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AES and TDS Study of the Adsorption of NH_3 and NO On V_2O_5 and TiO_2 Surfaces: Mechanistic Implications

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The adsorption of NH_3 and NO on pure V_2O_5 and on TiO_2 samples at pressures (ca. 25 Torr) and temperatures (room temperature to 675 K) close to those used in industry with V_2O_5/TiO_2 catalysts to carry out the NO reduction with NH_3 has been studied by Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS), using a UHV chamber equipped with a built-in high pressure cell (up to 1 atm). NH_3 adsorption takes place over the whole range of temperatures studied on TiO_2 and on V_2O_5 as well as on reduced V_2O_5 surfaces. NO adsorption occurs only on TiO_2 and on reduced V_2O_5 but not on oxidized V_2O_5 surfaces. It is shown that NH_3 reduces the vanadium pentoxide surface resulting in the production of N_2O. The presence of N_2O, NO, and O_2 results in the reoxidation of the vanadium surface with the nitrogen oxides being converted into N_2. No evidence for the NO + NH_3 reaction has been obtained on the TiO_2 surface. However, NO adsorption on TiO_2 appears to be a main factor for the catalyst effectiveness in V_2O_5/TiO_2 samples since it may provide a source of NO at the interface of vanadia islands on TiO_2 in the actual catalyst. Finally, from TDS and AES data a reaction mechanism is suggested that may explain the reduction of NO to N_2 as well as the side reaction responsible for the production of N_2O.

INTRODUCTION

Interest in air quality and emission control has resulted in considerable research dealing with the selective reduction of nitrogen oxides. An extensive review of this subject has recently been published (*1*). Among the catalysts tested, vanadium oxides supported on TiO_2 seem to be preferred for catalyzing the $NO_x + NH_3 + O_2$ reaction. Although NO_x can be reduced to N_2 with the use of reducing gases such as CH_4, H_2, and CO, ammonia is preferred since the other gases are readily consumed by reaction with O_2. The characterization of the supported vanadium species by different techniques, such as extended X-ray absorption fine structure (EXAFS) (*2, 3*), high resolution electron microscopy (HREM) (*4*), X-ray photoelectron spectroscopy (XPS) (*5–8, 34*), laser Raman spectroscopy (*9, 10*), and electron spin resonance (ESR) (*11, 13*), has been reported. Kinetic studies directed toward the elucidation of the reaction mechanism (*14, 27*), in some cases supported by theoretical approaches (*28*), have been undertaken and the preparation of titania-supported V_2O_5 with improved redox properties (*29*) has been described.

Although surface sensitive electron spectroscopies are excellent tools for studying the catalyst surfaces, little has been reported on the use of surface science techniques for studying the adsorption of NH_3 and NO on V_2O_5 and on V_2O_5/TiO_2 surfaces. Only Tsai *et al.* (*30, 31*) have reported an AES study of the surface of supported Group VIII metals for the NH_3 + NO reaction after SO_2 poisoning. Most pa-

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pers assume that reduction of supported V_2O_5 occurs during the NO + NH_3 reaction, but the mechanism through which the reduction takes place has not been verified.

The aim of the present work was to study the adsorption of NO and NH_3 on pure V_2O_5 and on TiO_2 by means of Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS). On the basis of our findings, elementary steps are proposed for the NO + NH_3 + O_2 reaction on V_2O_5 and V_2O_5/TiO_2. As will be shown later, NO cannot adsorb on fully oxidized V_2O_5 surfaces. The experimental techniques utilized in this work allowed us to demonstrate the reduction of the vanadium oxide catalyst in the presence of NH_3, which in turn is oxidized to N_2O. In addition, the role of oxygen in the reactant mixture has been established mainly as a participant in the NO and NH_3 competition for the reduced surface sites improving the catalyst life.

EXPERIMENTAL

In this study a powdered vanadium oxide catalysts (V_2O_5) from Aldrich Chemical Co. (99.999% pure) was employed. High purity gases, NH_3, NO, and O_2, were obtained from Matheson and used without further purification. Pure TiO_2 (99%) as anatase was supplied by Südchemie.

The apparatus used for the AES and TDS studies has been previously described (*32*). It consists of a stainless-steel bell jar, evacuated to pressures below 5×10^{-9} Torr by a Varian VHS6 diffusion pump, backed by a rotary pump. A built-in high pressure cell isolates the sample from the UHV environment accounting for sample treatments under different atmospheres up to 1 atm (*32*).

The sample holder is part of the high pressure cell. When it is open, the cell exposes the sample to ultrahigh vacuum (UHV) for AES and/or TDS analysis, and when it is closed, it becomes a part of the reactor used for sample treatments. The sample is pressed against a gold coated stainless-steel grid, and it is in intimate contact with a chromel–alumel thermocouple. The grid is held against a gold foil by two lateral flaps. By passing current through the foil, the sample can be heated to the desired temperature.

