Mechanism of interaction of NO with NH_3 on vanadium-containing catalysts based on IR spectroscopic data

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Adsorption of ammonia and nitrogen oxide on V_2O_5/Al_2O_3 samples of different degrees of reduction has been studied by IR spectroscopy. On an oxidized surface, ammonia is coordinated by V^{3+} and V^{4+} ions to form ammonium ions; NO is not adsorbed. On a reduced surface, the coordination of NO by V^{3+}, V^{4+}, and V^{5+} ions is observed, which results in the formation of nitrosyl complexes. A strong mutual influence between NO and NH_3 occurs during coadsorption or consecutive interaction on a reduced catalyst surface.

Key words: IR spectroscopy, adsorption, ammonia, nitrogen oxide, coordination, degree of oxidation, electron exchange, vanadium-containing catalysts.

Different viewpoints exist concerning the mechanism of the interaction of NO with NH_3 in the presence of oxygen on vanadium-containing catalysts:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

It is believed that two adsorbed particles, *viz.*, $NO_{2(ads)}$ and $NH_4{}^+{}_{(ads)}$, participate in reaction (1) in the presence of V_2O_5 and V_2O_5/Al_2O_3 (Ref. 1). Probably,[2] one of the stages of this reaction, the oxidation of NO into NO_2, can easily occur at room temperature even before adsorption. Based on the results of IR- and ESR-spectroscopic, adsorption, kinetic, and isotope (^{15}N) studies, the following mechanism of reaction (1) was suggested:[2,3] 1) NH_3 is adsorbed as $NH_4{}^+{}_{(ads)}$ with participation of $V^{5+}{=}O$ groups; 2) NO from the gas phase reacts with $NH_4{}^+{}_{(ads)}$ according to the Ili-Ridil mechanism to form N_2, H_2O, and V—OH groups; 3) V^{4+}—OH groups are peroxidized into $V^{5+}{=}O$ by gaseous oxygen. Similar results are obtained[4,5] with the use of labeled NH_3 and O_2 in the presence of V_2O_5, V_2O_5/TiO_2, $V_2O_5/Al_2O_3/SiO_2$, and V_2O_5/Al_2O_3.

It has been suggested[6] on the basis of EXAS, IR spectroscopy, and data on the activity of V_2O_5 monocrystals and polycrystals with different morphology that not V=O, but V—OH groups participate in the reaction. According to the data of thermodesorption spectrometry and Auger-spectroscopy,[7] the reaction occurs according to the Langmuir—Hinshelwood mechanism through the spillover of NO_{ads} particles from the carrier to reduced vanadium centers on which ammonia is adsorbed. The forms of the adsorption of NH_3 and NO on vanadium-containing catalysts have been studied previously.[8—10]

As a result of IR-spectroscopic studies of the adsorption of NO, NO_2, and NH_3 on V_2O_5/TiO_2 at different temperatures, the following mechanism is suggested (see Ref. 11):

$$VO^{2+} + NH_3 = HO{-}V{-}NH_2{}^{2+}$$
$$NO + HO{-}V{-}NH_2{}^{2+} = HO{-}V{-}NH_2{-}NO^{2+}$$
$$HO{-}V{-}NH_2{-}NO^{2+} = N_2 + H_2O + VOH^{2+}$$
$$VOH^{2+} + {}^1\!/\!_4O_2 = VO^{2+} + {}^1\!/\!_2H_2O$$

The analysis presented does not allow us to choose a preferential scheme of reaction (1) because in neither of the works cited was the kinetics of transformations of the surface compounds studied, nor were the conditions realized *in situ*. Also the studies were performed, as a rule, on oxidized samples.

However, one cannot rule out the reduction of the catalyst during its interaction with the reaction mixture, and there are some indications[12] that the character of the adsorption of NH_3 and NO depends essentially on the degree of reduction of the vanadium-oxide catalyst.

Here we present data on the forms of the adsorption of NH_3 and NO and the subsequent interaction of NO_{ads} with NH_3 and $NH_{3\,(ads)}$ with NO on vanadium-containing catalysts with different degrees of reduction.

