

On the role of oxygen in the reaction of NO reduction by NH_3 over monolayer $\text{V}_2\text{O}_5\text{-TiO}_2$ catalyst

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Abstract

The selective catalytic reduction of NO by NH_3 over monolayer $\text{V}_2\text{O}_5\text{-TiO}_2$ catalyst has been investigated by transient response technique and IR spectroscopy. Ammonia adsorption–desorption processes on the catalyst surface proceed with participation of both Brønsted and Lewis acid sites. Sharp ammonia desorption caused by vanadia oxidation was observed in the reaction of O_2 and $\text{NO} + \text{O}_2$ flows with ammonia treated catalyst. This phenomenon results in the increase of the reaction rate. The reasonable mechanism of oxygen effect on the reaction rate is proposed.

Keywords: SCR reaction; Vanadia monolayer; Transient response technique; IR spectroscopy

1. Introduction

Selective catalytic reduction (SCR) of nitrogen oxides by ammonia is one of the effective postcombustion techniques to remove nitric oxide from man-made sources. The most commonly used catalyst for this process is vanadium pentoxide supported on the anatase phase of titania. Monomeric vanadyl and polymeric vanadate surface species dispersed on the support surface are considered to be more preferable as active sites than the bulk (or crystalline) V_2O_5 [1,2]. It is also known that addition of oxygen into the feed gas at concentration up to 0.1–1.0% causes a substantial increase of NO conversion. For vanadium pentoxide this effect

was firstly demonstrated by Inomata et al. [3]. They concluded that NH_4^+ formed on dual sites involving $\text{V}^{5+}\text{-OH}$ and adjacent $\text{V}^{5+}\text{<O}$ which assists in the activation of NH_3 acts as the active ammonia species and reacts with NO from the gas phase. The rate of SCR reaction is proportional to the amount of $\text{V}^{5+}=\text{O}$ species in the catalysts. Oxygen, thus reoxidises the reduced V-OH species to $\text{V}^{5+}=\text{O}$. Recently Topsoe and co-workers [4,5] showed, however, that correlation between reaction rate and concentration of $\text{V}^{5+}=\text{O}$ species is revealed at low partial pressures of oxygen only, when surface reoxidation is slow. In line with this Janssen et al. [6] using isotopic methods found that ammonia does not react with O_2 or oxygen from any source during the reaction. Promoting effect of oxygen confirmed by numerous investigators [7–10] thus can be explained by faster reoxida-

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tion of reduced vanadia species in O_2 than in NO.

Despite impressive progress achieved in mechanistic studies the authors propose that namely Brønsted-bound ammonia is involved in the SCR reaction. For example, Schneider et al. [8] used DRIFT spectroscopy coupled with mass spectrometry under reaction condition to prove the participation of NH_4^+ in the reaction. As a consequence, proposed reaction mechanisms don't include ammonia adsorbed on the Lewis sites, although the latter being the $V^{5+}=O$ species also. According to data presented in Refs. [3,5], these species are involved in the activation of adsorbed ammonia and in reoxidation processes under the action of O_2 . In view of this situation we have used transient response technique in combination with IR spectroscopy to elucidate the mechanism of oxygen effect on SCR reaction.

2. Experimental

Catalyst used in study was prepared by a 'grafting' technique, as described in [11]. Titania of anatase modification with $S_{BET} = 88$ m^2/g used as the support was prepared by precipitation of $TiCl_4$ with ammonia with subsequent washing, drying and calcination at 773 K. TiO_2 was initially treated by $VOCl_3$ in the gaseous phase at 293 K. The excess of $VOCl_3$ was removed by heating in a He flow at 523 K. Then the surface was hydroxylated by moist air at 340 K for 2 h, physically adsorbed water was removed by heating in the He flow up to 410 K. To increase the vanadium coverage the above mentioned procedure was repeated. After three $VOCl_3$ supporting cycles vanadium weight loading was 3.16%, that corresponds to 4.2×10^{18} atom V/ m^2 or to 0.83 of monolayer (which is equal to 5.1×10^{18} V atoms/ m^2) coverage by vanadium species [12]. According to ^{51}V -NMR, XPS, and TEM data [12,13], two types of surface complexes with vanadium in the distorted tetrahedral environment of oxygen atoms

are formed, one of them containing an OH group in the coordination sphere.

