Ammonia Oxidation on a Stepped Platinum Single-Crystal Surface

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The reactions of oxygen with ammonia have been studied over the $Pt(S) - 12(111) \times (111)$ surface for pressures between 10^{-10} and 10^{-8} Torr over the temperature range -75 to $600°C$. These steady-state reaction studies were performed in an ultrahigh vacuum system equipped with low-energy electron diffraction for determination of surface structures, Auger electron spectroscopy (AES) for surface composition determinations, and mass spectroscopy for determination of gas-phase compositions. The oxidation of ammonia proceeds rapidly above $150°C$ on the $Pt(S) - 12(111) \times (111)$ surface; the products observed are molecular nitrogen, nitric oxide, and water. For a stoichiometric mixture of ammonia and molecular oxygen, nitrogen formation predominates at low temperature (150 to $400°C$) while nitric oxide formation predominates above $400°C$. Kinetic studies done with excess ammonia reveal that the nitrogen formation rate is first order in gas-phase oxygen pressure but saturates with increasing ammonia pressure. Under these conditions the surface is primarily covered with nitrogen-containing species. Kinetic studies done in excess oxygen indicate that nitric oxide formation is first order in ammonia pressure but saturates with increasing adsorbed oxygen pressure. Under these conditions the surface is covered with adsorbed oxygen (as determined by AES). Thermal desorption of oxygen adsorbed on the platinum surface during ammonia oxidation indicates that the oxygen is present as oxygen atoms bound to the step edge sites. The observations that the reaction rates for both branches of this reaction saturate with respect to increasing reactant pressure just as the step edge sites become saturated indicate that the step edge sites play a predominant role in both reaction branches.
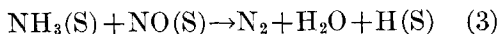
INTRODUCTION

The reaction between molecular oxygen and ammonia over platinum wires is important in the manufacture of nitric acid and has been the object of several studies (1–4). The reaction between oxygen and ammonia to form molecular nitrogen is an undesirable side reaction in that process, but may become an important reaction for the purification of industrial and automotive effluents. As part of a program to characterize the surface chemistry of the nitrogen–hydrogen–oxygen system over noble metals and to determine the effects

of variations in surface structures on this surface chemical system, a study of ammonia oxidation has been undertaken using a well-characterized platinum single-crystal surface as the catalyst.

Much of the work done on ammonia oxidation before 1960 has been summarized by Chilton (1). Pignet and Schmidt studied the kinetics of ammonia oxidation over platinum wires (2, 3) in the 0.1- and 1.0-Torr pressure region and found that the reaction rates observed can be modeled by several Langmuir–Hinshelwood kinetic forms based on the overall chemical reactions proposed by Fogel (4).

$$NH_3(S) + O_2(S) \rightarrow NO + H_2O + H(S) \quad (1)$$

and/or

$$NH_3(S) + O(S) \rightarrow NO + H_2 + H(S) \quad (2)$$

$$NH_3(S) + NO(S) \rightarrow N_2 + H_2O + H(S) \quad (3)$$

Pignet and Schmidt studied the decomposition of both NO and NH_3 over polycrystalline platinum wires (3) and reported that neither decomposition reaction is important below 600°C. Fogel and co-workers (4) studied ammonia oxidation over platinum using an ion microprobe to study the surface composition. They concluded that oxidation of NH_3 by O_2 proceeds directly without formation of long-lived surface intermediates as indicated by Eqs. (1), (2), and (3). Nutt and Kapur (5, 6) support the Langmuir–Hinshelwood mechanism proposed by Fogel (4) and propose that the rate of nitric oxide formation is first order in pressure for both ammonia and oxygen. They (6) also observe maxima in the nitric oxide formation rate with respect to both ammonia pressure and oxygen pressure.

Several recent papers dealing with ammonia oxidation over platinum on alumina catalysts have stated that crystallite size effects occur (7, 8); however, the primary products in these studies run at 100 to 300°C were nitrous oxide and nitrogen rather than nitric oxide and nitrogen. Nitric oxide and nitrogen are the predominant products when supported platinum catalysts are run at higher temperature.

