

## The Catalytic Reduction of Nitric Oxide by Ammonia over a Clean and Vanadium Oxide-Coated Platinum Foil

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The reduction of NO by NH<sub>3</sub> could be readily monitored over a 2-cm<sup>2</sup> area platinum foil in the temperature range of 450–560 K. The reaction is first order in NO and zero order in NH<sub>3</sub> partial pressures, and the rate is given by  $r_{\text{NO}} = 5 \times 10^7 [\text{NO}] \exp(-E/RT)$  (mol/cm<sup>2</sup>.s) with  $E = 113 \pm 20$  kJ/mol. Vanadium oxide forms three-dimensional islands on Pt with a stoichiometry near V<sub>2</sub>O<sub>4</sub>. Its presence does not alter the activation energy appreciably but reduces the rate by blocking the active platinum sites. © 1991 Academic Press, Inc.

### INTRODUCTION

The catalytic reduction of nitric oxide by ammonia, in both the absence and presence of oxygen, has been the subject of many investigations due to its importance in the removal of nitrogen oxides from the flue gases of power plants and nitric acid plants.

Although both platinum group metal and base metal catalysts are capable of reducing NO by ammonia, presently base metal catalysts are used. This is partly due to the high temperatures of the flue gases produced (typically 350°C for thermal power plants and 170–500°C for HNO<sub>3</sub> plants (1, 2)) and the presence of oxygen. In this study the reaction between NO and NH<sub>3</sub> was monitored in the absence of oxygen in order to avoid the possibility of ammonium nitrate formation in our reaction system (4, 5). Some examples of commercial catalysts used for reducing the level of nitric oxide in flue gases are V<sub>2</sub>O<sub>5</sub> on Al<sub>2</sub>O<sub>3</sub> supports (2) and WO<sub>3</sub>–V<sub>2</sub>O<sub>5</sub> on TiO<sub>2</sub> (6), the latter being highly resistant to poisoning by sulfur compounds present in the flue gases from stationary sources. Since platinum, vanadia,

and titania reach optimum nitric oxide conversion at quite different temperatures, it is interesting to study the behavior of a combination of two or all three of these components (3). This could ultimately lead to the formulation of a new catalyst which operates at high efficiency in a broad range of tail gas temperatures and compositions.

In this paper we explored the catalytic behavior of a small 2-cm<sup>2</sup> platinum foil for the NO/NH<sub>3</sub> reaction. Ultrahigh vacuum (UHV) surface science techniques were utilized for cleaning and characterizing the surface composition. The catalytic reaction could be readily monitored in the temperature range of 450–560 K. Vanadium oxide was deposited on Pt from the vapor phase and characterized, and its influence on the reaction rate was also studied.

### EXPERIMENTAL

In order to study the reaction over both platinum foils and a platinum foil partly or entirely covered by vanadium oxide, an ultrahigh vacuum chamber equipped with a high-pressure reaction cell was used (Fig. 1). In this way both surface analysis tech-

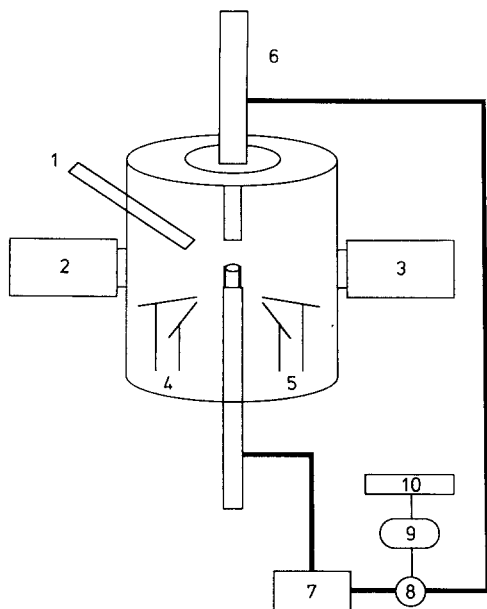


FIG. 1. Schematic representation of the ultrahigh vacuum system equipped with high-pressure reaction cell used in the study of the NO reduction by NH<sub>3</sub>. (1) Ion gun, (2) Auger electron gun, (3) mass spectrometer, (4) titanium source, (5) vanadium source, (6) hydrolic piston, (7) pump, (8) sampling valve, (9) photo ionization detector, (10) integrator.