The Auger electrons were detected by a double-pass cylindrical mirror analyzer (CMA) equipped with a coaxial electron gun (Physical electronics 15-255G). A 6 eV peak-to-peak modulation and a response time of 20 ms were selected. The electron gun was always operated at 1 kV and 0.8 mA at normal incidence.

For TDS studies, the adsorbate was introduced into the high pressure cell at pressures close to those usually achieved under actual industrial conditions (ca. 25 Torr), allowing it to circulate at the temperature chosen (room temperature to 675 K) for 15 min. After that, the sample was cooled in the adsorbate atmosphere and outgassed in the UHV chamber, at the adsorption temperature, until the system base pressure was achieved. The sample was then heated under UHV conditions at a constant heating rate (15 K s^{-1}). A mass spectrometer (UTI 100C) monitored the gas evolution of a given mass, and a plot of the signal intensity versus temperature was generated on an XY recorder (Hewlett–Packard 7044B). Alternatively, the sample was exposed to the reactant gases in a UHV environment in which case the gases were introduced into the UHV chamber through a leak valve at pressures below 1.10^{-6} Torr.

RESULTS

(*i*) *Studies on* V_2O_5

The adsorption of NH_3 and NO on V_2O_5 has been studied by AES and TDS. The presence of carbon contamination on V_2O_5 has been described as responsible for the reactivity of thin films of V_2O_5 on gold foils (*33*). The formation of CO and/or CO_2 that desorbs at ca. 675 K might be responsible for the generation of oxygen vacancies on the V_2O_5 surface leaving exposed V^{4+} species that can then react with the adsorbates

(*3*, *33*). To avoid any interference from coadsorbed species we carried out an oxidation treatment that would leave a clean V_2O_5 surface, before adsorbing NH_3 and/or NO. Figure 1 shows the AES spectrum of the vanadia sample after oxidizing it under 40 Torr of O_2 at 675 K for 15 min followed by heating at the same temperature for 10 min in the UHV chamber; this results in a clean V_2O_5 sample characterized by the presence of the $V(L_3M_{23}M_{23})$ and $V(L_3M_{23}M_{45})$ transitions at 430 and 469 eV, respectively, and at 510 eV for the O(*KLL*) transition.

Unfortunately the oxidation state of the vanadium species is not unequivocally obtainable by AES. Even at low peak-to-peak modulation (2 eV), the intensity ratio between the O(*KLL*) and $V(L_3M_{23}M_{23})$ lines is the same, 2.4, for the oxidized and reduced vanadia samples. Various authors (*33*, *35*–*37*) have drawn conclusions from the relative intensity of the lines but they used oxidized vanadia films. In our study bulk vanadia was used and to observe a change in the AES spectrum, much of the sample would have had to be reduced rather than just the surface.

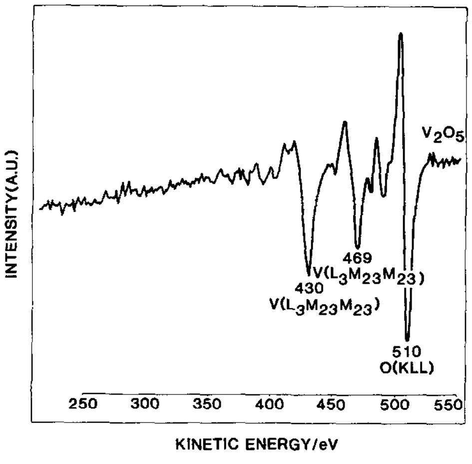

FIG. 1. AES spectrum of a clean oxidized V_2O_5 sample. Peak-to-peak modulation 2 eV.

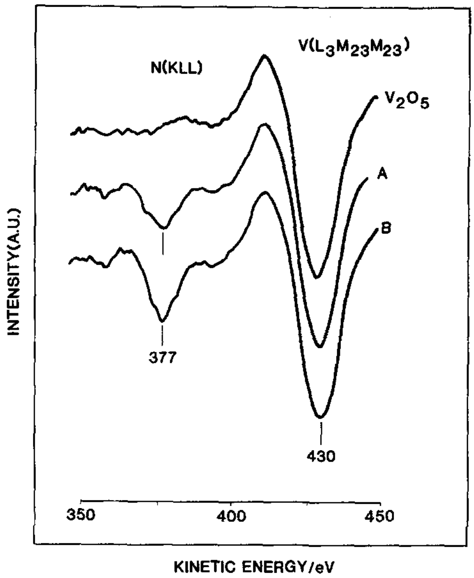

FIG. 2. AES spectra for the adsorption of NH_3 at RT (A) on a clean oxidized V_2O_5 sample, (B) on a NH_3-reduced V_2O_5 sample, compared to the AES spectrum for clean oxidized V_2O_5 (Fig. 1).

