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The Catalytic Reduction of Nitric Oxide with Ammonia over a Stepped Platinum Single Crystal Surface

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The reduction of nitric oxide by ammonia has been studied over a stepped platinum single crystal surface in a vacuum system equipped with Auger electron spectroscopy, low-energy electron diffraction, and mass spectrometry. The reaction proceeds rapidly in the temperature range 150 to 550°C; the only product observed is molecular nitrogen. The rate-limiting step of this reaction scheme occurs between an adsorbed fragment of ammonia and adsorbed molecular nitric oxide. The reaction rate is inhibited by large excesses of nitric oxide. The observed reaction kinetics can be modeled using a single site Langmuir–Hinshelwood reaction scheme. Analysis of the surface during steady-state reaction studies supports the proposed Langmuir–Hinshelwood behavior.

INTRODUCTION

The reduction of nitric oxide by ammonia is an interesting technique for removing nitric oxide from gas streams since ammonia reacts selectively with nitric oxide in the presence of oxygen using platinum catalysts (*1–5* and references therein). A study of the reaction between nitric oxide and ammonia has been undertaken as part of a program to characterize the surface chemistry of the nitrogen–hydrogen–oxygen system over noble metal surfaces with well-determined surface properties. This paper reports the results of steady-state kinetic studies of nitric oxide reduction with ammonia using a stepped single crystal platinum surface as the catalyst. A single crystal sample was used so that the effects of surface structure variation could be determined following similar studies on different single crystal surfaces. Several experiments concerning the effects of oxygen on the ammonia–nitric oxide reaction are also reported.

The mechanism of the ammonia–nitric oxide reaction has been studied over supported platinum catalysts primarily by two groups (*3*, *6–8*). Both groups worked in the temperature range 150 to 250°C. They observed both N_2 and N_2O production. The mechanism proposed by Otto *et al.* (*7*, *8*) was formulated using isotopic labeling of the nitrogen. Basically, the reaction proceeds via a Langmuir–Hinshelwood mechanism which branches with dissociative adsorption of ammonia. The NH_2 (ads) species reacts with NO (ads) to yield N_2. The adsorbed hydrogen fragment of the ammonia reacts with NO (ads) to yield a surface intermediate HNO (ads) which reacts with another NHO to yield N_2O. They indicate that addition of excess hydrogen causes the latter sequence to yield N_2 also.

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workers (*3*, *6*) support and extend the proposed mechanism (*7*, *8*) by fitting their kinetic data with a rate law derived from the proposed mechanism. They model the rate using a single-site Langmuir–Hinshelwood kinetic model involving associative adsorption of NO and dissociative adsorption of NH_3. This indicates that the rate-limiting step occurs between adsorbed NO and an adsorbed nitrogen containing fragment of NH_3.

EXPERIMENTAL

The steady-state reactivity experiments were done in a stainless-steel ultrahigh vacuum system equipped with several gas inlets, a cylindrical mirror analyzer for Auger electron spectroscopy (AES), a low-energy electron diffraction (LEED) unit to determine surface structure, and a quadrupole mass spectrometer to monitor gas-phase composition. Typical background pressures were 1 to 3×10^{-10} Torr during these experiments. This system has been used exclusively for studies with compounds containing nitrogen, hydrogen, and oxygen; therefore, the background contained very little carbon monoxide. The system was pumped exclusively by ion pumps so that the pumping speed would remain fairly constant during the reactivity experiments. The experimental system has been discussed in detail in an earlier publication (*9*).

The platinum single crystal sample was prepared using usual metallographic techniques. The exposed surface has been characterized using Laue X-ray back-reflection and LEED. The sample has a stepped surface with (111) terraces 12 atomic rows wide linked by monotonic height steps with (111) orientation. The same sample was used previously in a study of ammonia oxidation by molecular oxygen (*10*). Periodic examination of the surface with LEED during these studies indicates that this surface structure is stable during the reaction between ammonia and nitric oxide. The sample was heated resistively with direct current and was cooled through a 0.50-mm platinum wire attached to a liquid nitrogen-cooled alumina tube. The sample temperature was monitored with a 0.25-mm Pt–Pt 10% Rh thermocouple spot-welded to the bottom edge of the sample.

A typical Auger spectrum of the clean surface taken at 300°C is shown in Fig. 1.

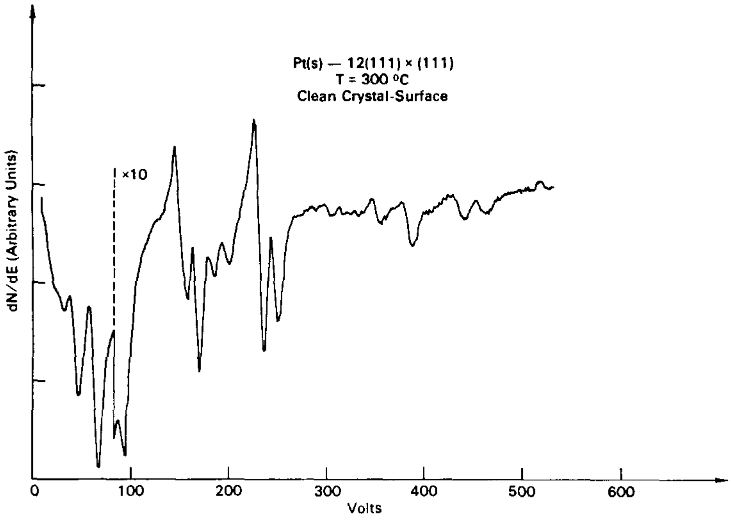

FIG. 1. Auger spectrum of the clean surface taken at 300°C.