The experimental setup to perform the transient response measurements consists of a gas-mixing system, a reactor and a quadrupole mass-spectrometer to analyse the reagents concentration in time. The gas mixtures of NO, NH_3 and O_2 in helium were prepared in stainless cylinders by conventional static partial pressures method. The gas flows of desired composition were made up of these mixtures and He by means of flow controllers. The flow rates of all the gasses passing the reactor were kept constant at 2 ml/s. Gas flows were replaced stepwise with four-port pneumo-operated valve (operation time is 0.1 s). Catalyst sample was loaded into the tubular reactor ($l = 150$ mm, ID 3 mm) made of inert with respect to the reagents Be-ceramics. The gases exiting the reactor were continuously analysed by a quadrupole mass spectrometer 'SENSORLAB 200 D' coupled with an IBM AT personal computer for data acquisition and processing. Resolution time of the kinetic setup determined by diffusion smearing of response curve in the blank experiment was about 0.5 s. The mass spectrometric data were quantitatively analyzed using the fragmentation patterns determined experimentally from calibration gases. The concentrations of H_2O , N_2 , NO, O_2 and N_2O were determined from the intensities of mother peaks at m/e 18, 28, 30, 32 and 44, respectively. The concentration of N_2O was negligibly small (less than several ppm). Water concentration was determined by comparison with the intensity of $m/e = 18$ peak in the He flow saturated by water vapour at controlled temperature. The accuracy of such calibration procedure did not exceed 30%. Measurement of NH_3 concentration using the intensity of mother peak with $m/e = 17$ or its fragment at $m/e = 16$ was not so easy due to overlapping of these peaks with the fragments from water and oxygen with the same masses. So, we subtracted from intensity at $m/e = 16$ and 17 the known intensities of fragments from O_2 and H_2O . The contribution

of both NO and H₂O fragments at $m/e = 16$ was negligible (less than 5%). Then we compared the obtained value of intensities ratio at $m/e = 16$ and 17 with that for pure NH₃. If these two values coincided, we accepted these relaxation curves as a correct.

Three types of the transient experiments have been carried out: (1) ammonia adsorption (0.25% or 0.75% NH₃ + He for balance) and desorption in He in the temperature range from 300 to 623 K, (2) interaction of different gas mixtures (3.6% O₂ + He, 0.25% NO + He and 1.2% O₂ + 0.25% NO + He) with adsorbed ammonia, (3) changing of the feed gas: 0.25% NH₃ + 0.25% NO + He to a feed gas containing oxygen: 0.25% NH₃ + 0.25% NO + 1.2% O₂ + He. Experiments (1) and (2) were carried out with 0.31 g and experiments (3) with 0.152 g of the catalyst. Prior to every experiment the catalyst sample was oxidised at 623 K for 15 min in 3.6% O₂ + He flow and then cooled up to the operative temperature.

IRS studies were carried out by Specord M80 spectrometer with movable high vacuum quartz cell. This cell is a T-type tube. One section of the cell is used for sample heating, second one for registration of IR spectra. The third section consists of a stopcock to seal it off from air and had a ground joint to connect (disconnect) the cell to (from) the vacuum system. Catalyst samples for IRS study were pelletised ($m = 0.024$ – 0.03 g). Catalyst pellet attached to the quartz holder can be transferred fast from the measurement section ($T = 293$ K) to hot section ($T = 623$ K) and back by tilting of the cell preliminary disconnected from the vacuum system. Special experiments showed that the sample is heated (cooled) up to the temperature of hot (cold) section for 50–60 s. For comparison, in standard static cells with fixed position of the sample the maximal heating rate does not exceed 50 K/min. Before adsorption the pellet was oxidised at 623 K (200 Torr of O₂) for 1 h and then outgassed at the same temperature for 1 h. Ammonia was adsorbed at 293 K and 10 Torr pressure for 15 min. Then the samples

were evacuated at different temperatures (293, 423, 523 and 623 K) for 1 h. In the experiments imitating the fast oxidation the sample outgassed at 623 K was cooled up to 293 K, then the ammonia (10 Torr) was adsorbed again and evacuated at room temperature for 1 h. Following oxygen admission (50 Torr) on the reduced by this way catalyst was performed at 293 K. Then the cell was disconnected from the vacuum system and the holder with pellet was transferred into the preheated at 623 K section and held there for 2 min. Taking into account the time for the sample heating and transferring we believe that the catalyst oxidation at 623 K proceeded for about 1 min.