Experimental

A V_2O_5/Al_2O_3 (10 % of V_2O_5) catalyst was prepared by impregnating γ-Al_2O_3 (S_{sp} = 220 m^2 g^{-1}) with ammonium metavanadate. The system comprises monolayer catalysts containing octahedrally coordinated V^{5+} cations in an oxidized state linked by V—O—V-bonds, which completely shield active centers of Al_2O_3 (both coordination-unsaturated Al^{3+} and surface hydroxyl groups[13]).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 236—241, February, 1994.

1066-5285/94/4302-0214 $12.50

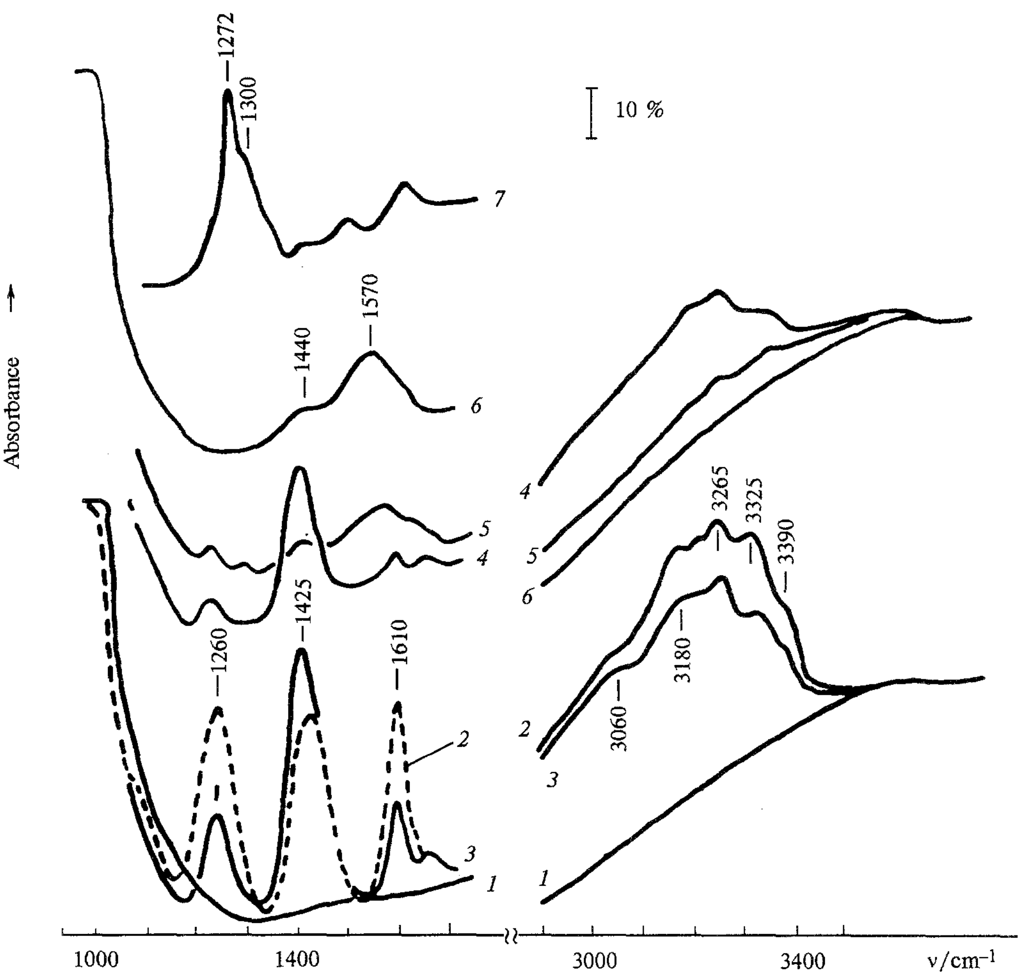

Fig. 1. IR spectra of NH$_3$ adsorbed on oxidized V$_2$O$_5$/Al$_2$O$_3$ and Al$_2$O$_3$: background (*1*); 2.7·10^3 Pa of NH$_3$ at 300 K (*2*); subsequent desorption at 300, 373, 473, and 573 K (*3—6*); adsorption at 293 K with subsequent desorption at 523 K on Al$_2$O$_3$ dehydrated at 773 K (*7*).

