

Temperature-Programmed Desorption/Reaction and *in Situ* Spectroscopic Studies of Vanadia/Titania for Catalytic Reduction of Nitric Oxide

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Temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR) studies were conducted to probe the catalytic chemistry of nitric oxide reduction by ammonia on thin films of titania, vanadia, and vanadia/titania at vacuum conditions, as well as on powdered catalysts under flow conditions. The activation energies and enthalpies of ammonia desorption estimated in vacuum and powder TPD studies, respectively, are comparable, consistent with nonactivated ammonia adsorption. The enthalpies of ammonia desorption range from about 18 to 26 kcal/mol over vanadia, vanadia/titania, and titania, with the enthalpy increasing with decreasing vanadia content. *In situ* IR measurements of the surface ammonia coverages under reaction conditions for the selective catalytic reduction (SCR) of nitric oxide suggest that ammonia adsorption on Lewis acid sites is stronger than on Brønsted acid sites and ammonia adsorption is not rate determining for the SCR reaction. Significant amounts of adsorbed NO are not present on vanadia/titania surfaces under SCR reaction conditions. Vacuum and powder TPR studies indicate that the activation energy for the formation of N₂ from NO and NH₃ is about 20 kcal/mol, independent of whether the NO species is strongly adsorbed (under vacuum TPR conditions) or weakly adsorbed (under powder TPR conditions). © 1992 Academic Press, Inc.

INTRODUCTION

An effective option for control of NO_x emissions from stationary sources is the use of chemical reducing agents such as NH₃ at temperatures above about 570 K (1, 2). Normal operation of furnaces and many other sources of NO_x produce gas streams containing substantial (>1%) quantities of dioxygen. Since NH₃ oxidation by O₂ first becomes significant at temperatures above about 650 K (3, 4), this reducing agent is effective for selective catalytic reduction (SCR) of nitric oxide.

The most widely studied catalysts for the SCR reaction have been based on titania-supported vanadia, as discussed in detail in

a recent review (4). It is generally believed that the catalytic reaction involves the adsorption of ammonia on Lewis and/or Brønsted acid sites, followed by reaction of nitric oxide with adsorbed ammonia in a Eley–Rideal (5–9) or a Langmuir–Hinshelwood step (10–14). Further understanding of this reaction requires quantitative measurements and comparisons of the rates of adsorption/desorption and surface reaction processes associated with the SCR reaction.

The approach of the present study is to use temperature-programmed desorption (TPD) to study adsorption/desorption processes involving NH₃, NO, and H₂O, temperature-programmed reaction (TPR) spectroscopy to probe the reaction between NH₃ and NO, and *in situ* infrared spectroscopy to monitor surface coverages by various species under reaction conditions. The cata-

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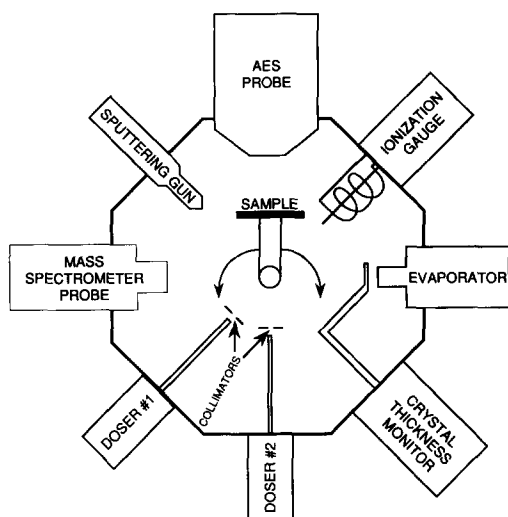


FIG. 1. Schematic diagram of vacuum TPD apparatus.

lysts employed in these studies were titania, vanadia, and vanadia/titania. A unique aspect of this work is the combined use of temperature-programmed desorption/reaction methods for high-surface-area catalysts at atmospheric pressure reaction conditions, as well as low-surface-area model catalysts at ultrahigh-vacuum conditions. The combination of the information obtained from these temperature-programmed measurements with the results of *in situ* IR spectroscopy over a range of reaction conditions provides an effective strategy for studying the essential surface chemistry of the catalytic process.

EXPERIMENTAL

Vacuum Temperature Programmed Studies

The apparatus used for temperature programmed desorption/reaction (TPD/R) studies of model catalysts at ultrahigh-vacuum conditions is shown schematically in Fig. 1. The system consists of a high-capacity ion pump and a titanium sublimation pump connected to an ultrahigh-vacuum stainless-steel chamber via a poppet valve. A UTI 100C quadrupole mass spectrometer, an Auger electron spectrometer (Physical

Electronics Instruments system), an argon ion sputtering gun, an ionization gauge, and gas dosers are arranged circumferentially around the sample position in the chamber. The chamber is also equipped with a heated evaporation unit and a crystal thickness monitor (Kronos QM-301) for deposition of vanadia on catalyst surfaces.

Samples for study were based on a 0.25-mm-thick tungsten foil, upon which a non-porous, 200 to 250-nm layer of titanium dioxide was deposited. The titania sample was prepared by first sintering commercially available titanium dioxide (Toho Titanium, extra pure) at 1000 K for 48 h. The pelleted product was then used as the source for reactive sputtering at the Thin Films Laboratory at the University of Wisconsin–Madison to deposit titania on the tungsten foil support.

The titania sample was treated in the TPD/R chamber in oxygen at a pressure of 10^{-5} – 10^{-7} Torr to minimize carbon contamination. Surface cleanliness was monitored by Auger electron spectroscopy. Treatment temperatures near 1000 K over several hours were required to remove carbon. X-ray diffraction spectra of the titania film before and after vacuum treatment indicated that the fresh film consisted of anatase primarily, whereas the annealing treatment transformed the anatase phase into rutile.

Comparison of published Auger electron spectra with spectra obtained for the titania sample used in these studies indicated that the model titania surface was fully oxidized. The 418-eV titanium Auger transition on the sample closely resembled that of TiO_2 rather than the spectrum of TiO_2 reduced by Ar-ion bombardment. Additionally, the ratio of the peak height for the oxygen transition near 510 eV to the titanium transition near 380 eV is the same as observed in the literature for TiO_2 (15). No elements other than Ti, O, and trace C were observed.

Temperature-programmed desorption/reaction experiments were initiated by dosing gases onto the surface at cryogenic temperatures (120–150 K). The heating rate during

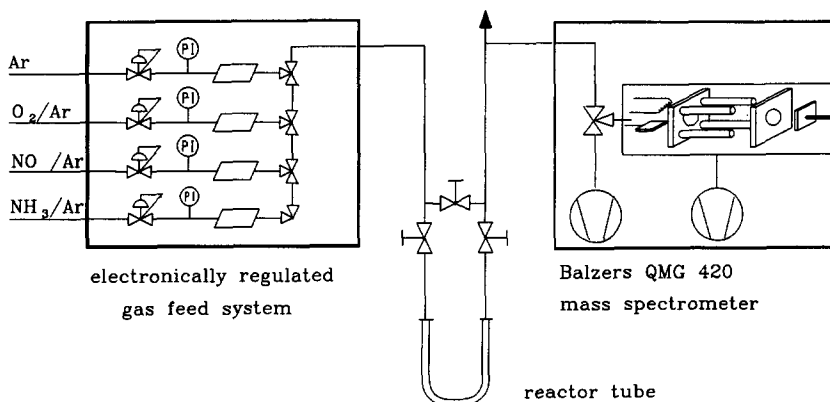


FIG. 2. Schematic diagram of powder TPD apparatus.