The spectra were taken with a 10-V peak to peak modulation, 5 μA of incident current, 2.00 keV of incident electron energy, a defocused beam (diameter $\simeq$ 1.5 mm), and sweep rates of about 3 V/sec. The nitrogen peak to peak height ratio has been used in this work to indicate approximate surface concentration of nitrogen-containing species. The nitrogen ratio "RN" is the ratio of the nitrogen plus platinum peak to peak height at 390 V to the platinum peak to peak height at 238 V. The value of the ratio is 0.174 ± 0.005 (*9*, *10*) for a clean surface and is independent of temperature (*10*). Approximate calibration of the nitrogen ratio using LEED and thermal desorption results was discussed in earlier papers (*9–11*). As discussed previously (*10*) the nitrogen Auger ratio RN taken at low resolution (10-V modulation) has approximately the same sensitivity for nitrogen regardless of the chemical environment of the nitrogen. Therefore, the Auger ratio RN has been used to measure the surface concentration of "nitrogenic" surface species during reactivity experiments. This assumption is justified if all ammonia derived species (NH_3, NH_2, NH), nitrogen (N_2, N), nitric oxide, and possible mixed species (NHO) have approximately similar Auger sensitivities and peak positions. This assumption may not be analytically correct but should give reasonable qualitative results using low-resolution spectra. Nitric oxide is identified as a nitrogenic species since most of the oxygen in molecular NO cannot be observed due to electron beam desorption at these current levels (*9*).

The reaction rates were determined using the stirred tank formulation for a *flow* reactor as discussed previously (*10*). The steady-state reaction rates are related to the observed product partial pressure by an equation of the form

$$r_i = \frac{\Delta P_i S}{R T_g A} = B \Delta P_i, \qquad (1)$$

where r_i is the specific rate of formation of product "*i*" in units of molecules per square centimeter per second, ΔP_i is the change in partial pressure of species *i* during reaction, *S* is the pumping speed (flow rate), *R* is the gas constant, T_g is the gas temperature, and *A* is the catalyst area. The catalyst area was 2 cm^2 and a gas temperature of 300 K was used for calculation of rates.

Partial pressures were measured using a quadrupole mass spectrometer calibrated against the ion gauge for gases of interest. Changes in product partial pressure during reaction were determined by subtracting product background pressures determined with the cold platinum sample from product pressures determined with the platinum sample at reaction temperature. The background corrections for this reaction are substantial; however, the background is fairly constant. Background pressures were usually taken before and after reactivity determination. The pumping speed or flow rate was determined by measuring the exponential decay of pressure following the rapid flash of a tungsten or platinum filament. Apparent pumping speeds are fairly low (about 40 liter sec^{-1}) during reactivity experiments because all the exposed surfaces are saturated with adsorbed gas. Consistent approximate pumping speeds and ion gauge calibrations have been used to estimate the absolute rates given in the figures. The absolute accuracy of the number is poor; however, the data indicate the calibration is reasonable. The internal consistency of the data is quite good; points taken several weeks apart while searching various parameters agree. These data are directly comparable to the data concerning the reaction of ammonia and molecular oxygen (*10*) since the same Pt single crystal, experimental system, and calibrations have been used in both analyses. The reactivity experiments were run using a number of introduction sequences for the reactants. Below

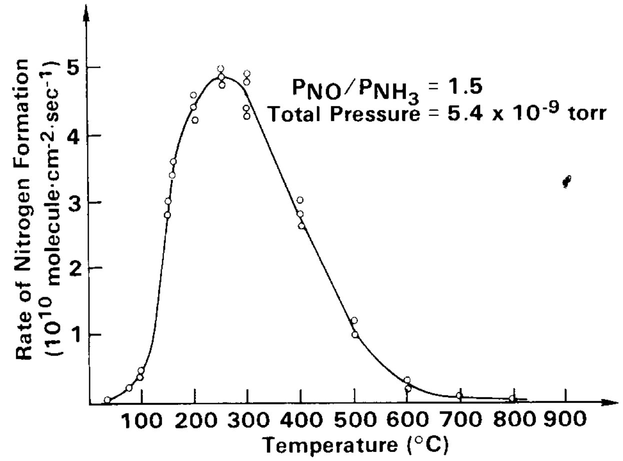

FIG. 2. Nitrogen formation rate as a function of platinum temperature for an approximately stoichiometric mixture of ammonia and nitric oxide.

500°C the steady-state rates were a unique function of temperature and reactant partial pressure. Above 500°C the situation is more complex because nitric oxide can oxidize the platinum surface. Oxidation of the platinum surface can be detected using AES (*9*, *10*). The reactivity experiments reported here were run on an oxide-free surface. For temperatures below 250°C prolonged induction periods were required to attain steady-state rates because the concentration of adsorbed species becomes important in determining the overall reaction rate. In this temperature range the reaction rate can also be reversibly affected by prolonged exposures to the electron beam used for AES. Therefore, electron beam exposures were minimized. This change in reaction rate is probably caused by electron beam induced dissociation of either or both of the reactants as has been reported previously (*9*). The reactivity versus temperature data were taken so that monotonic increases or decreases in temperature were avoided. The concentration data were taken in the same manner by choosing non-progressive concentrations.