niques and techniques to follow the catalytic reaction could be applied. The pumps used to establish UHV in the chamber were a diffusion pump in combination with a titanium sublimation pump, and the manipulator was pumped by a mechanical pump. To ensure good vacuum the entire UHV system was baked every night for about 10 h to remove ammonia, nitric oxide, and water from the walls of the chamber. The UHV chamber was equipped with an ion gun for Ar ion bombardment, an Auger electron gun with retarding field analyzer (RFA), and a mass spectrometer (UTI precision gas analyzer model 100C).

When NO alone was passed over a platinum foil at 523 K the NO signal remained constant after the equilibration period.

In order to determine the background reactivity of the system, the reduction of NO by ammonia was followed using a gold foil.

The Au and Pt foils had a thickness of 0.001 in. and a total surface area of 2 cm<sup>2</sup>. The foils were mounted on a manipulator which could be rotated to position the foils in front of a metal evaporation source or the RFA. The mounting of the samples is shown in detail in Fig. 2.

Two copper rods ending in a small platinum rod support the sample. Two platinum wires (thickness 0.015 in.) are spotwelded on the metal foils and on the platinum support rods. A chromel–alumel thermocouple is spotwelded on the foils for regulation of the reaction temperature with a precision temperature controller. The foils can be heated resistively by applying a current to the copper rods. These rods are hollow to allow cooling with cold nitrogen gas to reduce background reactivity. For the study of metal oxide overlayers a source shape shown in Fig. 2 was used. Vanadium wire (99.99% metallic purity) with a thickness of 0.005 in. was wrapped around a tungsten wire of thickness 0.03 in. The special shape of this tungsten wire allowed the metal evaporator to come close to the foils. A conical tantalum shield helped to restrict metal deposition to the foils. Prior to reaction or deposition, the Au and Pt foils were cleaned by alternating cycles of high-temperature oxidation during 60 min in  $1 \times 10^{-6}$  Torr of

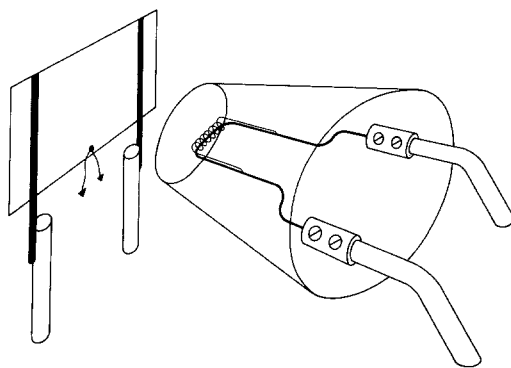


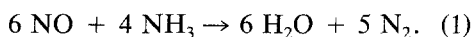
FIG. 2. A schematic representation of the vanadium evaporation source and sample mounting used in this study. Because of its shape it can be positioned close to the sample surface. The source is shielded by Ta.

oxygen at 900 K and Ar ion bombardment at a pressure of  $1 \times 10^{-4}$  Torr and with an ion energy of 2 kV until the surface was free of contaminants as judged by AES.

The chamber was equipped with a vanadium and a titanium source. For this study only the vanadium source was used. The copper feedthroughs on which the sources were mounted allowed resistive heating of the tungsten wires. Before being used in an experiment a new source was outgassed for at least 24 h. in UHV at a current level slightly below the onset of metal evaporation. In this way impurities like carbon and sulfur were removed. The platinum foil was heated in  $1 \times 10^{-6}$  Torr of oxygen at 900 K in order to check if during previous vanadium deposition some vanadium had diffused into the bulk of the platinum. Under our conditions no vanadium diffusion into the bulk was ever found. The vanadium was evaporated in an atmosphere of  $1 \times 10^{-6}$  Torr of oxygen and the base pressure of the chamber before an experiment was below  $1 \times 10^{-9}$  Torr. The substrate was kept at a temperature of 370 K to accomplish rapid vanadium oxidation.