Both the adsorption of NH_3 and of NO have been carried out as a function of temperature. Figure 2, curve A, displays the AES spectrum of V_2O_5 after adsorption of 25 Torr of NH_3 at room temperature. The presence of a new peak at 377 eV, with respect to the pure V_2O_5 spectrum, is now noticeable; this peak can be assigned to the N(*KLL*) transition indicating that NH_3 can be adsorbed at room temperature. After heating of the sample to 775 K the nitrogen peak disappears. On this presumably reduced vanadium surface, the adsorption of NH_3 also occurs (Fig. 2 curve B). No conclusions can be drawn about the nature of the resulting ammonia species on the basis of the AES spectrum.

Evidence for the reduction of the V_2O_5 surface can be obtained from TDS experiments. One of the possible mechanisms for the NH_3 + NO reaction includes a redox process, which implies the oxidation of NH_3 to N_2O using oxygen from the V_2O_5 lattice. To test the possibility of such a mechanism several experiments were performed in which, after adsorbing 25 Torr of NH_3 at room temperature, amu's 44 (N_2O^+) and 30 (NO^+) were monitored and the signal corresponding to amu 15 (NH^+) was analyzed as well. In both cases, similar TDS profiles were obtained showing peaks at 643 K (Fig. 3), indicating that V_2O_5 is reduced by NH_3 which in turn is oxidized to N_2O.

The adsorption of NH_3 on V_2O_5 has also been studied at 575 and 675 K. AES spectra of the interaction under 25 Torr of NH_3 at 575 and 675 K are shown in Fig. 4; the experimental procedure was as follows: after oxidizing the V_2O_5 sample, 25 Torr of NH_3 was introduced in the high pressure cell, heated to the reaction temperature for 15 min, and then cooled to room temperature in such an atmosphere and outgassed in the UHV chamber until the chamber base pressure was reached. After this treatment a nitrogen peak appears in the AES spectrum that cannot be eliminated by heating at the reaction temperature in UHV, as shown in Fig. 4; only by heating at 775 K under vacuum does the nitrogen peak disappear. However, this nitrogen peak, which cannot be eliminated by heating in UHV at the reaction temperatures, readily disappears by heating in O_2 at 675 K.

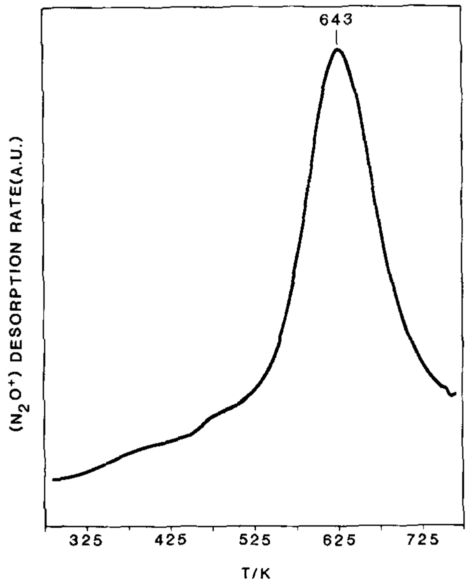

FIG. 3. TDS spectrum for the desorption of N_2O after adsorbing 25 Torr of NH_3 at RT on a clean oxidized V_2O_5 sample.

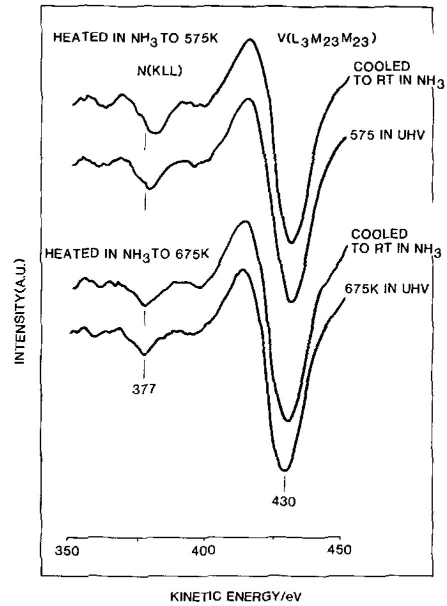

FIG. 4. AES spectra for the adsorption of NH_3 on a clean oxidized V_2O_5 samples at 575 and 675 K.