The thermal desorption results used in this study were obtained by first saturating the surface during steady-state reaction studies (at reaction temperature). The temperature of the sample was then increased, and the desorbing species were monitored mass spectrometrically. The species desorbed are a result of both reaction at the initial temperature of adsorption and reaction during the thermal desorption process. They have been used as a qualitative indication of surface conditions at the steady-state reaction condition. If the desorption maxima occur at the same temperature during simple adsorption–desorption experiments and desorption experiments following saturation during steady-state reaction, no "new" rate-limiting reaction step is involved in the desorption process following saturation with the reaction mixture.

DATA

The reaction between ammonia and nitric oxide proceeds rapidly over this stepped platinum single crystal surface in the 150 to 500°C temperature range. Maximum reaction probabilities (rate of product formation/collision rate of limiting reactant) in the range 0.03 to 0.07 have been observed at 200 to 250°C. Molecular

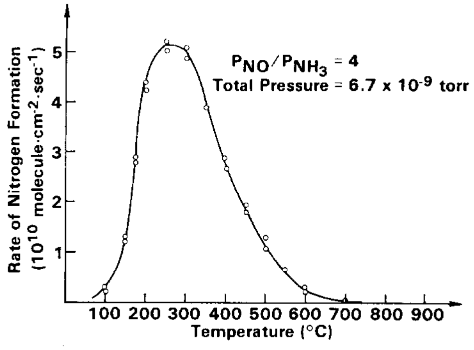

FIG. 3. Nitrogen formation rate as a function of platinum temperature for a reaction mixture containing excess nitric oxide.

nitrogen was the only nitrogen-containing product observed during these studies. During all the steady-state reactivity experiments reported here, data were taken to check for nitrous oxide formation; however, no catalytic nitrous oxide formation was observed during any of the experiments reported. The mass spectrometer sensitivity for N_2O was confirmed by adding N_2O to the gas phase. The overall chemical reaction which describes this reaction is:

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O. \quad (2)$$

The nitrogen formation rate as a function of platinum temperature is shown in Fig. 2 for an approximately stoichiometric mixture of ammonia and nitric oxide. The reaction rate increases rapidly from approximately 100°C until the maximum rate is attained at approximately 250°C. Above 250°C the reaction rate decreases with increasing temperature. Analysis of the surface using AES during these reactivity studies indicates that the surface coverage of nitrogen-containing species decreases as temperature increases for fixed gas-phase composition.

The nitrogen formation rate as a function of platinum temperature is shown in Fig. 3 for a reaction mixture containing excess nitric oxide. The shape of this curve is very similar to the reactivity curve for a stoichiometric ratio of ammonia and nitric oxide; however, the reaction initiation temperature is shifted to a slightly higher temperature. Figure 4 shows the nitrogen formation rate as a function of temperature for a reaction mixture with excess ammonia. The maximum nitrogen formation rate occurs at about 200°C and is approximately half the maximum rate observed in Figs. 2 and 3.

Detailed kinetic studies have been performed in two temperature ranges. A set of kinetic studies has been performed at 400°C. Surface analysis by AES during these kinetic studies at 400°C indicates that the surface is essentially vacant. Small concentrations of nitrogen-containing surface species were observed (RN $\approx$ 0.19) depending on the precise reaction conditions. The data in Fig. 5 indicate that the nitrogen formation rate is first order in nitric oxide pressure at 400°C. Figures 6a and 6b show that the nitrogen formation rate is half-order in ammonia pressure at 400°C in excess nitric oxide.

Kinetic studies have also been run at lower temperatures (150–200°C). In this temperature range AES indicates that the surface is covered with a considerable concentration of adsorbed nitrogen-containing species during reaction (RN $\gtrsim$ 0.25). The surface concentration detected by Auger

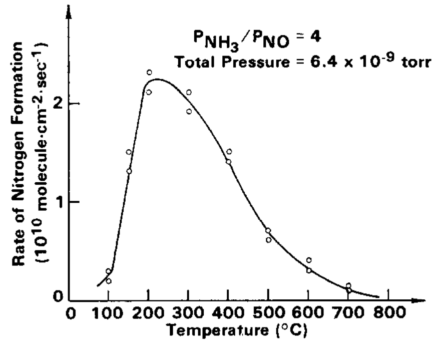

FIG. 4. Nitrogen formation rate as a function of platinum temperature for a reaction mixture containing excess ammonia.

depends on the exact reaction conditions. The data in Fig. 7 show the nitrogen formation rate as a function of nitric oxide pressure at 150 and 200°C. In excess ammonia the reaction rate increases with increasing nitric oxide pressure. In excess nitric oxide the reaction rate saturates and decreases with increasing nitric oxide pressure. The data in Fig. 8 show that the nitrogen formation rate saturates with increasing ammonia pressure in excess ammonia at 150 and 200°C. No inhibition of the reaction rate is observed with the addition of excess ammonia.

