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CATALYTIC REACTION MECHANISMS

Theoretical and Experimental Studies of the Nature of the Catalytic Activity of VO_x/TiO_2 Systems

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Abstract—The states of supported vanadium and the nature of activation of ammonia adsorbed on vanadium sites of VO_x/TiO_2 catalysts are studied by ^{51}V NMR spectroscopy and diffuse-reflectance IR Fourier-transform (DRIFT) spectroscopy using cluster quantum chemical calculations of NH_3 adsorption. We employ the VO_x/TiO_2 catalyst of two types: the monolayer catalyst in which vanadium is located on the surface of well-crystallized anatase and the catalyst in which vanadium embedded in the anatase lattice at a rather great depth. It is shown that ammonia is predominantly adsorbed on Lewis acid sites of the monolayer catalyst, whereas most of NH_3 adsorbed on the catalyst containing bulk vanadium is in the form of ammonium ions. Analysis of experimental and calculated data suggests that, in the monolayer catalyst, NH_3 molecules in the selective reduction of nitrogen oxides are activated on Lewis acid sites. Ammonia activation involves the dissociation of the N–H bond in a coordinated molecule, which results in the formation of the amide $V–NH_2$ group and a water molecule coordinated by a V^{5+} ion. It is likely that, in the case of the catalyst containing bulk vanadium, this reaction occurs with the predominant participation of ammonium ions.

INTRODUCTION

Selective catalytic reduction (SCR) of nitrogen oxides by ammonia over VO_x/TiO_2 catalysts belongs to the most important industrial processes. Many studies have been devoted to this catalytic system, and these reports are reviewed in part in [1, 2]. The catalysts that contain nearly monolayer or smaller amounts of the active component are of primary interest. The surface layer of a catalyst, 1–2 nm thick, is amorphous [1, 3]; therefore, when considering the state of vanadium ions, the coordination number with respect to oxygen (tetrahedral or octahedral coordination, the type of ligands (=O, -OH, -OV, or -OTi)), and the geometric features of the site are the main structural parameters. One can expect a certain difference in the adsorption and catalytic activity for single VO_x species on the anatase surface and for polyvanadate fragments containing adjacent vanadium ions. The specified characteristics of the surface layer can essentially depend on the method of catalyst preparation (the way of introducing the active component and its concentration) and its subsequent activation. These factors complicate the structural study of the active surface layer of catalyst and are also partially responsible for the uncertainty of the molecular mechanism of NO_x reduction by ammonia over VO_x/TiO_2 catalysts. Apparently, the fact that the active site includes V^{5+} ions may be thought of as being established rather reliably. The activation of ammonia is the initial moment of the catalytic reaction, and the interaction of ammonia with NO occurs by the Eley–Rideal mechanism. Different mechanisms of SCR of nitrogen oxides by ammonia over VO_x/TiO_2 catalysts were proposed depending on the type of ammonia activation [2]. One of the most popular mechanisms is based on the assumption of the key role of NH_3 activation on Brönsted acid sites [4, 5]. The mechanism of the dissociative adsorption of ammonia on vanadyl sites (O)V–O–V(O) that is accompanied by the formation of VOH and VO–NH_2-groups was also proposed [6]. The modification of this mechanism was discussed in [7]. The authors of [8] considered the mechanism of activation that was initiated by the coordination interaction between NH_3 and V^{5+} ion followed by the formation of an amide group.

This paper is devoted to the study of vanadium sites of titanium–vanadium catalysts by ^{51}V NMR spectroscopy, diffuse reflectance IR Fourier-transform spectroscopy (DRIFT), and quantum chemistry. The following catalysts of two different types are considered: the catalysts prepared by grafting vanadium from the $VOCl_3$ gas phase onto the anatase surface and the catalysts prepared by the spray drying of the suspension of anatase and a solution of vanadyl oxalate. The goal of this work is to reveal the effect of catalyst preparation on the structure of the active component, on the modification of active sites in ammonia adsorption, and on the activation nature of adsorbed NH_3 in the SCR of nitrogen oxides by ammonia. Another aim of this work is to carry out cluster DFT calculations of NH_3 adsorption on vanadium sites. We intended to elucidate the mechanism of the SCR of nitrogen oxides by ammonia over titanium–vanadium catalysts by comparing experimental and theoretical data for the active sites of VO_x/TiO_2 catalysts studied in this reaction.

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EXPERIMENTAL AND THEORETICAL

Monolayer vanadium catalysts were prepared by grafting gas-phase $VOCl_3$ onto the surface of well-crystallized anatase that was obtained by the hydrolysis of $TiCl_4$. Catalysts were prepared in a helium atmosphere to avoid the decomposition of chloride precursors by the atmospheric moisture. This procedure provides homogeneous, monolayer vanadium coverage of the anatase surface. Depending on the conditions of catalyst surface pretreatment, different types of vanadium complexes can be formed on it. The procedure is described in detail in [9]. The concentration of vanadium in these catalysts was 0.96 wt %, and their specific surface area was 76 m^2/g.