Figure 5 shows a plot of the TDS profile for the desorption of NH_3 from the V_2O_5 sample previously heated to 675 K under 25 Torr of NH_3. One peak is obtained, giving the same desorption energy as that obtained after ammonia adsorption at room

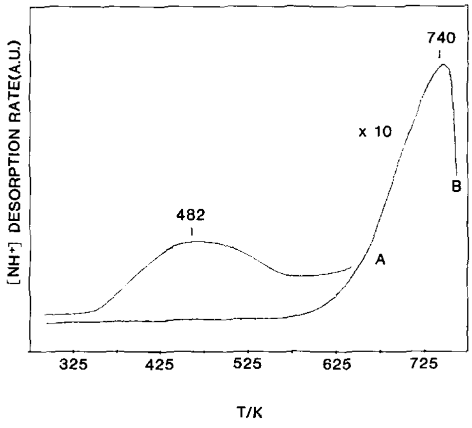

FIG. 5. TDS spectra for the desorption of NH_3 after adsorbing 25 Torr of NH_3 at 675 K. First run: the sample was heated to 675 K and cooled in UHV (A). Second run: heated to 775 K in UHV after the first run (B).

temperature. Since after the heat treatment in ammonia the sample is cooled down in an ammonia atmosphere, this peak may correspond to the adsorption of NH_3 at room temperature. However, after heating under vacuum at 675 K for 10 min the nitrogen peak remains in the AES spectrum, as shown in Fig. 4. After heating to 775 K a new TDS peak appears at 740 K, as shown in Fig. 5. On the basis of TDS and AES experiments, the identification of this peak remains uncertain. However, XPS and ESR spectra of V_2O_5/TiO_2 samples after treatment with NH_3 at reaction temperatures showed additional evidence for the dissociation of NH_3 (*38*). After reaction with ammonia, the V_2O_5 sample showed a sharp signal in the ESR spectrum that may be ascribed to electrons trapped in oxygen vacancies; at the same time a N(1*s*) signal at 399.6 eV can be observed in the XPS spectrum; this binding energy is 1.3 eV lower than that reported for NH_4VO_3 or NH_4^+ adsorbed on V_2O_5 (*15*) suggesting the dissociation proposed. The observed value (399.6 eV) is close to that reported by Au and Roberts (*39*) for NH_2 species adsorbed on clean and oxidized Mg(0001) crystals (399.0 eV) in the presence of O_2. However, although reporting the amide species, they do not characterize the bonding of the NH_2 species to the Mg(0001) surface.

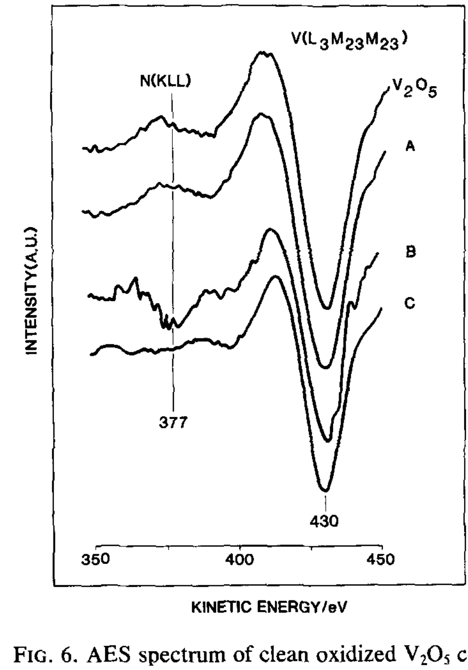

FIG. 6. AES spectrum of clean oxidized V_2O_5 compared to AES spectra for the adsorption of NO at RT (A) on a clean oxidized V_2O_5 sample, (B) on a NH_3-reduced V_2O_5 sample heated in UHV to 775 K, and (C) after heating (B) to 775 K in UHV.

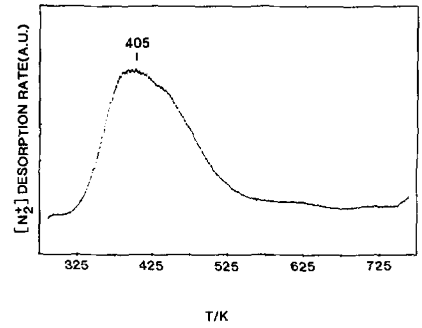

FIG. 7. TDS spectrum for the desorption of N_2 after adsorbing 25 Torr of NO at RT on a NH_3-reduced V_2O_5 sample.

NO was not adsorbed on a clean oxidized V_2O_5 surface under our experimental conditions; NO could also not be adsorbed on V_2O_5 that was covered with a monolayer of preadsorbed NH_3 (Fig. 6). NO adsorption at room temperature was observed on a V_2O_5 sample previously reduced with ammonia and outgassed in UHV at 775 K (Fig. 6). Heating the sample after NO adsorption to 775 K, the adsorbed species disappears. This result indicates that NO can interact with the reduced vanadium sites. In Fig. 7 the TDS (following amu 28 (N_2^+)) of that adsorbed species is shown. A peak centered at 405 K is observed which indicates that at reaction temperatures the NO can reoxidize the reduced vanadium sites while being reduced to N_2.

