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The Structure of the VO_x Oxo Complexes on the Surface of the Al_2O_3 of Various Structural Modifications

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Abstract—The structure of the surface VO_x oxo complexes prepared by deposition from aqueous solutions on alumina in various modifications (γ, η, χ, θ, and δ) is studied using ^{51}V and ^1H NMR. The crystal structure and acidic properties of the surface of the starting phases of Al_2O_3 do not substantially affect the structure of the surface VO_x compounds. This is explained by the reconstruction of the surface layer of the support and a change in its acidic properties caused by the action of impregnating aqueous solutions.

INTRODUCTION

The V_2O_5/Al_2O_3 system is an efficient catalyst for the partial oxidation of hydrocarbons, reduction of nitrogen oxides by ammonia, and other processes [1, 2]. The study of the interaction between V_2O_5 and support is of great scientific and practical interest because the nature of the compounds formed determines their catalytic properties. In particular, the predominant formation of the surface vanadium oxo complexes VO_x enhances the selectivity of the catalysts in the reactions of the partial oxidation of hydrocarbons as compared to V_2O_5. The structure of VO_x complexes in the $V_2O_5/\gamma\text{-}Al_2O_3$ system depends on the vanadium concentration in samples and the conditions of its deposition [3]. The structure of the VO_x oxo complexes also depends on the crystal structure of alumina. Several structural modifications of alumina are known: γ-, η-, χ-, θ-, δ-, κ-, and $\alpha\text{-}Al_2O_3$ [4]. The aluminum cations in $\alpha\text{-}Al_2O_3$ occupy only octahedral positions. All other modifications contain the cations in both octahedral (Al_o) and tetrahedral (Al_t) coordination with respect to oxygen atoms and differ by the Al_t/Al_o ratio and the distribution of cationic vacancies in the lattice [4]. Experimental [5–11] and theoretical [6, 12–14] data are available on the dependence of the acidic properties of alumina on its structure. Thus, the electron-acceptor properties of Al_2O_3 are determined by the coordination numbers of the aluminum cations in the subsurface layer.

Coordination numbers vary from 3 to 6, depending on the distribution of the cations between the octahedral and tetrahedral positions in the crystal lattice [5, 6]. The electron-acceptor ability of aluminum cations increases with a decrease in their coordination numbers. Hence, the strength of Lewis acid sites on the surface increases [6, 8, 11, 12].

The effects of the crystal structure of Al_2O_3 on the structure of the surface VO_x complexes have not been studied systematically. Deo G. *et al.* reported significant differences in the structure of the VO_x oxide compounds formed upon vanadium deposition from nonaqeous media on the surface of $\gamma\text{-}Al_2O_3$ (polymeric tetrahedral and distorted octahedral species), δ, and θ phases (monomeric tetrahedra and distorted octahedra) and on $\alpha\text{-}Al_2O_3$ (only monomeric tetrahedra) [15]. This was explained by a decrease in the surface acidity when going from low-temperature $\gamma\text{-}Al_2O_3$ to high-temperature δ-, θ-, and α-phases. Deo G. *et al.* used commercial alumina containing sodium admixtures [15]. The authors explained a decrease in the acidity of high-temperature modifications of alumina by an increase in the concentration of sodium on the surface due to the migration of the admixture from the bulk to the surface rather than by the specific features of their crystalline structure.

In this work, the structure of the surface VO_x complexes formed upon the deposition of the active component from aqueous solutions on γ-, η-, χ-, θ-, and α-alumina, which differ in the preparation procedure and the content the sodium admixture, was studied by ^{51}V NMR.

EXPERIMENTAL

To obtain various phases of Al_2O_3, three modifications of aluminum hydroxide (boehmite, bayerite, and hydrargillite) were calcined at temperatures of 600–1250°C for 12 h. The crystalline boehmite and bayerite were prepared by us in laboratory conditions. Hydrargillite was prepared by the standard Bayer process. The phases were identified by XRD on a DRON diffractometer (CuK_α monochromatic irradiation; a graphite monochromator).