3. Results

3.1. Ammonia adsorption

As seen on Fig. 1, the ammonia adsorption on oxidised catalyst surface proceeds very fast. The quantity of adsorbed ammonia is determined mostly by the temperature of its adsorption. As the temperature rises, then the quantity of ammonia adsorbed decreases, like in Ref. [2]. Maximal possible quantity of ammonia is adsorbed at room temperature and corresponds to about monolayer surface coverage if we accept

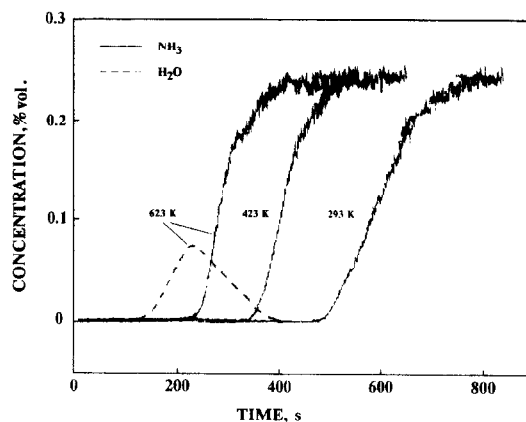


Fig. 1. Concentrations of NH₃ and H₂O in time at different temperatures of ammonia (0.25% NH₃ + He) adsorption on oxidized catalyst.

the ratio $\text{NH}_3:\text{V} = 1$. At 623 K this value is about 0.35–0.4 of monolayer, which is similar to that observed in Ref. [6]. When 0.25% $\text{NH}_3 + \text{He}$ flow was stepwise changed by He one some of reversibly adsorbed ammonia was desorbed.

Ammonia adsorption is accompanied by water evolution into the gas phase. As the water concentration passes the maximum, then the ammonia appears in the gas phase. One can suppose the competitive adsorption of water and ammonia on the same sites, ammonia being more strongly bound with these sites. The quantity of the water desorbed at 623 K is equivalent to about 0.1 of monolayer surface coverage, 4 times less than total amount of adsorbed ammonia. This means, that only part of ammonia is irreversibly (chemically) bonded with the surface. Another part of NH_3 is, thus, reversibly adsorbed. At lower temperature of adsorption not all the water formed desorbs into the gas phase. Water molecules seem to be coordinated on vanadia tetrahedra, thus completing their oxygen environment up to the octahedral one [13]. This water is bonded strong enough and can be removed from the surface at elevated temperatures only.

Similar to the data obtained earlier for other monolayer vanadia–titania catalysts (e.g., Refs. [3–5,8,14]), up to four different forms of adsorbed ammonia were identified on the oxidised surface of the sample under study. In the temperature interval from 293 to 623 K we observed by IRS (Fig. 2): (a) NH_4^+ ions that are stable on the surface up to 473–523 K (absorption bands at 1430, 1450 and 1670 cm^{-1}), (b) weak donor-acceptor Lewis-bound (or Brønsted-bound) complexes that were observed

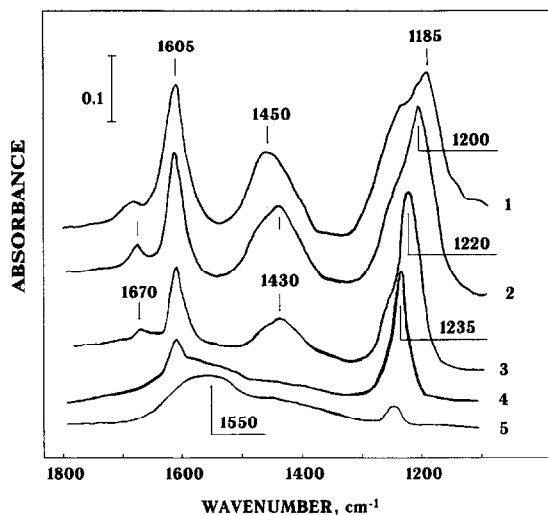


Fig. 2. IR spectra of ammonia adsorbed at 293 K on the oxidized (200 Torr of O_2) at 623 K for 1 h catalyst (1) and then evacuated for 1 h at different temperatures (K): (2) 293, (3) 423, (4) 523, and (5) 623.

up to 423 K (1200–1180 cm^{-1}), (c) strong Lewis-bound complexes existing up to 573 K (1235 cm^{-1}) and (d) the most stable amide species (1550 cm^{-1}). The first three forms were reversibly adsorbed, because they disappeared gradually as the sample was evacuated at elevated temperature. Thus, our catalyst reveals the typical properties with respect to the ammonia adsorption.