Figure 9 shows the reaction rate at 150 and 200°C as a function of the concentration of nitrogen containing surface species as detected by AES. These data were taken during the steady-state reactivity studies shown in Fig. 7. The variation in nitrogen Auger signal was induced by changes in nitric oxide pressure. The surface data indicate that initially the addition of nitric oxide to the reaction mixture causes an increase in the concentration of adsorbed nitrogen-containing species and an increase in the reaction rate. With addition of excess nitric oxide the concentration of adsorbed nitrogen-containing species increases even further. The reaction rate reaches a maximum and then decreases as the concentration of nitrogen-containing surface species increases due to addition of excess nitric oxide. A comparison of the data at 150 and 200°C indicates that the surface contains a larger concentration of adsorbed nitrogen-containing species at 150°C for a given reactivity level. As mentioned the clean platinum surface has a nitrogen Auger ratio of RN $\simeq$ 0.174 (*9*) and a nitrogen ratio RN $\simeq$ 0.54 for a (2 $\times$ 2) nitrogen or nitric oxide overlayer containing about 4 $\times$ 10^{14} nitrogen atoms or nitric oxide molecules.

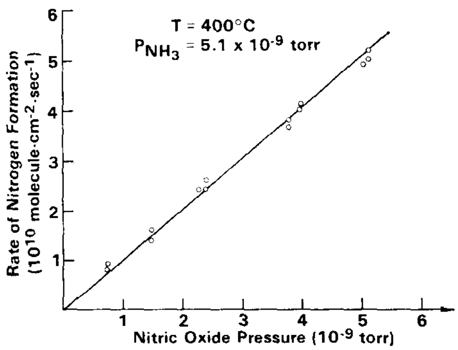

FIG. 5. Nitrogen formation rate as a function of nitric oxide pressure. The rate is first order in nitric oxide pressure at 400°C.

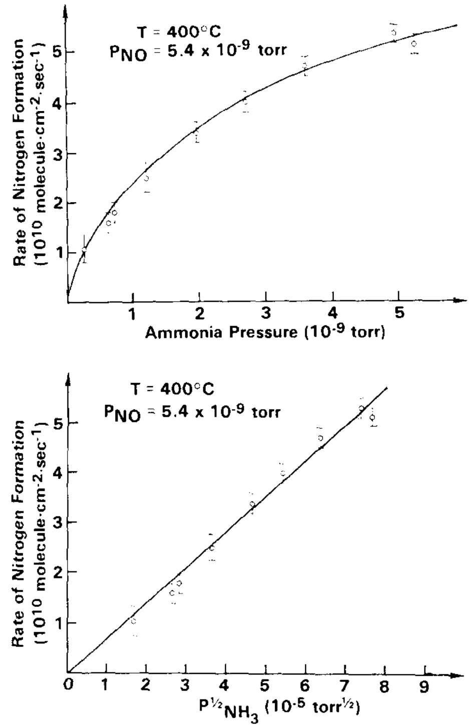

FIG. 6. (a and b) Nitrogen formation rate as a function of ammonia pressure. The nitrogen formation rate is half order in ammonia pressure at 400°C in excess nitric oxide.

A series of Auger and thermal desorption experiments was done during the steady-state reactivity experiments. Below the reaction initiation temperature (~100°C) a large concentration of nitrogen-containing species are adsorbed on the platinum surface (RN $\simeq$ 0.6–0.9) during exposure to the reaction mixture. Thermal desorp-

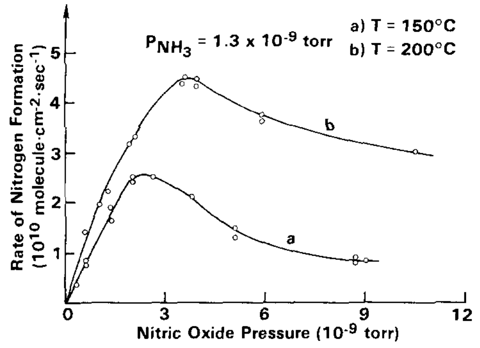

FIG. 7. Nitrogen formation rate as a function of nitric oxide pressure at 150 and 200°C. In excess nitric oxide, the reaction rate saturates and decreases with increasing nitric oxide pressure.

tion spectra indicate that the primary species desorbing for a surface saturated by exposure to the reaction mixture below 100°C are nitric oxide and molecular nitrogen. (The water formed during the reaction desorbs rapidly in the temperature range studied.) The peak temperatures for desorption correspond to the peak temperatures observed during simple adsorption studies of NO (*9*) and nitrogen (*10*). Nitric oxide desorption yields two peaks at about 75 and 165°C while the maximum nitrogen desorption rate occurs at about 210°C. Approximately equal amounts of nitric oxide and nitrogen were desorbed from a surface saturated by exposure to any reaction mixture below 100°C regardless of the relative pressures of ammonia and nitric oxide in the reaction mixture. Small amounts of desorbing ammonia and hydrogen were also observed (~10% of desorbing nitrogen or nitric oxide) following saturation of a cool surface with reaction mixture. The desorbing ammonia appeared as a very broad (~300°C) shallow peak unlike ammonia desorption spectra observed in simple adsorption–desorption experiments.

In the 150 to 200°C temperature range the identity of the major species desorbing from a surface saturated by exposure to the reaction mixture depends strongly on the stoichiometry of the reaction mixture. In excess ammonia the primary desorbing species is molecular nitrogen. The amounts of desorbing nitric oxide and ammonia are similar but significantly smaller than the amount of desorbing nitrogen. Following saturation of this surface at 150 to 200°C with the stoichiometric reaction mixture or mixtures containing excess nitric oxide the primary desorbing species are molecular nitrogen and nitric oxide.