TPD/R studies was typically 5–40 K/s. The TPD/R peaks from all samples were rather broad, precluding detailed peak shape analyses. Further, the difficulty in removing the gases from the chamber (e.g., resulting from adsorption/desorption processes on the walls of the chamber) made it difficult to control precisely the gas dosages on the sample. For these reasons, we have not attempted to determine preexponential factors from TPD/R spectra. A reasonable value of 10^{13} s^{-1} has been assumed for all surface processes.

Powder Temperature-Programmed Studies

Temperature-programmed desorption/reaction studies on high-surface-area powder catalysts were conducted using the apparatus shown schematically in Fig. 2. These measurements were made using about 0.1 g of powdered material sieve fraction 300 to 850 μm . Samples were loaded in a glass-lined stainless-steel reactor (length of catalyst bed $\sim 15 \text{ mm}$).

The gases used were mixtures of O_2/Ar (15% O_2), NH_3/Ar (3580 ppm NH_3), NO/Ar (3890 ppm NO), and Ar (99.999%), with no additional purification. The gas flow through the reactor was controlled and monitored by use of electronic mass flowmeters (Brooks), and the temperature of the reactor was controlled and monitored by means of a micro-

processor (Euroterm 820). The gas components were monitored on-line by a Balzers QMG 420 quadrupole mass spectrometer equipped with a heated, continuous gas inlet.

Catalysts containing 0.6 and 6.0% vanadia supported on titania were prepared by impregnating the titania support (anatase form, surface area of $90 \text{ m}^2/\text{g}$) with an oxalic acid solution of ammonium metavanadate, followed by drying at room temperature and calcination at 674 K. Unsupported vanadia was prepared using a similar route, without the titania support. After the samples were loaded in the reactor, they were treated for 3 h at 673 K in a flow of 100 N ml/min O_2/Ar . After cooling to room temperature, the reactor was bypassed and the gas was exchanged with NH_3/Ar at a flow of 50 N ml/min . When the intensities measured with the mass spectrometer had stabilized, this gas mixture was then passed through the reactor for about 1 h. Subsequent to this ammonia adsorption step, the gas was exchanged with pure Ar at 50 N ml/min while bypassing the reactor. After the mass spectrometer intensities had stabilized, the argon gas was passed through the reactor and ammonia TPD was carried out by increasing the temperature linearly at 2 K/min to 673 K.

After completion of the ammonia TPD ex-

periments, each sample was reoxidized for 3 h at 673 K, followed by exposure to ammonia (50 N ml/min NH₃/Ar) for about 1 h at room temperature. The gas was then exchanged with NO/Ar and temperature-programmed reaction experiments were carried out by heating the catalyst at 2 K/min to 673 K in a flow of 50 N ml/min NO/Ar.

Infrared Spectroscopic Studies

The state of the catalyst surface during the various adsorption and *in situ* reaction studies was monitored by FTIR measurements. Spectra were collected on a Digilab FTS80 FTIR spectrometer with an MCT (mercury-cadmium-telluride) detector at a spectral resolution of 4 cm⁻¹.

The vanadia/titania catalyst used for *in situ* IR studies was the 6% vanadia/titania sample described above for powder TPD/R studies. The sample was ground and pressed into a self-supporting wafer and mounted into a quartz *in situ* IR cell/reactor with CaF₂ windows. The experimental configuration allowed *in situ* IR measurements of the samples during pretreatments, adsorption, and desorption under vacuum, as well as during the SCR reaction at various temperatures.

In adsorption experiments, the sample was pretreated under vacuum (10⁻⁶ Torr) for 1 h at 673 K, followed by treatment at this temperature in 400 Torr of O₂ for 2 h. The sample was then cooled in O₂ and evacuated at room temperature before adsorption of gases at the same temperature.

For *in situ* reaction studies of the catalyst, the sample was activated in a stream of reaction feed gas at the reaction temperature, as described elsewhere (16). The reaction feed gas concentrations chosen in the present studies for NO and NH₃ were 340 and 500 ppm, respectively. These gases were mixed with 8% O₂ and Ar to maintain a total pressure of 1 atm. The concentrations of the various gas components of both the inlet and outlet gas stream were analyzed with the mass spectrometer system used for the powder TPD/R studies.

TABLE 1

Desorption Activation Energies (kcal/mol) Estimated from Vacuum TPD Studies

Adsorbed Species	TiO ₂	V ₂ O ₅ /TiO ₂ ^a	V ₂ O ₅ ^b
NO	22	20	16
H ₂ O	11, 18	11, 17	10, 14
NH ₃	14, 27	12, 24	12, 24

^a 4 equivalent monolayers vanadia on titania.

^b 12 equivalent monolayers vanadia on titania.

RESULTS

Vacuum TPD Studies

Vacuum TPD studies were conducted on titania, vanadia/titania, and vanadia thin-film samples. Experiments were initiated on the nonporous titania substrate prior to deposition of vanadia. To ensure a consistent catalytic surface from one experiment to another, the titania was treated with oxygen at 10⁻⁵–10⁻⁷ Torr and 1000 K for 30 min before each experiment. The results of these studies are summarized in Table 1. Nitric oxide adsorption at 120–150 K was observed to lead to a broad distribution of desorption states, as shown in Fig. 3. No reduction products, such as N₂ or N₂O, nor oxidation products, such as NO₂, were observed. The desorption kinetics can be described with an activation energy of 22 kcal/mol. The broad nature of the TPD spectrum for NO desorption is in agreement with the results of Odriozola *et al.* (10) for a powdered titania catalyst. The TPD peak observed by these authors, however, was at higher temperatures than the present study. It is probable that this difference may be attributed to differences in the types of titania employed in these two studies, i.e., a nonporous titania film used in the present study and a porous titania powder used by Odriozola *et al.*

Figure 3 shows two states for water desorption. These states can be described with activation energies of 11 and 18 kcal/mol. Two states of ammonia desorption from titania were also observed, as shown in Fig. 3. These states can be described with activa-

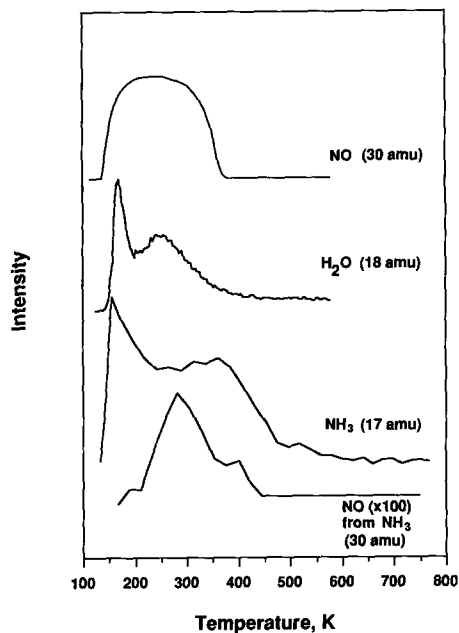


FIG. 3. Vacuum TPD spectra of NO, H₂O, and NH₃ from titania at heating rates of 12, 9, and 40 K/s, respectively.

tion energies of 14 and 27 kcal/mol. A small extent of ammonia decomposition to nitric oxide occurred, corresponding to less than 1% of the desorption observed during TPD from a saturation dose of NO onto the titania surface, as seen in Fig. 3.

