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An Infrared and Electrical Conductance Study of $V_2O_5/SiO_2–TiO_2$ Catalysts Active for the Reduction of NO by NH_3

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A series of $V_2O_5/SiO_2–TiO_2$ catalysts (vanadia content 2–30 wt%) was evaluated for the selective reduction of NO by NH_3. Activities at 200°C determined on a per gram vanadia basis were nearly equal for catalysts containing 5–20% vanadia. The 10% catalyst exhibited the highest activity at 350°C. Characterization of the catalysts with FTIR and XRD showed that the vanadia was highly dispersed on the carrier as an amorphous phase for all catalysts with 20% or less vanadia. Electrical conductance measurements were made to study the dispersion of the vanadia on the support and the effect of different gases on the degree of vanadia reduction. Conductances for the catalysts in 1.5% O_2/Ar carrier gas increased with increasing vanadia content for catalysts with 15% or more vanadia indicating a decreasing distance between V(IV) centers. Exposure of the catalysts to NH_3 in the carrier gas resulted in reversible increases in conductance for all vanadia concentrations. Exposure of the catalysts to NO resulted in reversible conductance increases for the 15, 20, and 30% catalysts. Exposure of the catalysts to NH_3 + NO resulted in conductance changes which indicated a reaction at 350°C between adsorbed, laterally mobile NH_3 and gaseous NO for all catalysts with the most effective reaction occurring on the 10% catalyst. At 200°C, the conductance measurements indicated a reaction between strongly bound NH_3, which exhibited little lateral movement, and gaseous NO.

INTRODUCTION

Selective catalytic reduction of nitric oxides with ammonia is becoming increasingly employed as a process to reduce pollution from stationary power sources. Vanadium oxide catalysts are currently used because of their resistance to poisoning by SO_2 and their high activity in the presence of oxygen (1–5%) in flue gases. Titanium oxide is incorporated in the support for the catalyst primarily because of the intimate interaction between V_2O_5 and TiO_2 which may give rise to an epitaxial growth of vanadia exposing the (010) plane (*1*) or, at monolayer or less coverage, results in highly dispersed vanadate species individually attached to the support (*2*).

Mechanistic work done on the NO–NH_3 reaction has shown that the formation of N_2 and H_2O occurs by an Eley–Rideal mechanism between NH_3 adsorbed on the catalyst and gaseous NO. Surface V=O sites play an important role in the reaction, and they are partially reduced during the reaction and subsequently oxidized by gaseous O_2 (*3*). While it is known that the reaction rate is dependent on O_2 concentration, only a few studies about the behavior of O_2 during the reaction have been published (*4*).

In order to investigate the adsorption of NO and NH_3 and the role of O_2 in the NO–NH_3 reaction, we have made infrared and electrical conductance studies of a series of $V_2O_5/SiO_2–TiO_2$ catalysts. It was previously reported that 20 wt% vanadia on $SiO_2–TiO_2$ as support was a very active catalyst for NO reduction (*5*). Our purpose in the present study was to observe the effect of the three principal gases involved in the

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reaction, NO, NH_3, and O_2, on the catalyst conductances for vanadia concentrations from 2–30 wt%.

Conductance measurements on powdered, nonsintered samples of high surface-to-volume ratio are a convenient way to monitor the adsorption of gaseous reactants but results are difficult to analyze quantitatively. For semiconducting oxide powders, adsorbed oxygen species play a key role in determining intergranular contact resistances. Oxygen adsorbing on *n*-type oxides extracts electrons from the near surface regions of the grains and thus the O^- concentration on the surface determines the conductance of a pressed pellet (*6*). Reducing gases which remove O^- can be expected to raise the conductance of the pellet. Vanadium pentoxide is normally an *n*-type semiconductor but there is a problem in using the above description of O^- control of conductivity because there is some disagreement over the existence of such charged oxygen species on the V_2O_5 surface. Grzybowska *et al.* (*7*) detected O_2^- and O^- on pure V_2O_5 and V_2O_5–TiO_2 samples using surface potential measurements. However, other studies using ESR and TPD have concluded that no such species exist on V_2O_5 surfaces (*3, 8, 9*). A recent study of the role of O_2 in the NO–NH_3 reaction found no evidence for isotopic scrambling between gaseous and lattice oxygen between 300 and 400°C for supported V_2O_5 catalysts and the authors proposed that molecular oxygen was responsible for oxidation of V=O reduced in the reaction (*4*).

The adsorption of NH_3 and NO on the catalyst surface is an important step in the reaction mechanism and is also the subject of some disagreement. It is generally agreed that NH_3 is strongly adsorbed on the catalyst surface, but the actual adsorption site is unclear. Inomata *et al.* (*3*) proposed that NH_3 was adsorbed as NH_4^+ on surface hydroxyl V_s–OH sites. This view was supported by Gasior *et al.* (*10*) who concluded from their XPS and IR measurements that V^{5+}–OH sites on the crystal planes perpendicular to (010) served as adsorption centers for NH_3. However, Janssen *et al.* (*4*) proposed that ammonia chemisorbed on the surface at 400°C producing NH_2 and OH groups which were observed to desorb as N_2 and H_2O. Both adsorption mechanisms entail the reduction of vanadia and since the ratio $c = V(IV)/[V(IV) + V(V)]$ determines the electrical conductivity in amorphous vanadium oxides (*11*), it was our plan to use electrical conductance measurements to follow NH_3 adsorption on the catalysts both alone and together with NO.

Several studies have found that NO adsorbs only weakly on V_2O_5 surfaces (*3, 4, 10*). However, it has been observed from ^{18}O labeling experiments that a small fraction of NO interacted with the surface during the selective reduction reaction (*12*). For our own conductivity studies, the previous work of Solymosi and Kiss (*13*) on the reduction of NO with CO over *n*-type SnO_2 has been a useful guide. Their electrical conductance measurements showed that both negatively and positively charged species were present on activated surfaces. Nitric oxide was observed to both donate electrons to SnO_2 upon adsorption as NO^+ and also accept electrons leading to formation of adsorbed NO^-.

