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Study of the NO_2–NH_3 Interaction on a Titania (ANATASE) Supported Vanadia Catalyst

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The adsorption and coadsorption of nitrogen dioxide and ammonia on an anatase-supported vanadia catalyst prepared by ion exchange from an acidic aqueous solution of ammonium vanadate are investigated by IR spectroscopy and ESR. The sequence of formation of adsorbed species and the thermal stability of the surface complexes are studied. It is established that the active sites for selective catalytic reduction (SCR) of NO_2 by NH_3 on vanadia-titania catalysts are (i) the V^{5+}=O groups, which interact with NO_2, and, as a result, vanadium is reduced to V^{4+}, while the nitrogen dioxide is oxidized to a nitrate coordinated to the vanadium (IV); and (ii) the V^{5+}–OH groups, which react with NO_2, thus giving rise to a strong Brønsted acidity. Ammonia is adsorbed with the participation of the induced Brønsted acid sites as NH_4^+, whereas NH_3 coordinatively bound to the Lewis acid sites is displaced by NO_2. The presence of delocalized protons on the sample surface is registered. It is found that these protons play an essential role in the occurrence of the SCR process. Some conclusions are drawn concerning the mechanism of SCR of NO_x by NH_3. A scheme is proposed according to which the reaction takes place between a NO_3^- ion, having a more pronounced symmetry, and a NH_4^+ ion, both coadsorbed on the catalyst active phase, with $NH_4^+NO_2^-$ appearing as an intermediate.

INTRODUCTION

The most used catalysts for selective catalytic reduction of NO_x from combustion gases by NH_3, are vanadia–titania catalysts (1). In spite of the large number of investigations on this catalytic system by different methods, there is still no agreement on the nature of the active sites and the mechanism of the DeNOx process. It is generally accepted that the vanadia part of the catalyst is essential for this reaction. Inomata and co-workers (2–5) have found that the sites responsible for the catalytic activity of bulk and supported vanadia toward the NO–NH_3 reaction in the present of oxygen under dilute gas condition are the V^{5+}=O groups, whose concentration correlates with the catalytic activity. On the basis of their isotopic transient studies (6, 7), Jannsen *et al.* have proposed a dual-site mechanism for the NO–NH_3 reaction in the presence of oxygen with the participation of two neighboring V^{5+}=O groups as active sites. Ramis *et al.* (8) have stated that this reaction is likely to occur at the vanadyl sites identified as VO^{2+} on the basis of the fact that vanadium is present almost completely as V^{4+} in vanadia–titania submonolayer samples (9). On the other hand, Gasior *et al.* (10) have concluded, from their studies on V_2O_5 that not the V=O species but the acid hydroxyl groups on the vanadia surface could be the active sites. Pointing out the importance of the acidic surface V–OH groups as the principal reaction sites in the catalytic reduction of NO, Topsøe *et al.* (11, 12) have noted that the V=O groups are also involved in the reaction. Their results indicate an interconversion between the Brønsted and Lewis acid sites on the vanadia–titania surface or a transformation between V–OH and V=O caused by the reagents during the reaction. On the basis of TPD/TPR and *in situ* IR spectroscopic studies Srnak *et al.* (13) point out the unique role of the vanadia component in V_2O_5/TiO_2 catalyst for catalytic reduction of NO. They propose that vanadia participates in an oxidation/reduction process which leads to ammonia activation.

There is a variety of views on the mechanism of the selective reduction of NO_x by NH_3 catalyzed by V_2O_5/TiO_2. A large majority of papers is focused on the SCR of NO, and little attention has been paid to the NO_2–NH_3 reaction on vanadia-titania catalysts. Measurements on the adsorption of the components have shown that NH_3 is chemisorbed with the participation of the Brønsted and/or Lewis acid sites (2–8, 10–21), while NO is not adsorbed or is only weakly adsorbed on oxidized vanadia or vanadia–titania surfaces (3, 4, 11–13, 17–19). This is one of the important reasons for a great number of authors to adopt an Eley–Rideal mechanism for the reaction (2, 3, 6, 7, 11, 12). Srnak *et al.* (13) have established that, depending on the reaction conditions, both Langmuir–Hinshelwood and the Eley–Rideal mechanism are effective for selective catalytic reduction of NO. However, strong adsorption of NO on bulk and supported vanadia

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in the presence of gaseous oxygen (17–19) or after a continuous contact of NO with the oxidized catalyst surface (8, 21, 22) have been observed. Moreover, it has been established that the SCR of NO_x by NH_3 is much more accelerated in the presence of oxygen and that oxygen is involved in the reaction (2, 6, 23). Takagi *et al.* (17–19) have concluded from their studies by IR, XPS, mass spectrometry, and kinetic and volumetric measurements that in the presence of ambient oxygen, NO is adsorbed as NO_2(ad), which reacts, according to a Langmuir–Hinshelwood mechanism, with the ammonia chemisorbed on the acid V–OH as NH_4^+ to form nitrogen and water. Recent IR studies (8, 21, 22, 24–27) have shown that both NO and NO_2 react with the oxidized surface of anatase and anatase-supported vanadia to form nitrates rather than NO_2(ad). Dines *et al.* (21) have proposed a mechanism in which NO_2 as surface nitrate species and ammonia as ammonium ions adsorbed on adjacent surface sites interact via an intermediate V–O–N═N species to give nitrogen, oxygen, and water as reaction products. On the contrary, Ramis *et al.* (8) have concluded from their FTIR studies that NO_2 does not participate directly in the reaction; being a much stronger oxidation agent than O_2, it oxidizes (reoxidizes) the catalyst surface, and the resulting NO interacts further on with the ammonia adsorbed as NH_2^- on the VO^{2+} cations to give N_2 and H_2O.

The purpose of the present paper is to study the adsorption and coadsorption of NO_2 and NH_3 on an anatase-supported vanadia catalyst prepared by ion exchange, paying special attention to: (i) the sequence of appearance of the different surface compounds with adding the reagents, (ii) the way of formation of the surface compounds and their location, and (iii) the possibility of interaction of the adsorbates with one another and with the gas phase. The elucidation of these moments would help clarifying the mechanism of SCR of NO_2 by NH_3.

EXPERIMENTAL

The vanadia-titania sample was prepared by adsorption of VO_2^+ ions from a solution of ammonium vanadate in nitric acid (pH 0.5) on TiO_2 (P25 Degussa; phase composition: 85% anatase, 15% rutile; BET surface area 55 $m^2 \cdot g^{-1}$) as described elsewhere (28). Further on the sample will be denoted as VT. The nitrogen dioxide was synthesized by thermal decomposition of $AgNO_2$ in vacuum at 423 K. Oxygen was added to the gas in order to remove the NO impurity. Complete purification was achieved by fractional distillation. The other substances used were A.R.

Chemical analysis was made by atomic absorption analysis (AAA) with a Pye Unicam SP 1950 apparatus at the corresponding resonance wavelength. The XPS measurements were carried out with an ESCALAB MkII (VG Scientific, Ltd.) apparatus using Mg$K\alpha$ radiation. The ESR spectra were recorded with a Bruker ER 200 D-SRC apparatus using a DPPH marker. The IR spectra were registered with a Specord M 80 apparatus (spectral resolution 0.5% cm^{-1} in the 4000–400 cm^{-1} region). The vacuum apparatus used ensured a residual pressure below 10^{-4} Torr (1 Torr = 1.33.3 $N \cdot m^2$).

To carry out the IR adsorption measurements, the VT sample was pressed into pellets with a suitable thickness and placed in the IR cell connected directly with the vacuum apparatus. Activation of the sample was performed for 2 h by successive heating at 723 K in vacuum and in oxygen (100 Torr) in order to eliminate eventual organic contaminants and other adsorbed impurities.