In a semiquantitative approach the N/V peak-to-peak ratio has been obtained from the AES spectra plotted in Figs. 2, 3, and 6 (Table 1). From this ratio it is possible to state that at least two different nitrogenated species are held by the V_2O_5 surface in adsorbing NH_3: the first has its maximum desorption rate at temperatures between

TABLE 1

N/V Peak-to-Peak Ratio

Adsorbate	Treatment	Temperature (K)	N/V
NH_3	Oxidized	300	0.21
NH_3	NH_3-reduced	300	0.29
NH_3	Cooled to RT in NH_3	575	0.18
NH_3	Heated to 575 K in UHV	575	0.15
NH_3	Cooled to RT in NH_3	675	0.12
NH_3	Heated to 675 K in UHV	675	0.13
NO	Oxidized	300	0.00
NO	Reduced	300	0.22

room temperature and 575 K while the second has its maximum desorption rate between 575 and 775 K; this is in agreement with the TDS results (Fig. 5). Surprisingly, after reaction in NH_3 at 575 or 675 K the vanadia surface undergoes modifications that prevent any further NH_3 adsorption at room temperature. If we compare the N/V ratio for NH_3 adsorption at room temperature (0.21) with the value obtained after reaction at 675 K and further cooling to room temperature (0.12) we must assume modification of the surface relative to the original one. This surface modification of the clean oxidized V_2O_5 surface cannot be ascribed to its reduction since the reduced surface adsorbs even more NH_3 than the oxidized one, Table 1. Since the reaction proceeds in a closed system, the reaction products are present in the high pressure cell; these products, as demonstrated by TDS (Fig. 3) are N_2O and H_2O; assuming, according to Miyamoto *et al.* (*12, 18*), that N_2O may react with the reduced sites reoxidizing them, then only NH_3, N_2, and H_2O should be present in the reactor and the presence of water should be responsible for the difference observed in Table 1. From this result it is possible to deduce either that H_2O adsorption on the V_2O_5 surface prevents any further ammonia adsorption or that the interaction of the NH_3 molecules with the hydroxylated surface is so weak that NH_3 desorption takes place at room temperature in a UHV environment.

Furthermore, the N/V peak-to-peak ratio for NO adsorption at room temperature is similar to that obtained for ammonia adsorption (Table 1). This indicates that the number of adsorbed NO species is equal to the number of NH_3-adsorbed species, pointing to a NO to NH_3 ratio equal to one in the NO + NH_3 reaction.

(*ii*) *Studies on TiO_2*

The adsorption of NO on TiO_2 has been studied by TDS as a function of temperature. The shape of the TDS spectra is the same regardless of the adsorption temperature and is characterized by a peak centered at 385 K. Neither N_2 nor N_2O was observed, indicating that NO adsorbs molecularly on the TiO_2 surface (Fig. 8). However, the amount adsorbed decreases when the reaction temperature increases. If successive 18 L (1 Langmuir = 10^{-6} Torr ×

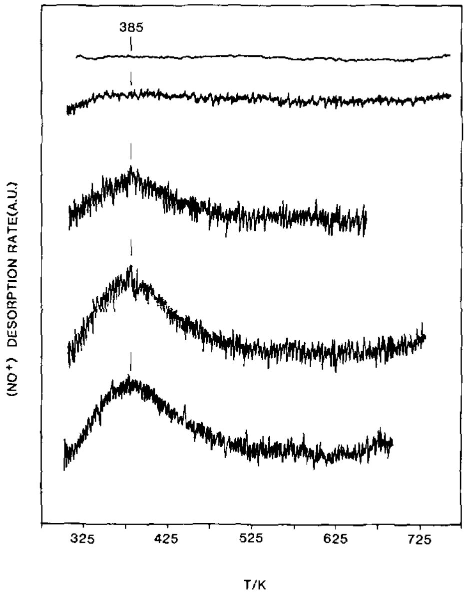

FIG. 8. TDS spectra for the desorption of NO after adsorbing successive 18-L doses of NO to an oxidized TiO_2 surface. The bottom profile corresponds to the first dose.

sec) doses of NO are provided to the TiO_2 surface, the amount adsorbed decreases to a level in which no more NO can be adsorbed, indicating a poisoning of the TiO_2 surface by NO species. When the adsorption is carried out in the high pressure cell under 25 Torr of NO, a single broad peak is observed in the TDS. This peak has higher desorption energy, the maximum appearing at 468 K.