EXPERIMENTAL

The catalyst support (Si/Ti = 1) was prepared by co-precipitation with urea of acidified solutions of $Na_2SiO_3 \cdot 5H_2O$ and $TiCl_4$ according to the procedure of Shikada *et al.* (*14*). The impregnations with vanadium were performed with aqueous solutions of NH_4VO_3 in oxalic acid. Catalysts were dried and then calcined for 1 h at 450°C before use (*5*). Infrared spectra of catalysts diluted in KBr (1 mg catalyst in 100 mg KBr) were recorded on a Bruker IFS 113 spectrometer.

Catalytic activities were determined in a conventional downflow fixed-bed reactor described previously (*5*). The following experimental conditions were used: 600 ppm

NO, 700 ppm NH_3, 2% O_2, and N_2 balance with a total flow through the reactor of 50 liters STP/h. Varying amounts of catalyst between 0.04 and 1.8 g were used, yielding space velocities in the range 38,000 to 1,710,000 h^{-1}. The conversions of NO were in this way kept within the range 5 to 20% at 200°C. Sample streams before and after the reactor were transported in heated teflon lines to a Beckman Model 955 Chemiluminescence NO_x meter. In order to avoid interference in the analysis, a scrubber with concentrated H_3PO_4 supported on alumina was used to remove NH_3 ahead of the NO_x meter. Rate constants were calculated, using a first-order dependence on NO concentration, from conversions of NO determined between 200 and 400°C. The BET surface areas were measured at liquid N_2 temperature in a gravimetric apparatus (*5*). X-ray diffraction was used to study the crystalline phases present in the catalyst and also to determine the crystallite size of the support particles (*15*).

Electrical conductance measurements were made in a stainless-steel cell (0.5 ml volume) which we have described previously (*16*). Catalyst powders were first ground in an agate ball mill for 10 min and then pressed into thin tablets at 400 kg/cm² pressure for 10 min. Gold contacts were evaporated onto both sides of small tablets (about 0.2 × 0.2 × 0.03 cm, weight about 5 mg) which were then positioned in the measurement cell two at a time and heated to 350°C in flowing 10% O_2 in Ar and held for 16 h. Gases used were Ar, O_2, 21% O_2/Ar, 2600 ppm NO/Ar, and 2700 ppm NH_3/Ar from Alfax AB. Several mass flow regulators from Bronkhorst High-Tech, BV, were used to vary the concentration of the different gases at a total constant flow through the cell of 100 ml/min. Switching valves from Bürkert were used to introduce and take away gases from the carrier flow. All flow regulators and valves could be controlled manually or by computer. Conductivity measurements were made at a constant dc potential of 1 V.

RESULTS AND DISCUSSION

Catalyst Characterization and Activity Testing

Surface areas were determined for calcined catalysts, and results are listed in Table 1. The surface area decreased with increasing vanadia loading. Since the surface area decreases when calculated per gram catalyst and per gram support were about the same, we consider that the decrease was the result of filling the smallest pores (*5*) and was not caused by the increase in density of the loaded support. V_2O_5 was visible in the XRD spectra only for the 30% catalyst which could be the result of vanadia covering the pore walls to more than a monolayer thickness. The monolayer capacity of the support is 26 wt% V_2O_5 using the recommended value of 0.10 wt% V_2O_5 per m² of support proposed by Bond *et al.* (*17*).

FTIR analysis of the catalysts indicated that V_2O_5 was highly dispersed on the carrier. Figure 1 shows spectra for the 2, 7, 15 and 30% catalysts in the 1050–750-cm^{-1} region of the spectrum. Peaks in the 1000–950-cm^{-1} region can be attributed to surface vanadate species as has been previously reported for amorphous two-dimensional

TABLE 1

Surface Areas and First-Order Rate Constants for the NO–NH_3 Reaction at 200 and 350°C

V_2O_5 (%)	BET surface area (m^2/g)	Rate constants (cm^3/s/g V_2O_5)		
		k(200)	k(350)	k'(350)[a]
0	259	0	–	–
2	251	15	1400	2234
5	237	64	1280	4481
7	209	51	–	–
10	212	77	1640	9720
15	183	85	913	4902
20	159	77	625	3010
30	86	42	–	–

[a] Rate constants corrected for diffusion effects by assuming a first-order dependence on NO concentration and using the data presented in Ref. (*5*).

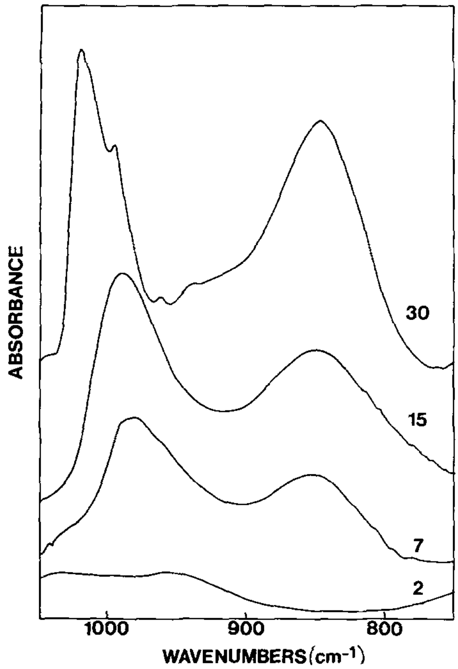

FIG. 1. Infrared spectra for 2, 7, 15, and 30% catalysts after calcination at 450°C. The contribution of the support has been subtracted from the spectra.