RESULTS

Characterization of the Sample VT

According to the AAA data, the sample VT contained 2.65 wt% V_2O_5. The vanadium content did not exceed a monolayer coverage (according to Ref. (29)). The vanadium atom surface concentration calculated with this value was 2.3 V^{5+} nm^{-2}, i.e., much lower than the mean surface concentration of the coordinatively unsaturated titanium cations on the anatase (ca. 5 Ti^{4+} nm^{-2} (30)). According to the XPS data, the V : Ti ratio was 2.5 : 100, i.e., considerably higher than that calculated using the AAA data. This was an indication of the surface localization of the adsorbed vanadium oxo-species. On the basis of Ref. (28), vanadium was distributed on the anatase as monomeric surface species containing V^{5+}═O and O═V^{5+}–OH structures.

The position of the V $2p_{3/2}$ peak maximum at 516.7 eV indicated the five valent state of vanadium (28, 31). This was in agreement with the absence of a signal in the ESR spectrum of the activated VT sample (see Fig. 1).

The IR spectrum of the activated VT sample (Fig. 2) was similar to that described earlier (28). Bands at 3668 and 3640 cm^{-1} were observed in the ν(OH) region and were related, according to previous studies (9, 16, 28, 32), to the OH stretching modes of V^{5+}–OH surface hydroxyl groups. A very weak and broad absorbance in the 3600–3000 cm^{-1} region showed the existence of a certain amount of hydrogen-bonded hydroxyls. A sharp and intense band at 1032 cm^{-1} characteristic of the V^{5+}═O stretching vibration (9, 16, 28, 32) was registered in the 2000–1000 cm^{-1} region.

The spectrum recorded after adsorption of CO (40 Torr) on the activated sample VT revealed the presence of Ti^{4+}–CO surface carbonyls (band at 2188 cm^{-1} corresponding to ν(CO)) formed with the participation of the β-Lewis acid sites of anatase (28, 33, 34). No (α)Ti^{4+}–CO carbonyls were detected, which indicated that the

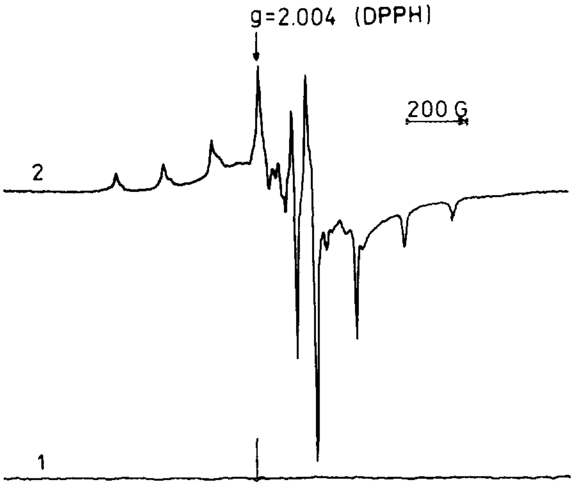


FIG. 1. ESR spectra of a VT sample at 110 K: a sample activated for 2 h successively in vacuum and in oxygen (100 Torr) at 723 K (1); and after adsorption of NO_2 (2 Torr, 10 min, followed by 15 min evacuation at room temperature) (2).

α-Lewis acid sites of the support were blocked by the deposition of vanadium.

Ammonia Adsorption

The introduction of ammonia (2 Torr) at room temperature, followed by 15 min evacuation in order to eliminate the hydrogen-bonded NH_3 molecules, led to the appearance in the IR spectrum of bands at 1598 and 1160 cm^{-1} (Fig. 2). These bands corresponded to $\delta_{as}(NH_3)$ and $\delta_s(NH_3)$ vibrations of coordinatively bound ammonia (34). The position of the latter band was indicative of $(\beta)Ti^{4+}$–NH_3 surface complexes (28, 33–36). The spectrum obtained by subtraction of the background spectrum from that of the NH_3 covered sample showed that the band at 1160 cm^{-1} possessed a high-frequency shoulder at ca. 1220 cm^{-1}, which may be ascribed to $\delta_s(NH_3)$ of complexes of the type V^{5+}–NH_3 (28, 37). A broad and weak band was visible at ca. 1458 cm^{-1}, which characterized $\delta_{as}(NH_4)$ modes of the ammonium ion. The band position revealed the presence of weak or moderate Brønsted acidity (28, 34), in addition to the Lewis acidity, on the VT sample.

In the high-frequency region there were overlapping bands due to symmetric and asymmetric N–H stretching vibrations of coordinatively bound ammonia and ammonium ion, as well as the Fermi resonance of $2\delta_{as}(NH_3)$ with $\nu_s(NH_3)$ (16, 34). The band at 3572 cm^{-1} could be assigned to ν(NH) vibrations of NH^+ species appearing after dissociation of part of the ammonia molecules during adsorption (28, 36, 38). The bands due to the V^{5+}–OH groups decreased in intensity. This indicated also a moderate acidity of the protonic sites of the sample VT, on which reversible ammonia adsorption proceeded. Besides, these bands were shifted to higher frequencies (3680 cm^{-1}), which implied an increased O–H bond order.

It was worth noting that the band at 1032 cm^{-1}, which characterized the V^{5+}=O stretchings, disappeared from the spectrum after ammonia adsorption.

Adsorption of Nitrogen Dioxide

The ESR spectrum obtained at 110 K after adsorption of NO_2 (2 Torr, 10 min, followed by 15 min evacuation) at room temperature on an activated VT sample is presented in Fig. 1 and is typical of V^{4+}-containing species (5, 9, 39). Hyperfine structures due to electron-nuclear spin coupling were observed in the spectrum. Two sets of eightfold parallel hyperfine components with $g_\parallel^{(1)}$ = 1.958, $A_\parallel^{(1)}$ = 156.3 G, and $g_\parallel^{(2)}$ = 1.946, $A_\parallel^{(2)}$ = 160.0 G, respectively, were clearly detected, while the corresponding perpendicular components were not distinguishable. These two signals characterized two kinds of surface vanadium–oxo species, in which four-valent vanadium was

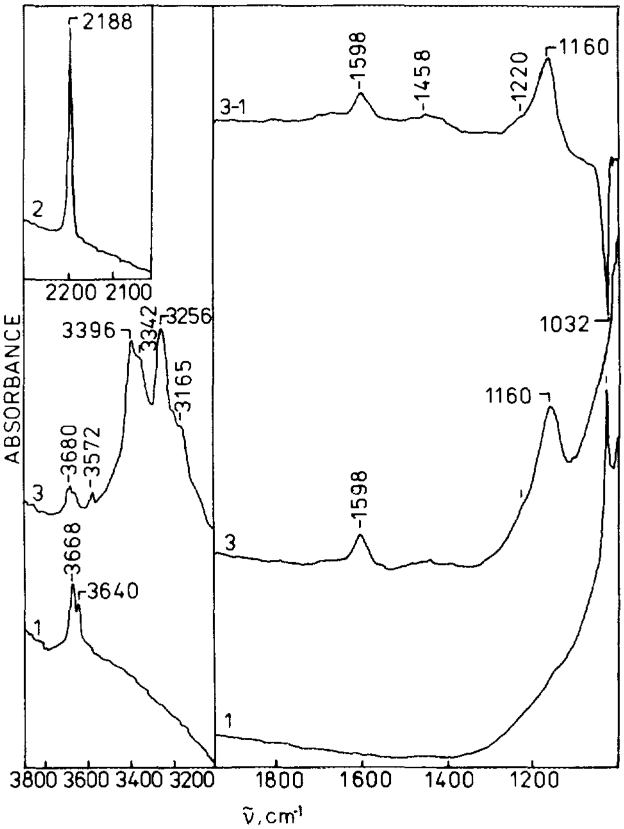


FIG. 2. IR spectra of an activated VT sample (1); adsorption of CO (40 Torr, room temperature) (2); subsequent evacuation and adsorption of ammonia (4 Torr, 10 min, followed by 15 min evacuation) (3); and the difference spectrum obtained by subtraction of spectrum (1) from spectrum (3) (3 − 1).