NH_3 adsorption also takes place on TiO_2 (Fig. 9). The TDS spectrum of ammonia is characterized by a single broad peak which is centered at 445 K after 5 L adsorption at RT. The temperature corresponding to the maximum in the TDS peak shifts to higher values when increasing the NH_3 dose, indicating either a dependence of the binding energy on coverage or a population of different TiO_2 sites. On adsorbing NH_3 at either 373 or 473 K, a decrease in the amount adsorbed is observed as well as a shift to higher desorption temperatures (Fig. 9). When the NH_3 adsorption is at 373 K, an NH_3 desorption peak in the TDS profile at 495 K results; this peak position is independent of the NH_3 dose, pointing to the existence of different adsorption sites on the TiO_2 surface. The TDS after NH_3 adsorption at 473 K results in a hardly noticeable peak at about 600 K, indicating that at this temperature almost all the active surface sites on the TiO_2 surface have been removed.

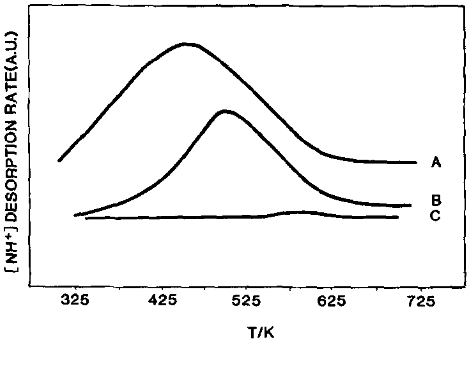

FIG. 9. TDS spectra for the desorption of NH_3. (A) 5 L at RT; (B) 5 L at 375 K; (C) 5 L at 475 K.

This points to an interaction between the ammonia molecule with the TiO_2 surface through weakly bound hydroxyl groups that are easily removed by heating at mild temperatures.

The reaction of NO and NH_3 on the TiO_2 surface has also been studied by leaking a NO + NH_3 (2:3 ratio) mixture into the UHV chamber at doses up to 20 L. This experiment showed that neither N_2 nor N_2O are desorbed from the TiO_2 surface in the temperature range 300–700 K and that, therefore, there is no reduction of NO by NH_3 occurring on TiO_2 in this temperature range.

DISCUSSION

Although the NH_3 + NO reaction has been the subject of numerous investigations (*1*), the nature of the active sites and of the reaction mechanism is still undetermined. The results described above provide some information on the role of the support and on the active phase of V_2O_5/TiO_2 catalysts for the removal of nitrogen oxides in stack and power gas exhaust systems.

The reduction of V_2O_5 in the presence of NH_3, either as a bulk oxide or when supported, is generally proposed in the literature (*18, 27*).

Our results clearly indicate that the surface of the V_2O_5 catalyst is reduced in the presence of NH_3 and in the absence of NO, leaving behind a surface vacancy according to the following scheme:

$$V_2O_5 + \frac{x}{2} NH_3 \rightarrow V_2O_{5-x} + \frac{x}{4} N_2O + \frac{3x}{4} H_2O. \quad (1)$$

The reduction of the V_2O_5 surface and the subsequent oxidation of the NH_3 molecule to N_2O has been demonstrated by TDS (Fig. 4). This result appears to contradict the NH_3 − NO adduct proposed by Miyamoto (*18, 28*) and agrees with the scheme proposed by Bosch *et al.* (*23*),

$$V_2O_5 + \frac{x}{2}NH_3 \rightarrow V_2O_5 - \frac{3x}{4} + \frac{x}{4}N_2 + \frac{3x}{4}H_2O, \quad (2)$$

in which case the oxygen defect may be present as a surface vacancy or a surface hydroxyl group.

Our results do not exclude the possible presence of hydroxyl groups or surface vacancies. However, the presence of a surface vacancy or a hydroxyl group should depend on the temperature at which the reaction is carried out. Dehydroxylation of V_2O_5 and V_2O_5/TiO_2 at temperatures below 550 K has been mentioned in the literature (*13, 40*). The reduction of the vanadium site by dehydroxylation has also been pointed out by Busca *et al.* (*13*).

Although it has been shown that the presence of water in the reactant mixture does not affect the temperature at which the maximum NO conversion occurs (*41*), it will be shown later in this article that surface hydroxylation is an important factor in the role of O_2 species during the reaction.

A difference between the stoichiometric scheme proposed by Bosch *et al.* (*23*) and that proposed here is the presence of N_2O instead of N_2. Thermodynamically, the N_2O species is stable with respect to its decomposition into N_2 and O_2 at the reaction temperatures (575–675 K) and the stability increases with increasing temperature. Thus, the presence of N_2 instead of N_2O in the reaction products, as postulated in (*23*), must be due to a further interaction of N_2O with surface vacancies:

$$V_2O_{5-x} + xN_2O \rightarrow V_2O_5 + xN_2. \quad (3)$$

Thus the surface is reoxidized to V^{5+}, while the N_2O in turn is reduced to N_2. In fact, by combining Eqs. (1) and (3) the scheme proposed by Bosch *et al.* (*23*), Eq. (2), is obtained. A reduction of N_2O with NH_3 to produce N_2 and H_2O which occurs on metals is not likely to occur on oxides.