The specific surface areas of the supports (S_{sp}, m^2/g) were determined by the BET method from data on the argon thermal desorption. The ^1H MAS NMR technique was used to evaluate the state of hydroxyls on the alumina surface. Spectra were recorded on a Brucker

Table 1. Specific surface area and phase composition of alumina samples prepared from boehmite, bayerite, and hydrargillite by calcination at various temperatures

Starting hydroxide			S_{sp}, m^2/g			
phase	content of admixtures, wt %		600°C	900°C	970°C	1250°C
	Na	Fe				
BM	0.020	0.010	130(γ)	23(δ)	20(δ)	4.5(α)
BA	<0.002	0.020	240(η)	140(η)	70(θ)	9.0(α)
HG	0.190	0.015	180(χ + γ)	112(χ + γ)	–	–

CXP-300 NMR spectrometer (7.1 T) by spinning the samples under a magic angle with respect to the external magnetic field (MAS) at a velocity of 4 kHz in sealed ampules positioned in a mushroom-shaped quartz rotor [7]. The ^1H NMR spectra were recorded at a frequency of 300.13 MHz, complete sweeping of 50 kHz, the pulse width of 5 μs, and a relaxation delay of 5 s. The number of scans was 500 for each spectrum. Chemical shifts were measured relatively to tetramethyl silane as the external standard with an accuracy of ±0.1–0.2 ppm. The accuracy of expanding a spectrum to the Gaussian components was ±10%. Before a run, weighed samples (150–200 mg) were treated in special glass ampules at 500°C and a residual pressure of $<10^{-3}$ torr for 14 h.

The V_2O_5/Al_2O_3 samples were prepared by the impregnation of the support by an aqueous solution of ammonium metavanadate (pH 7), which was followed by drying in air at 110°C and calcination at 500°C for 4 h. The vanadium content in impregnating solutions and supported samples was estimated by photocolorimetry with hydrogen peroxide [16].

The ^{51}V NMR spectra (static and MAS) were recorded on a Brucker MSL-400 spectrometer at a frequency of 105.8 MHz, a radiofrequency pulse width of 1–2 μs, and at 10–1 Hz pulses per second. For recording MAS spectra, a standard device with a mushroom-shaped rotor with the spinning velocity of ~4 kHz was used; the shifts were measured relatively to $VOCl_3$ used as the external standard. Before measuring, samples were evacuated in quartz 40-mm long ampules with a 10-mm diameter at 200°C. Then, they were additionally oxidized by O_2 at 500°C to exclude the effect of paramagnetic centers and sealed. The static NMR spectra were recorded on the samples placed in sealed quartz ampules; to measure MAS spectra, the ampules were opened and the samples were transferred into the rotor.

RESULTS AND DISCUSSION

Table 1 presents the conditions of preparation and some properties of the alumina samples. Note that the content of sodium admixtures in the starting boehmite (BM) and bayerite (BA) is small (< 0.02 wt %) and is equal to 0.2 wt % in hydrargillite (HG). The content of iron in alumina did not exceed 0.02 wt %.

As one might expect, a series of crystalline phases is formed depending on the nature of the starting hydroxides and the calcination temperature (Table 1).

After calcination of aluminum hydroxides at temperatures up to 950°C, the oxides formed contain the residual amounts of OH groups [8]. We studied the properties of the residual hydroxyl coverage of various structural modifications of alumina by high-resolution ^1H NMR. Three overlapped signals with the chemical shifts of 3.5, 1.2, and –0.2 ppm (±0.2) were observed in the spectra of all the samples studied (Fig. 1). Other lines in the spectra in Fig. 1 refer to side bands that appeared when a sample was turned at a magic angle. The ^1H NMR signals were assigned according to [7].

The low-field line with a chemical shift of 3.5 ppm (signal *1*) is a superposition of signals from the hydroxyl groups bound to aluminum cations in the octahedral and tetrahedral coordination: (OH_2Al_o), (OH_3Al_o), $(OHAl_oAl_t)$. These OH groups have an acidic nature and are relevant to Brönsted acid sites.

The narrow line with a shift of 1.2 ppm (signal 2) corresponds to the intraglobular water molecules that are not removed during evacuation.

The line with the chemical shift of –0.2 ppm (signal *3*) can be assigned to the OH groups in the octahedral coordination $(OH–Al_o)$. Its position indicates the basic nature of these OH groups.

Table 2 shows the relative intensities of signals *1*, *2*, and *3* (I_1, I_2, I_3) in the ^1H MAS NMR spectra of various crystalline modifications of alumina, as well as the overall content of OH groups per unit surface area of the sample (C_{OH}). This value varies by a factor of 2–3 depending on the Al_2O_3 structure. The relative content of OH groups exhibiting acidic or basic properties changes by a factor of 1.4–2.0.