3.2. Reaction of NO with ammonia treated catalyst

Chemisorbed, or strongly bound, ammonia desorbs neither in He flow nor during temperature programmed desorption. It can be removed from the surface only by the reaction with NO to produce N_2 , H_2O and traces of N_2O . We have calculated the quantity of NO consumed and that of N_2 formed at 623 K in the following

Table 1
Integral amounts of the components of reaction mixture in different experiments

Type of experiment	NH_3 adsorbed (molecules/g)	N_2 formed (molecules/g)	NO consumed (molecules/g)	NH_3 desorbed (molecules/g)
$\text{NH}_3/\text{He}-\text{NO}/\text{He}$	12.3×10^{19}	3.6×10^{19}	3.9×10^{19}	8.7×10^{19}
$\text{NH}_3/\text{He}-\text{He}-\text{NO}/\text{He}$	12.3×10^{19}	24.2×10^{18}	25.2×10^{18}	6.5×10^{19} (in He flow) + 3.2×10^{19} (in NO/He)
$\text{NH}_3/\text{He}-\text{O}_2/\text{He}-\text{NO}/\text{He}$	12.3×10^{19}	22.6×10^{18}	25.2×10^{18}	6.5×10^{19} (in He + O_2 flow) + 3.2×10^{19} (in NO/He)

experiments: (1) after the stepwise replacing of $\text{NH}_3 + \text{He}$ flow by $\text{NO} + \text{He}$ and (2) after admission of $\text{NO} + \text{He}$ flow on the surface treated by ammonia, like in (1), with intermediate blowing by He (or $\text{O}_2 + \text{He}$) flow for 15 min to remove some reversibly adsorbed ammonia. These results are listed in Table 1. It is seen, that independently on the quantity of ammonia adsorbed, the quantity of NO consumed and that of N_2 formed coincide. This means, that into N_2 molecule one nitrogen atom incorporates from NH_3 and another one from NO . The same conclusion was made in [6]. It is also evident, that the quantity of N_2 formed and that of ammonia desorbed does not depend on the oxygen presence in the blowing flow.

The same types of experiments were carried out at 300 and 423 K. Unlike the high temperature experiments, after stepwise replacing of $\text{NH}_3 + \text{He}$ flow by $\text{NO} + \text{He}$ none of reaction products were observed in the gas phase at 300 K and only traces at 423 K (Fig. 3). Ammonia adsorption at 423 K with further blowing in He during 15 min resulted in the desorption of some ammonia and water into the gas phase. Only after these reagents were partly desorbed, the reaction products (N_2 and water) were observed in $\text{NO} + \text{He}$ flow. This allows us to hypothesize, that two neighbouring vanadia

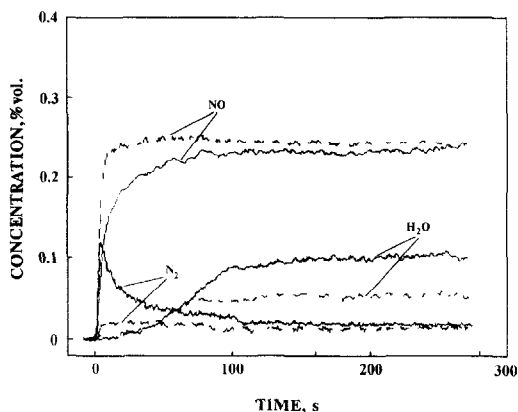


Fig. 3. Concentrations of N_2 , NO and H_2O in time at $T = 423$ K after admission of 0.25% $\text{NO} + \text{He}$ flow on the catalyst pretreated with 0.25% NH_3/He for 15 min at $T = 423$ K (dotted lines) and with intermediate blowing by He for 15 min (solid lines).

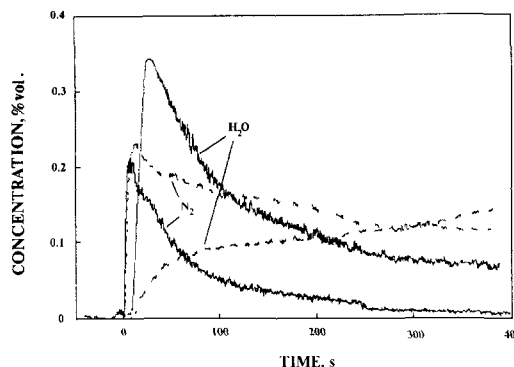


Fig. 4. Concentrations of N_2 and H_2O in time at 623 K after admission of 0.25% $\text{NO} + \text{He}$ (solid lines) and 0.25% $\text{NO} + 1.2\%$ $\text{O}_2 + \text{He}$ (dotted lines) flows on the catalyst pretreated with 0.75% $\text{NH}_3 + \text{He}$ flow for 15 min at the same temperature.

species are necessary for reaction to proceed: the first site adsorbs NH_3 , the second one is to be available for NO molecule. Ammonia or water, thus, can block these sites and inhibit NO activation and subsequent reaction.