Following the above TPD studies on titania, an amount equivalent to four monolayers of vanadia was deposited on the rutile surface, as estimated by the crystal thickness monitor. After oxidation, Auger electron spectroscopy indicated the presence of both vanadium and titanium. It was found that raising the temperature of the sample beyond 700 K resulted in desorption of vanadium oxide species. To maintain a consistent oxidation state of the catalyst surface, the sample was thus reoxidized at 650 K for 30 min in oxygen at 10^{-5} – 10^{-7} Torr following each TPD experiment. Periodic AES studies confirmed no loss of vanadium from the surface during these experiments. As discussed later, it is likely that a significant fraction of the vanadium was present in a reduced state, e.g., as V⁴⁺ cations.

Figure 4 shows that desorption of nitric oxide takes place in a single broad state. The activation energy can be estimated to be 20 kcal/mol. During desorption of NO, peaks for N₂, O₂, N₂O, or NO₂ were not observed, indicating that NO decomposition did not occur. Further evidence that nitric oxide was not reduced on the catalyst was obtained by repeating the TPD experiment without reoxidation of the catalyst. No change in the amount of nitric oxide adsorbed at saturation was observed, even after 10 TPD experiments.

Water desorption was observed to occur from vanadia/titania in two distinct states, as illustrated in Fig. 4. The activation energies for these states can be estimated to be 11 and 17 kcal/mol. Temperature-programmed desorption spectra for NH₃ showed states with activation energies of 12 and 24 kcal/mol, as seen in Fig. 4. In these experiments, ¹⁵ND₃ (21 amu) was employed to eliminate possible interference from other desorption species (such as H₂O) in the mass spectrometer. The decomposition products

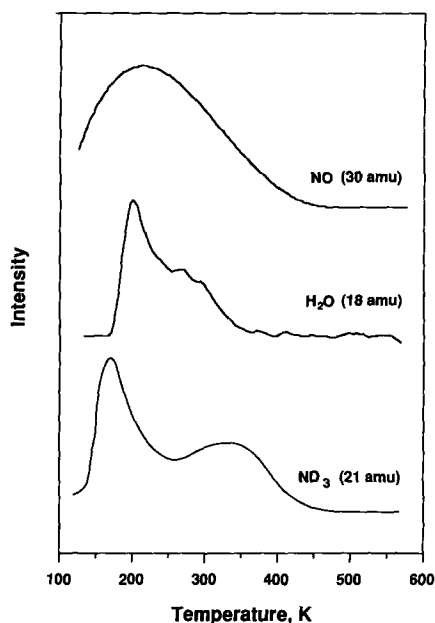


FIG. 4. Vacuum TPD spectra of NO, H₂O and ¹⁵ND₃ from vanadia/titania at heating rates of 10, 23, and 7 K/s, respectively.

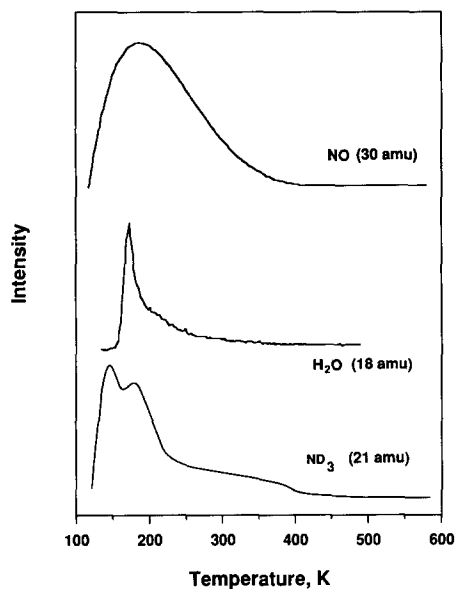


FIG. 5. Vacuum TPD spectra of NO, H₂O, and ¹⁵ND₃ from vanadia at heating rates of 10, 11, and 7 K/s, respectively.

N₂, N₂O, NO, and NO₂ were not observed. Measurements of the ammonia TPD peak area versus ammonia exposure indicated that the ammonia sticking coefficient was approximately equal to 0.1.

The equivalent of eight additional monolayers of vanadia was subsequently deposited onto the vanadia/titania catalyst, as monitored by the crystal thickness monitor. Following an oxidation treatment, Auger electron spectroscopy indicated that vanadium and oxygen were the only elements present on the surface. Periodic Auger electron spectra were taken to confirm that titanium had not been exposed and that impurities such as carbon had not accumulated. Thus, this sample will be denoted as being a vanadia surface.

Similar to nitric oxide TPD on the vanadia/titania catalyst, NO desorbs from vanadia in a single broad peak, as seen in Fig. 5. The activation energy was estimated to be 16 kcal/mol. This result represents a decrease of 4 kcal/mol relative to vanadia/titania. No evidence of NO decomposition (N₂ or N₂O) or oxidation (NO₂) was observed.

As on the vanadia/titania catalyst, water on the vanadia catalyst desorbs from two states, as shown in Fig. 5. The desorption activation energies are estimated to be 10 and 14 kcal/mol. Ammonia desorption spectra are illustrated in Fig. 5. As for the data of Fig. 4, ¹⁵ND₃ was employed in these studies. A high-energy state is apparent, with a desorption activation energy of 24 kcal/mol. A single state can be used to describe the low-temperature peaks, with an activation energy of 12 kcal/mol. No products, such as N₂O, N₂, NO, or NO₂ were observed.

Vacuum TPR Studies

Coadsorption experiments involving ammonia and nitric oxide were conducted to investigate the reaction between nitric oxide and ammonia on the above titania, vanadia/titania, and vanadia surfaces. The catalysts were exposed to near-saturation levels of ¹⁵ND₃, followed by saturation with NO, both at cryogenic temperatures (120–150 K). Reaction between ammonia and nitric oxide was not observed on the titania surface; i.e., neither ¹⁵N¹⁴N nor ¹⁵N¹⁴NO were detected.