Vanadium catalysts containing vanadium in the bulk of anatase were prepared by spray drying of the suspension of titania and a solution of vanadyl oxalate followed by drying it at 383 K and thermal treatment in the air flow in the temperature range from 473 to 973 K for 4 h. Titania used was produced by the sulfate technology, had the anatase structure, and had low sulfur content (<0.1 wt %). Excess V_2O_5 was removed using a 2 M HNO_3 solution. The description of the preparation procedure characterization of the catalysts were presented in [10]. After washing, the catalysts contained 2.5 wt % V. The specific surface area was 18 m^2/g.

The oxidative treatment of catalysts involved 1-h heating at 675 K first in vacuum and then in oxygen (150 Torr), cooling in oxygen atmosphere to room temperature, and 1-h evacuating.

^{51}V NMR MAS (magic-angle-spinning samples) spectra were recorded on MSL-400 and DSX-400 Bruker spectrometers at a frequency of 105.2 MHz, at a radio-frequency pulse duration of 1 μs, and at a frequency of pulse repetition of 1–10 Hz, the spinning rate of samples varied from 10 to 35 kHz. The chemical shifts are reported with respect to the external $VOCl_3$ standard. The NMR spectra were analyzed according to [11].

The diffuse reflectance infrared Fourier-transform spectra of catalysts and adsorbed molecules were recorded in the powder samples at room temperature using an Impact 410 Nicolet spectrophotometer supplied with a homemade IR diffuse reflectance attachment similar to that described in [12]. NO and NH_3 were adsorbed at room temperature and at an equilibrium pressure of 10 and 20 Torr, respectively. To lower the coverage of the catalyst surface by adsorbed ammonia, the preadsorbed ammonia was sequentially evacuated at 373, 413, 453, 493, 533, and 573 K for 0.5 h at each temperature. The catalysts were reduced by ammonia at 573 K and an equilibrium pressure of 20 Torr for 0.5 h.

The DFT calculations of the active structures of supported vanadia were carried out using the ADF computer program [13] and the local density approximation with the exchange-correlation Vosko–Wilk–Nusair (VWN) potential [14]. The basis functions were taken from the standard basis sets ADF II (for V and Ti) and III (for O and N), which corresponded to the DZ level. The choice of basis functions was described in detail in [15].

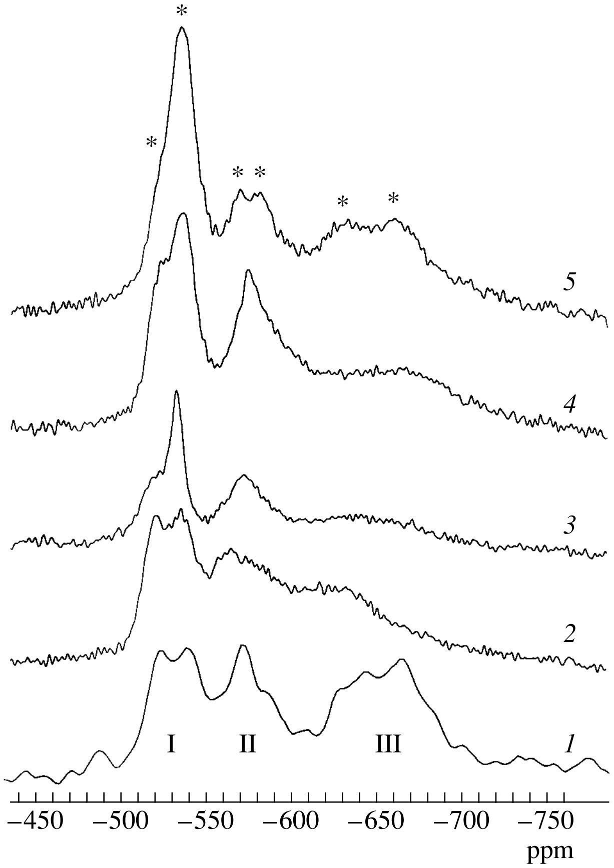


Fig. 1. ^{51}V NMR spectra of the monolayer VO_x/TiO_2 catalyst recorded at a frequency of 102.5 MHz and at a MAS frequency of 35 kHz: (*1*) oxidized sample and the sample after the adsorption of NH_3 on it at (*2*) 300, (*3*) 475, (*4*) 625 K, and (*5*) the sample after the SCR of NO by ammonia (reaction mixture composition: 1% NO + 1% NH_3 + 4.67% O_2, the rest, He; flow rate, 6.42 L/h; 625 K).

The fragment of the anatase (001) surface was chosen as a cluster model of the TiO_2 support. The broken bonds on the boundary of a cluster were saturated with pseudoatoms H*. Initially, these pseudoatoms were placed at a distance of 0.1 nm from the boundary oxygen atoms of the cluster in the direction of the broken oxygen–metal bonds. Then, the position of boundary pseudoatoms H* was fixed and geometry optimization of all cluster atoms was carried out.