After rehydration of the surface of γ- and η-Al_2O_3, one OH group in the filled monolayer occupied an area of 8 Å^2 [4]. Hence, the concentration limit of hydroxyl groups in a monolayer can be 1.25×10^{19} m^{-2}. Taking into account the data of Table 2 and those reported in [4], one can calculate that the coverage of the BA600 sample of η-Al_2O_3 by hydroxyl groups is only ~20% of a monolayer, including ~10% of a monolayer occupied by acidic OH groups. The concentration of the Lewis acid sites also depends on the structure of Al_2O_3 vary-

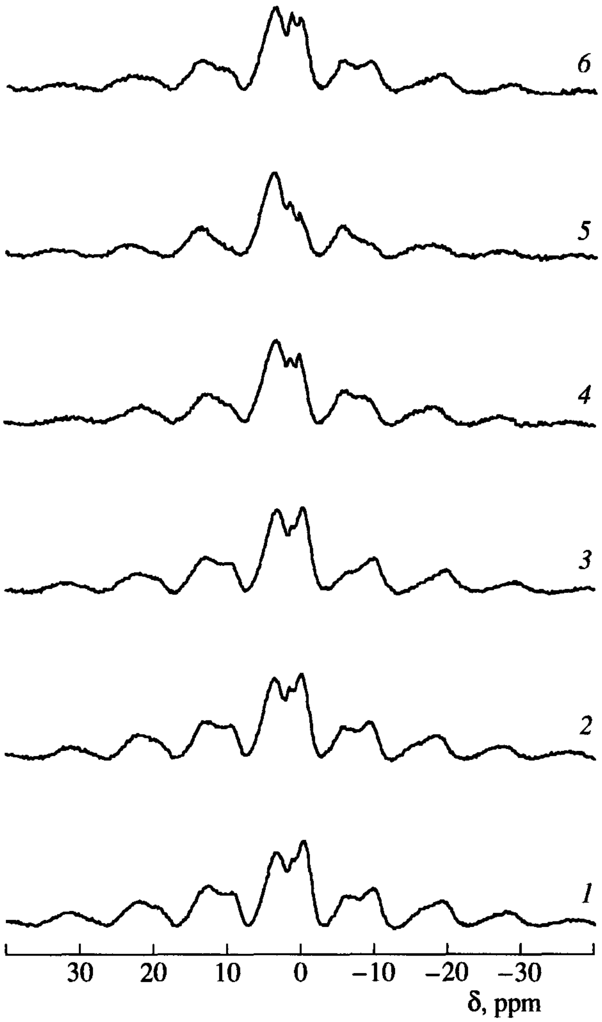


Fig. 1. ^{1}H MAS NMR spectra of various modifications of Al_2O_3: (*1*) γ(BM600), (*2*) η(BA600), (*3*) χ + γ(HG600), (*4*) δ(BM900), (*5*) η(BA900), (*6*) χ + γ(HG900). The starting hydroxide and its calcination temperature, °C, are shown in parentheses.

ing by a factor of 2–3 for various modifications [8]. This concentration was found to be 1.5×10^{18} m^{-2} for η-Al_2O_3.

Thus, as follows from Table 2 and data presented in [8], the concentration and strength of acid sites in alumina depend substantially on their crystalline structure.

Table 2. Specific content of OH groups and relative integral intensities of the lines in the ^{1}H MAS NMR spectra of various crystalline modifications of alumina evacuated at 500°C

Phase*	$C_{OH} \times 10^{-18}$, m^{-2}	I_1, %	I_2, %	I_3, %
γ (BM600)	4.2	57	4	39
η(BA600)	2.7	54	5	41
χ + γ(HG600)	2.2	61	2	37
δ(BM900)	5.6	70	2	28
η(BA900)	3.4	77	2	21
χ + γ(HG900)	2.0	58	4	38

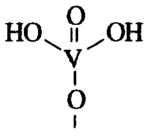
* The starting hydroxide and the temperature of its calcination in °C are shown in parentheses.

A series of the catalysts with various vanadium contents was prepared on the basis of the alumina modifications (Table 3). The vanadium concentration was chosen to minimize the amount of the V_2O_5 phase not bound to the support surface. According to [3], the V_2O_5 phase is observed on the surface of γ-Al_2O_3 at the surface vanadium concentration $C_{surf} > 3 \times 10^{18}$ atom/m^2. In this work, the constant vanadium concentration was 2.4×10^{18} atom/m^2 in the samples of series 1 and 1.2×10^{18} atom/m^2 in the samples of series 2. Because the specific surface areas of the alumina supports varied by more than an order of magnitude, the overall content of vanadium (C_V) was varied in the wide range from 0.2 to 5 wt % to ensure the constancy of the vanadium surface concentration (Table 3). We failed to study the state of vanadium in the samples based on α-Al_2O_3 because of the small specific surface area of this support (4.5–9.0 m^2/g). To maintain the above vanadium surface concentrations, its overall content should be <0.1 wt %, which is too small to obtain the NMR signals of sufficient intensity.