The samples were molded into pellets for IR-spectroscopic studies. Preliminary treatment of the surface of the samples tested involved their consecutive treatment in O$_2$ and *in vacuo* at 723 K until complete removal of admixtures.

The last portion of oxygen was removed at 293 K (the oxidized sample). Spectra were recorded on a UR-20 spectrophotometer. The spectral width of the slit at 100 cm^{-1} was 8 cm^{-1}. The sample was placed in a special cuvette, which allowed one to treat the samples, to perform adsorption and desorption of gases and vapors at different temperatures, and to record IR spectra at room temperature with the compensation of the spectrum of the gaseous phase of the adsorbate.

ESR spectra were obtained on a JES-3BX radiospectrometer at 77 and 300 K.

Adsorbates were chromatographically pure and were fractionally distilled *in vacuo* before adsorption.

Results and Discussion

Adsorption of NH$_3$. IR spectra of adsorbed NH$_3$ were interpreted on the basis of the available data on spectra of NH$_3$ adsorbed on oxides.[12,14] The changes in the IR spectra of ammonia adsorbed at 293 K on the oxidized V$_2$O$_5$/Al$_2$O$_3$ surface (Fig. 1, spectra *3—6*) during desorption testify that ammonia coordinated by V^{5+} ions (absorption band δ_s(NH$_3$) 1260 cm^{-1}) is completely desorbed below 573 K (spectrum *6*), and only a small number of oxidized ammonia complexes (absorption bands 1440 and 1570 cm^{-1})[15,16] are observed on the surface (Fig. 1, spectrum *6*). Comparison of data obtained for Al$_2$O$_3$ and V$_2$O$_5$/Al$_2$O$_3$ shows complete "shielding" of Al^{3+} by vanadium compounds, because no absorption bands at 1300 and 1275 cm^{-1}, which are characteristic of ammonia coordinated by Al^{3+} ions, are observed in the spectra (spectrum *7*). A considerable concentration of Bronsted acidic centers (BAC) (absorption band ~1440 cm^{-1}, δ(NH$_4^+$)) caused by the presence of vanadium compounds[13] is also noteworthy; it is known that BAC also protonate propylene and ethylene to form isopropoxide and ethoxide surface compounds.[17] No coordination of CO and NO by these oxidized vanadium ions was observed. ESR data of the original oxidized samples suggest the presence of V^{4+}—I type ions,[18] which are cations (V=O)$^{2+}$ in octahedral surroundings with covalently-linked oxygen ligands (*i.e.*, V—O—V structures are present).

The reduction of the oxidized samples by evacuation at 773 K results in the increase in the intensity (~1.5—2