RESULTS AND DISCUSSION

Figure 1 presents the high-resolution ^{51}V NMR spectra of the oxidized monolayer catalyst recorded at a frequency of 102.5 MHz and at a MAS frequency of 35 kHz. The use of high magnetic field and the high frequency of sample spinning allowed us to reliably sepa-

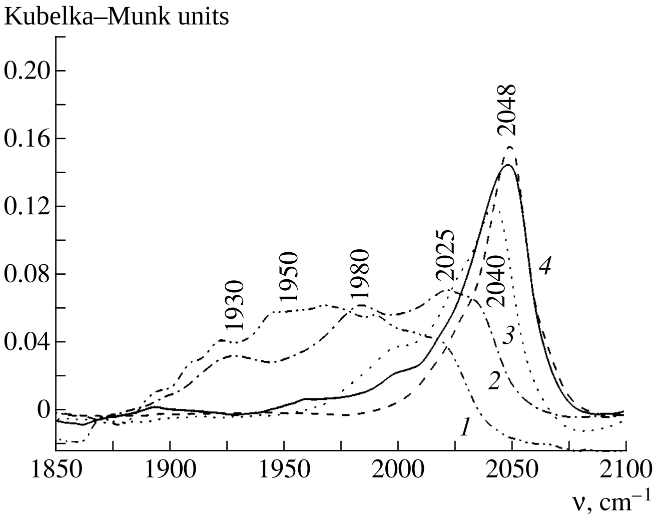


Fig. 2. (solid line) DRIFT spectrum of the first overtone of V=O bond vibrations in vanadyl groups of the oxidized monolayer VO_x/TiO_2 catalyst and DRIFT spectrum of the same sample after a 0.5-h evacuation of preadsorbed ammonia from its surface at (*1*) 373, (*2*) 473, (*3*) 573, and (*4*) 673 K. Ammonium was preadsorbed at room temperature and at an equilibrium pressure of 20 Torr. The spectra were recorded at room temperature.

rate for the first time the isotropic lines of central transitions in the ^{51}V NMR spectra of the VO_x/TiO_2 catalyst from spinning satellites. The spectrum of the oxidized sample (Fig. 1, spectrum *1*) contains three groups of signals for which isotropic chemical shifts measured with respect to $VOCl_3$ lie in the ranges from –515 to –530, from –560 to –580, and from –610 to –660 ppm. However, the assignment of ^{51}V NMR spectra of solids requires the detailed knowledge of not only the value of an isotropic shift but also all the parameters of the tensors of a chemical shift and a quadrupole interaction. Such detailed information can be gained from the current solid-state NMR spectroscopy (SATRAS and MQMAS). However, even these methods fail to analyze such a complex spectrum. It is only possible to evaluate the value and type of anisotropy and an approximate value of the quadrupole constant by comparing the spectra recorded at different rates of sample spinning (10, 15, 20, and 35 kHz) with the static spectra (we are going to publish these data elsewhere [16]). Such analysis permits the first group of signals (–515 to –530 ppm) to be assigned to V^{5+} ions in the coordination of a trigonal pyramid. Most probably, a large shift of the signal of the third group to the stronger field (–610 to –660 ppm) corresponds to the V^{5+} ions that most strongly interact with the surface of TiO_2 in the coordination of distorted octahedron (trigonal bipyramid). Most likely, the signals with a shift of –560 to –580 ppm correspond to distorted tetrahedral structures of the metavanadate type.

Each group of signals consists of two or three lines. This may point to the localization of V^{5+} ions not only on the most close-packed (001) faces of anatase but also on other splitting planes of TiO_2 crystallites. The presence of six to nine nonequivalent vanadium sites in the catalyst is also indicative of the possible association of vanadium structures at elevated temperatures.

Ammonia adsorption affected the ^{51}V NMR spectrum of the sample (Fig. 1, spectra *2*, *3*). Ammonia adsorption at room temperature resulted in a drastic decrease in the intensity of the signal from vanadium strongly bound to the surface. In higher-temperature adsorption (Fig. 1, spectra *3*, *4*), the intensity of the lowest-field line also decreased. The signal of group II (–560 to –580 ppm) was least affected by ammonia adsorption. After the SCR of nitrogen oxides by ammonia at 673 K and the removal of the reaction products at the same temperature by the helium flow, the lines of group III signal (–610 to –660 ppm) began to appear in the spectrum. After sample treatment in a helium flow at a higher temperature, its ^{51}V NMR spectrum almost regained its original shape. The evolution of spectra presented in Fig. 1 shows that most of the vanadium is accessible to adsorbed NH_3, that is, vanadium is located on the support surface. It also demonstrates that vanadium surface sites are nonuniform from the standpoint of their interaction with NH_3 and they are not rearranged during the SCR of nitrogen oxides by ammonia.