For the reaction 1% of NO in helium and 1% of NH<sub>3</sub> in helium were used (Matheson Certified Standard) without further purification.

After closing the reaction cell to isolate the reaction loop from the UHV chamber, the reaction gases were introduced and circulated at room temperature by a circulation pump to ensure a good mixing. Ten minutes after introduction of the gases, the foils were heated to the reaction temperature. The following reaction between NO and NH<sub>3</sub> takes place:



The decrease in NO concentration was monitored by a photoionization detector, (PID, HNU Systems model PI-51), equipped with a 9.5-eV ultraviolet lamp. This detector is very sensitive and of all gases present only NO is ionized.

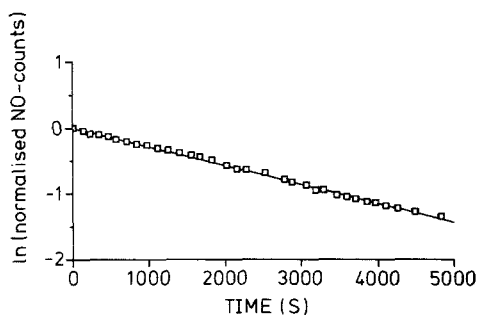


FIG. 3. The calculation of the reaction rate constant for the NO + NH<sub>3</sub> reaction over platinum at 489 K.

During reaction the pressure in the UHV chamber was about  $5 \times 10^{-8}$  Torr, caused by a small leak between both parts of the high-pressure cell. This leak was used to monitor the change in nitrogen concentration in the chamber.

In order to be able to subtract the rate of reaction of the background from that of the platinum foil, the rate constant for the reaction over gold was determined by assuming first order in NO and plotting  $\ln ([\text{NO}]/[\text{NO}]_{\text{initial}})$  versus time. The slopes of this type of plots give the rate constant at a certain temperature. These values were subtracted from the results obtained with platinum foils. It was found that the background reactivity at the lowest reaction temperature (474 K) was about 30% of the reactivity of the platinum foil at the same temperature, but that the background reactivity of the system remained almost constant with increasing temperature.

## RESULTS AND DISCUSSION

### 1. The Kinetics of the NO/NH<sub>3</sub> Reaction over Platinum

The partial pressures of NO and NH<sub>3</sub> in the reaction mixture were 3.8 Torr and the mixture was balanced with helium to a total pressure of 1 atm. The reaction order in NO was determined by varying the partial pressure of NO in the reaction loop while keeping the partial pressure of NH<sub>3</sub> constant at 3.8 Torr. The data obtained for the reaction over platinum are shown in Fig. 3 and

suggest that the reaction over platinum can be described on the basis of first-order kinetics in NO.

It was found that in a broad range of conversions the decrease in NO concentration as monitored with the PID detector could be described on the basis of first-order kinetics in NO, despite a drop in the partial pressure of ammonia during the reaction. Michailova (7) found that the reaction rate depends upon the ratio of the partial pressures of the reacting gases. Apparently this ratio does not change sufficiently during the reaction to influence the reaction orders.

Several investigators have found that the NO-NH<sub>3</sub>-O<sub>2</sub> reaction on supported V<sub>2</sub>O<sub>5</sub> catalysts can be modeled by pseudo-first-order kinetics in NO concentration (8-10, 26). Pusateri *et al.* (11) observed on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst a weak dependence on NH<sub>3</sub> pressure at 548 K for 0.25% NO and between 0.07 and 0.5% NH<sub>3</sub>, with a rate maximum at about 0.1% NH<sub>3</sub>. The data obtained by Meier and Gut (12) on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in the absence of O<sub>2</sub> indicate a zero order with respect to NH<sub>3</sub> at 515 K, for a NH<sub>3</sub>/NO molar ratio of 1.4, and a weak dependence around this ratio.