Several isotope exchange experiments were performed in order to confirm the validity of mechanistic proposals made in the discussion section. Adsorption–desorption experiments with mixtures of NH_3 and ND_3 indicate that dissociative adsorption predominates even at −190°C. The rate of ammonia recombination and desorption [$NH_2(ads) + H(ads) \rightarrow NH_3(gas)$] was also compared with the total molecular nitrogen formation rate during steady-state reactivity experiments. An equimolar mixture of NH_3 and ND_3 was oxidized with a stoichiometric amount of NO, and the catalytic production of ND_2H and N_2 was monitored. The rate of NDH_2 formation could not be monitored because the H_2O product formed during reaction has the same charge to mass ratio. The catalytic ND_2H formation rate was 0.7

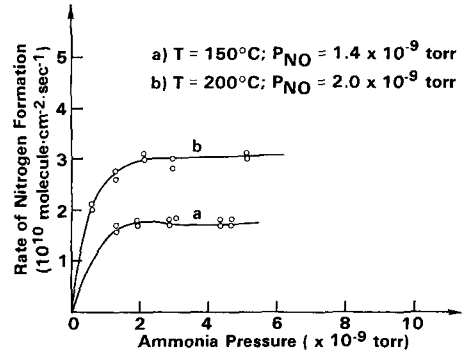

FIG. 8. Nitrogen formation rate as a function of ammonia pressure at 150 and 200°C. The rate saturates with increasing ammonia pressure in excess ammonia. No inhibition of the reaction rate is observed with the addition of excess ammonia.

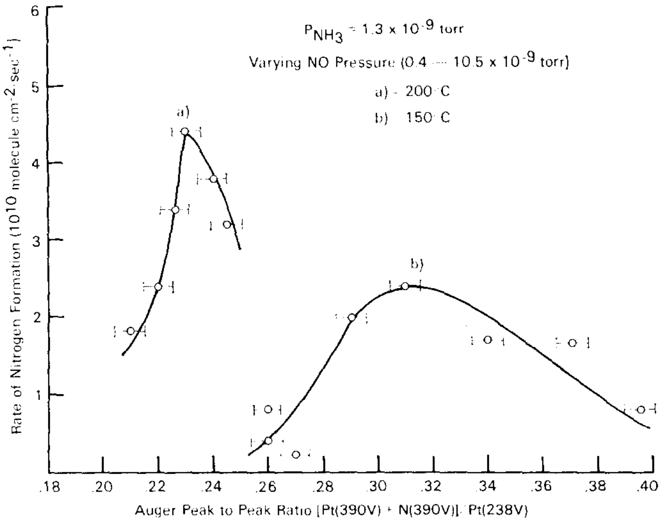

FIG. 9. Nitrogen formation rate at 150 and 200°C as a function of the nitrogen-containing surface species as detected by AES.

times the N_2 formation rate at 200°C. At 400°C the ND_2H formation rate was 1.0 times the N_2 formation rate. During this same series of experiments we observed *no* catalytic HD formation. The background levels were substantial at 3 amu; we estimate the recombination and desorption rate of hydrogen is at least 10-fold smaller than the total oxidation rate.

The data in Fig. 10 report the results of a study of the reaction between nitric oxide and ammonia in the presence of small amounts of oxygen. The data in curve a indicate the measured reactivity of this surface at 200°C for the reaction between NH_3 and O_2 as a function of oxygen pressure. As reported previously the only product observed under these conditions is molecular nitrogen (*10*). The ammonia oxidation reaction is first order in oxygen pressure confirming earlier results (*10*). The data in curve b relate the results of a series of experiments using NH_3, NO, and O_2 as reactants. These experiments were run on the same surface under the same conditions as the experiments shown in curve a except that 1×10^{-9} Torr of nitric oxide was added to the reaction mixture. The data in curve b indicate that the conversion of ammonia to nitrogen increases with addition of oxygen to the reaction mixture containing NH_3 and NO just as it did in the absence of nitric oxide. The slope of the two reactivity curves (in the presence and absence of NO) is the same. This data indicate that addition of oxygen to a NO and NH_3 reaction mixture does not seem to increase the reaction rate markedly (under these reaction conditions). Large increases in reaction rate were previously observed in studies (*2*, *4*, *5*) of this same reaction over supported catalysts at atmospheric pressure.

DISCUSSION

The results of the kinetic studies at 400°C (Figs. 5, 6a, and 6b) indicate that the reaction is half order with respect to ammonia pressure and first order with respect to nitric oxide pressure. These results imply that dissociated ammonia and molecular nitric oxide are participating in the rate-limiting reaction. These pressure dependences agree with earlier studies