EXPERIMENTAL

These steady-state reactivity experiments have been done in a stainless steel ultra-high 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 analyzer to monitor gas-phase composition. Details of the experimental system have been discussed in an earlier publication (12). The platinum single-crystal sample was prepared using the usual metallographic techniques. The exposed surface is composed of (111) terraces 12 atomic rows wide linked by monatomic height steps with (111) orientation. Periodic examination of the sample surface with LEED during reaction studies revealed that this surface structure is stable during ammonia oxidation. After 6 months of use the sample surface was examined with a stereo optical microscope at 70 power and no significant facetting or recrystallization was observed. 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. Auger spectra were taken with 10-V peak-to-peak modulation, 5 μA of incident current, a defocused beam (diameter ~1.5 mm), 2.00 kV of incident energy, and a sweep rate of 3 V/sec. A typical Auger spectrum of the clean surface taken at 300°C is shown in Fig. 1a. The nitrogen ratio "RN" is the ratio of the nitrogen plus platinum peak height at 390 V to the platinum peak height at 238 V. The value of this ratio for this clean platinum surface is 0.174 ± 0.004 (9, 12) and is independent of temperature (10). Approximate calibration of the nitrogen ratio against LEED and thermal desorption results was discussed in earlier papers (9, 12). A surface containing approximately 4×10^{14} N atoms/cm^2 gives rise to an Auger ratio of RN $\simeq 0.53 \pm 0.02$. The ratio RN is approximately linear in nitrogen surface concentration for adsorbed nitric oxide and nitrogen. The nitrogen Auger ratio RN also has approximately the same sensitivity for nitrogen adsorbed on the surface as atomic nitrogen or nitric oxide. Therefore, the Auger ratio RN has been used as a measure of the surface concen-
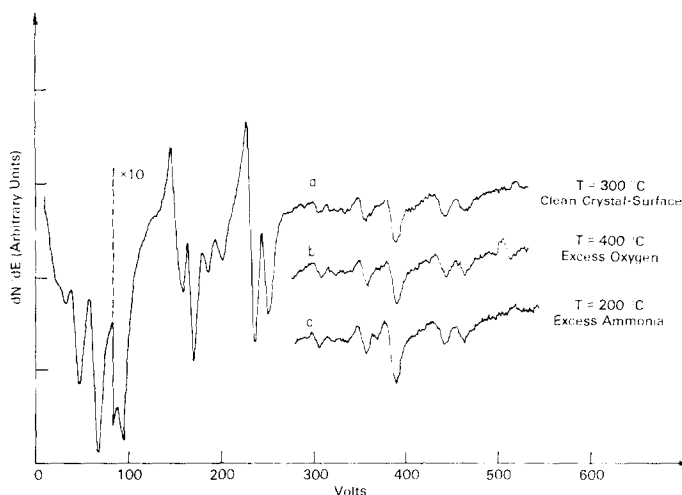
FIG. 1. Auger spectra of the $Pt(S) - 12(111) \times (111)$ surface taken: (a) with a clean surface at 300°C; (b) during steady-state ammonia oxidation of a reaction mixture with excess oxygen at 400°C; (c) during steady-state ammonia oxidation in a reaction mixture with excess ammonia at 200°C.

tration of "nitrogenic" species during reactivity measurement. Nitric oxide is identified as a nitrogenic species because most of the oxygen in molecular NO cannot be observed due to electron beam desorption at these current levels (*12*). The oxygen ratio "RO" is the ratio of the oxygen peak height at 510 V to the platinum peak height at 238 V. Approximate calibration of RO in terms of coverages, observed structures, and population of the step edge adsorption sites and terrace adsorption sites for this platinum surface has been discussed in detail in earlier papers (*10, 14*).

Steady-state reaction rates were determined using the stirred-tank formulation for absolute rates,

$$r_i = \Delta P_i S / R T_g A = B \ \Delta P_i,$$

where r_i is the specific rate of formation of product "i" in 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 cm² 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 the gases of interest. Changes in product partial pressure during reaction were determined by subtracting product concentrations determined with a cold catalyst sample from product concentrations determined with the catalyst at reaction temperature. Background levels were substantial, however, they were usually taken before and after each reactivity determination. The mass spectrometer ionizer and the ion gauge were run with reduced emission levels to minimize background contributions from the tungsten filaments. The pumping speed or flow rate was measured for the products and reactants during steady-state reaction studies by measuring the exponential decrease in pressure following the rapid flash of a tungsten or platinum filament. Consistent approximate pumping speeds and ion gauge calibration have been used to estimate the absolute rates presented in the figures. The internal consistency of the reactivity data over a 6-month period was quite good. Points taken several months
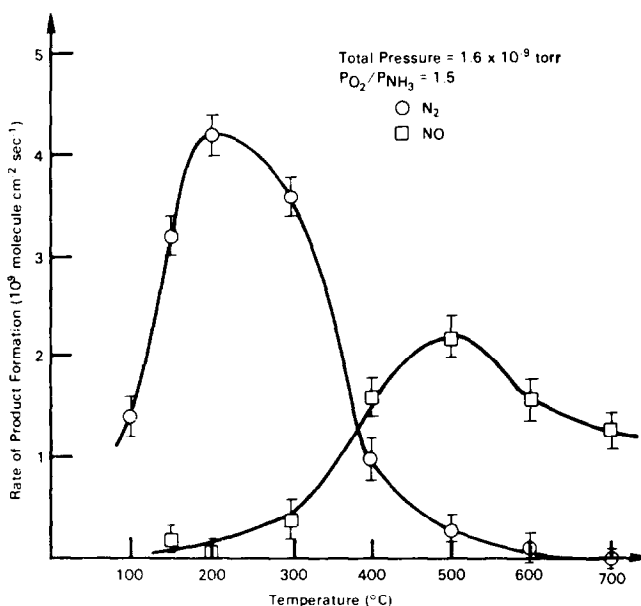
FIG. 2. Product formation rate as a function of temperature for a stoichiometric mixture of ammonia and oxygen.

apart while searching various parameters fall inside the error bars.