The desorption of N_2O at reaction temperatures, leaving behind a reduced site, raises the question of which species is able to reoxidize such vanadium sites. Since the adsorption of NO on the reduced sites is possible (Fig. 6) and results in NO being reduced to N_2 at reaction temperatures (Fig. 7), the following elementary step can also be proposed:

$$V_2O_{5-x} + xNO \rightarrow V_2O_5 + \frac{x}{2}N_2. \quad (4)$$

By combining Eqs. (1), (3), and (4) the overall reaction can be described as

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O. \quad (5)$$

This stoichiometry, proposed by Nam *et al.* (*26*) for the NH_3 + NO reaction on V_2O_5/TiO_2 catalysts, cannot account for the drop in NO conversion in the absence of O_2 reported in the literature (*11, 23, 25, 41*).

Taking into account the presence of O_2 in the reaction mixture, the following step can also be hypothesized:

$$V_2O_{5-x} + \frac{x}{2}O_2 \rightarrow V_2O_5. \quad (6)$$

The overall reaction may then be written

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (7)$$

which is in good agreement with the stoichiometries proposed in the literature (*43, 44*). This stoichiometry also fits the NO and NH_3 coverages obtained by AES on V_2O_5 (Table 1).

The kinetics of the NH_3 + NO reaction has been extensively studied (*14, 27*). While some disagreement appears in the literature data (*11, 16, 17, 19–26, 45*), the kinetic results may be summarized in an oversimplified manner: a positive order in NO and a zero or even slightly negative order in NH_3. These results, however, are obtained at temperatures lower than 590 K, while the rate order Nam *et al.* (*26*) proposed (first order in both NO and NH_3) fits the experimental results in the range 475–775 K. Further, it has been reported that in the presence of O_2 there is a change in the selectivity for the NO + NH_3 + O_2 reaction above 525 K (*23*).

Our results on V_2O_5 indicate that NO can interact at low temperatures with a reduced vanadia surface but that it cannot be adsorbed on an oxidized surface (Fig. 6). To comply with the kinetic results described in the literature, one needs to assume NO adsorption on the support. On anatase at least two different NO species can adsorb. The first is weakly bound to the titania surface (Fig. 8); the second remains adsorbed even at 775 K and poisons the titania surface preventing further adsorption of NO molecules. When the NO pressure increases the adsorption energy of the weakly bound NO species increases and the maximum in the TDS spectra shifts from 385 to 468 K; there is then a possible source of NO molecules for the reduced vanadium sites at the TiO_2 surface. Also, a positive dependence on the amount adsorbed with pressure is observed fitting the positive order in NO observed in kinetic experiments.

The elementary steps, Eqs. (1) to (7), described above cannot explain the presence of ammonia adsorbed on the vanadium catalyst in the high temperature range; in addition these ammonia species are unreactive toward NO. This strongly adsorbed species might be understood as NH_3 molecules that dissociate on the surface of the reduced V_2O_5 sample according to

$$V_2O_{5-x} + xNH_3 \rightarrow V_2O_5 - \frac{3x}{2}(NH_2)x + \frac{x}{2}H_2O. \quad (8)$$

Existence of this VNH_2 species finds support in XPS and ESR data (*38*). Moreover, Otto *et al.* (*14, 47*) claim that the primary step in the NH_3 + NO reaction is the formation of NH_2 species. In addition to this, spectroscopic evidence for the formation of NH_x species has also been extensively reported (*48–50*).

Janssen *et al.* (*27*) proposed the heterolytic dissociation of NH_3 over two adjacent VO groups, which after reaction with adsorbed NO is the source of N_2 in the products' mainstream. This proposal is in agreement with the observation of Faber and Harris (*42*) of the formation of NH_2NO. However, the fact that NH_3 can adsorb on a reduced vanadia surface, leading to an apparent oxidation of vanadium species as observed by XPS (*38*) and the presence of ESR signals corresponding to electrons trapped in oxygen vacancies after NH_3 treatments (*38*), supports the idea of a dissociative homolytic adsorption on the reduced surface activated at the reaction temperatures.

Table 1 shows that ammonia does not adsorb or does so very weakly on fully hydroxylated vanadia surfaces. In the absence of O_2 the removal of the adsorbed water is needed to reach a steady-state reaction (*18, 28*). If molecular oxygen is present, the oxidation of the hydroxylated reduced sites is easier than in the absence of O_2 according to Wehrli and Stumm (*46*).