Conclusions on the nonuniformity of vanadium sites in the ammonia adsorption follow from the results of studying the monolayer VO_x/TiO_2 catalyst by ^{51}V NMR spectroscopy and are consistent with DRIFT data. Figure 2 presents changes in the spectra of the first overtone of V=O bond vibrations in vanadyl groups of the oxidized catalyst that were observed as preadsorbed ammonia was evacuated from the sample at elevated temperatures. The spectrum of the oxidized sample obtained before ammonia adsorption exhibited the only absorption band at 2048 cm^{-1} that corresponded to the first overtone of V=O bond vibrations in the vanadyl groups [5] (the spectrum is presented in Fig. 2 by the solid line). This points to the absence of the bulk V_2O_5 phase from the catalyst, because the spectrum of the overtone of V=O bond vibrations for the bulk V_2O_5 consists of two absorption bands at 1975 and 2020 cm^{-1} that are comparable in intensity (the spectrum is omitted). The spectrum of the oxidized sample obtained before ammonia adsorption also shows that the nonuniformity of vanadium sites demonstrated above by ^{51}V NMR spectroscopy only slightly affected the frequency of the first overtone of V=O bond vibrations. The simultaneous disappearance of the absorption band at 2048 cm^{-1} and the appearance of the broad band with a maximum at 1950 cm^{-1} were observed in the spectrum of the sample from the surface of which preadsorbed ammonia was evacuated at 375 K. After the removal of ammonia at 473 K, this broad band transformed into the spectrum in which at least four absorption bands at 1930, 1980, 2025, and 2040 cm^{-1} were clearly defined. These bands were attributed to different vanadyl sites for the adsorption of molecular ammonia. After heating the sample in

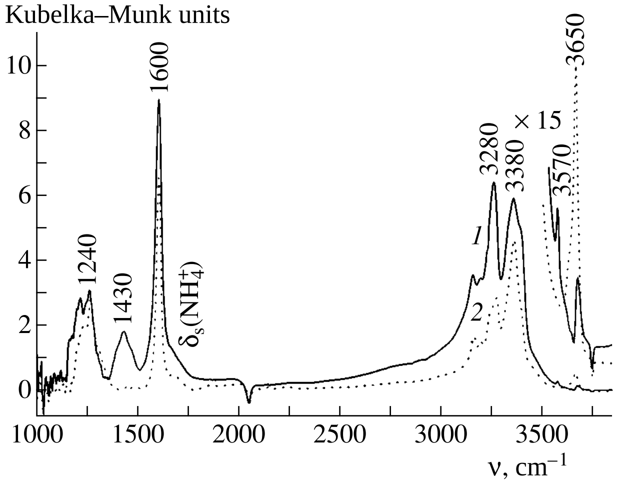


Fig. 3. DRIFT spectra of ammonia adsorbed on the monolayer VO_x/TiO_2 catalyst and remained on it after a 0.5-h evacuation at (*1*) 373 and (*2*) 475 K. Ammonium was preadsorbed at room temperature and at an equilibrium pressure of 20 Torr. The spectra were recorded at room temperature.

vacuum at higher temperatures, the intensity of the low-frequency absorption bands decreased; the spectrum gradually returned to its initial shape; and it contained the only absorption band at 2048 cm^{-1} (spectrum *4*).

Thus, changes in the spectra presented in Fig. 2 indicate that all vanadyl groups in the monolayer catalyst belong to the surface sites and to a greater or lesser extent are modified during the ammonia adsorption. Ammonia adsorption is accompanied by the perturbation of vanadyl groups instead of causing their disappearance. The perturbation of vanadyl groups results in the broadening and shifts of the absorption bands of the overtones of V=O bond vibrations to the low-frequency region. Different values of this frequency shift may be due to structurally somewhat different ammonia species, which will be considered later in the discussion of the quantum chemical results.

The spectra of ammonia strongly adsorbed on the monolayer VO_x/TiO_2 catalyst are presented in Fig. 3. After the evacuation of ammonia weakly bound to the catalyst surface at 373 K (spectrum *1*), the spectrum of fundamental vibrations of N–H bonds contained absorption bands typical of NH_3 molecules adsorbed on Lewis acid sites (symmetric δ_s = 1150–1250 cm^{-1} and asymmetric δ_{as} = 1600 cm^{-1} bending vibrations and symmetric ν_s(N–H) = 3200–3300 cm^{-1} and asymmetric ν_{as}(N–H) = 3300–3400 cm^{-1} stretching vibrations) [8, 17] and the absorption band of asymmetric bending vibrations of ammonium ions at 1430 cm^{-1} [8, 17]. The spectrum also contains the low-intensity narrow absorption band at 3650 cm^{-1}, which is assigned to V–OH groups [18, 19], and the band at 3570 cm^{-1}. The latter band most likely corresponds to asymmetric stretching vibrations of N–H bonds of surface amides, probably, V–NH_2 that are formed in the dissociation of ammonia molecules. A similar frequency of 3520–3530 cm^{-1} was observed for the vibrations of the surface Si–NH_2 groups [20, 21].