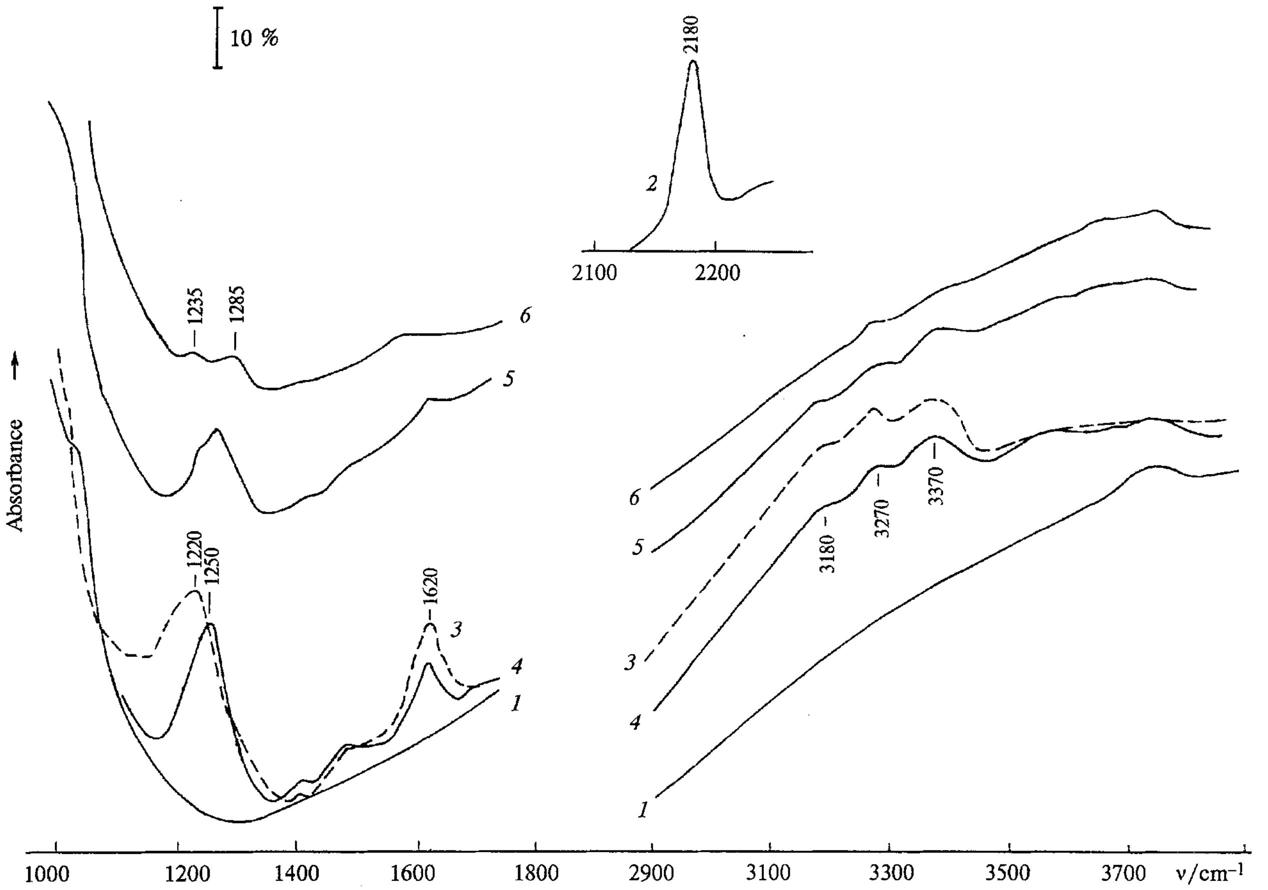

Fig. 2. IR spectra of CO and NH_3 adsorbed on V_2O_5/Al_2O_3 reduced in H_2 at 773 K: background (*1*); $3.3 \cdot 10^3$ Pa of CO at 300 K (*2*); $1.6 \cdot 10^3$ Pa of NH_3 at 300 K (*3*); subsequent desorption at 300, 393, and 523 K (*4—6*).

times) of ESR signals primarily due to the appearance of V^{4+}—II type ions in the coordination of the tetragonal pyramid (the covalently-linked ligand is removed from V—O—V).[18] The adsorption of CO on oxidized and evacuated samples does not result in noticeable changes in the ESR spectra. When the samples are heated in the presence of CO at $T \geq 423$ K, the intensity of the ESR signals of V^{4+}—I and V^{4+}—II type ions increases. This is mainly determined by the increase in the concentration of type II $(V{=}O)^{2+}$. For the samples reduced in CO at ~573 K, the broadened signal mainly contributes to the intensity of the ESR spectra of V^{4+}· For the samples reduced by interaction with CO at $T > 673$ K, a sharp decrease in the intensity of the ESR signal from V^{4+} ions is observed, which can be caused both by the formation of "clusters" of paramagnetic ions and consequent reduction of V^{4+} ions, for example, to V^{3+}.