monolayers on V_2O_5/TiO_2 catalysts (*18*). Andersson (*19*) has shown that a band at 995 cm^{-1} in V–Ti oxides is due to the boundaries between oxidized and reduced vanadia in which the V=O bond is weakened. Thus for catalysts containing 20% or less vanadia, no evidence for crystalline V=O was seen and all vanadia was present as an amorphous layer of slightly reduced character on the support. The 30% catalyst exhibited a strong absorption at 1020 cm^{-1} which can be assigned to crystalline V=O (*18*) in agreement with the XRD results. A small peak at 968 cm^{-1} was observed which has been previously reported in the spectrum of V_2O_5 (*19*). SEM investigations had shown that the catalyst support was made up of 75–150-nm particles. X-ray microanalysis using SEM indicated that the surface was enriched with TiO_2 containing 5% Si and 95% Ti (*5*). Measurements with diffuse reflectance FTIR detected a band at 3740 cm^{-1} which was assigned to the Si–OH stretching vibration of silica. The absorption intensity at 3740 cm^{-1} decreased with increasing vanadia concentration of the catalysts, the intensity for the 30% catalyst being $\frac{1}{10}$ the intensity for the support alone. Thus at least some of the vanadia interacts with SiO_2 in the support, although we conclude that most of the vanadia is in contact with TiO_2. Although the spectra in Fig. 1 for the submonolayer catalysts (7 and 15%) have features similar to those reported for V_2O_5/TiO_2 catalysts (*18, 19*), the presence of silica in the support yields high surface areas and thereby high monolayer capacities compared to the V–Ti system (*18*).

Rate constants for the NO–NH_3 reaction were measured at several temperatures, and the first-order rate constants at 200 and 350°C are presented in Table 1. The rate constants calculated per gram vanadia were nearly equal for vanadia concentrations from 5–20% at 200°C. The 10% catalyst exhibited the highest activity at 350°C. Possible explanations for these activity trends will be discussed later in this paper.

Electrical Conductance of Supported V_2O_5

Electrical conductances of the catalysts were measured at 350°C in a gas flow of 1.5% O_2 in Ar. As shown in Table 2, where conductance is designated as *G*, the conductance of the support alone was quite low

TABLE 2

Conductance (*G*) in Carrier Gas and Relative Conductance Changes (ΔG) after Exposure to 300 ppm NO and 300 ppm NH_3 at 350°C

V_2O_5 (%)	*G* (μS)[a]	$\frac{\Delta G(NO)}{G}$	$\frac{\Delta G(NH_3)}{G}$	$\frac{\Delta G(NO + NH_3)}{G}$
0	0.02	0.0	0.02	0.0
2	0.03	−0.1	1.5	1.2
5	0.02	0.0	1.5	1.1
7	0.03	0.0	1.8	0.9
10	0.02	0.0	1.8	0.7
15	0.05	0.2	3.3	2.7
20	0.15	0.6	4.8	3.6
30	25.	0.5	4.6	3.5
100	5000.	0.1	2.0	1.6

[a] Units in microsiemens (1 S = 1 ohm^{-1}).

and did not vary for up to 10% vanadia loading. The conductances increased sharply between 10 and 30% vanadia. Pure V_2O_5 had a significantly higher conductance than the supported catalysts. Varying the concentration of O_2 in the gas flow in the range 0–6% caused no change in conductance for the catalysts with 20% or less vanadia. Small changes in conductance (ΔG) were observed for the 30% catalyst and pure V_2O_5. The results presented in Table 2 are an average of measurements on at least three different samples of each catalyst. Variation in G and $\Delta G(NH_3)$ values was about 10–20%.

V_2O_5 exhibits n-type semiconductor properties due to the hopping of electrons between vanadium ions in different valence states (V(IV) and V(V)). Since the electron–phonon coupling is rather strong, the unpaired electrons are trapped in their own polarization wells and the charge carriers are actually small polarons (*20*). No difference was observed between the conductance of the support and conductances for catalysts of 10% or less vanadia in the carrier gas (Table 2). However, these catalysts all exhibited rather large changes in conductance ($\Delta G(NH_3)$) when exposed to NH_3 (Table 2, Fig. 2). V_2O_5 monolayers supported on titania (anatase) have been shown to be composed of isolated vanadate species individually attached to the titania surface (*21, 22*). Although the two systems are quite dissimilar, the formula of Austin and Mott (*20*) for describing small polaron conduction in glasses containing transition metal ions

$$\sigma = [\nu_0 e^2 c(1 - c)/kTR] \exp(-2\alpha R) \exp(-W/kT) \quad (1)$$

can serve as an illustrative model for conduction in vanadia catalysts. The expression for conductivity σ includes several terms where ν_0 is the optical phonon frequency, k is the Boltzmann constant, e is the electronic charge, T is the Kelvin temperature, R is the average distance between two transition metal ions, c is the fraction of sites occupied by an electron (V(IV)/[V(IV) + V(V)]), α is the decay component of the localized $3d$ electron wave function, and W is the activation energy. The two terms which are of interest for the supported vanadia catalysts are R, the dispersion of vanadia on the support, and c, the degree of reduction of the vanadia. The distance between V ions on the support is a function of the vanadia concentration. For the lowest concentration, 2 wt%, which corresponds to about $\frac{1}{10}$ monolayer coverage of the support, the average distance between V ions if they are evenly distributed in two dimensions, is about 20 Å. For such large R values, the $\exp(-2\alpha R)$ term dominates in Eq. (1) and the conductance is low.

