 3, curves *1*, *2*) shows absorption bands at 1564 and 1304 cm^{-1}, which characterize the stretching vibrations of the deprotonated carboxyl group of the oxalate ions. It is likely that the latter are weakly bound to OH groups of aluminum oxide by hydrogen bonds [24]. Upon 1800-min-long adsorption, the spectrum (Fig. 3, curve *3*) exhibits only absorption bands at 1720, 1693, 1405, 1293, and 1278 cm^{-1}, which are due to adsorbed aluminum oxalate complexes (Table 1).

Correlating our ATR-FTIR spectroscopy data with oxalic acid adsorption data from the literature [20, 23, 24] suggests that the aluminum oxalate complexes are chemisorbed on the alumina surface as bidentate five-membered ring structures [20], which are the most stable:



A
bidentate chelate species
$[Al(C_2O_4)_2(H_2O)_2]^-$



B
bidentate chelate species
$[Al(C_2O_4)_3]^{3-}$

(Al_s = surface aluminum atom of aluminum oxide).

This is accompanied by the replacement of surface OH groups and/or coordinated water molecules with the formation of five-membered chelate structures via Al_s–O bonding [24]:

$$[Al_s(OH)(H_2O)]^0 + [Al(C_2O_4)_3]^{3-} + H^+ \rightleftarrows \{Al_s[Al(C_2O_4)_3]\}^{2-} + 2H_2O,$$

$$[Al_s(OH)(H_2O)]^0 + [Al(C_2O_4)_2(H_2O)_2]^- + H^+ \rightleftarrows \{Al_s[Al(C_2O_4)_2(H_2O)_2]\}^0 + 2H_2O.$$

It is not impossible that the aluminum oxalate complexes are also anchored to electron acceptor sites.

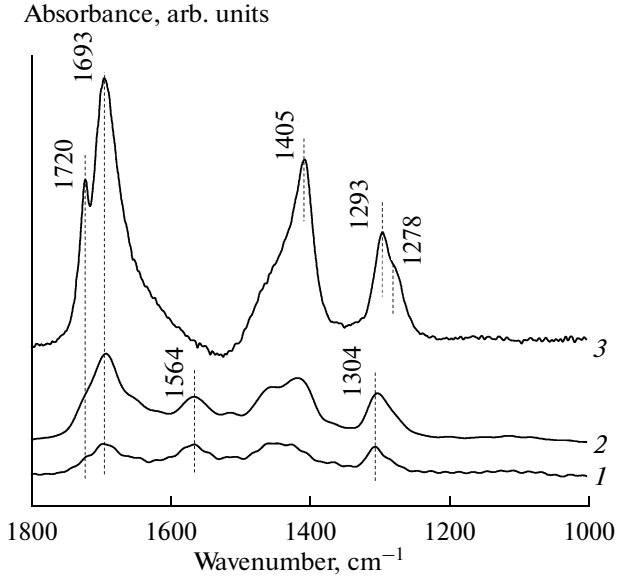


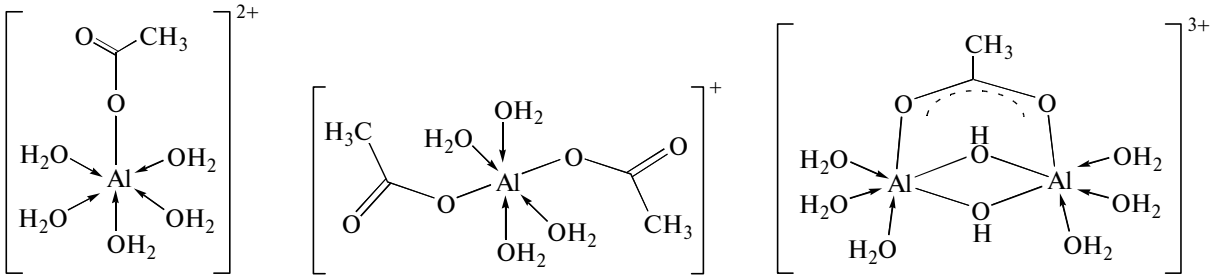
Fig. 3. ATR-FTIR spectra of the materials obtained by aluminum oxalate adsorption on alumina for (*1*) 30, (*2*) 60, and (*3*) 1800 min.