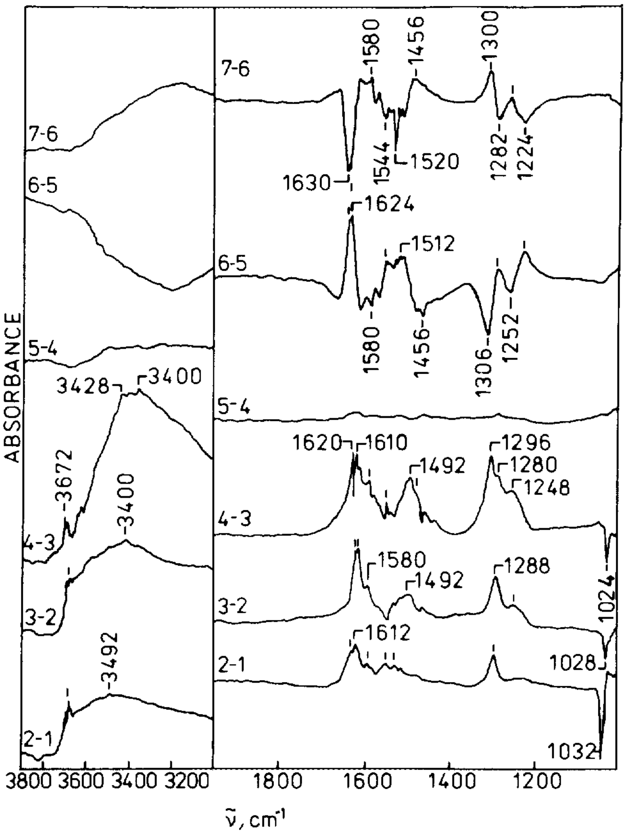


FIG. 3. IR difference spectra of various amounts of NO_2 adsorbed on a VT sample at room temperature. Each spectrum denoted as (j − i) is obtained by subtraction from spectrum (j) the preceding spectrum (i). Cumulative NO_2 dosages are 16 μmol/g (p_0 = 0.1 Torr) (2); 32 μmol/g (3); 64 μmol/g (4); and 128 μmol/g (5). Spectrum immediately after subsequent 15 min evacuation at room temperature (6); and 12 h later (vacuum, room temperature) (7). Background spectrum (1).

five (square-pyramidally) coordinated (9, 39). In addition, a broad and weak signal centered at g = 1.935, which was indicative of magnetically interacting V^{4+}-containing species (9), was detected.

The adsorption of NO_2 (2 Torr, 10 min, followed by 15 min evacuation) at room temperature on activated VT sample resulted in a very similar spectrum to that obtained for NO_2 on pure anatase (8, 26, 27, 40).

In order to establish the sequence of formation of the surface species during NO_2 adsorption on the activated VT sample, experiments have been carried out in which the gas has been introduced in small portions. Each portion corresponded to an initial pressure of 0.1 Torr in the cell. Each spectrum was recorded 10 minutes after the gas admittance, without intermediate evacuation. For the sake of clarity, the difference spectra obtained by subtraction from each spectrum the preceding one are presented in Fig. 3.

The first NO_2 dose (p_0 = 0.1 Torr) caused the appearance of a broad absorbance in the ν(OH) region of hydrogen-bonded hydroxyl groups with a maximum at ca. 3490 cm^{-1} (Fig. 3, spectrum (2 − 1)). The bands corresponding to ν(OH) vibrations of the original hydroxyl groups were shifted to the higher wavenumbers (around 3672 cm^{-1}). The bands in the low-frequency region had low intensities and revealed the beginning of nitrate formation. The band corresponding to the $\nu(V^{5+}{=}O)$ mode preserved its position but decreased in intensity, which was an indication that the vanadyl groups were involved in the adsorption process.

The next NO_2 portions led to an additional increase in intensity of the band corresponding to the hydrogen-bonded hydroxyls and to shift of the maximum to the lower frequencies (3400 cm^{-1}) (Fig. 3, spectra (3 − 2) and (4 − 3)). An additional increase in intensity of the isolated V–OH groups was also observed. At lower wavenumbers there were distinguished bands revealing the presence of bidentate (1620, 1610, 1580, and 1248 cm^{-1}) and monodentate (a broad band at ca. 1492 cm^{-1} and a band at 1288 cm^{-1}) nitrates (8, 22, 24, 25, 41, 42). The band corresponding to the $\nu(V^{5+}{=}O)$ stretching mode exhibited a still more pronounced drop in intensity and shift to lower wavenumbers.

Portions (Fig. 3, spectrum (5 − 4)), ensuring pressures of up to 1 Torr in the cell, led to saturation of the sample surface (the IR difference spectrum showed no changes in the low-frequency region (2000–1000 cm^{-1})). In the ν(OH) region a weak negative band around 3670 cm^{-1} was observed, which indicated that part of isolated OH groups has disappeared.

The evacuation of NO_2 for 15 min at room temperature resulted in an intensity drop of the bands in the ν(OH) region (Fig. 3, spectrum (6 − 5)). The amount of bidentate nitrates characterized by bands at 1624, 1544, and 1224 cm^{-1} as well as of the monodentate nitrates with bands at 1520–1504 cm^{-1}, and 1282 cm^{-1} increased, while the amount of bidentate nitrates (bands at 1610–1550 and 1252 cm^{-1}) and the surface species, characterized by bands at 1456 and 1306 cm^{-1}, decreased. Hence, the evacuation caused transformation of some surface species into others, and, probably, destruction of some of the species.

The spectrum recorded after 12 h displayed changes completely opposite to these caused by the evacuation (Fig. 3, spectrum (7 − 6)). The simultaneous appearance/disappearance of the bands at 1456 and 1300 cm^{-1} could indicate that these bands characterize the same surface species. They appear just before saturation of the surface (a shoulder at about 1470 cm^{-1} and an intense band at 1296 cm^{-1}), disappear after short evacuation, and are observed again a long time after the evacuation has been stopped.