Admission of the reactants sequentially (in either order) or simultaneously resulted in unique steady states which are a function of temperature and partial pressures below 500°C. Above 500°C the situation becomes more difficult because the platinum surface can become oxidized (*10*). The reactivity versus temperature and reactivity versus concentration data have been taken so that monotonic increases or decreases in temperature were avoided. The error bars shown include all the experimental data. Each point represents three to ten separate reactivity determinations.

RESULTS

Overall Characteristics of the Reaction System

The oxidation of ammonia with molecular oxygen over the Pt(S) − 12(111) × (111) surface proceeds rapidly in the pressure range 10^{-10} to 10^{-8} Torr above 150°C. Approximate reaction probabilities (rate of product formation/collision frequency of

limiting reactant) as high as 0.05 have been observed. Molecular nitrogen and nitric oxide are the only nitrogen-containing products observed; this conclusion agrees with earlier studies of this reaction system over polycrystalline platinum surfaces (*2–6*). Considerable effort has been expended searching for other nitrogen-containing products, especially N_2O and nitrogen atoms, with no success. The overall chemical equations describing the two observed reactions are:

$$4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O,$$
$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O.$$
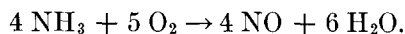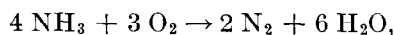
For a stoichiometric mixture of ammonia and oxygen Fig. 2 shows that molecular nitrogen formation predominates at low temperature (100 to 400°C) while nitric oxide formation predominates above 400°C. These changes in catalyst selectivity have been correlated with surface composition data taken using AES during steady-state reaction. Figure 1c shows an Auger spectrum taken at 200°C under conditions such