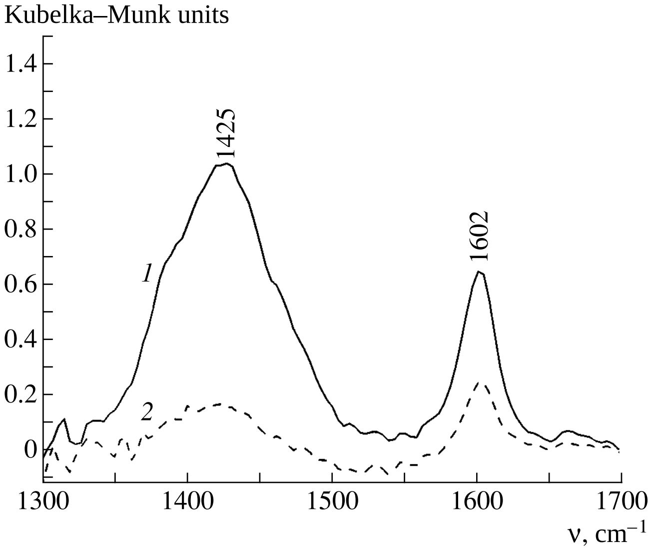


Fig. 4. DRIFT spectra of ammonia adsorbed on the VO_x/TiO_2 catalyst and remained on it after a 0.5-h evacuation at (*1*) 373 and (*2*) 475 K. Ammonium was preadsorbed at room temperature and an equilibrium pressure of 20 Torr. The spectra were recorded at room temperature. The catalyst was prepared by spray drying.

After the evacuation of adsorbed NH_3 at 473 K (spectrum *2*), the intensities of absorption bands of ammonia adsorbed on Lewis acid sites were somewhat reduced, whereas the absorption band of ammonium ions disappeared (Fig. 3, spectrum *2*). The disappearance of this band was accompanied by a sharp increase in the intensity of the narrow absorption band at 3650 cm^{-1} that corresponds to isolated V–OH groups. This indicates that the protonation of ammonia most probably involves these isolated V–OH groups. After heating the catalyst with adsorbed ammonia in vacuum at 473 K, the absorption band at 3570 cm^{-1} that corresponds to N–H vibrations of amide groups also disappeared. Most probably, the small intensity of this band and the low thermal stability of amide groups that is comparable with the stability of ammonium ions are the main reasons why there is no consensus among researchers regarding the possibility of dissociative adsorption of ammonia over titanium–vanadium catalysts.

Figure 4 presents the spectra of the ammonia that was adsorbed on the VO_x/TiO_2 catalyst prepared by spray drying and remained on it after evacuating at 373 (spectrum *1*) and 473 K (spectrum *2*). The spectra were recorded in the region of bending vibrations of N–H bonds. The absorption bands at 1425 and 1600 cm^{-1} corresponded to the asymmetric bending vibrations of ammonium ions and the molecules coordinated by Lewis acid sites. The intensity ratio of these absorption

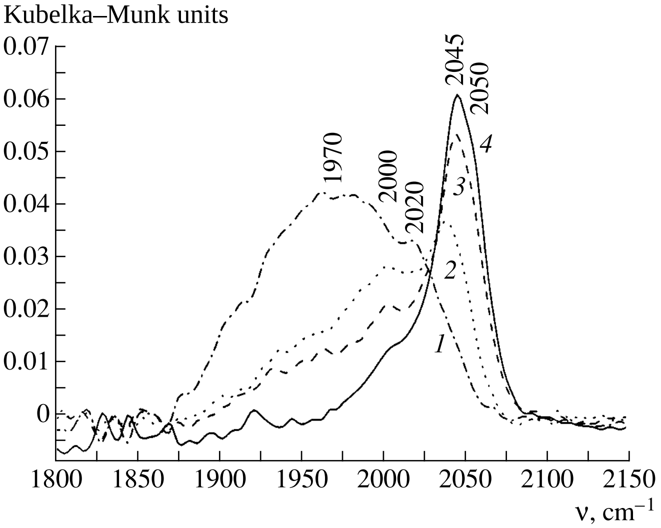


Fig. 5. DRIFT spectra of the first overtone of V=O bond vibrations of vanadyl groups in the VO_x/TiO_2 catalyst prepared by spray drying after a 0.5-h evacuation of preadsorbed ammonia from its surface at (*1*) 375, (*2*) 475, (*3*) 575, and (*4*) 675 K. Ammonium was preadsorbed at room temperature and an equilibrium pressure of 20 Torr. The spectra were recorded at room temperature.

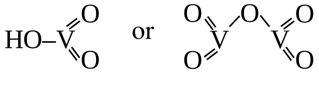
bands indicates that, after the evacuation of preadsorbed ammonia at 373 K (Figs. 3, 4, spectra *1*), the fraction of protonated molecules in this catalyst was significantly higher than that in the monolayer sample. It is also clear that, as in the case of the monolayer catalyst, most of ammonium ions adsorbed on the catalyst, which was prepared by spray drying, were decomposed by heating at 473 K.