The final spectrum, obtained after surface saturation with NO_2, did not differ from spectrum 1 in Fig. 4, which

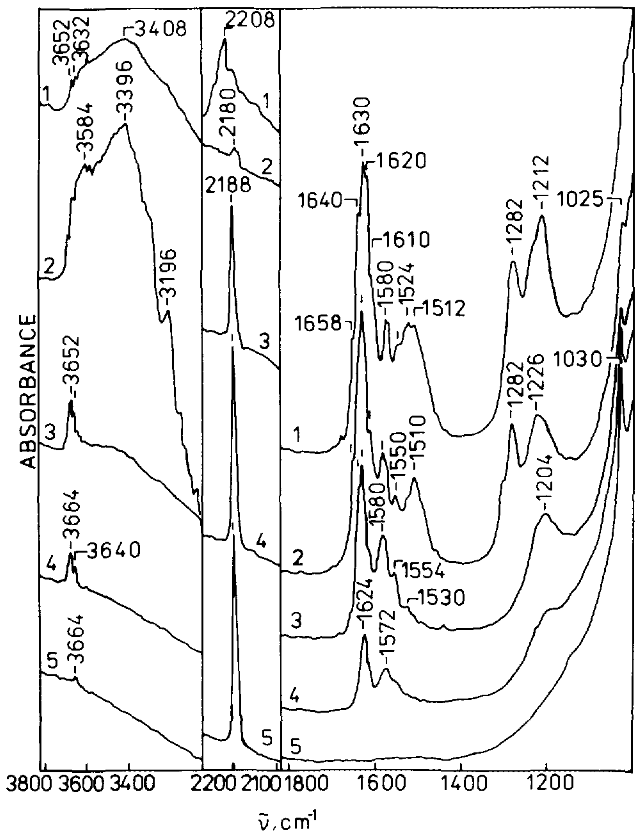


FIG. 4. IR spectra of NO_2 adsorbed on a VT sample (2 Torr NO_2, 10 min, followed by 15 min evacuation at room temperature) (1); after 30 min outgasing at 353 K (2); 423 K (3); 493 K (4); and 623 K (5). All spectra are registered in an atmosphere of 40 Torr CO at beam temperature.

was observed after dosage of 2 Torr NO_2 for 10 min followed by 15 min evacuation. Only, during the portion adsorption of NO_2 the band at 2208 cm^{-1} characteristic of NO^+ species (34, 41, 42) was not detected. The shoulder at 1658 cm^{-1} was assigned to δ(HOH) of water molecules formed as a result of NO_2 adsorption (40).

Heating of the sample in vacuum at 353 K for 30 min after NO_2 dosage (2 Torr, 10 min, followed by 15 min evacuation) resulted in a fourfold increase in intensity of the broad band in the ν(OH) region (Fig. 4, spectrum 2). Hence, the slight increase of temperature led to spectral changes in the ν(OH) region analogous to those obtained after keeping the sample in vacuum at room temperature (see Fig. 3, spectrum (7 − 6)). On the contrary, in the region of 2000–1000 cm^{-1} all bands demonstrated an intensity decrease after heating in vacuum. A low-intensity band at 1025 cm^{-1} appeared, which could be assigned to the ν(V=O) vibrations. The band due to NO^+ vanished. Testing with CO (40 Torr) of the sample surface resulted in appearance of a weak absorbance at 2180 cm^{-1}, which evidenced the presence of a small amount of unoccupied Lewis acid sites on the support (Fig. 4, spectrum 2).

Rising the temperature up to 423 K (Fig. 4, spectrum 3) led to a sharp drop in intensity of the strong band corresponding to the ν(OH) vibrations of the hydrogen-bonded hydroxyls: a negligible absorbance was observed at about 3400 cm^{-1}. Bands at 3652 and 3640 cm^{-1} corresponding to the ν(OH) modes of isolated V–OH groups were registered. The bands due to the monodentate nitrates have almost vanished: a weak absorbance at 1530 and ca. 1270 cm^{-1} was established.

The alterations caused by the increase of the outgassing temperature (493–553 K) were the most pronounced in the region of ν(NO) stretching modes of the nitrates (Fig. 4, spectrum 4). Bands corresponding to the bidentate nitrates and exhibiting a significantly decreased intensity were detected at 1624, 1572, and ca. 1200 cm^{-1}. The ν(V=O) band was shifted to 1030 cm^{-1} and has increased in intensity. The admittance of CO (40 Torr) evidenced that the coordinatively unsaturated surface Ti^{4+} ions, i.e., the β-Lewis acid sites of anatase were completely deblocked and accessible to CO adsorption: the intensity of the respective carbonyl band was completely restored. This indicated that the nitrates observed under these conditions were situated on the vanadium ions. It was worth noting that the intensity of the bands characterizing the OH stretchings of the V–OH groups decreased.

As the desorption temperature rose up to 623 K, the bands due to the isolated surface V–OH groups almost completely disappeared from the spectrum (Fig. 4, spectrum 5). In addition, no nitrates were established. The band characteristic of the ν(V=O) stretching mode restored its initial intensity. The NH_3 adsorption on the sample thus treated, revealed the presence of a certain Brønsted acidity ($\delta_{as}(NH_4)$ at 1444 cm^{-1}) as well as the presence of coordinatively bound ammonia (a bands at 1598 and 1160 cm^{-1}). The latter spectrum differed from that obtained after NH_3 adsorption on a freshly activated sample (Fig. 2) by a somewhat higher concentration of the protonic sites. The disappearance of the bands due to the isolated hydroxyl groups from the spectrum was also observed after evacuation of the activated VT sample at 723 K for 30 min, while no changes in intensity and position of the V=O band were detected. Calcination of the sample under 100 Torr oxygen at 723 K for 30 min, followed by evacuation of O_2 at room temperature, resulted in complete restoration of the original V–OH bands.

Adsorption of NH_3 on a NO_2 Precovered VT Sample

The adsorption of ammonia (4 Torr, followed by 15 min evacuation) at room temperature on a sample with preadsorbed NO_2 (2 Torr, 10 min, followed by 15 min

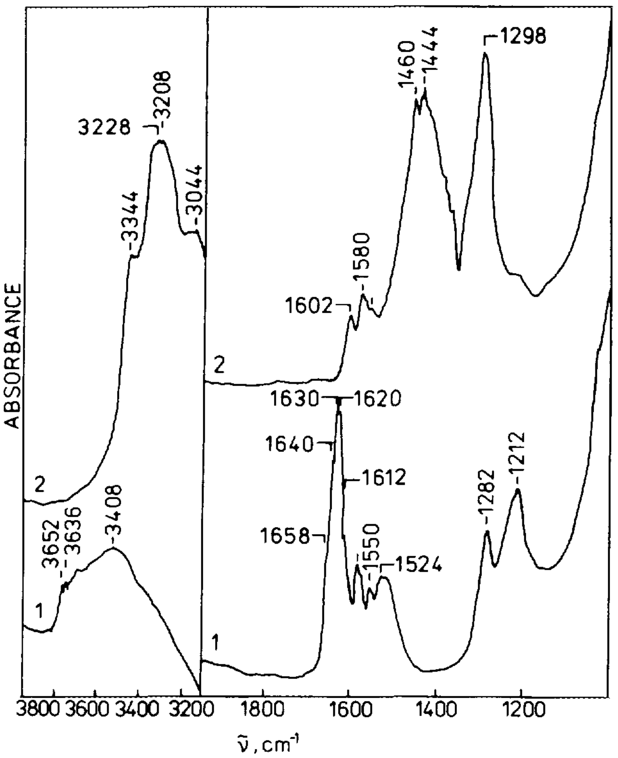


FIG. 5. IR spectra of NO_2 adsorbed on a VT sample (2 Torr NO_2, 10 min, followed by 15 min evacuation at room temperature) (1); and subsequent ammonia adsorption (4 Torr, 10 min, followed by 15 min evacuation at room temperature) (2).

evacuation) caused strong changes in the IR spectral region of nitrate ν(NO) modes (Fig. 5). The bands corresponding to the different nitrates disappeared or reduced in intensity. It was not clear whether there was coordinatively bound ammonia on the sample surface. In the 3900–3000 cm^{-1} region the spectrum contained a very intense complex band with a maximum at 3228–3208 cm^{-1}. Very intense bands at 1460–1440 cm^{-1} and 1298 cm^{-1} were also observed.

Ammonia portion admitting to a NO_2 precovered sample allowed easier investigation of the occurring processes and assignment of the IR bands. Again, each gas portion corresponded to an initial pressure of 0.1 Torr in the cell. In the 2000–1000 cm^{-1} region, difference spectra obtained by subtracting from each spectrum the preceding one were presented in Fig. 6.