that molecular nitrogen is the only reaction product. A nitrogen-containing adsorbate is the only surface species detected using Auger. Figure 1b shows an Auger spectrum taken during a steady-state reaction run at 400°C under conditions such that nitric oxide is the only reaction product. The primary species detected by Auger is adsorbed oxygen. These observations indicate that the selectivity of this catalyst is correlated strongly with composition of the adsorbed layer during reaction. In fact, AES analysis run during the generation of the reactivity profile shown in Fig. 2 indicates that, as the selectivity changes, the surface composition also changes for fixed gas-phase composition with varying catalyst temperature. Catalyst selectivity is also a function of gas-phase composition as shown in the next figure. Figure 3a shows
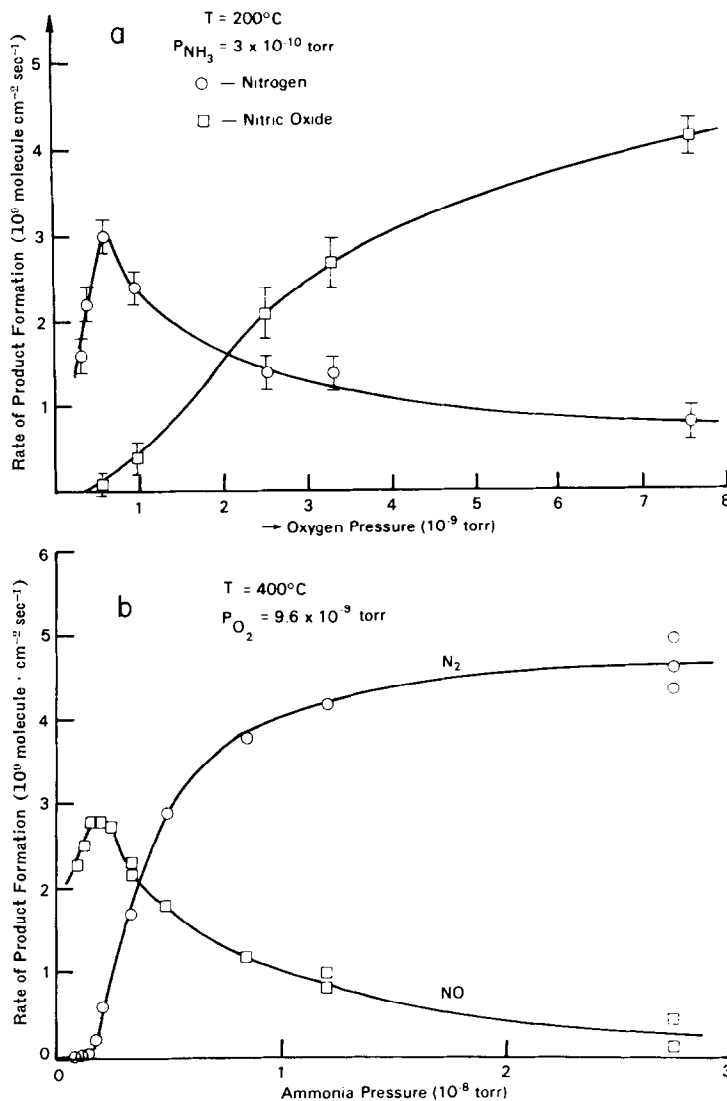
FIG. 3. Product formation rate as a function of: (a) oxygen pressure at 200°C; (b) ammonia pressure at 400°C.
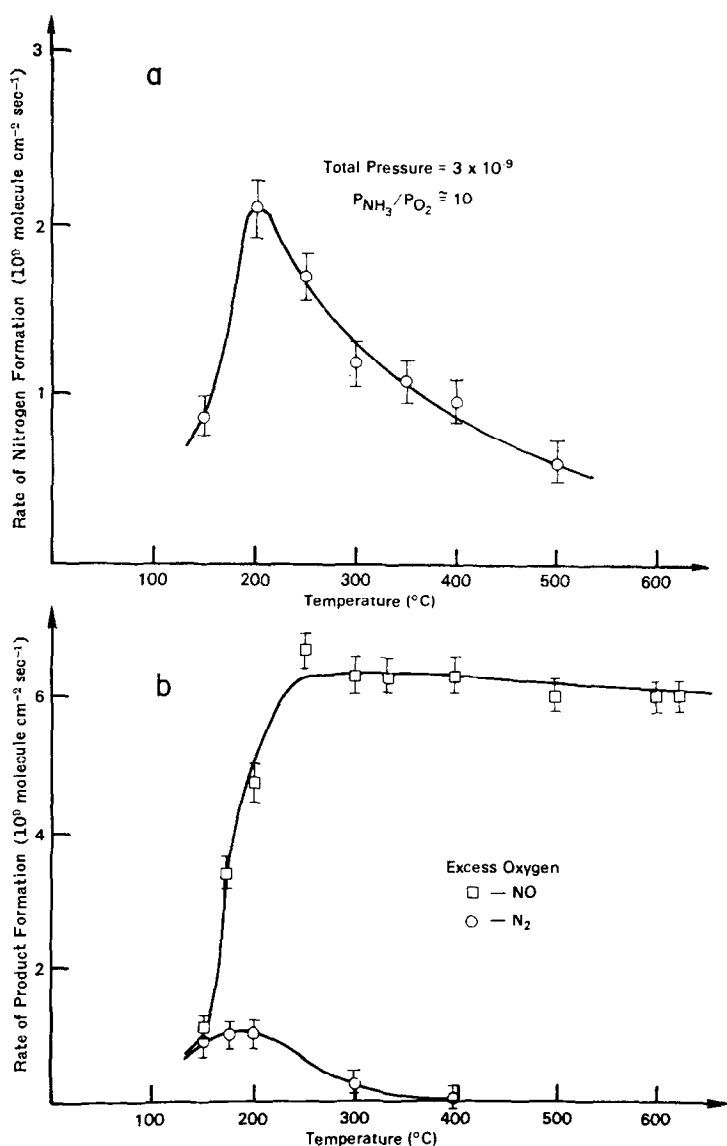
FIG. 4. Product formation rate as a function of temperature for a reaction mixture with: (a) excess ammonia; (b) excess oxygen.

the variation in product formation rate at 200°C (the peak of the N_2 production curve) for fixed ammonia pressure as a function of oxygen pressure. Figure 3b shows the product formation rates at a catalyst temperature of 400°C with fixed oxygen concentration as a function of ammonia pressure. Further experiments have been performed in order to charac-terize the reactivity–temperature profiles for mixtures with excess ammonia and excess oxygen. In excess ammonia the nitrogen formation branch of this reaction system predominates as shown in Fig. 4a. No catalytic nitric oxide formation was observed. Figure 4b shows the catalyst activity as a function of temperature for a reactant mixture containing excess oxygen

$(P_{O_2}/P_{NH_3} = 10)$. A small amount of molecular nitrogen is formed in the temperature range 100 to 300°C; however, the primary reaction product is nitric oxide.

All three reactivity–temperature profiles (Figs. 2, 4a, and b) have a rapidly increasing rate between 100 and 200°C. Earlier studies with adsorbed nitrogen and nitric oxide indicate that the desorption rate begins to be quite significant in this temperature range (12). If the platinum surface is exposed to the reaction mixture below the reaction initiation temperature, the surface becomes saturated with nitrogen as indicated by Auger. This nitrogen desorbs at the same temperature as the nitrogen which desorbs following adsorption of atomic nitrogen formed by gas-phase electron-impact dissociation of molecular nitrogen (12). As the temperature increases above the reaction initiation temperature the reaction rate increases and the concentration of nitrogen-containing surface species decreases as indicated by Auger and thermal desorption. All of these observations support the contention that reaction rate is affected strongly by the desorption rate for temperatures below about 200°C.