After adsorption of NH_3 on the reduced catalyst, the absorption bands at 1220 cm^{-1} (asymmetric from the high-frequency range) and 1620, 3270 and 3360 cm^{-1} appear in the IR spectrum (Fig. 2, spectrum *3*), which characterize deformational (δ) and stretching (ν) oscillations of the coordinated ammonia, most likely, on reduced vanadium ions. Actually, $\delta_s(NH_3)$, which is the most sensitive to the electron-acceptor state of the adsorption centers, decreases with the decrease in the acceptor ability of the cation. The decrease in the value of $\delta_s(NH_3)$ of coordinated ammonia from 1260 cm^{-1} for the oxidized sample to 1220 cm^{-1} for the reduced one can be related to the decrease in the acceptor ability of vanadium ions during its reduction. The change in the electronegativity of vanadium cations on going from V^{5+} (1.9) to V^{3+} (1.7) also attests to this fact. The lower thermal stability of the coordinated ammonia in the case of the reduced catalyst is also in favor of this. After desorption at room temperature, the absorption band at 1220 cm^{-1} is not observed in the IR spectrum of this sample, but an absorption band at 1250 cm^{-1} (Fig. 2, spectrum *3*) appears, which likely characterizes $\delta(NH_3)$ for the ammonia coordinated by V^{4+} ions. After desorption at 373 K the concentration of coordinated ammonia decreases both on the reduced sample and the oxidized catalyst. However, this form cannot transform into NH_4^+, and in the case of the reduced surface the concentration of coordinated ammonia remains fairly high compared with that on the oxidized catalyst surface. At 473 K, almost complete desorption of this complex is observed. Increasing the desorption temperature results in the appearance of absorption bands in the spectra, which were absent in the spectra of the oxidized samples and which are close to those observed in the spectra of ammonia adsorbed on Al_2O_3 (see Fig. 1, spectrum *7*). It should be mentioned that the formation of oxidized ammonia complexes (absorption bands 1440 and 1570 cm^{-1}) is not observed on the reduced sample in appreciable amounts. The adsorption of ammonia on the reduced sample, as in the case of the reduced V/SiO_2 and V/TiO_2 samples with a higher content of vanadium,[18] is not accompanied by the appearance of absorption bands of the ammonium ion in the IR spectrum, *i.e.*, the reduction of the catalyst leads by itself to the loss of Bronsted acidity. The results obtained show that the formation of clustered V^{4+} cations , *i.e.*, cations linked by V—O—V bridges, occurs during "mild" reduction of catalysts; the retention of proton acidity is also characteristic of these samples. During more drastic reduction, V^{3+} cations are observed. Apparently, this process is accompanied by the formation of isolated vanadium polyhedra (most likely, the formation of coordination-unsaturated tetrahedra of vanadium with the degree of oxidation 3+). In this process, the carrier partially opens.

Adsorption of NO. The study of the adsorption of NO on V_2O_5/Al_2O_3 (10 % of V_2O_5) shows that samples oxidized or reduced in CO below 573 K do not adsorb NO. No coordination of CO was not found for these samples either. The changes in the IR spectrum were observed only after adsorption of NO on reduced samples containing coordination-unsaturated V^{4+} or V^{3+} ions. Figure 3 shows a change in the IR spectrum of adsorbed NO in the range of 1700—1950 cm^{-1} depending on the degree of reduction of the sample. Only two absorption bands are observed in the spectra of the "moderately" reduced sample: 1785 and 1910 cm^{-1} (Fig. 3, spectrum *1*). When the sample was heated in CO at 673 and 773 K, new absorption bands appeared in the spectrum of the adsorbed NO: 1705 and 1835 cm^{-1}, and the intensities of absorption bands at 1785 and 1910 cm^{-1} increased (spectra *2*, *3*). As the moderately reduced samples contain coordination-unsaturated V^{4+} ions (see Ref. 12), the appearance of the absorption bands at 1785 and 1910 cm^{-1} in the spectrum of adsorbed NO can be related to the formation of dinitrosyl complexes of NO with V^{4+}ions.* The sample reduced by heating in CO at 773 K possesses coordination-unsaturated V^{3+} ions, which can coordinate CO molecules (νCO ~2182 cm^{-1}) (see Ref. 15). Therefore, the appearance of the maxima 1705 and 1835 cm^{-1} in the spectrum of NO adsorbed on such a sample[12] is associated with the formation of dinitrosyl type complexes with V^{3+} ions. The possibility of the formation of V^{3+}—NO (absorption band at ~1723 cm^{-1}) also cannot be excluded (see Ref. 19).