Aluminum Acetate: Speciation in Aqueous Solution and Adsorption on the γ-Al_2O_3 Surface

The ^{27}Al NMR spectrum of the solution of basic aluminum acetate (Fig. 4) shows two resonances at $\delta = 0$ and 2 ppm. The first one is due to the aquated aluminum cation $[Al(H_2O)_6]^{3+}$. The broad line at 2 ppm is due to the presence of cationic aluminum acetate complexes in the solution [17, 18, 25], among which the dominant species is the dinuclear, triply charged cation with a dawsonite structure [25]:

Table 1. Frequencies and assignment of the absorption bands of the aluminum oxalate complexes

ν, cm^{-1}	Assignment	Reference
1720	ν_{as} (C=O)	21–23
1693	ν_{as} (C=O)	21–23
1564	ν_{as} (C–O) [in COO^-]	22, 23
1405–1424	ν_s (C–O) + ν (C–C)	21–23
1304	ν_s (C–O) [in COO^-]	22, 23
1293, 1278	ν_s (C–O) + δ (O–C=O)	21–23



The AAS determination of the aluminum concentration in the aluminum acetate solution before and after its contact with γ-Al_2O_3 (contact time of 24–190 h) demonstrated that, at $C_{Al} = 0.12$ mol/l and pH 4.5, the aluminum acetate complexes, as distinct from the oxalate complexes, are not chemisorbed by γ-Al_2O_3. This observation can be explained both by the formation of only cationic forms of acetate complexes in aqueous solution and by these complexes having no carbonyl groups capable of forming surface chelate structures.

Thus, the study of the aluminum oxalate and acetate solutions demonstrated that the complexes brought into contact with alumina under similar conditions (concentration and pH) interact with the alumina surface in different ways. The anionic oxalate complexes are chemisorptively bound to the γ-Al_2O_3 surface. For this reason, these complexes were chosen for γ-Al_2O_3 modification.

Modification of the γ-Al_2O_3 Surface

The effect of modification on the acid–base surface properties and texture of aluminum oxide was studied by comparing those of γ-Al_2O_3 and 2.9%Al_2O_3/γ-Al_2O_3.

For selecting conditions for oxide formation from adsorbed aluminum oxalate complexes, we investigated the thermal decomposition of the crystalline hydrate $Al_2(C_2O_4)_3 \cdot nH_2O$ as the model compound by thermogravimetric analysis with mass spectrometric identification of volatile decomposition products. DTG data and the mass spectrometric identification of the gaseous products indicate that the thermal decomposition of aluminum oxalate consists of several steps. Between 70 and 220°C, the elimination of water of crystallization takes place. The greatest weight loss, observed at 320–400°C, is mainly due to the release of CO and CO_2. These data are in agreement with the results of an earlier study [26]. According to X-ray diffraction data, the solid product of the thermal decomposition of aluminum oxalate is γ-Al_2O_3 or a mixture of γ- and η-Al_2O_3 [27]. Thus, in order to decompose the

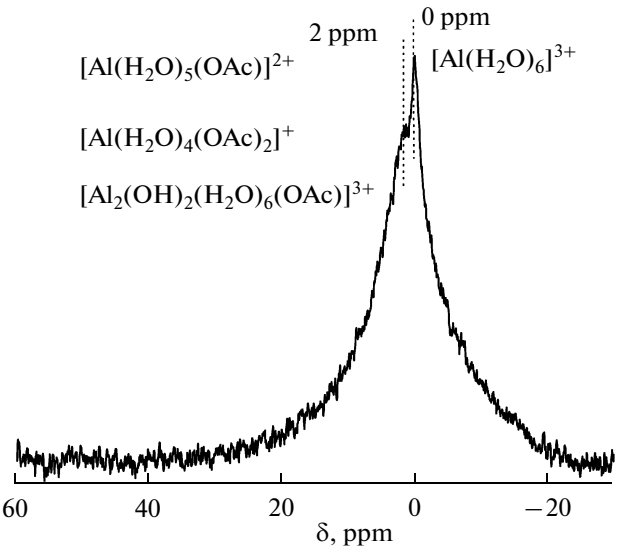


Fig. 4. ^{27}Al NMR spectrum of the solution of basic aluminum acetate ($C_{Al} = 0.12$ mol/l, pH 4.5).