The results of TPR experiments involving ¹⁵ND₃ and NO over vanadia/titania are illustrated in Fig. 6. The dinitrogen product observed was ¹⁵N¹⁴N. The activation energy

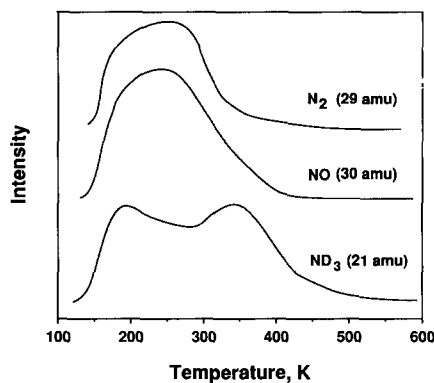


FIG. 6. Vacuum TPR spectra following coadsorption of ¹⁵ND₃ and ¹⁴NO on vanadia/titania at a heating rate of 13 K/s.

for the formation of N_2 from adsorbed NO and NH_3 (i.e., $NO^* + NH_3^* \rightarrow N_{2(gas)}$) can be estimated to be 20 kcal/mol. No ^{15}NO , $^{14}N^{15}NO$, or $^{15}N_2O$ were observed. The presence of $^{15}N_2$ could not be determined due to interference with the NO also present. Efforts were made to detect the reported gas-phase adduct NH_2NO (17), but no evidence for this species could be found.

Reaction between $^{15}ND_3$ and NO on the vanadia surface gave results similar to those for the vanadia/titania catalyst. The activation energy for the formation of N_2 from adsorbed NO and NH_3 is about 20 kcal/mol.

Powder TPD Studies

Ammonia TPD spectra are shown in Fig. 7 (mass 15) for the different catalysts studied (titania, vanadia, 0.6% vanadia/titania, 6% vanadia/titania). The ammonia TPD spectrum for titania shows a broad feature near 400 K, followed by a broad peak at 550 K. The TPD spectrum for the 0.6% vanadia/titania catalyst shows a broad feature starting at about 350 K, peaking at about 460 K, and vanishing at about 625 K. The corresponding spectrum for the 6% vanadia/titania catalyst shows a sharp increase at 360 K, peaking at about 395 K and disappearing at 575 K. The TPD spectrum for vanadia is less intense than the titania-based materials, due to the lower surface area of unsupported vanadia, i.e., $10\text{ m}^2/\text{g}$ for vanadia compared to $60\text{--}75\text{ m}^2/\text{g}$ for the titania-containing materials. The spectrum shows a peak near 400 K and a broad feature near 450 K.

The TPD spectra in Fig. 7 show that ammonia is held most strongly on the titania surface, followed by the 0.6% vanadia/titania catalyst, and it is bonded most weakly on the 6% vanadia/titania catalyst and on vanadia. It is likely that these broad TPD spectra are superpositions of several contributions originating from different sites, e.g., Lewis and Brønsted acid sites. Since titania shows primarily Lewis acidity, whereas high loadings of vanadia on titania show primarily Brønsted acidity (e.g., (18)), it may

be suggested that ammonia adsorption is stronger on the Lewis acid sites.

Numerical simulations of the experimental TPD spectra incorporating readsorption of ammonia were conducted to estimate energetics of ammonia desorption. It is apparent that the TPD spectra are broad, showing spectral features at temperatures from about 400 to 600 K. For simplicity, we have chosen to describe the broad range of ammonia desorption states in terms of three sites. It is important to note that these three sites do not necessarily have physical significance, but they are used instead to capture the essential features of the broad ammonia desorption distribution. The numerical simulations were conducted by solving simultaneously the three differential equations describing ammonia adsorption and desorption on each of the three sites, combined with the differential equation describing the material balance for ammonia in the non-steady-state TPD cell. This cell was treated for simplicity as a well-mixed reactor. Readsorption on the sites was assumed to be non-activated with a sticking coefficient of 0.1. The desorption of ammonia was assumed to occur with a preexponential factor of 10^{13} s^{-1} for all sites, the same value used in the analysis of the vacuum TPD spectra. It is important to note that the high value of the ammonia sticking coefficient leads to fast readsorption during the powder TPD experiment; therefore, the TPD spectrum provides information about the desorption equilibrium constant (19). Accordingly, we refer to energetics obtained in powder TPD experiments as desorption enthalpies, in contrast to the desorption activation energies obtained in vacuum TPD studies where readsorption is negligible.

The results of the simulations of the powder TPD spectra are summarized in Table 2. The enthalpies for ammonia desorption estimated for the three sites were 18, 22, and 26 kcal/mol. We estimate that the uncertainty in these estimated ammonia desorption enthalpies is ± 2 kcal/mol, since this is

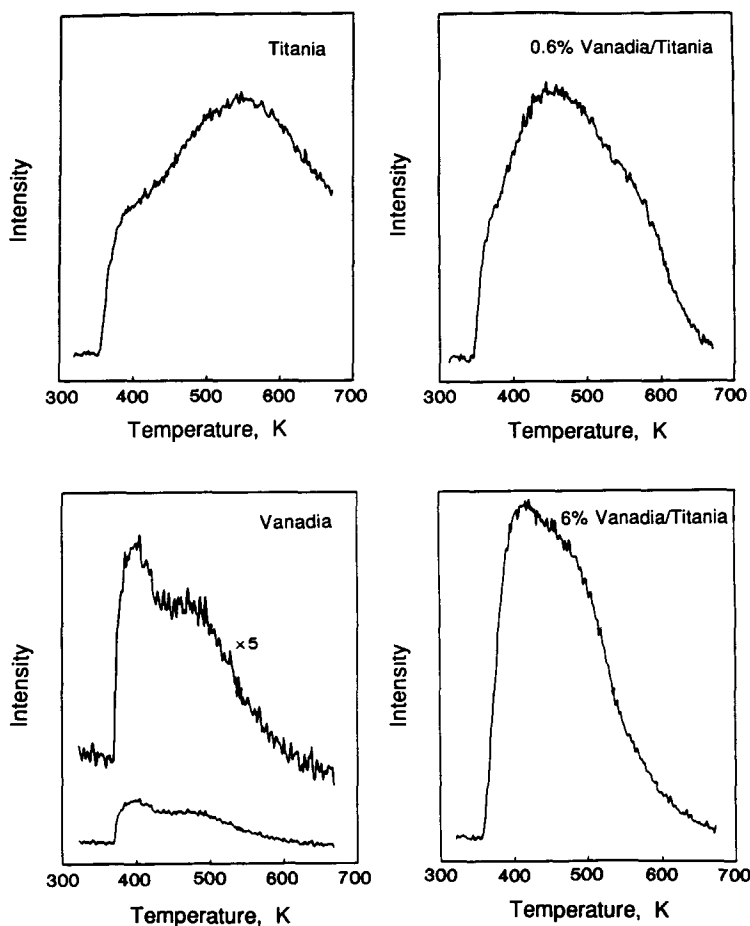


FIG. 7. Powder TPD spectra of ammonia (15 amu) from titania, vanadia, 0.6% vanadia/titania, and 6% vanadia/titania.

the variation that is produced by varying the ammonia sticking coefficient from 0.01 to 1. It can be seen in Table 2 that the fractional

TABLE 2

Fractional Amounts of Ammonia Adsorption Sites
Estimated from Powder TPD Studies

Catalyst	Site 1 (18 kcal/mol)	Site 2 (22 kcal/mol)	Site 3 (26 kcal/mol)
TiO ₂	0.20	0.50	0.30
0.6% V ₂ O ₅ /TiO ₂	0.20	0.53	0.27
6% V ₂ O ₅ /TiO ₂	0.47	0.43	0.10
V ₂ O ₅	0.60	0.35	0.05

amount of the weakest adsorption site increases as vanadia is added to titania, while the fractional amount of the strongest site decreases. However, it is not necessarily possible to associate a particular site to titania or vanadia sites alone. For example, all three sites are present on the titania surface in the absence of vanadia.