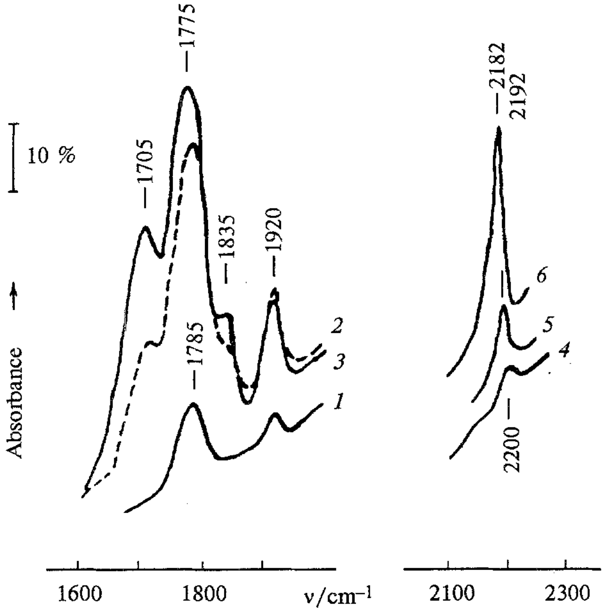

Fig. 3. IR spectra of CO and NO adsorbed on V_2O_5/Al_2O_3: $1.3\cdot10^3$ Pa of NO (*1*) and $6\cdot10^3$ Pa of CO (*4*) on samples reduced by desorption of toluene at 773 K; $5\cdot10^2$ Pa of NO (*2*) and $2\cdot10^3$ Pa of CO (*5*) on samples reduced in CO at 673 K; $5\cdot10^3$ Pa of NO (*3*) and $1.6\cdot10^3$ Pa of CO (*6*) on samples reduced in CO at 773 K.

The nitrosyl complexes observed are partially desorbed by evacuation at room temperature, however, their complete removal from the catalyst surface occurs during prolonged evacuation at 373 K (see Fig. 3, spectrum *2*). The spectra of repeatedly adsorbed CO and NO (spectra *4* and *5*) indicate partial oxidation of the reduced centers in the adsorption of NO, which is confirmed by the liberation of N_2O. It is noteworthy that reoxidation of the surface by NO, as follows from the appearance of N_2O, occurs in the desorption of NO even on the sample containing only V^{4+} ions. In our opinion, this also testifies to the existence of associated (clustered) states of the vanadium-oxide phase, *i.e.*, vanadium ions are located at distances providing the formation of V—O—V species.

Interactions of NO_{ads} + NH_3 and $NH_{3(ads)}$ + NO. When NO is introduced to a reduced sample with preadsorbed ammonia, a shift of the absorption band $\delta_s(NH_3)$ in the IR spectrum from 1220 cm^{-1} ($V^{3+} \leftarrow NH_3$) to 1245 cm^{-1} ($V^{4+} \leftarrow NH_3$) is observed and two new absorption bands appear at 1570 and 1705 cm^{-1} (Fig. 4, spectra *1*, *2*). Absorption bands in the 1800—2000 cm^{-1} range are not observed. If the sequence of the adsorption of gases is reversed, the resulting spectrum is similar to spectrum *2* in Fig. 4. The results obtained attest that when NO is introduced to a catalyst with preadsorbed ammonia, on the one hand, reoxidation of the V^{3+} centers on which ammonia

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* Analysis of the relative intensities of the absorption bands in the spectra of adsorbed NO unambiguously points to the presence of those characteristic of mononitrosyl NO complexes. The absorption band at ~1775 cm^{-1} is complex in nature, and its decomposition shows that it consists of three components, including absorption bands at 1765 and 1745 cm^{-1} characteristic of V^{4+}—NO complexes.[16]