Examination of the reactivity–temperature profile taken in excess oxygen (Fig. 4b) reveals that significant nitrogen production occurs in the 100 to 250°C temperature range (when the rate is desorption limited). Thermal desorption spectra indicate that significant amounts of nitric oxide can be desorbed following saturation of the surface at 150 or 200°C during steady-state reaction. Thus, the nitrogen formation rate in excess ammonia is significant when the surface concentration of nitric oxide is significant. A separate study of the reaction between nitric oxide and ammonia over this platinum surface reveals that the reaction proceeds rapidly in the temperature range 100 to 500°C and that molecular nitrogen is the only product observed (13). These observations support the contention made by earlier authors (2–4) that, during

the ammonia–oxygen reaction, molecular nitrogen formation may proceed through a nitric oxide surface intermediate as indicated by reaction (3) in the Introduction. Thermal desorption spectra taken from a surface saturated by exposure to ammonia–oxygen mixtures below 100°C indicate that the surface is covered with nitrogen no matter how much excess oxygen is present in the reaction mixture. This result can be explained by considering that reaction occurs between ammonia and adsorbed nitric oxide formed by previous oxidation of ammonia. This process continues until the surface is saturated with nonreactive nitrogen.

The nitrogen formation rate has a maximum at about 200°C in the three temperature profiles run with excess ammonia, at stoichiometry and with excess oxygen. The decrease in rate with increasing temperature occurs when nitrogen production is the only reaction pathway available, indicating that the decrease of the rate with increasing temperature cannot be caused solely by competition for surface sites by adsorbed oxygen. The decreasing rate is probably affected by a rapidly decreasing surface concentration of reactive species. That is, the residence time for the reacting species is decreasing more rapidly than the mean time necessary for reaction of the species. When both reaction pathways are open, the decrease in nitrogen formation rate with increasing temperature is more severe, indicating either a change in the nitrogen formation mechanism or competition between the reaction pathways. In the transition region where both nitrogen and nitric oxide are being formed, the surface contains both nitrogen and oxygen as indicated by Auger electron spectroscopy. A series of experiments was run at 200°C with a variable NH_3/O_2 ratio; as ammonia pressure increased the surface nitrogen Auger signal increased and the surface oxygen decreased. The rate of the N_2 reaction followed the surface nitrogen con-
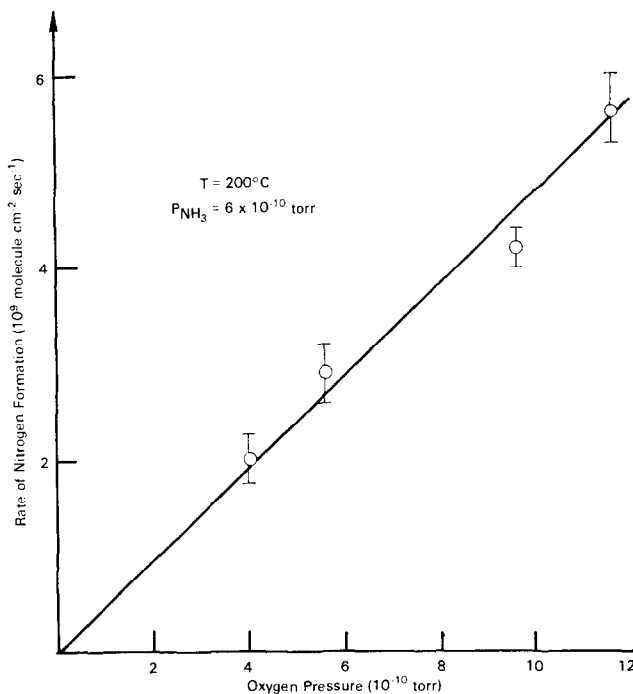
FIG. 5. Nitrogen formation rate as a function of oxygen pressure at 200°C in excess ammonia.

centration and the NO rate followed the oxygen surface concentration. The total concentration of adsorbed species was approximately constant, $RN + RO = K$, as was the total of the two reaction rates. This observation further supports the contention that the reaction rates are competitive.

The nitric oxide branch of this reaction network increases with increasing temperature at low temperatures, but the reaction rate decreases only slightly with increasing temperature above 250°C for a reaction mixture with excess oxygen (Fig. 4b). The surface is covered with oxygen in this temperature range as indicated by Auger. The oxygen surface concentration remains essentially constant with increasing temperature; that is, the oxygen desorption rate, or adsorbed oxygen residence time, is not an important reaction parameter for reaction mixtures with large excesses of oxygen above 250°C. The fact that the rate remains essentially constant with increasing temperature implies that the nitric oxide formation reaction is not an activated process.