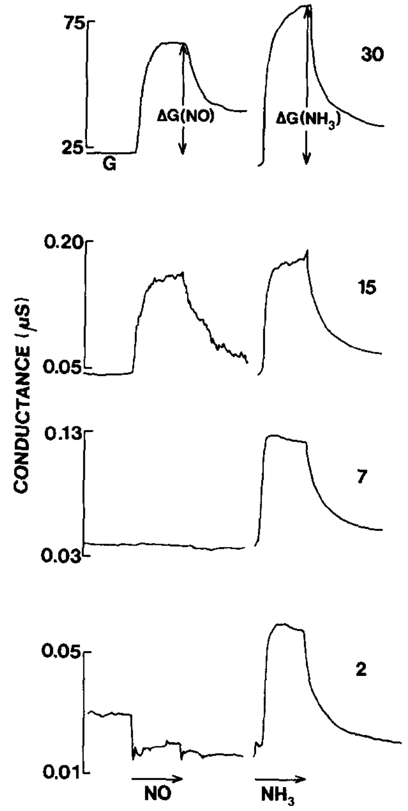

FIG. 2. Changes in conductance during exposure of 2, 7, 15, and 30% catalysts to 300 ppm NO or 300 ppm NH_3 in 1.5% O_2/Ar for 1 h at 350°C. Conductance scale shown is for the NH_3 exposures. The scale was expanded for the NO exposures.

With increasing vanadia content, the distance between V centers decreases, falling to about 4 Å at monolayer coverage (26 wt%), and the conductance thus increases. This simplified description is a possible explanation for the conductance data in Table 2. For catalysts with 10% or less vanadia content, the large R values result in low conductances in the oxidizing carrier gas and no difference is observed in conductance between the support and the vanadia catalysts. For catalysts with 15% or more vanadia, the decreasing R values result in increasing conductances. It should be pointed out that the simple polaron theory encounters problems when describing glasses with low vanadia content (*23*). The assumption that the vanadium ions are equally spaced does not hold, and Eq. (1) must be modified to account for the percolation of the current carriers through irregular paths, a situation which would not be surprising for a supported vanadia catalyst.

The second term in Eq. (1) which is of interest for the current study is c, the degree of reduction of the supported vanadia. Exposing the catalysts to NH_3 increased the conductances for all catalysts as a result of reduction of vanadia. Thus even catalysts with large R values were found to increase conductance during NH_3 exposure because of the increase in the $c(1 - c)$ term in Eq. (1). We made no attempt to use Eq. (1) to quantify conductance changes observed for the catalysts in different gases in terms of c since the pressed powder catalysts are not such suitable materials for electrical measurements as the sintered, dense glasses. However, it is our judgement that Eq. (1) provides a good introduction for using conductance measurements to study supported vanadia catalysts.

There are additional models available to describe conductance in pressed catalyst pellets. For nonsintered powders, the intergranular contact resistance is an important factor and the extraction of conduction electrons from the near-surface region upon oxygen adsorption on n-type semiconductors creates a barrier which electrons must overcome in order to hop to a neighboring grain. For catalysts supported on semiconducting oxides, the support can take part in the conduction mechanism by so-called Fermi energy control (*6*). Adsorbed, partially reduced oxygen species play a prominent role in the conduction mechanism, but since such species have so far not received much attention in the mechanism for the $NO–NH_3$ reaction, we will continue to use Eq. (1) in discussing our results and return to this issue in the final section.

It was also observed that the activation energies derived from the temperature dependence of the conductances in 1.5% O_2/Ar were between 63 and 84 kJ/mole for catalysts containing 20% or less vanadia. The 30% catalyst had an activation energy of 21 kJ/mole, very near to the 17 kJ/mole measured for the pure V_2O_5 samples. This is in agreement with the XRD and FTIR results showing crystallinity in only the 30% catalyst. It also corresponds well with the variation in W observed for vanadia-containing glasses (*23*). When R increased from 4.5 to 5.3 Å, a sharp increase in W was observed followed by a more gradual increase at higher values of R. Increasing vanadia concentration from slightly below (20%) to slightly above (30%) monolayer coverage would be about in the R range where W changes rapidly.

Adsorption of NO

After the catalysts had reached a constant conductance level in the carrier gas, they were exposed for 1 h to 300 ppm NO. As shown in Fig. 2, the 2% catalyst exhibited an irreversible decrease in conductance upon exposure to NO, the 7% catalyst showed no change in conductance and the 15 and 30% catalysts showed increases in conductance which were reversible in the carrier gas after the NO exposure was stopped. Table 2 lists the relative changes in conductance upon exposure to NO, $\Delta G(NO)/G$ (see Fig. 2).

It is generally agreed that NO is either not adsorbed or only weakly adsorbed on V_2O_5 during the NO–NH_3 reaction (*3, 4, 10*). Our conductance measurements are in agreement with this conclusion for vanadia concentrations of 10% or less. The small irreversible decrease observed with the 2% catalyst is similar to what was observed by Solymosi and Kiss on SnO_2 (*13*). They attributed the conductance decreases to adsorption of NO as NO^- which was strongly held on the SnO_2 surface.

The conductance increases observed for the higher vanadia loadings indicate a different type of NO adsorption. The low ionization potential of NO, 9.5 V, allows the conversion of the nitric oxide molecule to the nitrosonium ion, NO^+. Adsorption of NO^+ has been observed by electrical conductivity on SnO_2 (*13*) and by infrared spectroscopy on metal oxides (*24*) and zeolites (*25*). However, catalysts that were exposed to 300 ppm NO at 350°C and then cooled to room temperature in Ar exhibited no IR bands which could be assigned to NO or NO^+-adsorbed species.

Another possibility to explain the conductance increase upon NO exposure is that the catalyst surface was reduced by the NO. Since our conductance measurements showed no evidence for O^- being present on the surface, the mechanism described by Morrison (*6*) of a reducing gas removing O^- and thereby raising the conductivity of the oxide is not applicable. A direct reduction of the catalysts by NO with formation and desorption of NO_2 is a possible explanation for the conductance increases. Odenbrand *et al.* (*5*) have reported the production of about 30 ppm NO_2 when 630 ppm NO was passed over the 20% catalyst at 350°C in a 2% O_2/N_2 carrier gas. Although it is difficult to analyze the conductance changes observed quantitatively, this low conversion of NO to NO_2 seems suitable for causing the ΔG(NO) values shown in Table 2. Infrared studies have shown that NO adsorbs as a chelating NO_2 species on partially reduced CeO_2 (*26*) and Cr_2O_3 (*27*). Desorption of this species would result in the formation of oxygen vacancies and an increase in conductance.