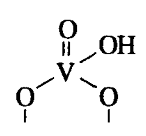
The signals of three types (*A*, *B*, and *C*) are present in the ^{51}V NMR spectra of all the samples studied (Figs. 2, 3), which were observed earlier for the V_2O_5–γ-Al_2O_3 system [3].

A chemical shift of the signal of type *A* changes from −520 to −590 ppm, and its shape is typical of vanadium in a nearly perfect tetrahedral environment. This signal corresponds to the isolated species [VO_4] adsorbed on the surface of Al_2O_3 through the formation of one or two bonds with the surface oxygen atoms that have some H_2O molecules in the second coordination sphere. A negligible scattering in the chemical shifts can be due to the different extents of solvation of these complexes in various samples.

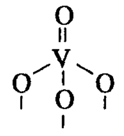
Signal *B* has a maximum at −700 ppm and the shape typical of vanadium in the distorted tetrahedral environment. This signal can be assigned to isolated [VO_4] tetrahedra strongly bound to the Al_2O_3 surface probably via the bonds with at least two surface oxygen atoms.



A



A



B

Signal *C* characterized by nearly axial anisotropy of the chemical shift ($\sigma_\perp = 350$ ppm) was assigned to the polynuclear vanadium species on the Al_2O_3 surface in which vanadium is in the distorted octahedral environment. This axial anisotropy of the spectrum is typical of the distorted octahedral oxygen environment of vanadium with one shortened V=O bond.

Note that the surface species found in this work coincide with those identified by the Raman spectroscopy in [15] in which the monomeric and polymeric tetrahedrally coordinated species were revealed at the