3.3. Reaction of $\text{NO} + \text{O}_2$ with ammonia treated catalyst

Let us compare the shape of relaxation curves of the reaction products monitored at 623 K in the $\text{O}_2 + \text{NO} + \text{He}$ flow and $\text{NO} + \text{He}$ one without oxygen (Fig. 4). The relaxation curve for N_2 is characterised by steep rising (practically stepwise) at the initial moment. This means that the reaction rate is very high. It is significant that the initial reaction rates in both cases are practically the same. The relaxation curves of N_2 formation are similar and pass the maximum. In the absence of oxygen concentration of N_2 dropped very fast, in step with ammonia desorption, so that NO has appeared in the gas phase in 20 s, but substantially earlier than complete ammonia desorption. In the presence of O_2 the concentration of N_2 falls down much slower than NH_3 desorption so that the complete conversion of NO was observed over prolonged (ca. 9 min) period. As soon as all the ammonia was desorbed, then N_2 concentration fell down to zero very fast and NO appeared.

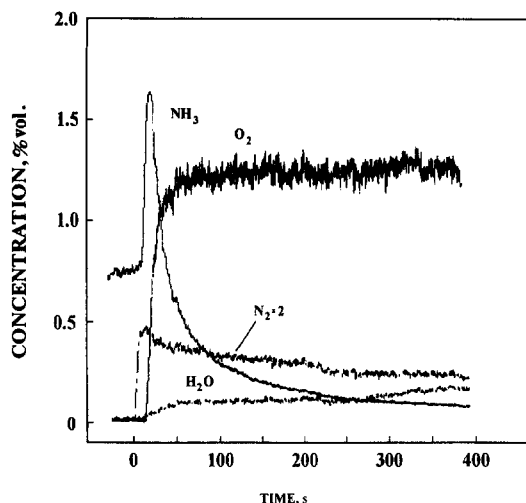


Fig. 5. Concentration of the reagents in time after admission of $\text{NO} + \text{O}_2 + \text{He}$ flow on the catalyst pretreated with ammonia. The reaction conditions are the same as in Fig. 4.

Quite a different behaviour of H_2O relaxation curves also took place. In $\text{NO} + \text{He}$ flow H_2O concentration passes the sharp maximum while in $\text{NO} + \text{O}_2 + \text{He}$ one the water is not observed at the initial period, then its concentration increases monotonously.

The prolonged period of higher reaction rate in the presence of O_2 seems to be the evidence of the well-known fact of the reaction promotion by oxygen [3,7–10]. This effect can be explained by higher concentration (or faster regeneration) of active sites and is undoubtedly associated with redox processes. Indeed, at the initial period after admission of $\text{NO} + \text{O}_2 + \text{He}$ flow on the reduced catalyst the period of complete oxygen conversion was observed (Fig. 5). Time delay for oxygen depends on the temperature. At 623 K about 8.1×10^{19} oxygen atoms per g of catalyst reacted with the reduced sites. This value corresponds to 18% of surface vanadium atoms. As the temperature decreased, then the time delay decreased also, and at 423 K it disappeared completely.

It should be noted another interesting fact that was found in these experiments and, to our mind, never reported earlier. Complete oxygen consumption at the initial period was accompa-

nied with sharp ammonia desorption (Fig. 5). Then the slower process of desorption proceeds, so that ammonia relaxation curve passes the maximum. This effect can explain the different character of H_2O relaxation curves recorded in NO and $\text{NO} + \text{O}_2$ flows (Fig. 4). During fast ammonia desorption the water formed in the reaction can occupy vanadia species being cleared from NH_3 , due to competitive adsorption of NH_3 and H_2O on the oxidised catalyst surface (Fig. 1). In the absence of oxygen the vanadia species remain occupied with adsorbed ammonia. Therefore, water formed in the reaction of NO with adsorbed ammonia is to desorb into the gas phase.