At temperatures below 525 K, provided NH_3 has reduced the vanadia surface and water has been formed, ammonia and nitric oxide can compete for the reduced surface sites, which in the absence of O_2 leads to a decrease in the rate of NO reduction. This explains the generally agreed on effect of O_2 on the rate of NO reduction (*1, 23, 25, 45*), namely, a sharp increase in the NO conversion in the presence of O_2.

O_2 treatment at 675 K restores the original V_2O_5 surface, suggesting the oxidation of such VNH_2 species in the presence of O_2. The stoichiometric step should be described by

$$V_2O_5 - \frac{3x}{2}(NH_2)x + xO_2 \rightarrow V_2O_{5-x} + \frac{x}{2}N_2O + H_2O. \quad (9)$$

By combining the elementary steps described by Eqs. (5) and (7) to (9), the side reaction that leads to the increase in N_2O

concentration as the reaction temperature increases is obtained:

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O. \quad (10)$$

Over V_2O_5, the evolution of N_2O at temperatures above 675 K in the oxidation of NH_3 has been reported (*51*). This side reaction may explain the change in selectivity for the NO reduction at temperatures above 525 K (*23*). If a competitive adsorption takes place, the number of sites available for the reduction of NO may decrease, leading to a drop in NO conversion; additionally, in the presence of O_2 the VNH_2 species are oxidized to V^{5+} and N_2O, increasing the N_2O concentration in the reaction products.

On the basis of the large number of observations reported, the two simultaneous reaction mechanisms proposed by Nam *et al.* (*26*) seem to agree with our results.

However, for the case of supported V_2O_5 other pathways for the production of N_2O may be considered, particularly the report that TiO_2 is able to produce N_2O (*25*). But, as shown earlier, N_2 or N_2O is not produced by the reaction of NO and NH_3 on the TiO_2 surface. Thus, the reported production of N_2O in the NO + NH_3 reaction over TiO_2 samples (*25*) could be associated with the reduction of the TiO_2 surface by NH_3 at high temperatures, leading to the formation of N_2O which is thermodynamically stable at temperatures of ca. 675 K. In fact, Busca *et al.* have reported the presence of NH_3 species held by TiO_2 at temperatures higher than 750 K, and the presence of Ti^{3+} ions on vanadia/titania catalysts after reduction (*52*) gives support to the following step:

$$TiO_2 + xNH_3 \rightarrow \frac{x}{2} N_2O + \frac{3x}{2} H_2O + TiO_{2-2x}. \quad (11)$$

Interaction of two NO molecules at the titania surface should be dismissed as a source of N_2 or N_2O since it has not been possible to detect either species by TDS or TPRS.

SUMMARY AND CONCLUSIONS

The adsorption of NH_3 and NO on pure vanadia and on TiO_2 under pressures (up to 25 Torr) and at near-industrial temperatures (room temperature to 675 K) has been studied by AES and TDS, using a UHV chamber equipped with a built-in high pressure cell (up to 1 atm).

NH_3 adsorption takes place over the whole range of temperatures studied on both V_2O_5 and reduced V_2O_5 surfaces while NO adsorption occurs only on reduced V_2O_5 surfaces. TiO_2 adsorbs NH_3 as well as NO.

The V_2O_5/TiO_2 catalyst currently employed for reducing NO_x emissions from power plants can be understood as a bifunctional catalyst. Extrapolating from the data with pure V_2O_5 and pure TiO_2 to V_2O_5/TiO_2 catalysts, one can propose that the adsorption of ammonia takes place mainly on the vanadium component causing the reduction of the original V^{5+} species. In turn the NO adsorption takes place on the TiO_2 support, since oxidized vanadia samples are completely unable to adsorb NO. The reduction of NO to N_2 would occur through a Langmuir–Hinshelwood mechanism or a spillover onto the surface of the vanadia component that implies the migration of the adsorbed NO species from the support to the reduced vanadium sites. In the absence of O_2, however, the catalyst loses activity since the reduced vanadium species can interact with ammonia molecules in the gas phase, leading to the formation of VNH_x species which are completely unreactive towards NO.

Furthermore, oxidation of the NH_3 to N_2O has been demonstrated by TDS on oxidized vanadium species. It has also been shown that reduced vanadia can be oxidized by reduction of N_2O to N_2. Since TiO_2 was not able to generate N_2O after heating in NO at reaction temperatures, a similar redox cycle on the surface of the support involving ammonia is proposed. This also leads to the formation of NH_x species on the surface of the catalyst that, in the presence of O_2, leads to the formation of N_2O, as has been reported in the literature. This process also explains the decrease in the catalytic activity as a function of the temperature because of the poisoning of active surface sites.

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