Nitrogen Formation

A detailed examination of the nitrogen formation branch of this reaction system has been undertaken at 200°C in excess ammonia (Fig. 5). These conditions were chosen so that no gas-phase nitric oxide would be produced. The reaction to form nitrogen from ammonia and oxygen is first order in oxygen pressure as indicated in Fig. 3. However, the nitrogen formation rate saturates with increasing ammonia pressure as indicated in Fig. 6a. The first-order dependence of the rate on oxygen pressure indicates that molecular oxygen participates in the rate-limiting reaction. This molecular oxygen may be weakly adsorbed or it may react directly from the gas phase. Significant concentrations of oxygen-containing species were not de-

tected using Auger. Thermal desorption spectra taken after saturation of the surface during steady-state reaction at 200°C also failed to detect oxygen, although oxygen may react before it can desorb. For low ammonia pressures the rate of nitrogen formation increases with increasing ammonia pressure; however, the rate of nitrogen formation saturates with further increases in ammonia pressure as indicated in Fig. 6a. Simultaneous measurement of the surface composition by AES during reaction indicates that the surface is covered with nitrogenic species. The kinetic results suggest that the rate-limiting reaction is occurring between molecular oxygen and an adsorbed nitrogen species. Identification of the initial order for the nitrogen formation branch at very low ammonia pressures would aid in identifying the nitrogenic species which participates in the rate-limiting step; however, this information is not accessible because nitric oxide formation interferes when the ammonia pressure is decreased substantially. Thermal desorption spectra taken from surfaces saturated during reaction in excess ammonia show that the primary desorbing species is molecular nitrogen; small amounts of desorbing ammonia and hydrogen are also detected. These results suggest

that ammonia or an ammonia-derived species is the primary nitrogen-containing participant in the rate-limiting step of this reaction. With large excesses of ammonia the reaction follows the pattern described by Eley–Rideal or noncompetitive Langmuir–Hinshelwood kinetics. Saturation of the rate occurs when the active surface is covered with the adsorbed reactant. After saturation, the rate remains constant because there is no competition between the two reactants for surface sites. A measurement of the surface concentration of reactive intermediates should give a measure of the concentration of active surface centers if the measurement is done when the reaction rate is saturated with respect to gas-phase ammonia pressure and the reaction is not desorption limited. The coverage of nitrogenic species which corresponds to saturation of the rate does not depend on oxygen pressure as long as ammonia is in excess. That is, the surface concentration of nitrogenic species is not limited by oxygen pressure (however, the rate is first order in oxygen for all the observed surface concentrations of nitrogenic species.)

The data from Fig. 6a are shown in Fig. 6b where the nitrogen formation rate is plotted as a function of RN, the nitrogen
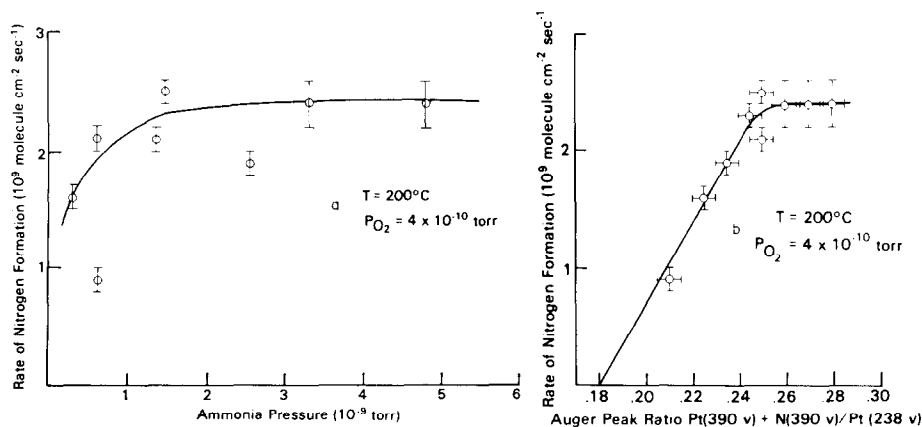

FIG. 6. Nitrogen formation rate for reaction mixtures containing excess ammonia at 200°C as a function of: (a) ammonia pressure; (b) nitrogen Auger ratio Pt(390 V) + N(390 V)/Pt(238 V).
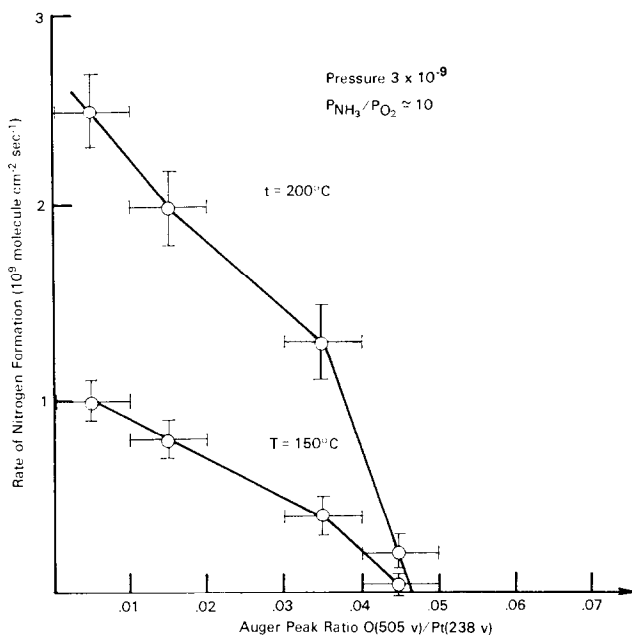
FIG. 7. Nitrogen formation rate as a function of surface oxide concentration measured by the oxide Auger ratio O(505 V)/Pt(238 V). The steady-state reaction was run at 200°C with excess ammonia.