3.4. Replacing of $\text{NO} + \text{NH}_3$ mixture by $\text{NO} + \text{NH}_3 + \text{O}_2$

Sharp ammonia desorption was observed also after replacing of the $\text{NO} + \text{NH}_3 + \text{He}$ flow by $\text{NO} + \text{NH}_3 + \text{O}_2 + \text{He}$ (Fig. 6). As for reaction of $\text{NO} + \text{O}_2 + \text{He}$ mixture with adsorbed ammonia, sharp NH_3 desorption was also observed and caused by oxidation of vanadia. Thus, at 623 K the quantity of oxygen reacted with the reduced active sites is about two times more (1.4×10^{20} atoms/g) compared with experiments shown in the Fig. 5. So, as the ammonia

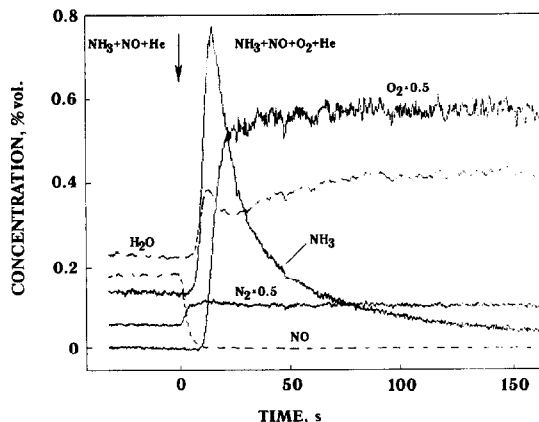


Fig. 6. Concentrations of reagents in time after stepwise replacing (noted by the arrow) of 0.25% $\text{NH}_3 + 0.25\%$ $\text{NO} + \text{He}$ flow to the 0.25% $\text{NH}_3 + 0.25\%$ $\text{NO} + 1.2\%$ $\text{O}_2 + \text{He}$ one at 623 K.

from the gas phase adsorbs and reacts permanently on the surface, then the additional quantity of oxygen is necessary for reoxidation of the active sites. As a consequence the two-fold increase of nitrogen concentration was observed in oxygen containing mixture. At 423 K we did not observe the oxidation of vanadium species (no time delay for oxygen), as well as sharp ammonia desorption. As a result, there was no substantial change in the reaction rate. Thus, the increase of catalyst activity in the presence of O_2 can be explained by the creation of new vacancies due to desorption of large amounts of NH_3 blocking the active sites. Therefore, studies of the reaction of O_2 at different temperatures with ammonia saturated catalyst were carried out.

3.5. Reaction of O_2 with ammonia treated catalyst.

After replacing $NH_3 + He$ mixture by the $O_2 + He$ one without NO none of reaction products were evolved into the gas phase. Similar observation was made by Janssen et al. [6]. Thus, at 623 K the integral quantity of N_2 and H_2O evolved into the gas phase does not exceed the value of 3.2×10^{18} molecule/g (about 0.5% of surface vanadia atoms). For comparison, the quantity of oxygen consumed is about 4.5×10^{19} atoms/g (10% of vanadia sites). At 523 K this value is about 6.5×10^{18} , and at 423 K less than 3×10^{17} . As in the reaction of $NO + O_2$ mixture with ammonia treated catalyst, at the temperatures higher than 523 K we observed the sharp ammonia desorption (Fig. 7). Quantity of ammonia desorbed in the initial period increases with the temperature and correlates quite well with the quantity of oxygen consumed.

One can suppose, that namely reversibly adsorbed ammonia was desorbed under the action of oxygen. Firstly, integral amounts of ammonia desorbed during 15 min in He and $O_2 + He$ flows are very close. Secondly, the integral amounts of the products formed in the reaction with NO were the same and did not depend on

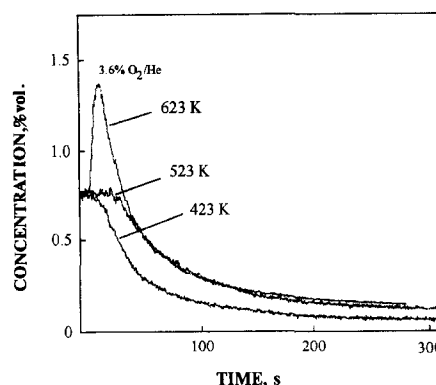


Fig. 7. Relaxation curves of ammonia desorption at different temperatures after stepwise replacing of 0.75% $NH_3 + He$ flow to the 3.6% $O_2 + He$ one.

the oxygen's presence in the gas flow (see Table 1).