From these indications it can be deduced that under our reaction conditions the order with respect to NH<sub>3</sub> is probably close to zero, and may become negative when high conversions are attained in the system. If the stoichiometry of reaction (1) is assumed, a molar ratio between NH<sub>3</sub> and NO of  $\frac{4}{3}$  is reached at 50% NO conversion. The reaction orders determined in our experiments hold well in a broad range of temperatures as shown in Fig. 4. Using the corrected rate constants for the reaction between NO and ammonia over platinum, an Arrhenius plot was constructed.

The slope of this line yields an activation energy for the disappearance of NO  $E_1 = 113 \pm 20$  kJ/mol, which is in agreement with literature data. Activation energies reported for alumina-supported platinum catalysts and polycrystalline platinum range from 90 to 117 kJ/mol (7, 11-14). Using the value

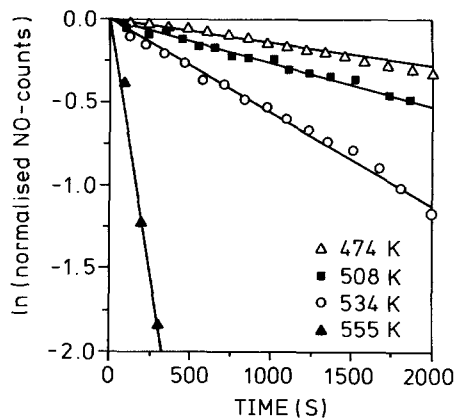


FIG. 4. Results obtained for the NO/NH<sub>3</sub> reaction over platinum at various temperatures.

for the preexponential factor calculated by extrapolation of the Arrhenius plot to  $1/T = 0$  gives the following rate expression:

$$r_{\text{NO}} = 5 \times 10^7 [\text{NO}] e^{-E_1/RT} \quad (\text{mol/s} \cdot \text{cm}^2) \quad \text{with } E_1 = 113 \text{ kJ/mol.}$$

At 473 K this gives an initial rate of  $3.5 \times 10^{-9}$  mol of NO per cm<sup>2</sup> of platinum per second. This is comparable to results obtained under similar conditions (7).

At 473 K values of ca.  $0.12 \times 10^{-9}$  were obtained for the reaction rate on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts by Pusateri *et al.* (11) and Otto *et al.* (15). At the same temperature, Takoudis and Schmidt (14) reported a value of  $0.56 \times 10^{-9}$  for a clean Pt wire treated at 1573 K in  $10^{-2}$  Torr of oxygen. These differences may be due to various pretreatments of the catalysts before reaction.

The formation of nitrogen was also monitored using the mass spectrometer. However, monitoring the decreasing NO signal by the photoionization detector was a more sensitive means to follow the reaction rate. The fast reaction rate of NO reduction by ammonia over platinum should be compared with the rates reported over vanadium oxide-titanium oxide catalysts at much higher temperatures (600-700 K). The reaction appears to be much slower over the oxide surface as compared to that over platinum.

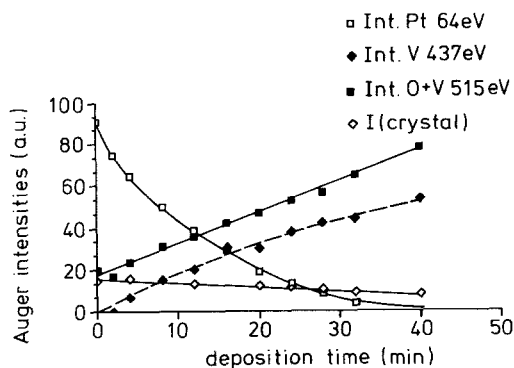


FIG. 5. Vanadium deposition curve on a platinum foil at a temperature of 373 K and in an atmosphere of  $1 \times 10^{-6}$  Torr of oxygen. The intensities of the Auger electron transitions for Pt (64 eV), V (437 eV) and the combination peak of O and V at 515 eV are plotted versus deposition time. The crystal current was monitored during deposition because it can reflect changes in surface composition or surface structure (21, 27).