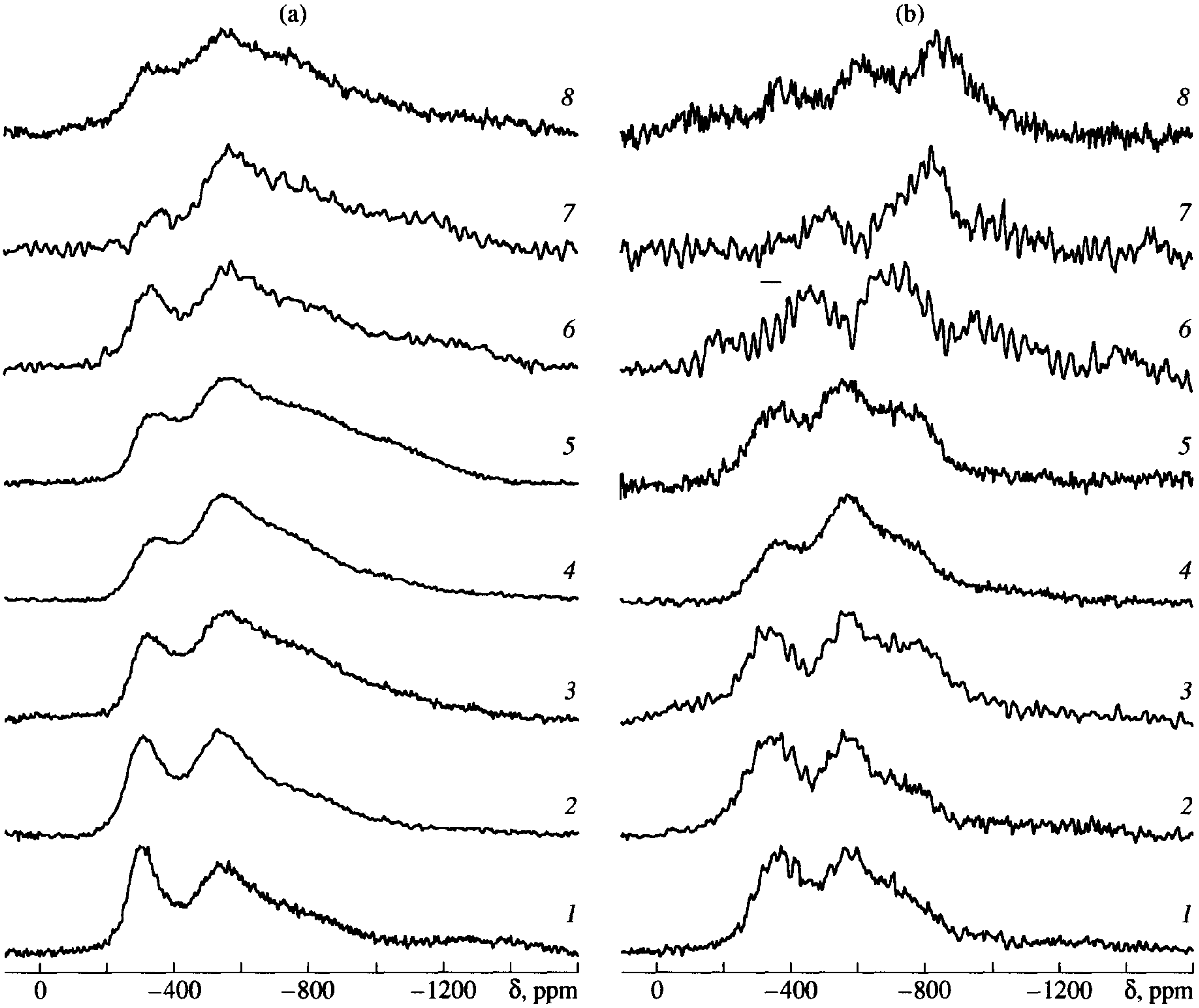


Fig. 2. Static (a) and MAS (b) ^{51}V NMR spectra of vanadium-alumina samples: (*1*) 1-3; (*2*) 1-1; (*3*) 1-4; (*4*) 1-2; (*5*) 1-5; (*6*) 1-6, (*7*) 1-8, and (*8*) 1-7. For notations of samples, see Table 3.

vanadium content of less than a monolayer. Based on the NMR data, it is possible to distinguish tetrahedra, which are weakly and strongly bound to the surface (signals *A* and *B*, respectively). The absorption bands assigned to the octahedrally coordinated polymeric species were observed in [15] at a higher vanadium content. The line *C* in the NMR spectra corresponds to this state of vanadium.

Table 3. Samples of the vanadium-alumina catalysts

Modification of Al_2O_3	η(BA600)	χ + γ(HG600)	γ (BM600)	η(BA900)	χ + γ(HG900)	θ(BA970)	δ(BM900)	δ(BM970)
$S_{Al_2O_3}$, m^2/g	240	180	130	140	112	70	23	20
Samples of series 1								
C_V, wt %	5.0	3.7	2.7	2.9	2.2	1.4	0.44	0.40
Notation	1-1	1-2	1-3	1-4	1-5	1-6	1-7	1-8
Samples of series 2								
C_V, wt %	2.5	1.8	1.4	1.5	1.1	1.2	0.22	0.20
Notation	2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8