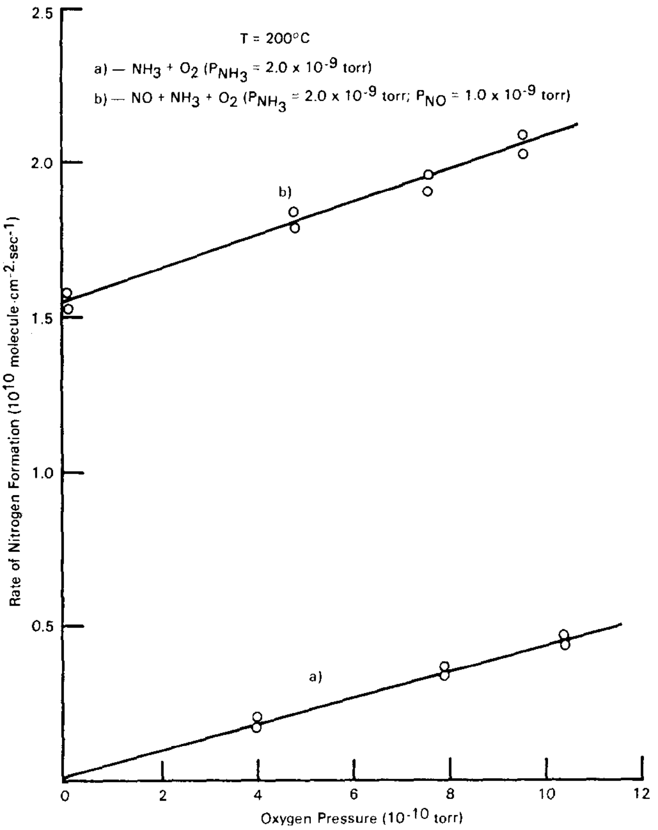

FIG. 10. Nitrogen formation rate at 200°C as a function of oxygen pressure.

of this same reaction studied on supported platinum catalysts (*3*, *6–8*). The fact that dissociated ammonia participates in the rate-limiting step implies that adsorption and dissociation of the ammonia is occurring prior to the rate-limiting reaction.

The isotope exchange results indicate that the dissociatively adsorbed ammonia fragments on the surface are in equilibrium with the gas-phase ammonia pressure since the rate of catalytic ND_2H formation indicates that the ammonia recombination and desorption rate is larger than the N_2 formation rate over the temperature range studied. (Adsorption studies indicate that statistical exchange occurs for ammonia adsorbed on this platinum surface. Therefore, the total exchange rate should be about 2.7 times larger than ND_2H formation rate since exchange should also yield NH_3, NDH_2, ND_2H, and ND_3.) The recombination and desorption of hydrogen occurs at a much lower rate than either the ammonia exchange reaction or the nitrogen formation reaction as indicated by the fact that no HD formation was observed during oxidation of NH_3, ND_3 mixtures. This result indicates that the NH_2 and H surface concentrations should be similar since they are determined by the gas-phase ammonia pressure.

Analysis of the surface during the steady-state reactivity experiments using Auger indicates that the surface is essentially clean at 400°C; very small concentrations of nitrogen-containing species are observed (RN $\simeq$ 0.17 to 0.19). The kinetic results taken at 150 and 200°C are more complex since the surface contains a significant concentration of adsorbed nitrogen-containing species. Qualitatively, the results shown in Fig. 7 indicate that the reaction rate decreases with addition of excess nitric oxide. This observation coupled with the observation that dissociated adsorbed ammonia participates in the rate-limiting reaction indicates that this reaction can be described by a Langmuir–Hinshelwood reaction scheme with the rate-limiting reaction occurring between adsorbed molecular NO and an adsorbed fragment of ammonia. This conclusion also agrees with earlier work done over supported platinum (*3*, *6–8*).

A more detailed examination of the rate data in Fig. 7 indicates that both the increase and decrease of the rate at 150°C is approximately first order with respect to increased nitric oxide pressure. However, the data taken at 200°C (Fig. 7) indicate that the decrease of the nitrogen formation rate is approximately half order with respect to nitric oxide pressure (0.5 ± 0.1). If the only inhibiting surface species were adsorbed nitric oxide, a simple first-order rate law should result at both temperatures. These results indicate that the reaction rate may be inhibited by some other surface species. Figure 8 indicates that the reaction is not inhibited by addition of excess ammonia to the reaction mixture. Below 200°C thermal desorption spectra taken from reaction-saturated surfaces show that significant amounts of molecular nitrogen desorb. Nitrogen desorption spectra taken from this surface after saturation with the reaction mixtures agree with nitrogen desorption spectra taken following adsorption of atomic nitrogen (*9*), nitric oxide (*9*), or ammonia (*9*). All the desorption spectra indicate that the maximum nitrogen desorption rate occurs at about 225°C. Therefore, nitrogen inhibition of this Langmuir–Hinshelwood reaction seems reasonable in the 150 to 200°C temperature range.

We have used the single site Langmuir–Hinshelwood reaction scheme proposed by earlier workers (*3*, *6–8*). However, we observe no nitrous oxide formation; therefore, we have used a previously proposed minor reaction pathway so that both reaction branches yield nitrogen (*3*, *6–8*). The isotope exchange results mentioned previously indicate that the reaction (3) controls the hydrogen and ammonia fragment concentration on the surface since the rate of the recombination–desorption reaction is larger than the total forward rate of ammonia oxidation.