The first NH_3 portion led to the most pronounced decrease in intensity of the bands at 1644, 1632, and 1210 cm^{-1} corresponding to bridge nitrates, along with an increase of the band intensities at 1624, 1506, and 1300 cm^{-1}, as well as appearance of a weak absorption at ca. 1450 cm^{-1} (Fig. 6, spectrum (2 − 1)). The next NH_3 portion produced the same changes in the spectrum, however to a smaller extent (Fig. 6, spectrum (3 − 2)). After the third portion of ammonia, the spectrum showed that bidentate (bands at 1620, 1550, and 1220 cm^{-1}) and monodentate (bands at 1520 and 1280 cm^{-1}) nitrates were attacked by NH_3 along with the bridge nitrates (Fig. 6, spectrum (4 − 3)). Simultaneously, a broad band at 1475–1420 cm^{-1} and a band at 1300 cm^{-1} appeared. Each successive portion led to gradual consumption of the nitrates, the last to be involved in the process being the bidentate nitrates with bands at 1612 and 1240 cm^{-1}. With increasing NH_3 portions, an enhancement of the intensity of the pair of complex bands at 1470–1430 and 1300 cm^{-1} was observed. After the surface saturation with ammonia the spectrum did not differ from that presented in Fig. 5. Coordinatively bound ammonia (band at 1160 cm^{-1}) was not registered. Bands at 1602, and 1574 cm^{-1}, and a weak band at ca. 1230 cm^{-1} revealed the presence of bidentate nitrates, which were especially resistant toward NH_3.

In the 3900–3000 cm^{-1} region the increasing amount of adsorbed ammonia led to rising intensity of the broad

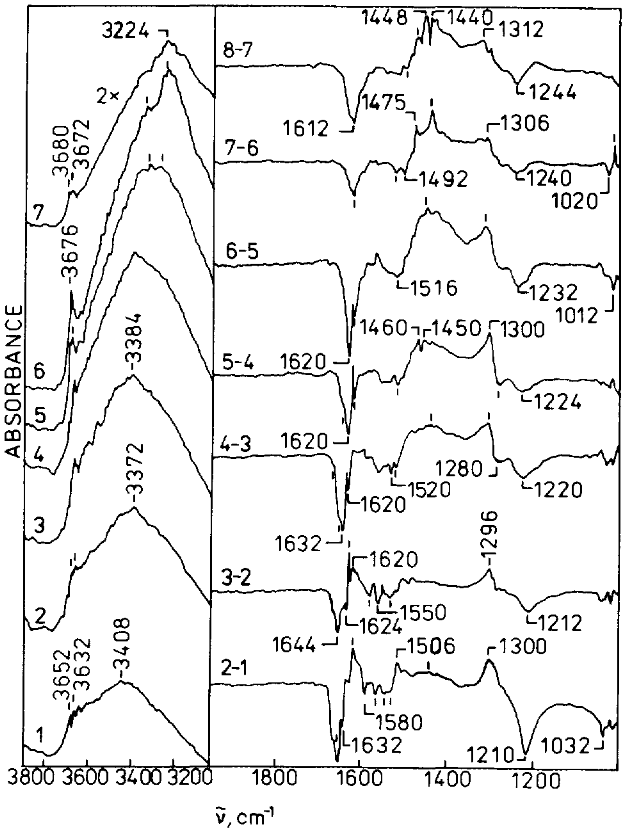


FIG. 6. IR spectra of various amounts of NH_3 adsorbed on a NO_2 precovered VT sample (2 Torr NO_2, 10 min, followed by 15 min evacuation) at room temperature. Each spectrum denoted as (j − i) is obtained by subtraction from spectrum (j) the preceding spectrum (i). Cumulative NH_3 dosages are 16 μmol/g (p_0 = 0.1 Torr) (2); 32 μmol/g (3); 48 μmol/g (4); 64 μmol/g (5); 80 μmol/g (6); 96 μmol/g (7); and 112 μmol/g (8). Spectrum before NH_3 addition (1).

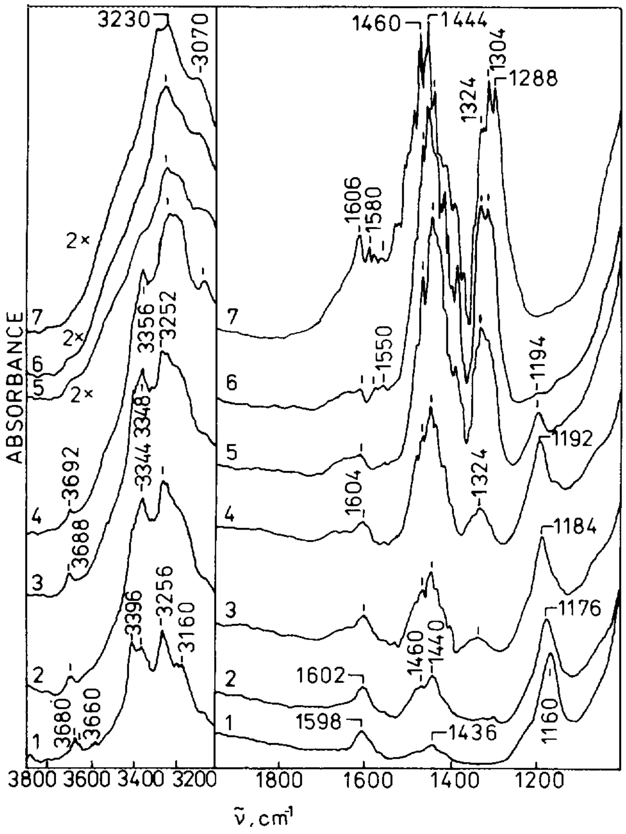


FIG. 7. IR spectra arising after the addition of different doses of NO_2 on an NH_3 precovered VT sample (4 Torr NH_3, followed by 15 min evacuation) at room temperature. Cumulative NO_2 dosages are 4 μmol/g (p_0 = 0.025 Torr) (2); 8 μmol/g (3); 24 μmol/g (4); 60 μmol/g (5); 80 μmol/g (6); and 200 μmol/g (7). Spectrum before NO_2 addition (1).

band whose maximum was gradually shifted to the lower frequencies (from 3408 to 3224 cm^{-1}). After the fourth NH_3 portion, bands corresponding to the isolated hydroxyl groups with a maximum at 3676 cm^{-1} were registered (Fig. 6, spectrum 5).

Adsorption of NO_2 on an NH_3 Precovered VT Sample

Portions of NO_2 were also adsorbed on an ammonia precovered VT sample. However, in this case each dose ensured an initial pressure of 0.025 Torr in the cell. The spectra (Fig. 7) evidenced that with increasing NO_2 amount the bands corresponding to $\delta_{as}(NH_3)$ and $\delta_s(NH_3)$ of the coordinatively bound ammonia lost gradually their intensity, the $\delta_s(NH_3)$ band being gradually shifted to higher wavenumbers. A complex split band with two maxima at 1460 and 1444 cm^{-1}, appeared in the spectrum and simultaneous formation of an initially weak band at 1340–1320 cm^{-1} was observed. As the NO_2 dosing proceeded, the latter band became intense and complex, revealing maxima between 1324 and 1288 cm^{-1}. When the pressure in the cell reached 1.25 Torr, the spectrum indicated formation of nitrates (bands at 1606 and 1580 cm^{-1} in Fig. 7, spectrum 7)). The strong increase of the NO_2 pressure (up to 10 Torr) resulted in a drop in intensity of the complex band in the region of 1450–1400 cm^{-1}, which has also been reported by other authors (8).