Powder TPR Studies

Temperature-programmed reaction profiles for powdered catalysts were obtained following the above TPD studies by first saturating the surface with ammonia, followed

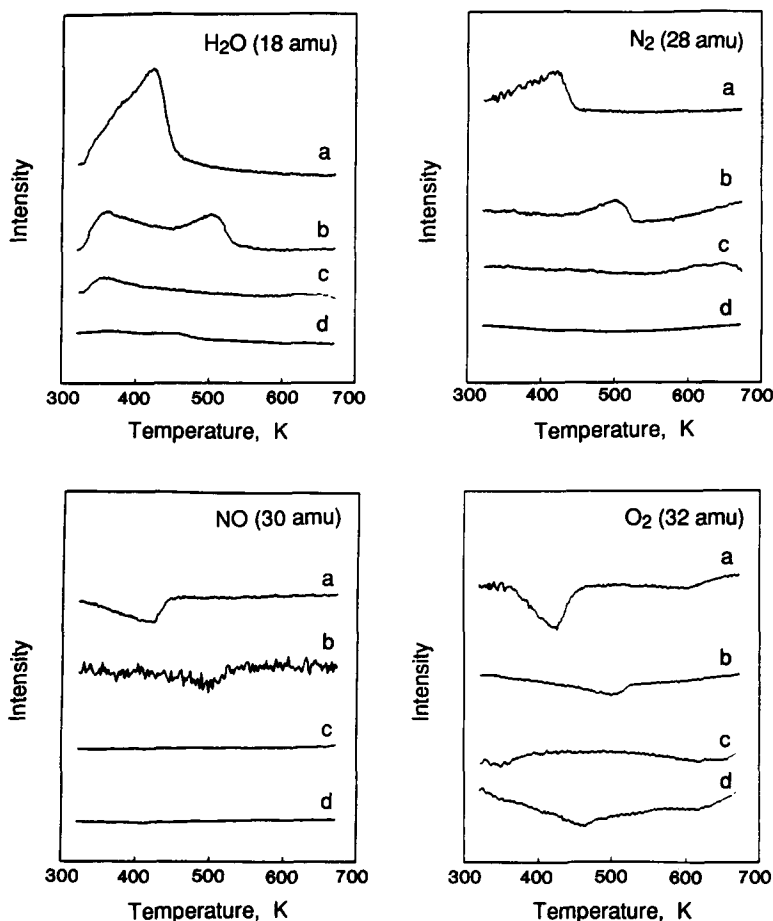


FIG. 8. Powder TPR spectra in flowing NO following saturation of the surface with ammonia for (a) 6% vanadia/titania, (b) 0.6% vanadia/titania, (c) titania, and (d) vanadia. The NO trace from 0.6% vanadia/titania (bottom left) is not of 30 amu but of 15 amu (doubly ionized NO).

by heating in the presence of gaseous nitric oxide. These TPR spectra obtained in flowing NO/Ar for masses 18, 28, 30, and 32 are compared in Fig. 8. The spectra show a decrease in NO pressure (mass 30) over a narrow temperature interval for the vanadia/titania samples, accompanied by a parallel increase in N_2 pressure (mass 28). Thus, the reaction between adsorbed NH_3 and NO to form N_2 is clearly demonstrated.

The TPR experiments over titania do not show evidence for reaction between NO and adsorbed ammonia, consistent with the vacuum TPR studies. In contrast, the TPR spectra for the two vanadia/titania samples pro-

vide evidence for the consumption of NO and production of N_2 . From the TPR profiles it is apparent that the activation energy for this reaction is different for the two vanadia/titania catalysts. The reaction starts near 450 K for the 0.6% vanadia/titania catalyst and it ceases near 525 K. For the 6% vanadia catalyst, the reaction begins near 325–335 K and it proceeds until the temperature reaches ca. 450 K. Finally, the TPR spectra over vanadia do not show evidence for reaction between NO and adsorbed ammonia. However, this result is probably due to the low surface area of the vanadia, which makes it difficult to detect in the mass spec-

trometer the consumption of NO or the production of N₂, as noted below.

The NO consumption curve in the TPR experiments can be simulated numerically using a mechanism that involves desorption and readsorption of ammonia ($\text{NH}_3^* \leftrightarrow \text{NH}_{3(\text{gas})} + *$) and reaction between adsorbed ammonia and gaseous NO ($\text{NO}_{(\text{gas})} + \text{NH}_3^* \rightarrow \text{N}_{2(\text{gas})}$). These calculations were conducted using a differential equation describing the material balance for consumption of nitric oxide in the TPD cell, combined with the same differential equations used for analysis of the TPD spectra, each equation modified with an additional term describing the reaction of nitric oxide with adsorbed ammonia. Using the parameters derived above for the desorption/adsorption of ammonia, the overall shapes of the NO consumption curve can be reproduced if a preexponential factor of $10^7 \text{ Torr}^{-1} \text{ s}^{-1}$ is used for the reaction between ammonia and NO with activation energies of about 24 and 20 kcal/mol for the 0.6 and 6% vanadia/titania catalysts, respectively. In these numerical analyses we have assumed that the three sites for each catalyst have the same reactivity with NO, since we noted above that it is not necessarily possible to associate a particular site to titania or vanadia. In particular, while all three sites are present on the titania surface, the ammonia on these sites does not react with nitric oxide. Thus, the activation energies reported above for the temperature-programmed reaction over the vanadia/titania catalysts should be considered to be average values for the ammonia adsorbed on these catalysts.