## 2. Vanadium Oxide Deposition on Platinum and its Effect on Reactivity

**A. Vanadium deposition.** Before starting vanadium deposition the foil was heated in UHV at 900 K for several minutes and the cleanliness of the foil was checked by AES. As soon as the foil was clean, vanadium was deposited slowly onto the platinum in an atmosphere of  $1 \times 10^{-6}$  Torr of oxygen. A typical deposition curve is shown in Fig. 5, where the intensity of the Pt Auger peak at 64 eV, the V 437 eV peak, the crystal current, originating from secondary electron emission, and the combination peak of V and O at 515 eV are plotted against deposition time. Vanadium was deposited for 2–4 min at a time and in between the depositions the Auger spectra were recorded. A gradual growth of vanadium oxide is observed. In Fig. 6 the intensity of the Pt Auger transition at 237 eV is plotted versus deposition time. When Figs. 5 and 6 are compared, it is clear that no breaks in the Auger curves or the crystal current are observed which would indicate Frank–van der Merwe growth (a layer-by-layer growth of vanadium oxide on the platinum foil resulting in a break in the Auger curves every time the

formation of a monolayer is completed). Most likely the vanadium oxide grows on top of the platinum foil by forming three-dimensional islands according to the Volmer–Weber mechanism. This means that the vanadium oxide which is deposited forms crystallites on top of the platinum without first completing one or more monolayers. This conclusion is supported by the fact that the intensities of both the surface sensitive Pt(64 eV) and the less surface sensitive Pt(237 eV) Auger electron transitions disappear at about the same deposition time. As discussed later, it was also found that even when very thick layers of vanadium oxide were deposited on Pt, the reactivity of the system could still be described by assuming that part of the platinum was not covered by vanadium oxide, thus resulting in a (low) reactivity of the vanadium oxide/platinum system. An Auger spectrum of a platinum foil partially covered by vanadium oxide is shown in Fig. 7.

**B. The characterization of the vanadium oxide overlayers.** As has been found by Lewis (16), it is hard to grow vanadium pentoxide overlayers on a metal substrate in the reducing environment of the ultrahigh vacuum. Furthermore, the oxide surface can be reduced by the impact of electrons, ions, or photons. In the UHV chamber, vanadium oxide can be reduced by residual  $H_2$  or CO in the ambient to form  $H_2O$  and  $CO_2$ . The

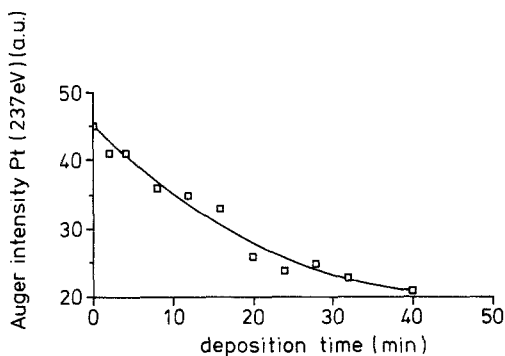


FIG. 6. The decrease in intensity of the Pt (237 eV) Auger electron transition versus deposition time.

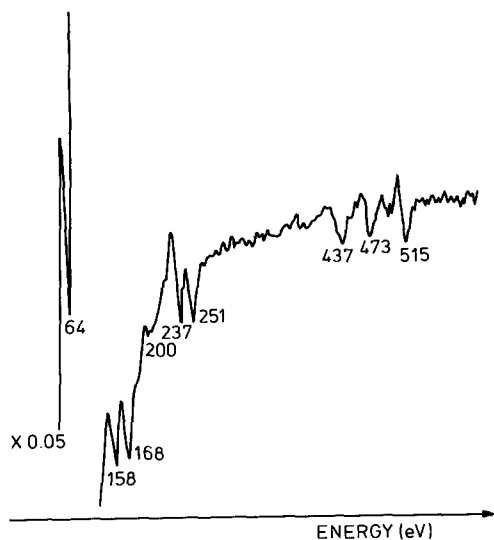


FIG. 7. An Auger electron spectrum of platinum partly covered by vanadium oxide.

presence of carbon impurity in the vanadium oxide must be avoided because of its reducing character and its possible impact on the catalytic behavior of the oxide overlayers (17).