$$NH_3(g) \overset{K_{NH_3}}{\rightleftarrows} NH_2(ads) + H(ads) \tag{3}$$

$$NO(g) \overset{K_{NO}}{\rightleftarrows} NO(ads) \tag{4}$$

$$NH_2(ads) + NO(ads) \xrightarrow{k_3} N_2(g) + H_2O(g) \tag{5}$$

$$NO(ads) + H(ads) \xrightarrow{k_4} [HNO(ads)] \tag{6}$$

$$[HNO(ads)] + H(ads) \xrightarrow{k_5} N(ads) + H_2O(g) \tag{7}$$

$$N(ads) + N(ads) \xrightarrow{k_6} N_2(g). \tag{8}$$

The fractional coverages of all the surface species can be expressed in terms of the reaction rate (r), gas phase reactant pressures (P_{NO}, P_{NH_3}), the equilibrium constants, and rate constants defined in the preceding reaction scheme. The fractional coverage of vacant surface sites is denoted Θ in the following expressions; the surface coverage of each surface species is denoted Θ_A where A is the adsorbed species.

$$\Theta = \frac{r^{\frac{1}{2}}}{(k_3 + k_4)^{\frac{1}{2}}(K_{NH_3}{}^{\frac{1}{2}}P_{NH_3}{}^{\frac{1}{2}}K_{NO}P_{NO})^{\frac{1}{2}}} \tag{9}$$

$$\Theta_{NO} = \frac{r^{\frac{1}{2}}K_{NO}{}^{\frac{1}{2}}P_{NO}{}^{\frac{1}{2}}}{(k_3 + k_4)^{\frac{1}{2}}(K_{NH_3}{}^{\frac{1}{2}}P_{NH_3}{}^{\frac{1}{2}})} \tag{10}$$

$$\Theta_N = \frac{r^{\frac{1}{2}}(k_4)^{\frac{1}{2}}}{k_6{}^{\frac{1}{2}}(k_3 + k_4)^{\frac{1}{2}}} \tag{11}$$

$$\Theta_{\mathrm{NH_2}} = \Theta_{\mathrm{H}} = \frac{r^{\frac{1}{2}} K_{\mathrm{NH_3}}{}^{\frac{1}{4}} P_{\mathrm{NH_3}}{}^{\frac{1}{4}}}{(k_3 + k_4)^{\frac{1}{2}} (K_{\mathrm{NO}} P_{\mathrm{NO}})^{\frac{1}{2}}} \qquad (12)$$

$$\Theta_{\mathrm{NHO}} = \frac{r^{\frac{1}{2}} k_4 K_{\mathrm{NO}}{}^{\frac{1}{2}} P_{\mathrm{NO}}{}^{\frac{1}{2}}}{k_5 (k_3 + k_4)^{\frac{1}{2}} (K_{\mathrm{NH_3}}{}^{\frac{1}{4}} P_{\mathrm{NH_3}}{}^{\frac{1}{4}})}. \qquad (13)$$

If we consider the case where the predominant surface species are nitric oxide and nitrogen atoms (as indicated by the thermal desorption results), the relevant rate equation is:

$$r = \frac{k_6 (k_3 + k_4)(K_{\mathrm{NH_3}}{}^{\frac{1}{2}} P_{\mathrm{NH_3}}{}^{\frac{1}{2}} K_{\mathrm{NO}} P_{\mathrm{NO}})}{[k_6{}^{\frac{1}{2}}(1 + K_{\mathrm{NO}} P_{\mathrm{NO}} + k_4{}^{\frac{1}{2}} K_{\mathrm{NH_3}}{}^{\frac{1}{4}} P_{\mathrm{NH_3}}{}^{\frac{1}{4}} K_{\mathrm{NO}}{}^{\frac{1}{2}} P_{\mathrm{NO}}{}^{\frac{1}{2}})]^2}. \qquad (14)$$

The second term in the denominator corresponds to the surface coverage of NO; the third term corresponds to the nitrogen surface coverage. This rate equation indicates that the nitric oxide inhibition pressure dependence should range from first order to zero order depending on the relative importance of the second and third terms in the denominator. The rate expression also indicates that the rate should not depend on ammonia pressure in excess ammonia (third term in the denominator). In summary, all the kinetic observations made during this study can be explained using a simple Langmuir–Hinshelwood reaction scheme. The elementary reaction steps and intermediates are considered reasonable, but other sets of elementary step and/or reaction intermediates might also explain the observed data. Further studies of this reaction using isotope labeling and more explicit surface spectroscopies are currently underway in order to determine the details of the reaction mechanism.

The qualitative features of the reaction temperature profiles shown in Figs. 2, 3, and 4 can also be explained using this simple Langmuir–Hinshelwood reaction scheme. The rapid increase in the reaction rate above 100°C may be caused by reduced inhibition of the reaction rate by adsorbed species or the reaction rate may be limited by the product desorption rate. The thermal desorption results indicate that nitric oxide and nitrogen are the primary desorbing species. Inhibition of the reaction by adsorbed nitric oxide and/or nitrogen is reasonable since nitric oxide has a desorption maximum at 165°C and nitrogen has a desorption maximum at 225°C in simple adsorption–desorption experiments run on this same surface (*9*).

The decrease in the reaction rate above 250°C may be the result of a decreasing surface concentration of reactant molecules or reactive fragments. Surface analysis by Auger electron spectroscopy in this temperature range indicates that the surface concentration of nitrogen-containing species decreasing with increasing temperature for fixed gas-phase composition.

Data taken at 400°C by AES during steady-state reactivity experiments indicate that the surface coverage of nitrogen-containing species is very low. Therefore, inhibition of the reaction rate by adsorbed species is minimal as evidenced by the simple rate law observed at 400°C: $r \alpha k P_{\mathrm{NO}} P_{\mathrm{NH_3}}{}^{\frac{1}{2}}$.