The structural changes in the catalysts caused by the NO exposures were investigated by FTIR. As shown in Fig. 3, a small increase in peak height at 984 cm^{-1} was observed for the 20% catalyst after the NO exposure. It has been reported that unsupported V_2O_5 reduced during the NO–NH_3 reaction exhibited absorption bands at 990 and 910 cm^{-1} (*3*); these bands were assigned to the lattice vibrations of V_2O_4. We have previously assigned the absorption bands in the 1000–950-cm^{-1} region to amorphous surface vanadate of slightly reduced character and, as indicated in Fig. 3, exposure to NO increases the degree of reduction slightly. However, the number of sites reducible by NO is apparently much smaller than the NH_3 reducible sites (see Table 2). Reduction by NO may be a new, interesting characterization technique for V_2O_5 catalysts but, as we discuss below, the sites involved do not seem to play an important role in the NO–NH_3 reaction.

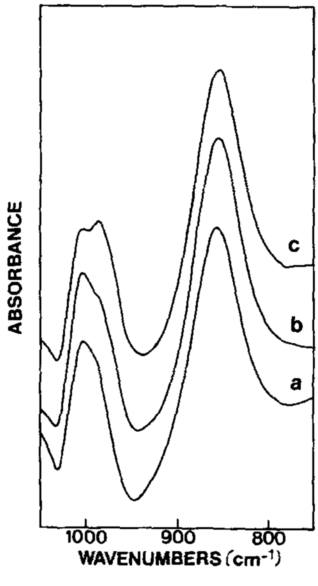

FIG. 3. Infrared spectra for 20% catalyst after exposure to (b) 300 ppm NO and (c) 300 ppm NH_3 at 350°C in a carrier gas of 3% O_2/Ar. Spectrum (a) is for the catalyst heated at 350°C in only the carrier gas.

Adsorption of NH_3

Conductances for all vanadia catalysts increased during exposure to NH_3. As shown in Fig. 2, there was a time lag of about 5 min between when the NH_3 was first switched into the gas stream and the initial increase in the conductance for the 15 and 30% catalysts. This time delay was a function of concentration, being about 90 min when the NH_3 concentration was 40 ppm, for example. For catalysts with the lower concentrations of vanadia, the conductance quickly reached its maximum value indicating a saturation of the adsorption sites (2 and 7% in Fig. 2). The increase was more gradual for the catalysts with higher vanadia concentrations. It was also observed for the 20 and 30% catalysts that $\Delta G(NH_3)/G$ (see Fig. 2) was a linear function of the NH_3 concentration up to about 600 ppm NH_3. The catalysts with lower V_2O_5 content exhibited a saturation of $\Delta G(NH_3)/G$ at about 300 ppm. These results are in agreement with a description of the supported V_2O_5 existing as isolated vanadate species for concentrations of 10% or less vanadia and a more complete coverage of the support for the 20 and 30% catalysts.

Table 2 lists the $\Delta G(NH_3)/G$ values for all catalysts. The support itself did not exhibit a significant conductance change during the NH_3 exposure. Relative changes for the supported catalysts increased with increasing vanadia content.

Fig. 3 shows the FTIR spectra for the 20% catalyst after exposure to NH_3. An increase in peak height at 984 cm^{-1} was seen after the exposure which, as we discussed above, indicates further reduction of the amorphous vanadia layer.

Two different NH_3 adsorption sites have been proposed for mechanisms describing the NO–NH_3 reaction. Janssen *et al.* (*12*) propose that (in the absence of NO) two NH_3 molecules chemisorb dissociatively on four adjacent V=O sites which are subsequently reduced when N_2 and H_2O desorb from the surface. However, Gasior *et al.* (*10*) disagree and claim that V=O does not participate in the reaction and that V^{5+}–OH is the adsorption site for NH_3. Both mechanisms propose the formation of oxygen vacancies and an increase in [V(IV)] upon NH_3 adsorption. We cannot discriminate between the two mechanisms based solely on our conductance measurements.

Several studies using infrared spectroscopy have shown that both chemisorbed NH_3 and physisorbed NH_4^+ are present on V_2O_5 catalysts after exposure to NH_3 under vacuum (*2, 3, 10*). Inomata *et al.* (*28*) found that NH_3 adsorbed on V_2O_5/TiO_2 at room temperature exhibited bands assigned to coordinatively held NH_3 (1610 cm^{-1}) and NH_4^+ (1420 cm^{-1}) ions. For vanadia concentrations of 10 mole% or more, only NH_4^+ was observed. We are unaware of any infrared results for NH_3 adsorption at temperatures above 300°C. For catalysts exposed to 300 ppm NH_3 in our measurement cell at 350°C and cooled to room temperature in the same gas flow (300 ppm NH_3, 1.5% O_2/Ar), bands at 1610 and 1400 cm^{-1} were observed. If the catalysts were cooled in Ar after NH_3 exposure, only the band at 1610 cm^{-1} was observed. This observation supports the idea that NH_3 is coordinatively held on the catalyst at 350°C and the mechanism proposed by Janssen *et al.* (*12*).

Adsorption of NH_3 + NO

Exposure of the catalysts to 300 ppm NH_3 + 300 ppm NO resulted in a conductance increase for all vanadia concentrations. For catalysts containing either 5% or less vanadia or 15% or more vanadia, the conductance increase was about 80–90% of that observed after exposure to only NH_3. For catalysts containing 7 and 10% vanadia, the increase was 40–50% of that observed after exposure to only NH_3. Table 2 lists the relative conductance changes for catalysts exposed to NO + NH_3 for 1 h.