In order to obtain information about the composition of the vanadium oxide overlayers on our platinum foil, AES and XPS were used. The use of AES for the determination of metal oxidation states has been reported in the literature (18–21). Using chemical shifts for the vanadium inner shell Auger transitions and the relative intensities of the oxygen and vanadium Auger peaks, Szalkowski and Somorjai were able to distinguish between the different oxidation states of vanadium in vanadium oxide (18). They were also able to observe the chemical shifts in other vanadium compounds (19). Rao *et al.* used metal Auger intensity ratios to study surface oxidation states (20). They found for example a relation between the ratio of the  $L_{2,3}M_{2,3}M_{4,5}/L_{2,3}M_{2,3}M_{2,3}$  vanadium Auger peak intensities and the oxidation state of the vanadium compounds studied.

In order to determine the oxidation state

of the vanadium in our overlayers, the Auger spectrum of a multilayer of the oxide on platinum was recorded. As a reference a vanadium foil (thickness 0.006 in. metallic purity 99.999%) was oxidized for 5 min in a furnace at 873 K under 1 atm of oxygen. The color of the vanadium oxide formed was blue. An XPS spectrum of this oxidized foil was recorded (Fig. 8) using  $MgK\alpha$  (1253.6 eV) radiation, and the binding energies were calibrated using the gold peaks, originating from the sample holder, in the XPS spectrum. The binding energies of the vanadium peaks were found to be 522.7 eV ( $2P_{1/2}$ ) and 515.8 eV ( $2P_{3/2}$ ) and for the oxygen peak 530.3 eV. Following the XPS measurements the foil was mounted on the UHV manipulator and an Auger spectrum was recorded. Both the Auger spectra of vanadium oxide on Pt and of the oxidized vanadium foil are shown in Fig. 9. The observed blue color of the thick oxidized vanadium layer might point to the presence of  $V_2O_4$  (22). The XPS data indicate that the vanadium oxide is not  $V_2O_5$  but a lower oxide of vanadium. The XPS data obtained are comparable to the binding energies reported by Sawatzky and Post for  $V_2O_3$  (23). Further information can be obtained from the Auger spectra.

Szalkowski and Somorjai calculated the O/V Auger ratios obtained for different vanadium compounds using the  $O(KLL)$  and  $V(L_{2,3}M_{2,3}V)$  peaks. They found different ratios for various vanadium oxide com-

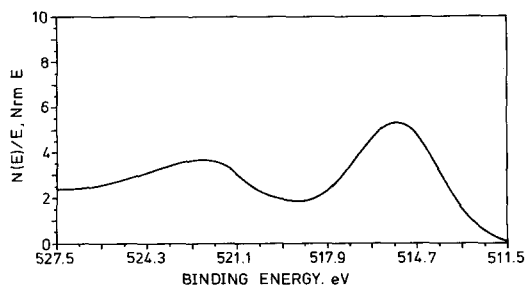


FIG. 8. The XPS data for vanadium obtained for a vanadium foil oxidized for 5 min in 1 atm of oxygen at 873 K.

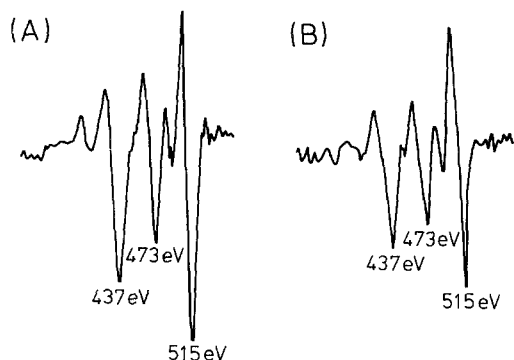


FIG. 9. The Auger spectra obtained for multilayers of vanadium oxide deposited on platinum (A), and of the vanadium foil that was oxidized for 5 min in 1 atm of oxygen at 873 K (B).

pounds. The O/V ratio in  $V_2O_4$  was 2.25 and for  $V_2O_3$  this ratio was 1.58, for example.