The shape of the spectrum in the 3900–3000 cm^{-1} region gradually changed from that typical of coordinatively bound ammonia to that obtained after saturation of a NO_2 predosed sample by NH_3 (Fig. 7, spectrum 4). The final spectrum in this region was also similar to that recorded after NO_2 adsorption on sample VT.

DISCUSSION

Adsorption of NO_2 on the VT Sample

The similarity of the IR spectra of NO_2 adsorbed on vanadia–titania and on anatase implies the existence of the same surface species in both cases. In agreement with the literature data (8, 21, 22, 24–27, 40), the main surface compounds arising during NO_2 adsorption in both cases are variously coordinated nitrates. Ramis *et al.* (8) has pointed out that because of the similarity of the Lewis acidity of the vanadium and titanium cations, the spectra of nitrate ions bridging or chelating on these two centers are expected to be almost indistinguishable. Different ways of formation of the surface nitrates may be assumed, depending on the localization of the nitrates.

According to the IR data exposed Ti^{4+} ions are present on the sample surface and they are involved in the process of nitrate formation. The simultaneous appearance of bands characteristic of NO^+ ions and nitrates as well as the results from the tests with CO, which reveal blocking of the anatase β-Lewis acid sites after NO_2 adsorption, permit assuming disproportionation of nitrogen dioxide according to the scheme:

$$-\mathrm{Ti}^{4+}-\mathrm{O}^{2-}-\xrightarrow{2\,\mathrm{NO}_2}-\overset{\mathrm{NO}_3^-}{\overset{|}{\mathrm{Ti}^{4+}}}-\overset{\mathrm{NO}^+}{\overset{|}{\mathrm{O}^{2-}}}-. \qquad [1]$$

This process has been considered to take place during NO_2 adsorption on pure anatase (26, 27), the α- and β-Lewis acid sites of anatase being involved. Since the anatase β-Lewis sites represent five-coordinated Ti^{4+} ions, formation of monodentate and bridge nitrates on the exposed titanium (IV) ions of the support may be suggested.

The portion adsorption of NO_2 causes a decrease of the intensity and gradual shift to low wavenumbers of the band characterizing the $\nu(V^{5+}{=}O)$ vibrations. After reaching saturation this band disappears. Such a behavior indicates that (i) coordination of NO_2 to vanadyl–oxo species occurs, which leads to changes in the vanadium surroundings and to decrease of the bond order of the vanadyl group, and (ii) subsequent reduction of the V^{5+}-ions by the adsorbed NO_2 according to the following scheme in agreement with Refs. (21) and (22):

$$V^{5+}{=}O + N^{4+}O_2 \rightarrow V^{4+}\text{–}O\text{–}N^{5+}O_2. \quad [2]$$

The occurrence of such a redox reaction on the VT sample surface is unambiguously confirmed in our experiments by the appearance of an intense ESR signal characteristic of V^{4+} after NO_2 adsorption on the activated sample. Moreover, the ESR data evidence the existence of two kinds of surface species, in which V^{4+}-ions are five-(square-pyramidally) coordinated. This is in accordance with the presence of two types of monomeric vanadyl species on the support (hydroxo–vanadyl species and monomeric vanadyl species without OH group), in which V^{5+}-ions are five-coordinated (28, 43). Obviously, the coordination degree of vanadium ion after its reduction by NO_2 is preserved and the nitrates formed are monodentate. These nitrates are better visible during dosage experiments and are characterized in IR spectra by not well resolved and complex band at 1470–1450 cm^{-1} together with a distinct band at 1296 cm^{-1}. In view of the value of spectral splitting ($\Delta\nu \approx$ 170–150 cm^{-1}) it may be assumed that these bands characterize a more symmetrical surface nitrates (8). Finally, formation of bridge nitrates coordinated to vanadium ions may also not be excluded.

The strong increase in intensity of the bands in the region of hydrogen-bonded OH groups, which is observed after keeping the NO_2-covered VT sample under vacuum at room temperature or after outgassing at 353 K could be explained by the assumption about existence of delocalized protons on the sample surface. These protons are not wholly detected by testing with ammonia. The most probable reason for this is that ammonia is a relatively weak proton accepter with respect to the mobile protons or that ammonia basicity is commensurable with that of the oxygen surface anions, among which the protons are distributed. For that reason, no stable protonation to NH_4^+ is possible. The presence of these protons may be judged indirectly, by investigating NO_2 adsorption. Owing to the existence of delocalized electric charges in the nitrates coordinated to the surface metal cations (according to reactions [1] and [2]), the electron density of the surface oxygen ions should increase. This would favor localization of the protons as hydrogen bonded OH groups. The localization process is slow at room temperature and is accelerated by raising the temperature, which results in the strong increase in band intensity of the hydrogen bonded surface hydroxyl groups despite the desorption.

By analogy with the results of experiments involving NO_2 adsorption on anatase (26, 27, 40) it can be proposed that the surface V^{5+}–OH groups also participate in the interaction with NO_2. The decrease in intensity of the bands characterizing ν(OH) modes of the V^{5+}–OH groups after NO_2 admittance and the appearance of broad band centered at ca. 3400 cm^{-1} evidence the occurrence of the following reaction:

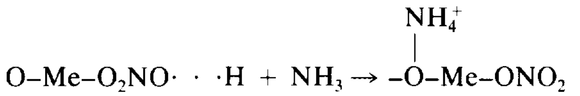
$$2V^{5+}\text{–}OH^- + 3NO_2 \rightarrow 2V^{5+}\text{–}NO_3^- + H_2O + NO. \quad [3]$$

However, the stronger acidity of the V–OH groups compared to that of the Ti–OH groups and the mobility of the protons on the vanadia–titania surface hinder the immediate proceeding of reaction [3]. Along with the proton localization and the appearance of hydrogen bonded OH groups, part of the protons are strongly bonded to the oxygen ions, which leads to an enhanced intensity of the bands characteristic of the isolated hydroxyl groups. An adsorbate induced alteration of the acid–base properties of the isolated OH groups is also observed, i.e., the OH groups acquire a more pronounced basicity, which is evidenced by the high-frequency shift of the respective bands in the ν(OH) region. The change in the hydroxyl group acid-base properties favors their interaction with NO_2. This suggestion is supported by the fact that with increasing NO_2 amount, the increase in intensity of the isolated hydroxyl groups becomes smaller and, after attaining saturation, these groups start to be consumed.

Finally, it could be noted the synchronous appearance/disappearance of the bands in the region of the hydrogen bonded hydroxyls and the bands at 1456 and 1300 cm^{-1}, which are ascribed to the peculiar monodentate nitrate coordinated to the vanadium (IV) ion. Hence, proton bonding to the nitrate oxygen atoms could be assumed, as a result of which this surface form is stabilized.

Adsorption of NH_3 on a NO_2 Precovered Sample

The addition of ammonia in portions to an NO_2 saturated VT sample leads to transformation of the bridge nitrates into bidentate and monodentate nitrates. The increasing ammonia amount is associated with the ammonium ion formation ($\delta_{as}(NH_4)$ at 1450–1400 cm^{-1}) as well as the appearance of the band pair at 1470–1460 and 1300 cm^{-1}. A similar pair of bands has been registered during NO_2 portion adsorption on a VT sample and have been already attributed to a nitrate with a more pronounced symmetry. For that reason, we are of the opinion that the nitrate formed by the interaction of adsorbed NO_2 with NH_3 is identical with that already described. The NH_4^+ species have emerged as a result of the interaction of ammonia (i) with the protons bonded to the nitrates according to the scheme



$$\text{O–Me–O}_2\text{NO}\cdot\ \cdot\ \cdot\text{H} + \text{NH}_3 \rightarrow \overset{\text{NH}_4^+}{\overset{|}{\text{–O}}}\text{–Me–ONO}_2 \quad [4]$$

or (ii) with the water molecules released in reaction (3), according to the scheme

$$\text{O–Me–O}_2\text{NO}\cdot\ \cdot\ \cdot\text{HOH} + \text{NH}_3 \rightarrow \overset{\text{NH}_4^+}{\overset{|}{\text{–O}}} - \overset{\text{OH}^-}{\overset{|}{\text{Me}}}\text{–ONO}_2. \quad [5]$$

Adopting the proceeding of reaction [5], one could explain the formation of isolated hydroxyl groups (bands at 3672–3680 cm^{-1}) with increasing ammonia amount. The complex spectrum of appearing ammonium ion indicates that these species are connected with the surface by at least two hydrogen bonds (34).