Comparing Figs. 2 and 3 we observe that the mixture containing more nitric oxide (Fig. 3) has a higher reaction initiation temperature. That is, at a given temperature the data in Figs. 3 and 4 indicate that addition of excess NO inhibits the rate. This confirms the kinetic data shown in Fig. 7. The data in Fig. 7 also indicate that the NO/$\mathrm{NH_3}$ ratio corresponding to maximum reaction rate increases with increasing temperature (for 150 and 200°C). This indicates that at 200°C the reaction is not being inhibited as severely by excess NO as it is at 150°C.

The reactivity data for reactions run in excess $\mathrm{NH_3}$ (Fig. 4) indicate that the maximum nitrogen formation rate is considerably smaller than that observed with stoichiometric or mixtures with excess nitric oxide. However, caution should be exercised in drawing this conclusion since the approximate reaction probability in terms of nitric oxide collisions is approximately 0.05 at the maximum in the reactivity curve. The reaction rate may be limited by nitric oxide pressure in this regime.

The data in Fig. 9 show the reaction rate at 150 and 200°C as a function of surface concentration of nitrogen-containing species as detected by AES. The Auger peak ratio should give a reasonable estimate of the sum of all the nitrogen-containing species on the surface as indicated earlier (*9, 10*). This change in concentration of nitrogen-containing species was induced by experimental changes in P_{NO}. Qualitatively, the data show the type of behavior expected for a Langmuir–Hinshelwood surface reaction. Initially the reaction rate increases with increasing surface concentration; the reaction then goes through a maximum and declines as the surface becomes covered with a larger concentration of adsorbed nitrogen-containing species. The surface coverage corresponding to the maximum reaction rate decreases with increasing temperature. There are several plausible explanations for these data. The type of adsorbed nitrogen-containing species may be changing with temperature. In this case the large concentration of nitrogen-containing surface species present during the reaction at 150°C (RN $\simeq$ 0.24–0.25) may be caused by the presence of a nonreactive surface species. In fact, the thermal desorption results support this explanation and suggest that the nonreactive surface species may be adsorbed nitrogen (the product). Another possible explanation would involve a change in the reactive site on this platinum surface. If several different types of surface sites (a minimum of two) with different heats of adsorption for the reactive surface species exist, a change in temperature may change the distribution and concentration of reactive species on the surface. For instance, a large concentration of adsorbed reactant adsorbed on a strong adsorption site could be unreactive at low temperature leading to the high concentration of nitrogen-containing species observed at 150°C. The evidence available at present strongly favors the first explanation; however, the second is certainly not excluded and may also be contributing.

As mentioned previously the mechanism used to explain this work was originally proposed to explain data obtained on supported catalysts operating at atmospheric pressure (*3, 6–8*). The reactivity temperature profiles and kinetic data taken using supported catalyst are surprisingly similar to the data presented in this paper. This similarity indicates that a similar mechanism may prevail over huge variations in operating pressure (from 10^3–10^{-8} Torr). Reaction initiation temperatures are higher using higher pressures presumably due to inhibition caused by increased surface concentrations of reactants or products. No nitrous oxide formation is observed in these low-pressure studies, although large concentrations are observed at high pressure. Using the mechanism postulated by Otto *et al.* (*7, 8*) nitrous oxide is formed by combination of two HNO surface species.

$$2HNO \rightarrow [\text{Surface Complex II}] \rightarrow N_2O + H_2O.$$

In our situation we proposed that the HNO formed reacts with another surface H to yield nitrogen atoms. That is, under low-pressure conditions the surface concentration of HNO may not become large enough to allow significant recombination rates to occur.

The experiments carried out with the ammonia, nitric oxide, and oxygen system indicate that at least under these conditions the two reactions $NH_3 + NO \rightarrow N_2$ and $NH_3 + O_2 \rightarrow N_2$ may simply be additive. The evidence is certainly not compelling but indicates that no large changes in reaction rates and probably reaction mechanism are occurring. An earlier study of the $NH_3 + O_2$ reaction in detail (*10*) indicates that the $NH_3 + O_2 \rightarrow N_2$ reaction may proceed at least partially via a nitric oxide surface intermediate in this temperature range. If this were the case, no dramatic increase in the N_2 formation rate would necessarily be observed for O_2 additions to $NO + NH_3$ reactant streams. A large increase in the catalytic activity of this surface for either reaction ($NH_3 + NO$ or $NH_3 + O_2$) seems unlikely under these experimental conditions since the reaction probability for each of these reactions separately at 200°C is very high ($\sim$0.05). This observation does not agree with earlier work done on supported catalysts at atmospheric pressure (*3*, *6–8*). The effects observed at higher pressure with supported catalyst may be caused by oxidation of the catalyst in the presence of gas-phase oxygen.

CONCLUSION

The reduction of nitric oxide by ammonia proceeds rapidly in the 150 to 550°C range; the only product observed is molecular nitrogen. The rate-limiting reaction occurs between an adsorbed fragment of ammonia and adsorbed molecular nitric oxide. The reaction rate is inhibited by addition of large excesses of nitric oxide to the reaction mixture. The observed reaction kinetics can be modeled using a single-site Langmuir–Hinshelwood reaction scheme.

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