To understand the possible mechanism of ammonia desorption in the presence of oxygen similar experiments were reproduced in the cell of an IR spectrometer. Firstly, the case of reduced surface with ammonia in the gas phase, like in the transient response experiments, was imitated. For this purpose reduced in ammonia catalyst outgassed at 623 K (Fig. 2, curve 5) was additionally treated with ammonia at room temperature. Like in Ref. [7], this procedure resulted in the increase of the intensity of the absorption bands at 1180 and 1200 cm^{-1} related to the most weakly bound forms of the

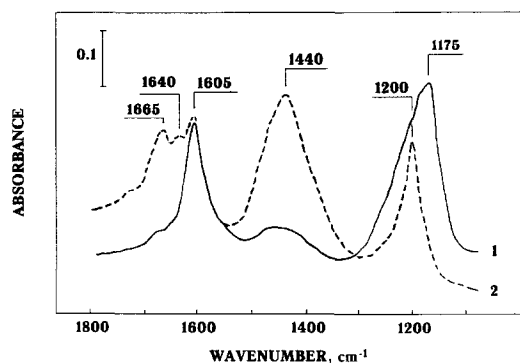


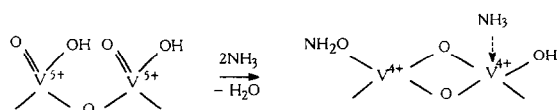
Fig. 8. IR spectra of adsorbed ammonia. The experiments were carried out successively. Spectrum 1: preliminary reduced catalyst treated with 10 Torr of NH_3 at 293 K with following evacuation for 1 h at the same temperature. Spectrum 2: following admission of O_2 (50 Torr) and heating (623 K, 2 min).

reversibly adsorbed ammonia (Fig. 8, spectrum 1). Spectrum recorded after the following treatment in O_2 in 2 min, as described in Section 2, is presented in Fig. 8 (spectrum 2). It is seen, that the intensity of the bands corresponding to the reversibly adsorbed ammonia decreases substantially, while those of NH_4^+ at 1440 cm^{-1} and water at 1640 cm^{-1} increase. If the catalyst was oxidised for half an hour, for example, these bands disappeared. Similar effect of increase of surface NH_4^+ concentration accompanied by decrease of that of coordinatively bonded NH_3 species in the presence of O_2 in the feed gas was observed by Topsoe et al. [5].

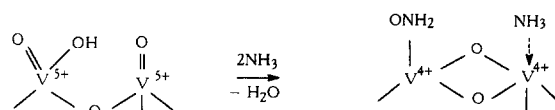
4. Discussion

Two types of vanadia tetrahedral species, that are capable to adsorb NH_3 , exist on the surface of monolayer catalyst. The first type without OH-groups serves as Lewis acid sites and the second one, that coordinates OH-groups, serves as Brønsted acid sites. At high vanadium coverage these species most probably form the extended surface structures (i.e., chains, islands) and can be located on the different cleavage planes of TiO_2 or interfacing. Taking into account that the ratio between these species depended on the prehistory of TiO_2 preparation and admixtures [13], then this assumption appears to be reasonable. So, two types of neighbouring vanadia sites active in redox processes can be considered: two neighbouring Brønsted acid sites (Scheme 1) and Brønsted and Lewis acid sites (Scheme 2).

The involvement of binuclear vanadium species in redox processes is supported by a number of authors. Firstly, upon ammonia adsorption at elevated temperatures $V=O$ groups



Scheme 1.

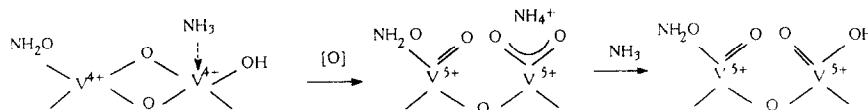


Scheme 2.

in polymeric species are reduced preferentially compared to monomeric ones [4,15]. Secondly, turnover frequencies of high-vanadia loading catalysts containing polyvanadate species mainly are significantly higher than those of low-vanadia loading catalysts with isolated vanadyls [9]. Binuclear vanadia species were also considered to be involved in SCR [3,5]. Our experiments showed clearly that the amount of water molecules evolved during ammonia adsorption is close to the amount of oxygen atoms consumed at further oxidation. The same stoichiometry (one oxygen atom removed per two vanadium atoms) was observed by Janssen et al. [6] during the catalyst reduction with ammonia. This means, that redox process in SCR proceeds via two-electron transfer. So, we suppose that reduction of vanadia included into the Brønsted acid site is to cause partial reduction of neighbouring vanadium (this can be either Lewis or Brønsted acid sites). So as the strength of the $H_3N \rightarrow V$ bond is determined by the oxidation state of vanadia, then one can suppose, that more weakly bound complexes of ammonia with V^{4+} are formed (weak donor-acceptor complexes at 1200 and 1180 cm^{-1}).