There are no data on displacement of nitrates by NH_3 leading to coordinatively bound ammonia in our experiments. With increasing NH_3 amount, a band with a maximum at 3224 cm^{-1} appears in the 3900–3000 cm^{-1} region, which might be attributed to physically adsorbed ammonia (44). Since there are no bands in the spectrum corresponding to coordinated NH_3, it may be assumed that in this case ammonia is bonded to the nitrate oxygen atoms by hydrogen bridges. The complexity of the spectrum in this region is due to overlapping of the described band with multiple bands corresponding to the ν(OH) modes of hydrogen bonds (a broad band centered at 3344 cm^{-1}) and to the ν_s(NH) vibration of the ammonium ion (intense bands grouped around 3044 cm^{-1}).

Adsorption of NO_2 on an NH_3 Precovered Sample

The results obtained by the NO_2 portion adsorption on an NH_3 saturated sample clearly show that nitrogen dioxide replaces the ammonia coordinated to the Lewis acid sites forming a nitrate with an enhanced symmetry (bands at 1470–1460 cm^{-1} and 1324–1304 cm^{-1}) on the metal cations. In addition, the presence of NH_4^+ is also registered (a complex band at 1444–1400 cm^{-1}). With increasing NO_2 concentration, the spectrum in the 3900–3000 cm^{-1} region trends to that recorded after admitting the components in an opposite order (as in the previous experiment). Hence, the displaced NH_3 is not desorbed and is bonded to the nitrates by hydrogen bonds.

Summary

The nitrate formation during the interaction of NO_2 with a Lewis acid site ($V^{5+}{=}O$) according to Eq. [2], leads to localization of the mobile surface protons and enhances the basicity of the V–OH groups. This favors disproportionation of NO_2 to occur according to Eq. [3], nitrates and water being yielded. Bidentate, bridge, and monodentate nitrates appear in these cases, and a nitrate with a more pronounced symmetrical structure, which is coordinated to vanadium (IV), is also detected. The latter is a predominant species in the presence of ammonia, irrespective of the succession of reagent adsorption. Therefore, it may be supposed that this nitrate is the active species in the SCR of NO_2 by NH_3. The following scheme might be proposed:

$$V^{4+}\text{–O–NO}_2\cdot\ \cdot\ \cdot NH_4^+ \rightarrow V^{5+}\text{–O}^\cdot + [NH_4NO_2] \xrightarrow[-VO^\cdot]{} N_2 + 2H_2O. \quad [6]$$

According to this scheme, the nitrate species coordinated to vanadium (IV) react with the ammonium ion located in the vicinity. The reactive $V^{5+}{=}O$ double bond, which is characterized by a mobility of its π-electron pair, is restored partially, the nitrate being decomposed by liberation of a nitrite ion, and an V–O$^\cdot$ radical being formed. The nitrite species are coupled with the NH_4^+ ions yielding nitrogen and water so fast that when the SCR process occurs, spectroscopic registration of the nitrite ion is difficult. It is well known that bulk ammonium nitrite decomposes easily already at 343 K to nitrogen and water. This supposition is confirmed by our additional coadsorption experiments carried out with (NO_2 + NH_3) gas mixtures varying the partial pressures of the components at both room and higher temperatures. The IR spectra characteristic of the reagent that is taken in an excessive amount are recorded in all cases, although with weak bands. This is an indication that the reaction has proceeded until the reagent present in an insufficient amount has been entirely consumed. Recently, Kudo *et al.* (45) have found nitrite formation on NiO/TiO_2 during the photocatalytic reduction of aqueous nitrate solutions.

Complete restoration of the $V^{5+}{=}O$ groups might be reached by selective oxidation of ammonia:

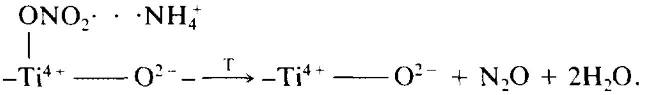
$$6\,V^{5+}\text{–O}^\cdot + 2\,NH_3 \rightarrow 6\,V^{5+}{=}O + 6\,H^+ + N_2. \quad [7]$$

Oxidation of ammonia to N_2 by the surface oxygen during the SCR proceeding has also been proposed by other authors (20, 46). Evidently, the combination of Eqs. [6] and [7] obeys the established stoichiometry of SCR of NO_2 by NH_3 (47, 48),

$$6\,NO_2 + 8\,NH_3 \rightarrow 7\,N_2 + 12\,H_2O,$$

and represents a redox mechanism of the process. The role of the surface hydroxyl groups (V–OH) is to ensure the necessary amount of protons for the initial formation of the ammonium ion. Part of the water released during the reaction is adsorbed dissociatively and restores the protons and the hydroxyl groups. Hence, the unique catalytic properties of this type of catalysts in SCR of NO_2 by ammonia is due to the joint effect of V–OH groups containing mobile protons and V=O groups in which vanadium easily changes its valence. Such a conjunction of the acidic and oxidizing function in the V–OH and V=O groups of an isolated hydroxo–vanadyl species is proposed by Bond (49) in the catalytic oxidation of *o*-xylene on vanadia/titania catalyst.

The formation of N_2O as a nonselective product of NO_2 reduction by NH_3 could be related to the reaction of NO_3^- species coordinated to the Lewis acid sites of the support ($(\beta)Ti^{4+}$ ions) with NH_4^+ species located in their vicinity, the oxidation state of titanium remaining unchanged (26, 27):



$$\overset{\mathrm{ONO_2\cdot\ \cdot\ \cdot NH_4^+}}{-\mathrm{Ti}^{4+}} \text{——} \mathrm{O}^{2-} \xrightarrow{T} -\mathrm{Ti}^{4+} \text{——} \mathrm{O}^{2-} + N_2O + 2H_2O. \qquad [8]$$

The absence in the support of bonds reactive towards redox processes is the reason for the decomposition of the $NH_4^+NO_3^-$-like species in a way different from that in the case of the active phase.

CONCLUSIONS

The results of the present study show that the active sites for the SCR of NO_2 by NH_3 on vanadia–titania catalysts are: (i) the V^{5+}=O groups on which chemisorption of NO_2 proceeds; this is a redox reaction which leads to the formation of V^{4+} and NO_3^- species with a more symmetrical structure coordinated to vanadium (IV); and (ii) the V^{5+}–OH groups which interact with NO_2, as a result nitrates and water molecules are formed; the latter give rise to a strong Brønsted acidity and favor ammonia adsorption as NH_4^+ species. The NH_3 coordinated to the Lewis acid sites is displaced by NO_2 which is adsorbed more tightly than ammonia.

An essential role for the SCR occurrence is played by the delocalized protons found on the sample surface. The presence of the mobil protons stabilizes the surface nitrate with enhanced symmetry, coordinated to the V^{4+}-ion. On the other hand the adsorption of NO_2 causes localization of the mobile protons due to the inducing effect of the nitrates formed, as a result OH groups with a more pronounced basicity appear, which favors their interaction with NO_2.