The O/V ratio calculated for the vanadium oxide overlayers on platinum (Fig. 10) was 1.69 and for the oxidized vanadium foil 1.87. These values are in between the values observed by Szalkowski and Somorjai for  $V_2O_4$  and  $V_2O_3$ .

Rao *et al.* (20) found a relation between the  $V(L_{2,3}M_{2,3}M_{4,5})/V(L_{2,3}M_{2,3}M_{2,3})$  Auger peak intensity ratio and the oxidation state of vanadium. The calculated ratio for vanadium oxide on platinum was found to be 0.87 and for the oxidized vanadium foil 0.9. According to Rao *et al.* this corresponds to an oxidation state of the vanadium of less than three, which could indicate the presence of a mixed oxide. When these results are compared for both the oxidized vanadium foil and the vanadium oxide overlayers on platinum, it is clear that the Auger spectra are similar. From the XPS data obtained it can be concluded that the vanadium oxide formed is not  $V_2O_5$  but a lower oxide  $VO_x$  with  $x \leq 2$ . Indications of the presence of  $V_2O_4$  and  $V_2O_3$  are found.

The stability of the vanadium oxide overlayers on Pt was checked by heating the platinum in steps of 50 or 100 K from 373 to 973 K in an atmosphere  $10^{-6}$  Torr of oxygen. After every temperature increase the

system was equilibrated for 5 min and then an Auger spectrum was recorded. The results obtained are given in Fig. 10. Until a temperature of about 650 K is reached, no appreciable changes in intensities are observed but above this temperature an increase in the platinum signal and crystal current are observed together with a decrease in vanadium and oxygen signal. These changes increase linearly with increasing temperature at temperatures higher than 770 K. The heating was stopped at 973 K.

The temperature was lowered to 810 K and an Auger spectrum was recorded. No differences from the spectrum recorded at 973 K were observed. Next, the sample was given 12 min to equilibrate at 523 K in the oxygen atmosphere of  $1 \times 10^{-6}$  Torr. Then, the oxygen pressure was increased to  $1 \times 10^{-5}$  Torr for 5 min, lowered to  $1 \times 10^{-6}$  Torr again, and an Auger spectrum was taken. The same procedure was followed for 10 min in  $5 \times 10^{-5}$  Torr of oxygen. In none of these cases were changes in the Auger spectra observed. Decreasing the temperature to 373 K had no effect either. Then, the sample was cooled down to room temperature, the chamber was evacuated, and the foil was sputtered for 30 min on both sides in  $1 \times 10^{-4}$  Torr of argon using argon ions with an energy of 2 kV. The Auger spectrum that was recorded after this treatment only showed platinum peaks. The foil was heated

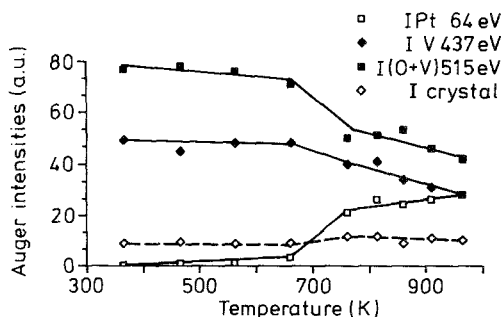


FIG. 10. The stability of vanadium oxide multilayers on Pt was checked by monitoring the Pt (64 eV), V (437 eV), and (O + V) (515 eV) Auger peak intensities and crystal current with increasing temperature.