Vanadium oxidation should result in strengthening of the $H_3N \rightarrow V$ bond, that is inconsistent with the observed sharp ammonia desorption. We propose another reaction pathway to compensate the increase of ammonia bond strength after oxidation of vanadium (Scheme 3).

Oxidation of vanadium bonded with amide group can result in the formation of NH_4^+ ion on the neighbouring site provided the latter being the Brønsted acid site. NH_4^+ ions are unstable at elevated temperatures and decompose with NH_3 evolution into the gas phase.



Scheme 3.

Thus, oxidation of Brønsted-bound ammonia complex by O_2 provides the sharp ammonia desorption and regeneration of Brønsted acid sites. The latter can adsorb additional ammonia as well as activate NO molecule to produce reaction products. That is why in the presence of O_2 the reaction rate is higher compared with that with NO only. Reaction runs both in $NO + O_2$ and in $NO + O_2 + NH_3$ flows involve the additional oxygen consumption (18% and 31% of vanadia surface atoms, respectively) and more sharp NH_3 desorption compared with experiments on O_2 admission on adsorbed ammonia. In line with this, the integral quantity of ammonia desorbed increases.

It is obvious that after the desorption of weakly bound ammonia the vacant oxidised sites for water adsorption are formed. Indeed, we did not observe water in the gas phase after the admission of $NO + O_2 + He$ flow on the surface reduced by ammonia (Fig. 4). In the absence of oxygen in the feed gas the surface concentration of weakly bound ammonia is higher. Therefore, water formed in the reaction of NO with Brønsted-bound ammonia is to desorb into the gas phase (Fig. 4). In the case of reaction mixture admission into the reactor the complex character of the H_2O relaxation curve is determined by superposition of two main factors (Fig. 6). Firstly, fast ammonia desorption makes the catalyst surface available for water adsorption. In this case H_2O relaxation curve should look like that in $NO + O_2 + He$ flow (Fig. 5). On the other hand, the presence of NH_3 in the feed gas should result in the exclusion of adsorbed water due to stronger ammonia bounding with the vanadium species. As a result, we obtain the superposition of H_2O relaxation curves presented on Fig. 4 and Fig. 6.

According to Scheme 2 (neighbouring Brønsted and Lewis acid sites) NH_3 desorption

is impossible or should proceed very slowly, because NH_4^+ ion can not be formed. Nevertheless, we suppose, that water formed in the reaction can favour conversion of Lewis acid sites into the Brønsted ones and thus increase the number of active sites. This is supported by recent data presented in [5,7] pointing to the increase of $V-OH$ species concentration in the oxygen containing feed gas. Water effect on the reaction rate is presently being under study.

5. Conclusion

Transient response technique and IR spectroscopy were used to study the nature of oxygen promoting effect in the reaction of NO reduction with NH_3 over monolayer $V_2O_5-TiO_2$ catalyst. Like in previous studies [3–5,8,14], both Brønsted and Lewis acid sites take part in the ammonia adsorption. It was found, that the reaction rate of NO with adsorbed ammonia is very high and does not depend on the oxygen presence in the reaction mixture. Thus, we supposed that promoting effect of oxygen can be caused, for example, by the change of concentration of active sites available for ammonia adsorption or NO activation.

In the reaction of oxygen-containing flow with adsorbed ammonia a sharp NH_3 desorption caused by vanadia oxidation proceeds. Both transient kinetics and IRS studies showed that upon vanadia oxidation more weakly bound (or reversibly adsorbed) ammonia complexes convert into Brønsted-bound NH_4^+ ions being unstable in the reaction conditions. Regenerated by this way oxidised active sites can adsorb additional ammonia as well as activate NO molecule thus resulting in the increase of reaction rate. However, water formed in the reaction

can occupy the sites freed from ammonia and seems to be capable to convert Lewis sites into the Brønsted ones.

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