The prevailing species appearing after a contact of an NO_2 precovered sample with NH_3 is the nitrate with a more symmetrical structure which is coordinated to the vanadium ion. The same species is predominant when the reagent are added in an opposite order. This nitrate is identified as the active species in the SCR of NO_2 by NH_3. It can interact with neighboring NH_4^+ ions yielding water and nitrogen due to the mobility of the π-electron pair of the V^{5+}=O double bond. This reaction may be presented as passing through $NH_4^+NO_2^-$ intermediate species, while the $NH_4^+NO_3^-$ species located on the support decompose directly to N_2O and water.

REFERENCES

1. Bosh, H., and Janssen, F., *Catal. Today* **2,** 369 (1988).
2. Inomata, M., Myamoto, A., and Murakami, Y., *J. Catal.* **62,** 140 (1980).
3. Myamoto, A., Kobayashi, K., Inomata, M., and Murakami, Y., *J. Phys. Chem.* **86,** 2945 (1982).
4. Inomata, M., Myamoto, A., and Murakami, Y., *J. Phys. Chem.* **85,** 2372 (1981).
5. Inomata, M., Mori, K., Myamoto, A., Ui, T., and Murakami, Y., *J. Phys. Chem.* **87,** 754 (1983).
6. Janssen, F., van den Kerkhof, F., Bosh, H., and Ross, J., *J. Phys. Chem.* **91,** 5921 (1987).
7. Janssen, F., van den Kerkhof, F., Bosh, H., and Ross, J., *J. Phys. Chem.* **91,** 6633 (1987).
8. Ramis, G., Busca, G., Lorenzelli, V., and Forzatti, P., *Appl. Catal.* **64,** 259 (1990).
9. Busca, G., Centi, G., Marchetti, L., and Trifirò, F., *Langmuir* **2,** 568 (1986).
10. Gasior, M., Haber, J., Machej, T., and Czeppe, T., *J. Mol. Catal.* **43,** 359 (1988).
11. Topsøe, N.-Y., and Topsøe, H., *Catal. Today* **9,** 77 (1991).
12. Topsøe, N.-Y., *J. Catal.* **128,** 499 (1991).
13. Srnak, T. Z., Dumesic, J. A., Clausen, B. S., Tornqvist, E., and Topsøe, N.-Y., *J. Catal.*, **135,** 246 (1992).
14. Rajadhyaksha, R., Hausinger, G., Zeilinger, H., Ramstetter, A., Schmelz, H., and Knözinger, H., *Appl. Catal.* **51,** 67 (1989).
15. Rajadhyaksha, R., and Knözinger, H., *Appl. Catal.* **51,** 81 (1989).
16. Busca, G., *Langmuir* **2,** 577 (1986).
17. Takagi, M., Kawai, T., Soma, M., Onishi, T., and Tamaru, K., *J. Phys. Chem.* **80,** 430 (1976).
18. Takagi, M., Kawai, T., Soma, M., Onishi, T., and Tamaru, K., *J. Catal.* **50,** 441 (1977).
19. Takagi-Kawai, M., Soma, M., Onishi, T., and Tamaru, K., *Can. J. Chem.* **58,** 2132 (1980).
20. Odriozola, J. A., Heinmann, H., Somorjai, G. A., Garcia de la Banda, J. F., and Pereira, P., *J. Catal.* **119,** 71 (1989).
21. Dines, T. J., Rochester, C. H., and Ward, A. M., *J. Chem. Soc. Faraday Trans.* **87,** 1473 (1991).
22. Dines, T. J., Rochester, C. H., and Ward, A. M., *J. Chem. Soc. Faraday Trans.* **87,** 1617 (1991).
23. Wu, S. C., and Nobe, K., *Ind. Eng. Chem. Prod. Res. Dev.* **16,** 137 (1977).
24. Ramis, G., Busca, G., Lorenzelli, V., and Forzatti, P., *Appl. Catal.* **64,** 243 (1990).
25. Dines, T. J., Rochester, C. H., and Ward, A. M., *J. Chem. Soc. Faraday Trans.* **87,** 643 (1991).
26. Bushev, V., Hadjiivanov, K., Kantcheva, M., and Klissurski, D., *Z. Phys. Chem.* **173,** 217 (1991).
27. Hadjiivanov, K., Bushev, V., Kantcheva, M., and Klissurski, D., *Langmuir*, in press.
28. Kantcheva, M., Hadjiivanov, K., and Klissurski, D., *J. Catal.* **134,** 299 (1992).

29. Bond, G. C., Zurita, J. P., Flamerz, S., Gellings, P. J., Bosch, H., van Ommen, J. G., and Kip, B. J., *Appl. Catal.* **22,** 361 (1986).
30. Hadjiivanov, K., Klissurski, D., and Davydov, A., *J. Catal.* **116,** 498 (1989).
31. Nag, N. K., and Massoth, F. E., *J. Catal.* **124,** 127 (1990).
32. Busca, G., Marchetti, L., Centi, G., and Trifirò, F., *J. Chem. Soc. Faraday Trans. I* **81,** 1003 (1985).
33. Hadjiivanov, K., Davydov, A., Klissurski, D., *Kinet. Katal.* **29,** 161 (1988). [In Russian]
34. Davydov, A. A., "IR Spectroscopy of Adsorbed Species on the Surface of the Transition Metal Oxides." Wiley, New York, 1990.
35. Busca, G., Saussey, H., Saur, O., Lavalley, J. C., Lorenzelli, V., *Appl. Catal.* **14,** 245 (1985).
36. Hadjiivanov, K., Busca, G., Klissurski, D., and Lorenzelli, V., *J. Chem. Soc. Faraday Trans.* **87,** 174 (1991).
37. Davydov, A. A., and Budneva, A. A., *Theor. Eksper. Khim.* **19,** 240 (1983).
38. Tsyganenko, A. A., Pozdnyakov, D. V., and Filimonov, V. N., *J. Mol. Struct.* **29,** 2991 (1975).
39. Davydov, A. A., Budneva, A. A., and Maksimov, N. G., *React. Kinet. Catal. Lett.* **20,** 93 (1982).
40. Kantcheva, M. K., Bushev, V. Ph., and Hadjiivanov, K. I., *J. Chem. Soc. Faraday Trans.* **88,** 3087 (1992).
41. Nakamoto, K., "IR Spectra of Inorganic and Coordination Compounds." Mir, Moscow, 1966.
42. Pozdnyakov, D. V., and Filimonov, V. N., *Kinet. Katal.* **14,** 760 (1973). [In Russian]
43. Kantcheva, M., Davydov, A., and Hadjiivanov, K., *J. Mol. Catal.*, **81** (1993).
44. Kung, M. C., and Kung, H. H., *Catal. Rev.-Sci. Eng.* **27,** 425 (1985).
45. Kudo, A., Kazunari, D., Maruya, Ken-ichi, and Onishi, T., *J. Catal.* **135,** 300 (1992).
46. Bosch, H., Janssen, F. J. J. G., van der Kerkhof, F. M. G., Oldenziel, J., van Ommen, J. G., and Ross, J. R. H., *Appl. Catal.* **25,** 239 (1986).
47. Ismagilov, Z. R., and Kerzhentsev, M. A., *Catal. Rev.-Sci. Eng.* **32,** 51 (1990).
48. Matsuda, S., and Kato, A., *Appl. Catal.* **8,** 149 (1983).
49. Bond, G. C., *J. Catal.* **116,** 531 (1989).