It was found that a sequential exposure of the catalysts to (a) NH_3 and O_2, (b) NH_3, NO, and O_2, (c) NO only, and (d) O_2 in the carrier gas provided information about changes in the catalysts during the NO–NH_3 reaction. Exposing the catalysts to NO (b) after the NH_3 exposure (a) had raised the conductance resulted in a relatively small lowering of the conductance for 2, 5, 15, 20, and 30% catalysts (5 and 15% shown in Fig. 4). The catalysts containing 7 and 10% vanadia exhibited much larger conductance decreases when NO was introduced (10% catalyst shown in Fig. 4).

The detailed mechanisms which have been proposed in the literature for the NO–NH_3 reaction involve active sites containing several surface vanadate species, V=O (*12*) or V^{5+}–OH (*10*). Janssen *et al.* (*12*) have proposed that in the temperature range 300–400°C chemisorbed NH_3 in the absence of NO results in a reduction/dehydration of the surface. Their mechanism requires that a certain number of vanadate species are located near each other and that there is sufficient lateral mobility of adsorbed species between these sites. If these requirements are met, then the following reaction occurs:

$$3V_2O_5 + 2NH_3(a) \rightarrow N_2 + 3H_2O + 3V_2O_4. \quad (2)$$

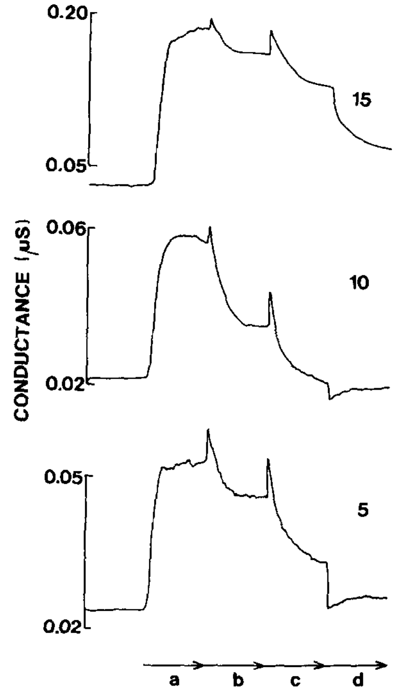

FIG. 4. Changes in conductance during exposure of 5, 10, and 15% catalysts to (a) 300 ppm NH_3, (b) 300 ppm NH_3 + 300 ppm NO, (c) 300 ppm NO, O_2 off, and (d) O_2 on, in 1.5% O_2/Ar carrier gas for 1-h intervals at 350°C.

When the partially reduced surfaces were exposed to NO (Fig. 4, segment b), a conductance decrease was observed for all catalysts. According to the mechanism of Janssen *et al.*, for this reaction step two gaseous NO molecules react with two chemisorbed NH_3 molecules and $2N_2$ + $2H_2O$ desorb. One oxygen vacancy is formed when an additional H_2O molecule is produced from the resulting V–OH sites:

$$V_2O_5 + 2NH_3(a) + 2NO(g) \rightarrow 2N_2 + 3H_2O + V_2O_4. \quad (3)$$

According to Eqs. (2) and (3), the admission of NO to an NH_3-reduced catalyst should ideally lower the steady-state conductance by $\frac{2}{3}$ when gaseous O_2 is present (transition from three oxygen vacancies to one oxygen vacancy). As shown in Table 2 and Fig. 4, only the 10% catalyst exhibited such a large conductance decrease when NO was admitted to the NH_3-reduced catalysts. One possible explanation for this is the variation in vanadia coverage of the support for the different catalysts. For the 2 and 5% catalysts, NO interacts mostly with the support between V sites and thus has only a small effect on the conductances of the NH_3-reduced catalysts. For the 15, 20, and 30% catalysts, the close packing of V sites is a favorable arrangement for the self-reaction of NH_3 described in Eq. (2), and this counteracts the fact that the higher vanadia concentrations improve the probability that NO approaches the surface near an adsorbed NH_3. We conclude that according to Fig. 4, NO is most effective for interrupting the self-reaction of NH_3 at 350°C on the 10% catalyst.

The activity data presented in Table 1 support this conclusion. At 350°C, the highest activity for NO conversion according to the observed rate constants, k, and the rate constants corrected for diffusion effects, k', was observed for the 10% catalyst which would indicate that the concentration of adsorbed NH_3 available to react with NO was highest on this catalyst. Increasing the reaction temperature to 400°C resulted in decreasing activities for the catalysts containing more than 10% vanadia and increasing activities for the catalysts containing less than 10% vanadia. This again emphasizes the importance of temperature and distance between V sites with regard to the reactions described in Eqs. (2) and (3).

Although it was not possible to measure conductances for the catalysts with the lower vanadia contents at temperatures much below 350°C, we have made measurements on the 15, 20, and 30% catalysts at 200°C. The results indicated that conductances increased very little during adsorption of NO or NH_3, but increased greatly during adsorption of NO + NH_3. Figure 5 compares the changes in conductance at 350 and 200°C for the 20% catalyst during exposure to the sequence of gases described above. During exposure to NH_3 alone, a much smaller relative increase in conductance was observed at 200°C than at 350°C. Upon introduction of NO in segment b, the conductance decreased at 350°C but increased considerably at 200°C. We interpret these results as indicating that at 200°C, the lateral mobility of adsorbed N species from NH_3 adsorption (Eq. (2)) is much less than at 350°C and the predominant reaction path during segment b to form oxygen vacancies on the surface is the direct collision of gaseous NO with adsorbed, relatively immobile NH_3 (Eq. (3)). It was also observed by FTIR that both chemisorbed and physisorbed NH_3 species were present on the catalyst surfaces at 200°C which would support the mechanism of Gasior *et al.* (*10*)

$$2V^{5+}ONH_4 + V^{5+}\text{–}O\text{–}V^{5+} + 2NO \rightarrow 2N_2 + 3H_2O + 2V^{5+}OH + V^{4+}\square V^{4+} \quad (4)$$

being operative at the lower temperature. If the collision between gaseous NO and strongly adsorbed NH_3 were the rate-limiting step at 200°C as has been proposed for V_2O_5 between 180 and 330°C (*3*), then the activity constants listed in Table 1 showing a nearly constant activity per gram vanadia for the 5–20% catalysts could be explained by the fact that since lateral interaction between adsorbed NH_3 species makes only a small contribution to the reaction at 200°C (Fig. 5) then the relative isolation of the vanadate groups in the submonolayer catalysts has no influence on the reaction rate. Only the extreme concentrations, 2 and 30%, exhibited significantly lower activities.