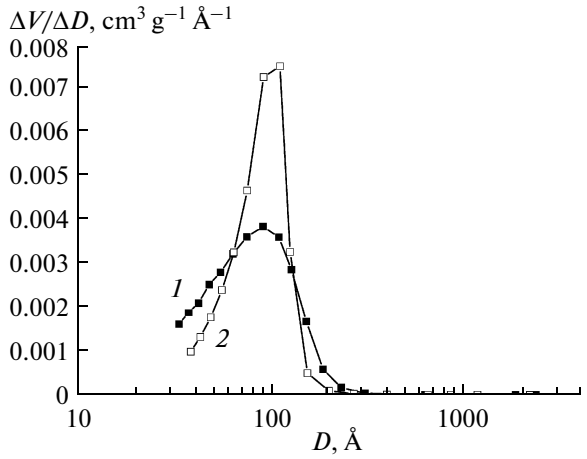


Fig. 5. Pore size distribution curves for (*1*) γ-Al_2O_3 and (*2*) 2.9% Al_2O_3/γ-Al_2O_3.

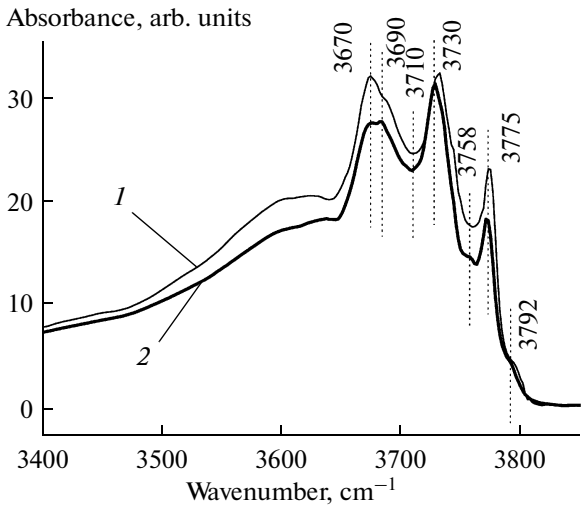


Fig. 6. IR absorption spectra in the region of hydroxyl stretching vibrations: (*1*) γ-Al_2O_3 and (*2*) 2.9% Al_2O_3/γ-Al_2O_3.

aluminum oxalate complexes adsorbed on the γ-Al_2O_3 surface and obtain a chemically uniform alumina surface, it is necessary to carry out heat treatment at 400°C or above. In subsequent experiments, the samples were calcined at 550°C for 3 h.

The textural characteristics of γ-Al_2O_3 and 2.9%Al_2O_3/γ-Al_2O_3 were studied by low-temperature nitrogen adsorption. It was demonstrated that the formation of aluminum oxide compounds (2.9% in terms of aluminum oxide) on the surface of the initial support via the thermal decomposition of supported aluminum oxalate complexes does not exert any significant effect on the specific surface area or pore volume: S_{BET} for γ-Al_2O_3 and 2.9% Al_2O_3/γ-Al_2O_3 is 202 and 200 m^2/g, and V_{ads} for these samples is 0.55 and 0.49 cm^3/g, respectively. At the same time, there is some difference in the pore size distribution. The distribution curves derived from nitrogen adsorption isotherms (Fig. 5) indicate that the modification causes no significant change in the total pore volume, but leads to a more uniform pore size distribution, reducing the proportion of pores smaller than 60 Å and larger than 150 Å.

The effect of the modification procedure suggested here on the surface properties of alumina was studied by IR spectroscopy. In the region of OH stretching vibrations, the spectra of the initial γ-Al_2O_3 and modified alumina (Fig. 6) show seven absorption bands characteristic of isolated OH groups: 3790–3795, 3775, 3758, 3730–3745, 3710, 3690, and 3670 cm^{-1}. The broad absorption band around 3600 cm^{-1} is due to hydrogen-bonded OH groups. The assignments of the absorption bands of the isolated surface OH groups [11] and the concentrations of these groups are listed in Table 2.