Auger ratio. In the following discussion the nitrogen ratio RN will be used as a measure of surface concentration for nitrogenic surface species as discussed in the Experimental section. The data in Fig. 6b show that the nitrogen formation rate increases linearly until RN reaches a value of 0.25. The reaction rate remains constant with further increases in the concentration of nitrogenic surface species. Using the approximate calibration of RN discussed in the experimental section an RN of 0.25 corresponds to a surface coverage of about 8×10^{13} nitrogen-containing species/cm². This surface contains about 1.5×10^{15} Pt atoms/cm² and was prepared with monatomic height steps spaced 12 atomic rows apart. Therefore, the concentration of step edge atoms is approximately 1.25×10^{14} atoms/cm². If we assume that the surface nitrogenic species can adsorb on every other platinum atom as was observed for the nitric oxide- and nitrogen-saturated surfaces [the (2×2) adsorbed overlayers]

the concentration of surface nitrogenic species required to saturate the step edge sites should be about 6×10^{13} nitrogen-containing species/cm². Thus, it appears that the rate of nitrogen formation increases with the concentration of nitrogenic surface species until the surface concentration of nitrogenic species is sufficient to saturate the step edge sites. After saturation of the step edge sites, the rate is virtually independent of the concentration of nitrogen-containing species. The specific rate of nitrogen formation in terms of concentration of nitrogenic surface species is at least *three times slower* above surface coverages of 8×10^{13} nitrogen-containing species/ cm² than below. The linear correlation between concentration of nitrogenic surface species and reaction rate does not prove that we are measuring only the concentration of reactive intermediates. There may be nitrogen-containing species generated which do not participate in the main reaction pathway. Reaction probabilities

based on the collision frequency of gas-phase oxygen with nitrogenic surface species reveal approximately half of these collisions would have to result in reaction to explain the observed rates. If the reactive oxygen molecules are adsorbed the reaction probability per collision could be approximately ten times lower. In either case the large reaction probabilities required to explain the observed rates suggest that most of the nitrogenic surface species are participating in the main reaction pathway.

The data in Fig. 6b indicate that adsorbed nitrogenic species are more effective in the nitrogen formation reaction when the concentration of surface species is low enough so that the step edge sites cannot be saturated. A series of experiments run with a partially oxidized platinum surface lends further support to the contention that only a small part of this platinum surface

accounts for most of the catalytic activity. The oxidized surface was prepared by treatment in oxygen or in reaction mixtures with excess oxygen above 600°C. As mentioned in a previous study of oxygen adsorption on this same platinum surface (10), oxidation of platinum gives rise to a state of oxygen which desorbs above 1000°C. This oxygen is difficult to remove by reaction and is stable in ammonia or hydrogen up to approximately 500°C (10). The oxide gives rise to an oxygen Auger transition which appears at 505 V instead of the usual 510 to 512 V for chemisorbed oxygen (10). The rate of nitrogen formation at low temperature is very sensitive to the presence of small amounts of surface oxide as shown Fig. 7. Comparisons made with the oxygen ratio (9) $O(510 \text{ V})/Pt(238 \text{ V})$ resulting from chemisorbed oxygen (assuming equal sensitivities) reveal that the
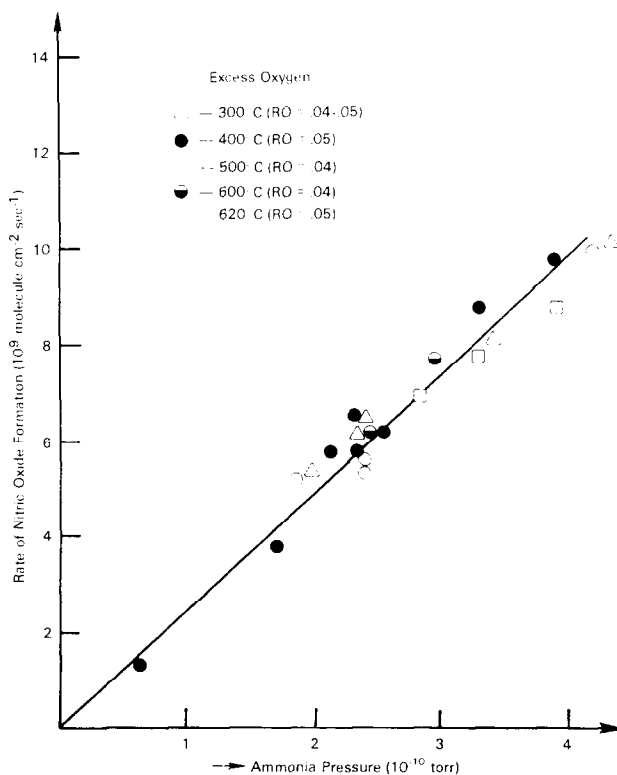