It was also observed that NO in the absence of O_2 could lower the conductance of reduced catalysts. As shown in Fig. 4, segment c, the conductance decreased when NH_3 and O_2 were removed from the carrier gas for all the catalysts. Catalysts with 7 and 10% vanadia content exhibited a decrease in conductance to the original conductance level during segment c.

We had shown earlier that NO was able to reduce oxidized catalysts containing 15% or more vanadia (Fig. 2, Table 2). However, catalysts which were first reduced with NH_3 were observed to have their conductances lowered when exposed to NO (Fig. 4). We conclude from these observations that the sites reducible by NO in the oxidized catalysts are also reducible by NH_3 and that in the steady-state with both NH_3 and NO present, the role of nitric oxide is to interrupt the reduction of the catalysts by NH_3 and not to further reduce the 15, 20, and 30% catalysts.

At 200°C, the oxidizing effect of NO was much less than what was observed at

350°C. This is shown in Fig. 5, segment c, where a large increase in conductance was seen after removal of NH_3 and O_2 from the gas flow. This result was also seen for the 15 and 30% catalysts at 200°C. It should be noted that the 20% catalyst also exhibited the lowest conductance decrease of all the catalysts at 350°C during segment c.

Segment d in Fig. 4 shows the effect of replacing NO with O_2 as the oxidizing gas. A further slow decrease in conductance for the catalysts with 15% or more vanadia and a rapid decrease for the 2 and 5% catalysts was observed during segment d. This is in agreement with the observation that reoxidation with O_2 is faster than reoxidation with NO (*12*). According to the mechanism of Janssen *et al.* (*4*), oxygen reoxidizes the surface by adsorbing as molecular O_2 on a single oxygen vacancy. When a vacancy arises nearby, the O_2 dissociates and one O atom migrates to the other vacancy. Reoxidation of the surface by NO requires the adsorption of two NO molecules on adjacent vacancies and subsequent desorption of N_2. This mechanism would presumably have a lower probability than O_2 reoxidation for most vanadia concentrations. However, this was not the case for the 7 and 10% catalysts. In a separate experiment, it was observed that NO was more effective than O_2 for the reoxidation of these catalysts. For these two catalysts, the distances between O vacancies were apparently favorable for the NO reoxidation mechanism.

At 200°C, the reaction of O_2 was clearly faster than the reaction of NO with the reduced catalysts, as shown in Fig. 5.

Effect of O_2 Concentration

Varying the O_2 concentration in the carrier gas had an effect on the conductance changes observed during the adsorption of NO or NH_3. The conductance increases caused by exposure to NO or NH_3 were always reversible when the gases were stopped and some O_2 was present in the carrier gas. The rate of decrease to the original conductance increased with increasing O_2 concentration.

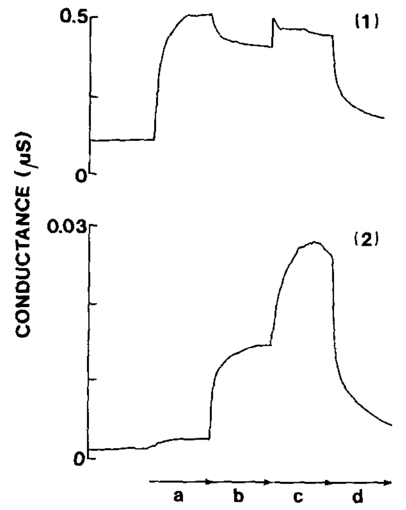

FIG. 5. Changes in conductance for 20% catalyst during exposure to (a) 300 ppm NH_3, (b) 300 ppm NH_3 + 300 ppm NO, (c) 300 ppm NO, O_2 off, and (d) O_2 on, in 1.5% O_2/Ar at 350 (1) and 200°C (2).

When both NO and O_2 were removed from the carrier gas after the NO exposures shown in Fig. 2, the conductances for the 15, 20 and 30% catalysts remained constant at the maximum value shown in the figure. When both NH_3 and O_2 were removed from the carrier gas after the NH_3 exposures there were sharp increases in the conductances. For the 20% catalyst the relative change in conductance, 4.8, after NH_3 exposure in 1.5% O_2 was followed by a further increase to 7.6 when both NH_3 and O_2 were stopped. This would seem to indicate that NH_3 remained on the surface and could further reduce the catalyst in the absence of O_2 whereas all NO species quickly desorbed from the catalyst when the gaseous NO was stopped. Janssen *et al.* (*12*) have reported that about 20% of the NH_3 adsorbed during reduction of catalysts remained on the surface after 1 h of flushing with helium.