The formation of the aluminum oxide compounds on the γ-Al_2O_3 surface alters the proportions of different types of OH groups and decreases their total concentration by 70 μmol/g. According to chemisorption data (Fig. 2), 290 μmol/g of the hydroxyl groups of the initial alumina are involved in the strong binding of oxalate complexes (at a complex : OH group ratio of 1 : 1). The actual decrease in the OH group concentration is much smaller (Table 2). This might be due to the formation of hydroxyl-containing oxide compounds on the modified γ-Al_2O_3 surface.

Table 2. Types and concentrations of hydroxyl groups in calcined Al_2O_3 samples

Sample	OH group concentration, μmol/g							
	Al_tOH (3790–3795 cm^{-1})	Al_pOH (3775 cm^{-1})	Al_oOH (3758 cm^{-1})	$Al_o(OH)Al_o$ (3730–3745 cm^{-1})	$Al_p(OH)Al_o$ (3710 cm^{-1})	$Al_o(OH)Al_t$ (3690 cm^{-1})	$Al_p(OH)Al_t$ (3670 cm^{-1})	ΣOH
γ-Al_2O_3	12	64	43	157	80	84	83	523
2.9%Al_2O_3/γ-Al_2O_3	11	49	35	150	72	77	58	452

Note: Al_t, Al_o, and Al_p designate a tetrahedrally coordinated, octahedrally coordinated, and pentacoordinated aluminum ion, respectively.

Table 3. Concentrations of Lewis acid sites characterized by different absorption bands in the IR spectrum of adsorbed CO

Sample	Lewis acid site concentration, μmol/g				
	2179 cm^{-1}	2191 cm^{-1}	2207 cm^{-1}	2225 cm^{-1}	Σ
γ-Al_2O_3	155	360	8	3	526
2.9%Al_2O_3/γ-Al_2O_3	155	330	7	2	494

It follows from the IR spectra of adsorbed CO (Table 3, Fig. 7) that the supporting of the aluminum oxalate complexes and their subsequent thermal decomposition to aluminum oxide compounds cause a slight decrease in the concentration of weak Lewis acid sites characterized by $\nu(CO) = 2191$ cm^{-1} (regular surface defects of alumina involving an octahedrally coordinated aluminum ion) [11]. It is possible that these weak Lewis acid sites also participate in the binding of aluminum oxalate complexes. Note that the strong and medium-strength Lewis acid sites of the initial alumina, characterized by $\nu(CO) = 2207$ and 2225 cm^{-1}, respectively, are not involved in the binding of the supported oxide compounds.

The effect of modification on the acid–base properties of the alumina surface was additionally estimated using the double-bond isomerization of 1-hexene as the model reaction, which is sensitive to the number and strength of Lewis acid sites [15, 28]. As a rule, the migration of a double bond in an olefin molecule is accompanied by the geometric isomerization of the product (conversion of the *cis* isomer into the *trans* isomer). Surface hydroxyl groups are necessary for this reaction to occur [28, 29]. According to our data, the only products of 1-hexene isomerization under the given conditions are *cis*- and *trans*-2-hexene. The supporting of the aluminum oxalate complexes followed by their transformation into surface aluminum oxide compounds leads to a decrease in the 1-hexene conversion (Fig. 8). Since the rate of double-bond isomerization is proportional to the number of electron acceptor sites [28], this result is in good agreement with the IR spectra of adsorbed CO (Fig. 7); that is, the decrease in the number of Lewis sites is accompanied by a decrease in the 1-hexene conversion.

In addition, the alumina samples examined here were found to differ in stereospecificity in the double-bond isomerization reaction. For γ-Al_2O_3 at 90°C and $\tau = 26$ s, the ratio of *cis*- to *trans*-2-hexene is 0.3; for the modified sample at the same temperature, this ratio is 0.4. (According to thermodynamic calculations, the equilibrium ratio of *cis*- to *trans*-2-hexene should be 1.0.) This can be due to the observed change in the hydroxyl cover of alumina (Fig. 6).