The TPR profile for mass 18 during the reaction between NO and adsorbed NH₃ is displayed in Fig. 8. This curve indicates that water is formed during the reduction of NO to N₂. Apart from a TPD peak at about 373 K caused by physisorbed H₂O, the TPD profiles for mass 18 for the vanadia/titania catalysts show that H₂O formation has a maximum at the same temperature (425 K for 6% vanadia/titania and 500 K for 0.6% vanadia/titania) as was observed for the reaction be-

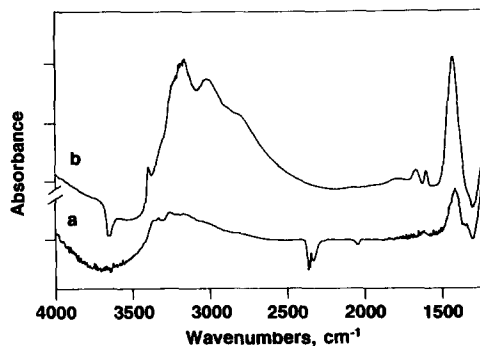


FIG. 9. Infrared spectra of the 6% vanadia/titania catalyst (a) under SCR reaction conditions at 573 K, 340 ppm NO, 500 ppm NH₃, and 8% O₂, and (b) after a saturation dose of ammonia at room temperature. Spectrum (a) is shown at a more expanded scale than (b) for clarity.

tween NO and adsorbed NH₃. This result suggests that water is formed in a reaction-limited step.

In the above TPR experiments, the NO/Ar gas mixture contained traces (<30 ppm) of O₂. The mass 32 panel of Fig. 8 shows that this oxygen is consumed at the same temperature at which NO is consumed for the two vanadia/titania catalysts. Thus, the measured TPR behavior for mass 32 strongly suggests that an important step in the SCR mechanism involves the oxidation of reduced surface sites in the reaction. It is interesting to note that the mass 32 trace shows evidence for small extents of reaction over vanadia, whereas the mass 30 trace does not show this reaction. This result can be understood by noting that mass 32 corresponds to <30 ppm of O₂, whereas mass 30 corresponds to 3890 ppm of NO. Thus, the mass 32 trace is a more sensitive indication of reaction over the low-surface-area vanadia catalyst.

In Situ FTIR Studies

Figure 9a shows an IR spectrum of the 6% vanadia/titania catalyst recorded during the SCR reaction at 573 K, while Fig. 9b shows the spectrum of the same catalyst with a saturation amount of NH₃ adsorbed

on the surface at room temperature. These spectra are reported with the background spectrum subtracted from the sample in flowing Ar at the same temperature. (This background spectrum in Ar is essentially the same as that in flowing Ar/O₂ under the conditions of this study.) The adsorption bands in Fig. 9 are primarily due to ammonia adsorbed on the surface and the accompanied disappearance of surface hydroxyl groups (16, 18, 20). The main features in the higher frequency region of the spectra are broadbands at 3019 and 2808 cm⁻¹ attributed to the stretching vibration of NH₄⁺ and bands at 3364 and 3334 cm⁻¹, which are due to the asymmetric and symmetric stretching vibrational frequencies of coordinated NH₃, respectively. The negative band near 3650 cm⁻¹ indicates the disappearance of surface hydroxyl groups upon ammonia adsorption. The adsorption bands in the frequency region below 1700 cm⁻¹ are due to the corresponding deformation modes. The bands at 1430 and 1670 cm⁻¹ in the room-temperature spectrum (Fig. 9b) are attributed to the asymmetric and symmetric bending vibrations of NH₄⁺, whereas the bands at 1606 and 1237 cm⁻¹ are due to the asymmetric and symmetric bending modes of coordinated NH₃, respectively. At the reaction temperature of 573 K (Fig. 9a) the NH₄⁺ band is shifted to 1419 cm⁻¹, reflecting a more strongly bonded NH₄⁺ species at the higher temperature. The negative band at 2041 cm⁻¹ is attributed to the first overtone vibration of V=O (18), indicating the disappearance of some V=O species during reaction.

The IR spectra show that Brønsted and Lewis acid sites on the vanadia/titania catalyst surface are partially covered with ammonia during the SCR reaction. From the intensity of the ammonia absorption bands, the ammonia coverages on the Brønsted and Lewis acid sites can be estimated, assuming that these sites are saturated after exposure to ammonia at room temperature. If ammonia adsorption/desorption is equilibrated under SCR reaction conditions, then the equilibrium constant for ammonia desorption

can be estimated by measuring ammonia coverages over the catalyst at various reaction conditions. Over the limited range of temperatures employed in these *in situ* studies, it is not possible to determine both the enthalpy and entropy of ammonia desorption. Instead, the enthalpy of desorption was estimated using the same preexponential factors for ammonia adsorption and desorption as those used in the above TPD studies, together with the ammonia coverages from the *in situ* IR measurements. For example, the fractional surface coverages by ammonia on the Brønsted and Lewis acid sites are found to be 0.26 and 0.39 at 573 K for an ammonia concentration of 500 ppm, corresponding to desorption enthalpies of 22 and 23 kcal/mol, respectively. These values are in good agreement with results of the TPD measurements.

Another important result from the *in situ* IR spectra shown in Fig. 9 is that adsorbed nitric oxide species are not detected on the catalyst surface under SCR reaction conditions, in agreement with the literature (21, 22).

DISCUSSION

Ammonia Adsorption Studies

The results of vacuum TPD experiments on the three surfaces examined in this study are summarized in Table 1. It can be seen in this table that ammonia desorbs at higher temperatures than water on titania, vanadia, and vanadia/titania surfaces. This behavior is consistent with the higher proton affinity of ammonia compared to water. The implication of this result for the SCR reaction is that water is not expected to block sites for ammonia adsorption, as discussed in detail elsewhere (23). In addition, the lower desorption activation energy of water compared to ammonia on these surfaces is consistent with the powder TPR result that water is formed in a reaction-limited step when preadsorbed ammonia is heated in the presence of nitric oxide.

The high sticking coefficient for ammonia adsorption (ca. 0.1) suggests that the activa-

tion energy for this process is small. Accordingly, the ammonia desorption activation energies estimated in vacuum TPD studies should be approximately equal to ammonia desorption enthalpies estimated in powder TPD experiments. The vacuum TPD spectra show evidence for two broad ammonia desorption states on the various surfaces studied. The desorption activation energy of the strongly adsorbed state decreases from 27 to 24 kcal/mol with the addition of vanadia to the titania. In addition, the relative intensity of this state decreases when extensive amounts of vanadia are deposited on the titania surface, and it becomes rather broad. These results are in general agreement with the powder TPD spectra, where the ammonia desorption features became more significant at lower temperatures as vanadia was added to titania, with the vanadia sample showing the most significant desorption contributions at low temperatures. This behavior observed in powder TPD studies was described by variations in the relative amounts of ammonia desorption states with enthalpies of 18, 22, and 26 kcal/mol. As shown in Table 2, the major contributions to the ammonia TPD spectrum for titania and the 0.6% vanadia/titania catalyst were from sites having enthalpies of 22 and 26 kcal/mol, while the major sites for the 6% vanadia/titania catalyst were sites with enthalpies of 18 and 22 kcal/mol. The most significant site for the vanadia sample was that with an enthalpy of 18 kcal/mol. Thus, these TPD studies show that addition of vanadia to titania leads to a slight weakening of the sites on which ammonia is adsorbed strongly (in the range from 22 to 26 kcal/mol) and the enhancement of sites that adsorb ammonia weakly (near 18 kcal/mol). The ammonia desorption states with activation energies near 12–14 kcal/mol observed in the vacuum TPD studies could not be detected in the powder TPD studies because temperatures below 300 K could not be achieved in the latter experiments.