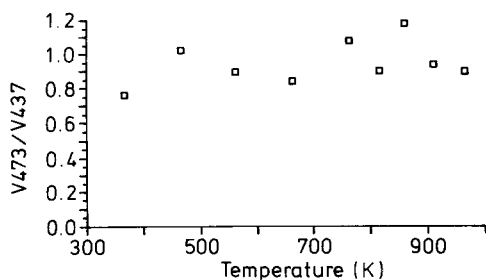


FIG. 11. The ratio of the vanadium Auger electron peak intensities at 473 and 437 eV in a multilayer of vanadium oxide as a function of the temperature of the platinum substrate.

to 900 K in  $1 \times 10^{-6}$  Torr of oxygen for 10 min and again an Auger spectrum was taken. It showed the presence of vanadium that had been pulled out of the bulk of the platinum by the high-temperature oxygen treatment. This vanadium had, apparently, disappeared into the platinum bulk when it was heated to a temperature higher than about 650 K. In Fig. 11 the ( $V_{473}/V_{437}$ ) ratio is plotted versus temperature and it is seen that this ratio does not change significantly. This ratio was the same under all conditions for all surface coverages of vanadium oxide and for all experiments. This indicates that vanadium oxide of the same stoichiometry was present on the platinum foil under all conditions.

*C. The reactivity of the vanadium oxide overlayers.* In Fig. 12 the results for the re-

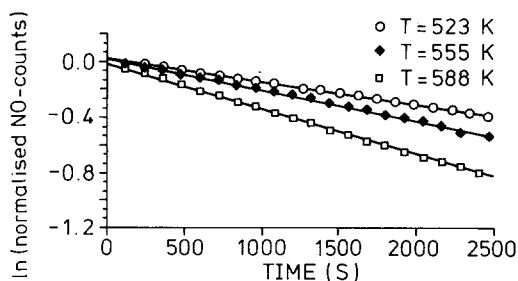


FIG. 12. The results obtained for the reaction between NO and NH<sub>3</sub> over a platinum foil covered with vanadium oxide multilayers. The reaction temperatures are 523, 555, and 588 K. From these data an activation energy of 98 kJ/mol can be calculated.

action between 3.8 Torr of NO and 3.8 Torr of NH<sub>3</sub> over vanadium oxide multilayers at various temperatures are presented. Again the reaction can be described assuming first order in NO. An Arrhenius plot was constructed and an activation energy  $E_2$  of  $98 \pm 15$  kJ/mol was calculated. This results in the rate expression

$$r_{\text{NO}} = 1.6 \times 10^4 [\text{NO}] e^{-E_2/RT} \text{ (mol/s} \cdot \text{cm}^2\text{)}$$

with  $E_2 = 98$  kJ/mol.

When these results are compared with those obtained for pure platinum it can be seen that the activation energy is the same within experimental error, but that the preexponential factor is a factor of 3000 smaller. It is possible that uncovered Pt sites are still present on the V<sub>2</sub>O<sub>4</sub>/Pt foil although there are no platinum peaks visible in the Auger spectrum. A careful examination of the results obtained by various groups on V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts for the selective reduction of NO by NH<sub>3</sub> in the presence of oxygen indicates that the reaction rate at 473 K is close to  $1.80 \times 10^{12}$  molecules NO per cm<sup>2</sup> V<sub>2</sub>O<sub>5</sub> per second ( $0.30 \times 10^{-11}$  mol of NO per cm<sup>2</sup> V<sub>2</sub>O<sub>5</sub> per second).

On the other hand, it is known that the reactivity of V<sub>2</sub>O<sub>4</sub> in the absence of oxygen for the same reaction is at least one order of magnitude lower (8, 9, 24, 25). It has been reported that in the absence of oxygen, V<sub>2</sub>O<sub>5</sub> is reduced to V<sub>2</sub>O<sub>4</sub> in a NO-NH<sub>3</sub> mixture at a temperature of 473 K (24). Taking this into account it can be deduced that V<sub>2</sub>O<sub>4</sub> is at least  $10^4$  times less active than Pt. It appears that platinum that remained uncovered during vanadium oxide deposition is responsible for the NO reduction by ammonia and that vanadium oxide participates mostly by blocking the active platinum sites. This is confirmed by the fact that it was found that the reactivity of the platinum foil decreases almost linearly with increasing vanadium oxide coverage.

#### ACKNOWLEDGMENTS

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