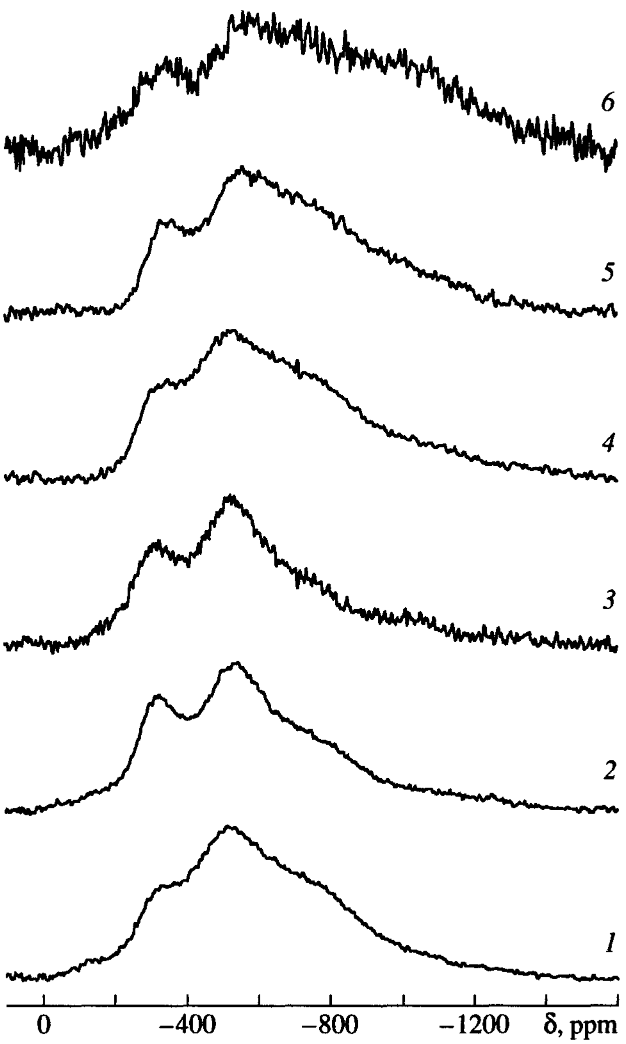


Fig. 3. ^{51}V NMR spectra of vanadium–alumina samples: (*1*) 2-3, (*2*) 2-1, (*3*) 2-4, (*4*) 2-2, (*5*) 2-5, and (*6*) 2-7.

Three broadened lines *A*, *B*, and *C* are present in the spectra of the samples of series 1 containing 2.4×10^{18} atoms/m^2 (Fig. 2a). The spinning of the samples under the magic angle only slightly narrows the lines, which is (Fig. 2b) likely due to the irregularity in the VO_x structures. Signal *C* from octahedrally associated complexes narrows most significantly, and this indicates some ordering of these condensed structures. The ratio of the intensities of signals *A*, *B*, and *C* is somewhat different for the phases of Al_2O_3. However, a pronounced correlation between their integral intensity and the crystalline structure of Al_2O_3 and hence the surface acidity is not observed. One can assume that variations in the line intensities are due to accidental factors, such as nonuniformity in the distribution on the support of the multilayered vanadium species most weakly bound to the surface (signal *C*).

One can expect that the fraction of multilayered vanadium species and hence the degree of nonuniformity in distribution should decrease when the vanadium content decreases. As is seen from Fig. 3, the spectra of the samples of series 2 in which the surface vanadium concentration is twice as low as that in the samples of series 1 have the following features: (a) the intensity of signal *C* decreases; (b) signal *A* from weakly bound tetrahedrally coordinated species becomes most intense; (c) signal *B* is pronounced. In general, the spectra of all samples of series 2 are very close to each other; that is, differences in the support structure do not unambiguously determine the position and the ratio of intensities of the main lines. Weakly bound species likely contain OH groups in the coordination sphere because signal *A* broadens and shifts to the high field upon evacuation under mild conditions (200°C, 10^{-4} torr).

Thus, by contrast to findings of [15], the structure of the surface layer of VO_x in the samples studied by us depends slightly on the type of the crystal structure of Al_2O_3. One can suggest that this is due to the procedure of vanadium deposition and the presence of admixtures in alumina. In [15], in the support, the content of sodium, which migrates to the surface under high temperatures, was comparatively high. It is possible that the poisoning of the acid sites by sodium as a result of the above-mentioned migration affects the acidic properties of the surface more substantially than the variations in the crystalline structure of alumina.

The second feature of the cited work [15] was the deposition of vanadium from nonaqueous media, namely, the impregnation of Al_2O_3 by the solutions of triisopropoxyvanadium in methanol. As Deo G. *et al.* [15] noted, even the small hydration of these samples, for example, during short contacts with an atmospheric moisture, changes the structure of the surface complexes due to additional coordination of the OH groups to vanadium.

In our study, the alumina prepared from boehmite and bayerite contained less sodium, and hence the differences in their acidic/basic properties can be associated only with the structure of the surface layer of the support. It should be taken into account that, unlike Deo G. *et al.* [15], we introduced vanadium by the impregnation of the supports with the aqueous solutions of vanadium salts. In this case, the rehydration of the support surface was probable, resulting in the smoothing of initial variations in the coordination of the surface aluminum cations and hence their acidic-basic properties. As follows from the high differential heats of adsorption (50–100 kcal/mol at small coverages on the surface of γ- and η-Al_2O_3 [17, 18]), water molecules initially dissociatively adsorb on the surface of dehydrated alumina. This causes an increase in the coordination number of the surface aluminum cations to 6, the surface reconstruction, and a change in its typical features determined by the crystal structure of the support. Smoothing of the surface acidic properties explains the formation of the same vanadium complexes on all structural modifications of alumina at both the stage of impregnation with aqueous solutions of vanadium compounds and during subsequent low-temperature (up to 500°C) calcination of the supported catalysts.

Thus, the crystal structure of alumina can affect the structure of the surface VO_x oxo complexes only when the conditions of preparation exclude the reconstruction of the surface due to the action of the solvent used for the precursors of the supported phase.

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