The infrared spectra of adsorbed ammonia on the 0.6 and the 6% vanadia/titania

catalysts showed that the fraction of the acid sites consisting of Brønsted centers was higher for the 6% vanadia/titania catalyst. Thus, the combination of this IR result with the powder TPD spectra for ammonia desorption suggests that ammonia is adsorbed more strongly on Lewis acid sites than on Brønsted acid sites. This result is also in agreement with previous work (20, 24).

Ammonia adsorption on pure titania occurs predominantly on Lewis acid sites (18). Vanadia supported on titania has IR absorption bands due to ammonia adsorbed on Lewis and Brønsted acid sites (11, 25, 26), in agreement with the present paper. At monolayer vanadia coverage, both Lewis and Brønsted acid adsorption sites are observed (18), but when the vanadia loading is increased to five to eight monolayers, only the band due to ammonia on Brønsted acid sites was observed (27). Pure vanadia has been reported to exhibit IR absorption bands due to ammonia adsorbed on Brønsted acid sites (8, 11–13).

Temperature-programmed desorption of ammonia from vanadia (8, 21, 28) gave an activation energy for desorption in the range from 24 to 28 kcal/mol. A separate study (24) reported that ammonia on Brønsted acid sites desorbed at a lower temperature than ammonia on Lewis acid sites, in agreement with the present findings of stronger ammonia adsorption on Lewis acid sites.

It should be noted that the titania surface used for the vacuum TPD studies was rutile, whereas an anatase/rutile sample of titania was used as the basis for powder TPD studies. The literature indicates that superior activity for SCR is found on vanadia supported on the anatase phase of titania (e.g., (4)), and laser Raman spectroscopy experiments suggest that the chemistry of the vanadia overlayer may be different for rutile versus anatase (29). However, the primary cause of higher activity of anatase-supported catalysts relative to rutile-supported catalysts for the selective catalytic reduction of nitric oxide is believed to be due to a higher active surface area for the former catalytic materi-

als (27, 30, 31). Accordingly, the essential surface chemistry of the active sites should remain unchanged, allowing general comparisons between vacuum and powder TPD results.

Comparison of the vacuum and powder TPD results with *in situ* IR results over a wide range of reaction conditions leads to the conclusion that ammonia adsorption is an equilibrated process under SCR reaction conditions. In particular, the intensities of the IR bands due to adsorbed ammonia in the presence of nitric oxide vary with reaction temperature and ammonia pressure according to a Langmuir adsorption isotherm with an equilibrium constant consistent with that determined from the TPD studies. Thus, the rate of ammonia adsorption cannot be rate limiting in the SCR process at typical reaction conditions. Indeed, the adsorption of ammonia on vanadia has been shown to follow the Langmuir isotherm in the absence of nitric oxide (21).

Nitric Oxide Adsorption Studies

A key result of the vacuum TPD study is the presence of adsorbed NO. While adsorption of NO on titania is expected (e.g., (10)), nitric oxide has been observed on vanadia surfaces only under reducing conditions (10, 32–35). Presumably NO adsorbs on reduced vanadium sites, as it has been observed to adsorb on reduced molybdena catalysts (36–41). Reduction of a vanadia/titania catalyst in hydrogen eliminates V–OH while generating Ti–OH species (18), producing sites that adsorb nitric oxide as nitrosyl and dinitrosyl surface species. A potential candidate for the reduced site would be V^{4+} , which has been observed under reaction conditions using ESR (8, 27, 42, 43). Apparently, the low pressures of oxygen (10^{-7} – 10^{-5} Torr) at 650 K used to pretreat the vanadia samples were insufficient to fully oxidize the surface prior to vacuum TPD studies. Accordingly, significant amounts of V^{4+} may be present under the conditions of the vacuum TPD studies.

Recent vacuum TPD studies have exam-

ined the interaction of nitric oxide and ammonia with pelleted vanadia and titania catalysts (10). These studies found the activation energy for nitric oxide desorption from titania to be 23 kcal/mol, in agreement with the value of 22 kcal/mol found in this study. Also, their TPD spectra were broad, indicating a distribution of adsorption sites, similar to the results reported here. Nitric oxide did not interact with a vanadia catalyst that was fully oxidized, which suggests further that the vanadia catalyst used in the present vacuum TPD studies was somewhat reduced.

Nitric oxide does not adsorb as nitrosyl species on fully oxidized vanadia, regardless of the support (8, 11–13, 18). If an alumina-supported vanadia catalyst is reduced to a stoichiometry of $V_2O_{3.6}$, then it can adsorb NO, with IR adsorption bands indicating nitrosyl, dinitrosyl, and nitrite species (32, 34). The activation energy for NO desorption from reduced vanadia/alumina was measured to be about 28 kcal/mol (33, 34), in general agreement with the present study.

SCR Reaction Studies

A fundamental difference exists between the reaction conditions employed during the vacuum TPR experiments and the powder TPR studies; i.e., gaseous nitric oxide is present during the powder TPR measurements. Therefore, reduction of NO must involve strongly adsorbed nitric oxide and ammonia species under vacuum TPR conditions, while gaseous (or weakly adsorbed) NO may also participate in powder TPR studies. In fact, various studies on vanadia/titania catalysts at SCR reaction conditions suggest that the reaction takes place via an Eley–Rideal step between adsorbed ammonia and gaseous NO (4–9). In agreement with these previous results, the *in situ* IR results of this study show that measurable amounts of adsorbed nitric oxide species are not present on the catalyst surface under SCR reaction conditions. Thus, we may suggest that different NO species may be responsible for reaction with adsorbed ammo-

nia during the vacuum and powder TPR studies. Accordingly, we must analyze the vacuum TPR results for the evolution of N_2 using a Langmuir–Hinshelwood step between adsorbed NO and NH_3 , while we must employ an Eley–Rideal step between gaseous (or weakly adsorbed) NO and adsorbed ammonia to describe the evolution of N_2 in the powder TPR studies.

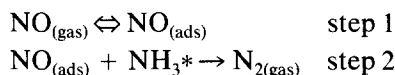
The vacuum and powder TPR studies show that a simple relation does not exist between the ability of a surface to adsorb NO and NH_3 and its reactivity for reduction of NO. For example, the titania surface adsorbs both NO and NH_3 under vacuum conditions, but it does not produce N_2 during subsequent heating. In addition, titania adsorbs ammonia most strongly in powder TPD studies, but this ammonia does not react with gaseous nitric oxide during subsequent heating. It is suggested that the vanadia component of the surface plays a unique role in the surface reaction between nitric oxide and ammonia; e.g., vanadia participates in an oxidation/reduction process which is necessary to activate at least one of the reactants, probably ammonia, as discussed below.