The IR spectra of the overtone of V=O bond vibrations for the catalyst sample, which was prepared by spray drying and from which the preadsorbed ammonia was evacuated at 373, 473, 573, and 673 K for 0.5 h, are presented in Fig. 5. After the evacuation of ammonia at 373 K, the spectrum contained a broad band with a maximum at 1970 cm^{-1}. The heating of the sample at 473 K in vacuum resulted in a drastic decrease in the intensity of this absorption band and in the appearance of rather narrow bands at 2000 and 2040 cm^{-1}. After evacuating the sample at 673 K, the spectrum transformed into the initial spectrum that consisted of two poorly resolved bands at 2045 and 2050 cm^{-1}. A sharp decrease in the intensity of the band at 1970 cm^{-1} and an increase in the intensity of the band at 3650 cm^{-1} observed in the spectrum (the spectrum is omitted) of the sample evacuated at 473 K, that is, at the temperature at which ammonium ions are decomposed indicate that the perturbation of V=O bonds in this sample was mainly due to their interaction with NH_4^+.

It can be assumed that the site on which ammonia is protonated contains the vanadyl oxygen atom and V–OH group. This site can be either mononuclear ((O)V–OH) or binuclear ((O)V–O–V–OH). The DFT calculations of ammonia adsorption on the clusters that model the binuclear structure on the surface of the bulk V_2O_5 and on the anatase surface in VO_x/TiO_2 confirmed the possibility of stabilizing NH_4^+ with a noticeable gain in energy [15, 22, 23]. In this case, ammonium ions were additionally stabilized by hydrogen bonds formed by two N–H groups of NH_4^+ and two terminal oxygen atoms of the cluster. Vanadyl oxygen and the oxygen atom from which a proton transferred to ammonia molecule became essentially equivalent. The bonds between such oxygen atoms and vanadium ions remained close to vanadyl bonds: their lengths (0.167–0.169 nm) were somewhat longer than the length of the true vanadyl V=O bond (0.160 nm) and much shorter than the length of a single V–O bond (0.19 nm). The elongation of the V=O bond during the protonation of a NH_3 molecule points to its weakening, which most likely is the reason for the low-frequency shift in the overtone of V=O bond vibrations of vanadyl groups in IR spectra (Figs. 2, 5).

It is known [24] that the specific activity of the VO_x/TiO_2 catalysts with a nearly monolayer vanadium coverage obtained by grafting $VOCl_3$ on the anatase surface was higher in the SCR of nitrogen oxides by ammonia than that of the bulk V_2O_5. Comparison of the stabilization energy of NH_4^+ ions on binuclear (O)V–O–V–OH sites grafted on the anatase surface with that of NH_4^+ ions on the cluster structures simulating bulk vanadium oxide showed that the Brönsted acidity of the active component weakly depended on the method of its supporting on the anatase surface. Some calculations [15] even demonstrated the trend toward a decrease in the acidity. This suggests that ammonium species (NH_4^+) on the monolayer VO_x/TiO_2 catalysts is not a key species in the SCR of nitrogen oxides and the activation of NH_3 molecules in this reaction occurs by another mechanism involving Lewis acid sites.

We carried out cluster calculations of the coordination interaction between NH_3 and vanadium ions to theoretically analyze the Lewis acidity of the active component and its change during supporting the active component on titania. The cluster structure of the anatase (001) surface is presented in Fig. 6. The next step involved the calculation of the active component structure and consisted in the stabilization of the fragment



on the TiO_2 cluster. The former case is depicted in Fig. 7. The energy of the coordination interaction of NH_3 with a mononuclear V^{5+} site was 97 kJ/mol. The corresponding energies for binuclear sites are summarized in the table, which also contains for comparison the calculated energies of NH_3 coordination by V^{5+} ion

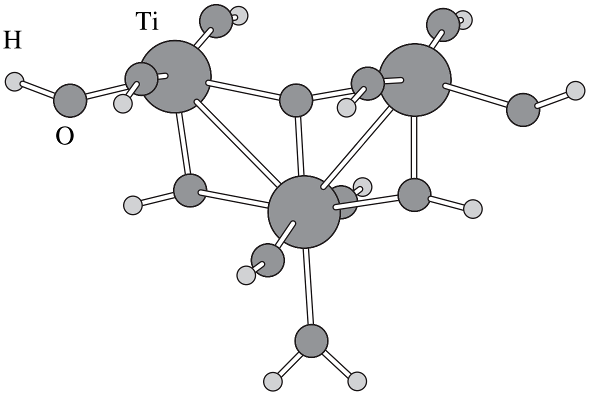


Fig. 6. Structure of cluster modeling the (001) anatase surface.

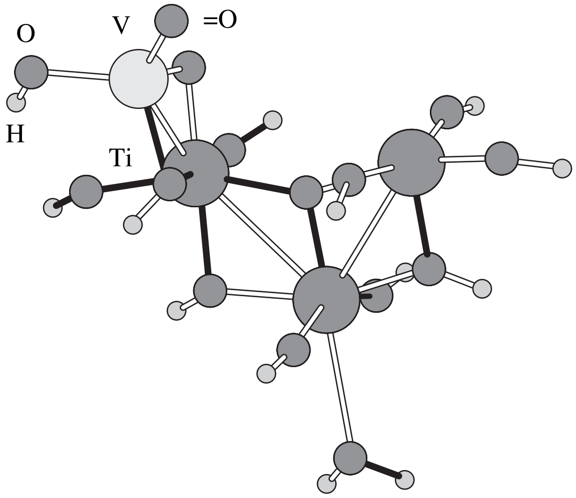


Fig. 7. Structure of cluster modeling a mononuclear vanadium cluster grafted onto the (001) anatase surface.