We have found that the formation of aluminum oxide compounds on the alumina surface alters both the proportions of hydroxyl groups of different natures and the Lewis acidity of the initial alumina. A subject of our further investigation will be the effect of the modification method suggested here on the adsorption properties of the support in the binding of platinum(IV) chloro complexes. We will also attempt controlled formation of the catalytic properties of the Pt/Al_2O_3 system.

Thus, the proportion of different types of surface sites in alumina can be varied by modifying the oxide surface with organic salts of aluminum. We have investigated the adsorption of aluminum oxalate complexes on the γ-Al_2O_3 surface. The chemisorption of these complexes on the γ-Al_2O_3 surface is possibly due to the formation of five-membered chelate structures via the replacement of surface OH groups of alumina. The amount of adsorbed aluminum (as oxalate complexes) and, accordingly, the degree of modification can be varied by introducing an excess amount of oxalate ligand into the modifier solution. Aluminum acetate complexes are not chemisorbed by γ-Al_2O_3.

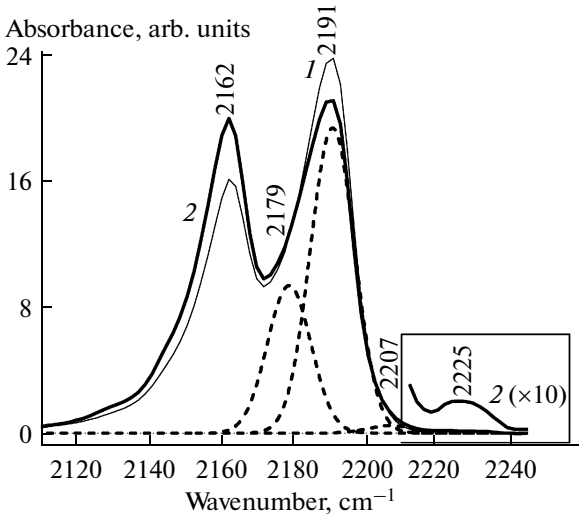


Fig. 7. IR spectra of CO adsorbed at 77 K and a CO pressure of 3 Torr: (*1*) γ-Al_2O_3 and (*2*) 2.9% Al_2O_3/γ-Al_2O_3. The dashed line shows the deconvolution of spectrum *2* into its components. Inset: portion of spectrum *2* magnified 10 times.

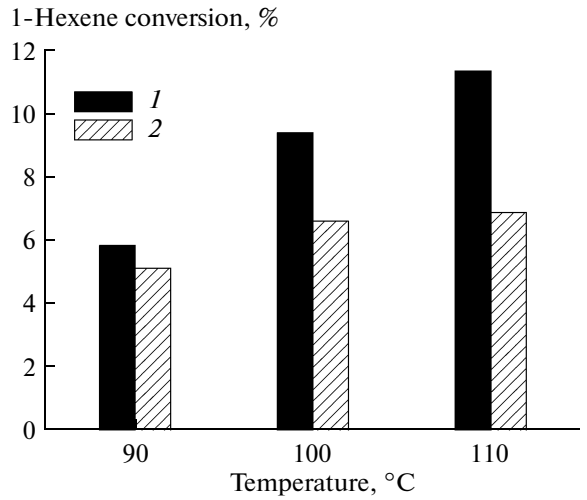


Fig. 8. Temperature dependence of the 1-hexene conversion: (*1*) γ-Al_2O_3 and (*2*) 2.9% Al_2O_3/γ-Al_2O_3.

Modifying the functional cover of the γ-Al_2O_3 surface (impregnation with an aluminum oxalate solution followed by heat treatment) changes the proportions of different types of surface hydroxyl groups and reduces their total number. In addition, this modification procedure decreases the number of weak Lewis acid sites. The change in the acid–base properties of the surface exerts an effect on the catalytic properties of alumina in the double-bond isomerization of 1-hexene. The modification affects the texture of alumina by altering the pore size distribution without changing the other parameters of the porous structure.

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