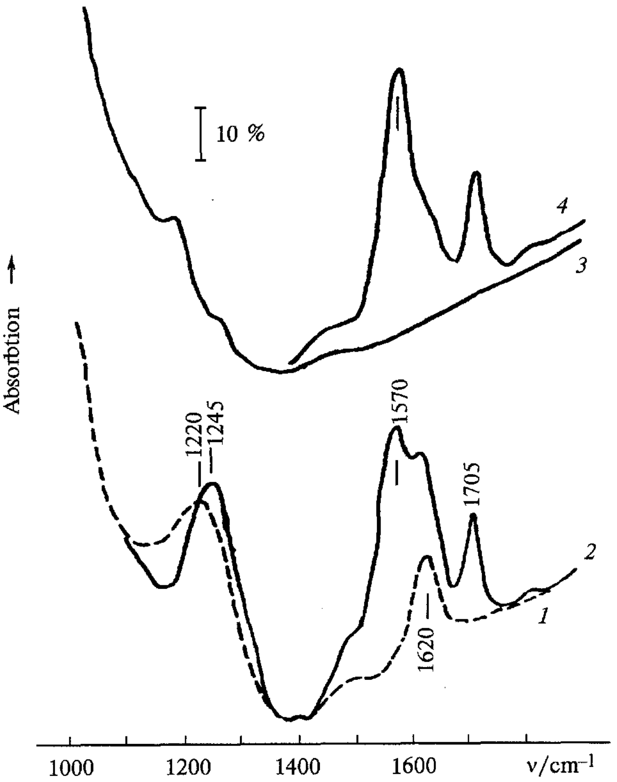

Fig. 4. IR spectra of ND_3 and NO adsorbed on V_2O_5/Al_2O_3 reduced in H_2 at 773 K: $7 \cdot 10^2$ Pa of NH_3 (*1*); introduction of NO to *1* (*2*); 10^3 Pa of ND_3 (*3*); introduction of NO to *3* (*4*).

is adsorbed, to V^{4+} occurs, and ammonia manifests itself on the reoxidized center ($\delta_s(NH_4)$ ~1245 cm^{-1}). On the other hand, dinitrosyl complexes form, which are characterized by much broader absorption bands than those for catalysts without preadsorbed ammonia. In order to reveal the absorption band $\nu_{as}(V(NO_2))$ we recorded the IR spectra of NO adsorbed on the catalyst with preadsorbed ND_3. The IR spectrum of ND_3, unlike that of adsorbed NH_3, has no absorption bands in the range studied (Fig. 4, spectrum *4*).* As can be seen from the spectrum obtained, virtually one dinitrosyl complex, which is characterized by absorption bands at 1570 and 1705 cm^{-1}, is observed on the surface. Most likely, these absorption bands correspond to ν_s and ν_{as} in the $V^{4+}(NO)_2$ dinitrosyl complex. The shift of ν(NO) observed in this case, as compared with ν(NO) in the IR spectrum of the catalyst, can be explained, in our opinion, by the influence of the adsorbed coordinationally-bound ammonia. Actually, ammonia as an electron donor is likely to increase the donation of electron density to NO π^*-orbitals, which causes the low-frequency shift of NO. It is difficult to explain the coordination of three molecules (two NO and one NH_3 molecules) on the same vanadium cation, although the value of the shift of ν(NO) is considerable and attests to direct electronic influence of ammonia (within the cluster).

Thus, in the present work we have found for the first time the inclusion of both of the reacting molecules (NO and NH_3) in a single complex with the possibility of electron exchange via vanadium cations, which makes possible the interaction of these molecules according the Langmuir—Hinshelwood mechanism.

It should be mentioned that this activation of molecules is facilitated by the specific state of the catalyst containing clusters of vanadium-oxide formations, which are easily reduced to V^{4+} and reoxidized to V^{5+}. The role of gaseous phase oxygen also becomes evident in this connection. This likely provides (maintains) a specific (V^{4+}) degree of oxidation of vanadium cations as a better oxidant than NO and does not allow them to be "overreduced" to V^{3+}.

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Received April 16, 1992;
in revised form September 29, 1993

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* Intense absorption bands at 1570 and 1705 cm^{-1} are present in the spectrum of NO adsorbed on the catalyst with preadsorbed ND_3. These bands most likely correspond to ν_s(NO) and ν_{as}(NO) in a dinitrosyl complex.