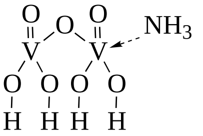
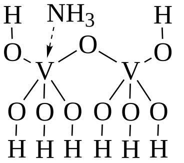
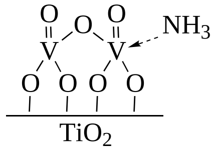
for unsupported clusters. The calculations showed a noticeable increase in the coordination interaction for supported VO_x species. The transfer of H atom from the adsorbed NH_3 molecule to the hydroxy group of V–OH with the formation of V–NH_2 and the coordinated water molecule V··OH_2 could be one of the possible pathways to amide species in the coordination sphere of vanadium ion. According to the results of calculation, this process is slightly exothermic (8.45 kJ/mol). The cited rearrangement corresponds to the reaction mechanism proposed in [8]. We believe that it is exactly this mechanism of ammonia activation that takes place over the model catalyst.

It should be noted that the coordination complex formed by NH_3 and surface V^{5+} ion may have different structures depending on the possibility of hydrogen bonding between the protons of adsorbed NH_3 and the lattice oxygen ions (Ti–O–Ti and Ti–O–V). It is interesting that, according to the calculations, a complex in which such a hydrogen bond is formed between a proton and the vanadyl oxygen is missing from these structures. The energetic estimates given above refer to the cases when the above-mentioned hydrogen bonds were absent. Different possible ammonia coordination complexes are probably responsible for different perturbations of the V=O bond; they lead to its ~0.1-nm elongation and can result in different frequency shifts of the first overtone of vanadyl bond as it is mentioned above in the discussion of the experimental IR spectroscopic studies of ammonia adsorption. Differences in complex formation mentioned here will lead to somewhat different values of NH_3 coordination energy and will slightly change the energetic characteristics of intermediates in the formation of the amide group. However, these differences are not fundamental.

Another mechanism assumed for NH_3 activation consists in the dissociative adsorption of NH_3 on the $(O)V^{(1)}$–O–$V^{(2)}(O)$ fragment of the active structure followed by the formation of $V^{(1)}$–ONH_2 and $V^{(2)}$–OH [6]. Our calculations revealed the high endothermicity of this process (~250 kJ/mol), which makes this mechanism of ammonia activation unlikely.

The ^{51}V NMR spectroscopic study of the VO_x/TiO_2 catalyst prepared by the spray drying of the suspension of TiO_2 and a solution of vanadyl oxalate showed that all V^{5+} ions in this system were in the coordination of a distorted octahedron [25] as it was in the case of the isomorphic replacement of titanium ions by vanadium ions. According to the DRIFT spectroscopic data, ammonia adsorbed on this catalyst is mainly present as ammonium ions (Fig. 4). The calculated stabilization energy of ammonium ions on the clusters that simulate the isomorphic substitution of V ions for Ti ions on the (001) anatase surface turned out to be ~20 kJ/mol

Characteristics of ammonia molecule coordination to Lewis acid sites of vanadium clusters

Cluster structure	Cluster composition	Coordination energy, kJ/mol
	$V_2O_7H_4$	26.53
	$V_2O_9H_8$	26.85
	$V_2O_5/Ti_3O_{12}H_{12}$	85.2