The observation that reaction between nitric oxide and ammonia takes place under vacuum and powder TPR conditions indicates that the strong adsorption of NO is not a necessary condition for the SCR reaction, since significant amounts of strongly adsorbed NO are not present on the surface under powder TPR or *in situ* IR reaction conditions. In addition, the presence of strongly adsorbed ammonia is not a sufficient condition for the SCR reaction, since titania adsorbs ammonia strongly, but this ammonia is not reactive under vacuum or powder TPR reaction conditions. Instead, it appears that strongly adsorbed ammonia is necessary for the SCR reaction; but as noted above, this ammonia must be near vanadia to undergo further reaction with nitric oxide.

In both the vacuum and powder TPR studies, the appropriate surface coverages by

strongly adsorbed species (i.e., θ_{NO} and θ_{NH_3} for vacuum TPD and θ_{NH_3} for powder TPD) can be estimated from the desorption and equilibrium constants determined in the vacuum and powder TPD studies, respectively. As noted above, we then use the peak for the evolution of N_2 in vacuum TPR experiments to estimate the rate constant for the Langmuir–Hinshelwood reaction between adsorbed nitric oxide and adsorbed ammonia ($NO^* + NH_3^* \rightarrow N_{2(gas)}$), whereas we use the peak for the consumption of NO in powder TPR studies to estimate the rate constant for the Eley–Rideal reaction between gaseous nitric oxide and adsorbed ammonia ($NO_{(gas)} + NH_3^* \rightarrow N_{2(gas)}$). Similar estimates for rate constants can also be made from *in situ* IR studies (44). The important result from these measurements is that the activation energies for the Langmuir–Hinshelwood and the Eley–Rideal reaction steps in the vacuum and powder TPR studies, respectively, are essentially the same (~ 20 kcal/mol). This is particularly true if one notes that the vanadia/titania sample studied in the vacuum TPR experiments and the 6% vanadia/titania catalyst studied in the powder TPR experiments both contained vanadia surface coverages near monolayer amounts, whereas the vanadia surface coverage on the 0.6% vanadia/titania catalyst was considerably lower than one monolayer.

A useful comparison between the Langmuir–Hinshelwood and the Eley–Rideal rate constants can be made if the Eley–Rideal reaction is written in terms of a weakly adsorbed, precursor state, $NO_{(ads)}$,



Assuming that step 1 is equilibrated, the overall rate of reaction is equal to $K_1 k_2 P_{NO}$, where K_1 is the equilibrium constant for step 1 and k_2 is the rate constant for step 2. Accordingly, the Eley–Rideal rate constant, k_{ER} , is equal to $K_1 k_2$. If we assume that the rate constant k_2 is equal to the Langmuir–Hinshelwood rate constant, k_{LH} , esti-

mated from the vacuum TPR studies, then the value of K_1 should equal k_{ER}/k_{LH} . This ratio of rate constants is equal to $10^{-6} \text{ Torr}^{-1} \text{ s}^{-1}$ (since the activation energies for both rate constants are equal to about 20 kcal/mol).

We see that the above estimate for K_1 is independent of temperature, as expected for a weakly adsorbed surface species (K_1 is proportional to $\exp(-\Delta H/RT)$, where the enthalpy of adsorption, ΔH , is small). The value of K_1 should be equal to about $10^{-7} \text{ Torr}^{-1} \text{ s}^{-1}$ for a sticking coefficient of one and a desorption preexponential factor of 10^{13} s^{-1} . This value agrees approximately with the above estimate of K_1 obtained from k_{ER}/k_{LH} , especially since the preexponential factors used in this study were simply order of magnitude estimates. This result suggests that the key aspect of the reaction between nitric oxide and ammonia is not the activation of nitric oxide, because both weakly and strongly adsorbed NO have similar reactivities. Instead, the key aspect of this reaction may be the activation of adsorbed ammonia, because this is the species that is common to both the vacuum and powder TPD measurements.

The important implication of the above result is that both Langmuir–Hinshelwood and the Eley–Rideal mechanisms may be effective for selective catalytic reduction of nitric oxide, depending on the reaction conditions. Furthermore, the reactivities appear to be comparable for the strongly and weakly adsorbed nitric oxide species in these two mechanisms, respectively, since the reaction is controlled by the activation of ammonia. Under typical SCR reaction conditions the amount of strongly adsorbed nitric oxide is negligible, and the Eley–Rideal mechanism would seem to be dominant.

The powder TPR results show that the activation energy for the Eley–Rideal reaction is higher for the 0.6% vanadia/titania catalyst compared to the 6% vanadia/titania sample. The 0.6% vanadia/titania catalyst also adsorbs ammonia more strongly. A sim-

ple correspondence between ammonia reactivity and the strength of ammonia adsorption does not exist, since the activation energies for the SCR reaction over these two catalysts are different while the ammonia TPD spectra for both catalysts can be described by linear combinations of the same three adsorption sites. Thus, we may suggest that the morphology of the vanadia site may be critical for its ability to activate ammonia. The nature of vanadia surface species on titania has been shown to depend on the vanadia loading (18, 45–50), and the catalytic activity of the vanadia/titania catalyst system for the SCR reaction has been found to exhibit an optimum at intermediate vanadia loadings (46, 48, 51, 52).

CONCLUSIONS

Vacuum and powder TPD studies indicate that the activation energies and enthalpies of ammonia desorption, respectively, are in agreement, consistent with nonactivated ammonia adsorption. These desorption energetic values range from about 18 to 26 kcal/mol over vanadia, vanadia/titania, and titania, with the enthalpy increasing with decreasing amounts of vanadia. Vacuum TPD spectra show that the activation energy for water desorption ranges from 14 to 18 kcal/mol over these same materials, with this value also increasing with decreasing amounts of vanadia. Accordingly, water should not significantly block ammonia adsorption under SCR reaction conditions. Comparison of the TPD results with *in situ* IR measurements of the surface coverages by ammonia under SCR reaction conditions suggests that ammonia adsorption on Lewis acid sites is stronger than on Brønsted acid sites and that ammonia adsorption is not rate determining for the SCR reaction. Nitric oxide adsorbs strongly on surfaces treated under vacuum conditions, with desorption activation energies varying from 16 to 22 kcal/mol in comparing vanadia, vanadia/titania, and titania, respectively. *In situ* IR studies indicate that significant amounts of adsorbed NO are not present on

vanadia/titania surfaces under SCR reaction conditions. Accordingly, TPR studies of the reaction between nitric oxide and ammonia probe a Langmuir–Hinshelwood step between adsorbed nitric oxide and ammonia species under vacuum conditions, whereas powder TPR studies involve an Eley–Rideal step between adsorbed ammonia and gaseous (or weakly adsorbed) nitric oxide. Both types of TPR studies indicate that the activation energy for reaction is about 20 kcal/mol, independent of the nature of the reactive NO species. This result suggests that a key step in the reaction between nitric oxide and ammonia may be the activation of the adsorbed ammonia species, probably by the vanadia component of the catalyst. The implications of these results for interpretation of the steady-state reaction kinetics of the SCR reaction over vanadia/titania catalysts under industrial reaction conditions will be addressed elsewhere (53).

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