The effect of O_2 on the NO–NH_3 reaction was studied by varying the O_2 concentration and observing the changes in conductance under different conditions. Figure 6

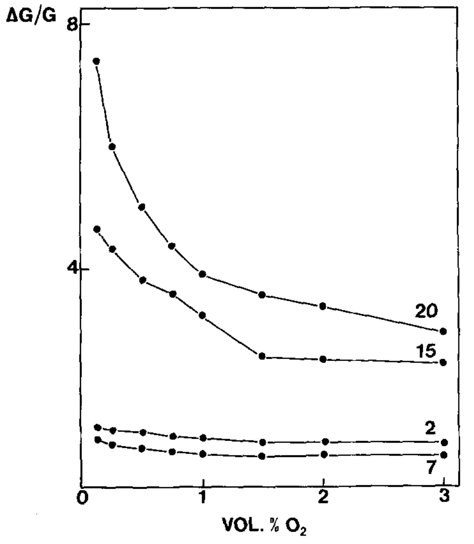

FIG. 6. Relative conductance changes for 2, 7, 15, and 20% catalysts during exposure to 300 ppm NH_3 + 300 ppm NO in different concentrations of O_2 at 350°C.

shows the effect of varying the O_2 concentration during exposure to NO + NH_3. For the catalysts with 10% or less vanadia concentrations, the conductances exhibited only a small dependence on O_2 concentration. The dependence was more pronounced for the catalysts with higher loadings. For the 15, 20, and 30% catalysts which exhibited conductance increases during exposures to NO or NH_3, only a small dependence on O_2 concentration during NO exposure and a much larger dependence during NH_3 exposure were observed.

Several studies have shown that the activity for the NO–NH_3 reaction increases with increasing O_2 concentration in the interval 0–1% O_2 (*3, 4, 5*). Inomata *et al.* (*3*) found good correlation between this result and the increase in the IR band at 1020 cm^{-1}, which is assigned to the $V^{5+}{=}O$ stretching vibration, for pure V_2O_5 catalysts during the NO–NH_3 reaction between 0–1% O_2. The mechanisms of Janssen *et al.* (*4, 12*) and Gasior *et al.* (*10*) account for this O_2 dependence of the reaction rate by the fact that O_2 reoxidizes the O vacancies formed during the reaction, regenerating $V^{5+}{=}O$ or $V^{5+}{-}O{-}V^{5+}$ surface sites.

The curves in Fig. 6 clearly show that the effect of the oxygen concentration on catalyst conductance during the NO–NH_3 reaction was greatest for the catalysts with the higher loadings and more closely packed surface vanadate species, 15 and 20%. Only small effects were seen for catalysts with 10% or less vanadia content. One possible explanation for this is that O_2 adsorbs on the support for catalysts with low vanadia content and has a relatively high concentration compared to the concentration of oxygen vacancies formed during the reaction. For the catalysts with higher vanadia contents, the surface concentration of O_2 is low relative to the number of oxygen vacancies formed in the reaction for gaseous O_2 concentrations of less than 1% and this affects the conductance. For this explanation to hold using the previously described molecular oxygen reoxidation mechanism (*4*), one must assume that the vanadia active sites are grouped together even on the catalysts with low concentrations of vanadia, as implied by Eqs. (3) and (4).

Whether partially reduced adsorbed oxygen species play a role in the NO–NH_3 reaction is an open question. None of the previous studies of the reaction on vanadia catalysts have reported evidence supporting their existence (*3, 4, 10*). Although our own conductance measurements indicated that there were no such O species on the calcined, submonolayer catalysts at 350°C, it has been reported that such species exist after O_2 adsorption on reduced silica-supported vanadia over a wide temperature range (*29*). Since vanadia catalysts are partially reduced in the steady-state of the NO–NH_3 reaction, it cannot be ruled out that reoxidation occurs by the scheme:

$$O_{2ads} \rightleftarrows O^{-}_{2ads} \rightleftarrows O^{2-}_{2ads} \rightleftarrows 2O^{-}_{ads} \rightleftarrows 2O^{2-}_{ads} \rightleftarrows 2O^{2-}_{lattice} \quad (5)$$

proposed by Shvets and Kazansky (*29*) instead of the one-step mechanism involving molecular oxygen described above (*4*). Indeed, the explanation given for the molecular oxygen mechanism on p. 5926 of Ref. (*4*) could also apply to reoxidation by Eq. (5). For the molecular oxygen reoxidation mechanism on supported vanadia catalysts, the rate-limiting step would most probably be in going from O_2 to 2O species because of the distances involved. For Eq. (5), the slow step would be that involving O^- since such radicals are highly reactive and would have a low concentration at 350°C in the presence of reducing gases (*29*). The fact that conversion of NH_3 to NO is low up to 400°C on titania-supported vanadia (*5, 30*) seems to indicate that O^- is not formed in the reaction.

CONCLUSIONS

V_2O_5 supported on SiO_2–TiO_2 was found to be highly dispersed on the carrier. Characterization of the catalysts by FTIR and XRD showed that the catalysts with 20% or less vanadia consisted of a surface amorphous vanadate phase dispersed on the carrier. Crystalline V_2O_5 was observed only in the 30% catalyst. The measured first-order rate constants calculated on a per gram vanadia basis for the NO–NH_3 reaction were nearly equal between 5 and 20% vanadia content at 200°C. The 10% catalyst exhibited the highest NO conversion at 350°C. Electrical conductance measurements were made in order to study the dispersion of vanadia on the support. The isolated surface vanadate species were close enough to each other to increase the conductance over that of the support alone when the vanadia concentration was more than 10%. Exposure of the catalysts to NH_3 caused reversible increases in conductance which were related to a reduction of the surface vanadate layer. This was observed even for the catalyst containing 2% vanadia. Exposure of the 15, 20, and 30% catalysts to NO resulted in reversible conductance increases probably caused by the formation of small quantities of NO_2.

Nitric oxide was observed to interrupt the reduction of catalysts which were under exposure to NH_3 at 350°C. An Eley–Rideal mechanism between gaseous NO and chemisorbed NH_3 in the presence of O_2 was found to occur on all catalysts with the most effective reaction between NH_3 and NO on the 10% catalyst. At 200°C, the adsorbed NH_3 exhibited little lateral mobility, and oxygen vacancies were produced mainly by reaction with NO.

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