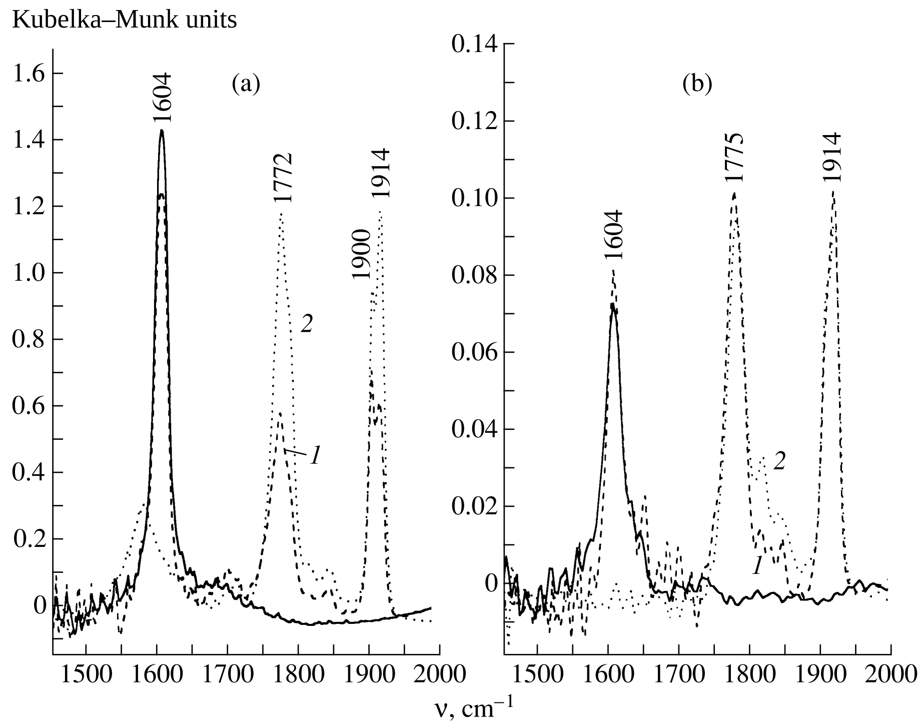


Fig. 8. DRIFT spectra of NO adsorbed on (a) the monolayer sample and (b) the catalyst prepared by spray drying; (*1*) DRIFT spectra of NO adsorbed on the same catalysts containing strongly adsorbed ammonia irremovable by a 30-min evacuation at 573 K; (*2*) DRIFT spectra of NO adsorbed on the same catalysts containing strongly adsorbed ammonia after heating them in NO (10 Torr) at 573 K for 30 min. The spectra of ammonia irremovable by evacuation at 573 K in the absence of adsorbed NO are presented by solid lines.

higher than that of ammonium ions on vanadium sites of the bulk V_2O_5 catalyst [23]. All these facts do not rule out the occurrence of the SCR of nitrogen oxides by ammonia over a real catalyst with the participation of ammonium ions by the mechanism proposed in [4, 5].

Figure 8 presents the spectra of NO adsorbed on ammonia-covered samples of the monolayer catalyst (a) and of the catalyst prepared by spray drying (b) (ammonia was preadsorbed at 573 K for 0.5 h). Spectra *1* refer to the above samples after the evacuation of adsorbed ammonia at 573 K, and spectra *2* were obtained after heating the catalysts containing strongly adsorbed NH_3 in an NO atmosphere (P_{NO} = 10 Torr) at 573 K for 30 min. The spectra of strongly adsorbed ammonia (solid lines) consist of the absorption bands at 1604 cm^{-1} that are typical of asymmetric bending vibrations of the molecules coordinated by Lewis acid sites. In addition to this band, spectra *1* of both samples contain a pair of bands at 1773 and 1912–1914 cm^{-1}. These bands are typical of asymmetric and symmetric stretching vibrations of the N–O bonds of dinitrosyl complexes that are formed with the participation of V^{4+} cations [17]. The occurrence of dinitrosyl complexes of V^{4+} ions in these samples indicates that, during the heating of the catalysts in the NH_3 atmosphere at 573 K, V^{5+} ions were partially reduced.

After heating the catalysts in an NO atmosphere (spectra *2*), the absorption band at 1604 cm^{-1} disappeared from the spectra. This is most likely due to the participation of strongly bound ammonia in the reduction of NO. In the spectrum of the monolayer catalyst, the absorption band at 1575 cm^{-1}, which can be assigned to the vibrations of nitrate ions [8], appears and the intensities of the bands of dinitrosyl complexes involving V^{4+} considerably increased. Thus, in the absence of oxygen, the reduction of NO over the monolayer catalyst by coordinated ammonia was accompanied by the additional reduction of surface V^{5+} ions. In the case of the catalyst prepared by spray drying, surface vanadium ions were not reduced. This follows from the equality of intensities of the absorption bands of V^{4+}–dinitrosyl complexes at 1772 and 1914 cm^{-1} in spectra *1* and *2* presented in Fig. 8b. To explain this phenomenon, one should assume that, in this catalyst, the surface V^{4+} ions resulting from the reaction were quickly reoxidized by mobile oxygen of the specific bulk phase. Apparently, the mixed vanadia–titania structures that were formed in the bulk of a support during the preparation of the catalyst can be such a phase. The presence of such structures may affect the rate of the catalyst reoxidation by oxygen. This stage can be rate-limiting in the SCR of nitrogen oxides by ammonia for vanadium-containing catalysts, for example, for V_2O_5–WO_3–TiO_2 [24, 26].

CONCLUSION

Ammonia is predominantly adsorbed on Lewis and Brönsted acid sites of the catalysts prepared by grafting $VOCl_3$ onto the anatase surface and those prepared by the spray drying of the suspension of anatase and a solution of vanadyl oxalate, respectively. Ammonium ions are formed with the simultaneous participation of vanadyl and terminal V–OH groups that are incorporated in the O=V–O–V–OH Brönsted acid sites. Vanadyl groups act as Lewis acid sites. The strength of such Lewis sites significantly enhances during the deposition of VO_x species onto the anatase surface. Apparently, amide species ($V–NH_2$) that were formed together with coordinated water molecules ($V\cdots OH_2$) by the transfer of H atom from adsorbed NH_3 molecule to V–OH group are intermediates in the SCR of nitrogen oxides by ammonia over the catalyst prepared by grafting $VOCl_3$ onto the anatase surface. NH_3 adsorbed on strong Lewis sites of both catalysts takes part in the SCR of nitrogen oxides by ammonia. However, it is most likely that, for the catalyst prepared by spray drying, this reaction predominantly involves ammonium ions.

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