FIG. 8. Nitric oxide formation rate as a function of ammonia pressure for constant surface oxygen concentration at various temperatures between 300 and 620°C.
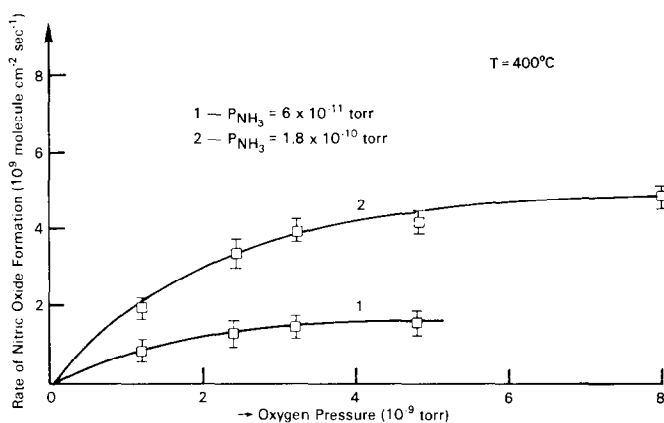
FIG. 9. Nitric oxide formation rate as a function of oxygen pressure at 400°C for a reaction mixture with excess oxygen.

nitrogen formation rate is severely curtailed by a smaller amount of oxygen than required to saturate the step edge site with chemisorbed oxygen. These data are presented here as support for the idea that a small part of the platinum surface is responsible for most of the catalytic activity. Nitric oxide formation does not increase with oxidation of the surface under these conditions; the ammonia oxidation reaction rate is poisoned by small amounts of surface oxide. The effect of oxide on the ammonia oxidation reaction network depends strongly on temperature; these results do not apply to higher temperature studies.

Nitric Oxide Formation

A detailed examination of the nitric oxide production branch of this reaction system has been undertaken at 400°C in excess oxygen. These conditions were chosen so that no detectable molecular nitrogen was formed. The nitric oxide formation rate is first order in ammonia pressure (Fig. 8). However, the rate of nitric oxide formation saturates as the oxygen pressure increases (Fig. 9). The first-order dependence of the nitric oxide formation rate on ammonia pressure indicates that molecular ammonia is probably the primary nitrogen-containing species involved in the rate-limiting reac-

tion step. The molecular ammonia may react from a weakly adsorbed state or directly from the gas phase. The kinetic behavior of this reaction can be rationalized using Eley–Rideal or noncompetitive Langmuir–Hinshelwood kinetics reaction schemes. Further support for this type of reaction scheme is shown in Fig. 8 which shows the nitric oxide formation rate for several temperatures as a function of ammonia pressure in excess oxygen. Auger measurements made during steady-state reaction reveal that the oxygen ratio "RO" remains constant during these experiments. Since the oxygen ratio RO has been shown to be proportional to surface oxygen concentration by Bonzel and Ku (14), the Auger data indicate that the rate of nitric oxide formation is independent of temperature over the temperature range 300 to 620°C for fixed oxygen surface coverage and ammonia pressure. This result indicates that the nitric oxide formation reaction does *not* have a substantial activation energy over this temperature range. This observation also confirms that ammonia decomposition is not involved in this reaction scheme since ammonia decomposition has been shown to have a substantial activation energy in this temperature range over similar platinum single-crystal surfaces (11). Analysis of Auger spectra taken

during the steady-state reactivity experiments (Fig. 9) indicates that the surface contains only oxygen. No significant concentrations of nitrogen-containing species were detected at 400°C by Auger; however, the sensitivity may not be adequate to detect small concentrations of weakly adsorbed molecular species.

The thermal desorption spectra shown in Fig. 10a indicate that the adsorbed oxygen is in an atomic state since the desorption kinetics are second order. The desorption spectra were taken by rapidly heating the platinum sample during a steady-state ammonia oxidation reaction. Several surface oxygen concentrations were obtained by varying the steady-state oxygen pressure. Second-order behavior is indicated by the peak shape and the observation that the peak temperature decreases with increasing coverage. The second-order behavior has been confirmed by observing that the desorption rate at

450°C depends parabolically on the initial surface oxygen concentration as measured by Auger electron spectroscopy (Fig. 10b). These observations indicate that the oxygen adsorbed on this platinum surface during the nitric oxide formation reaction is atomic. Oxygen adsorption has been studied on this same stepped platinum surface using thermal desorption spectroscopy and Auger electron spectroscopy (10). Two states of adsorbed oxygen have been observed by thermal desorption, low-energy electron diffraction, and by variations in sticking coefficient as a function of coverage. Adsorption occurs initially on the step sites as indicated by the formation of a one-dimensional ordered structure and by the simultaneous saturation of the high-temperature desorption peak. Saturation of this high-temperature form occurs at an Auger ratio of 0.09 (about 6×10^{13} molecules/cm²) and gives an approximate desorption energy of 45 kcal/mol using
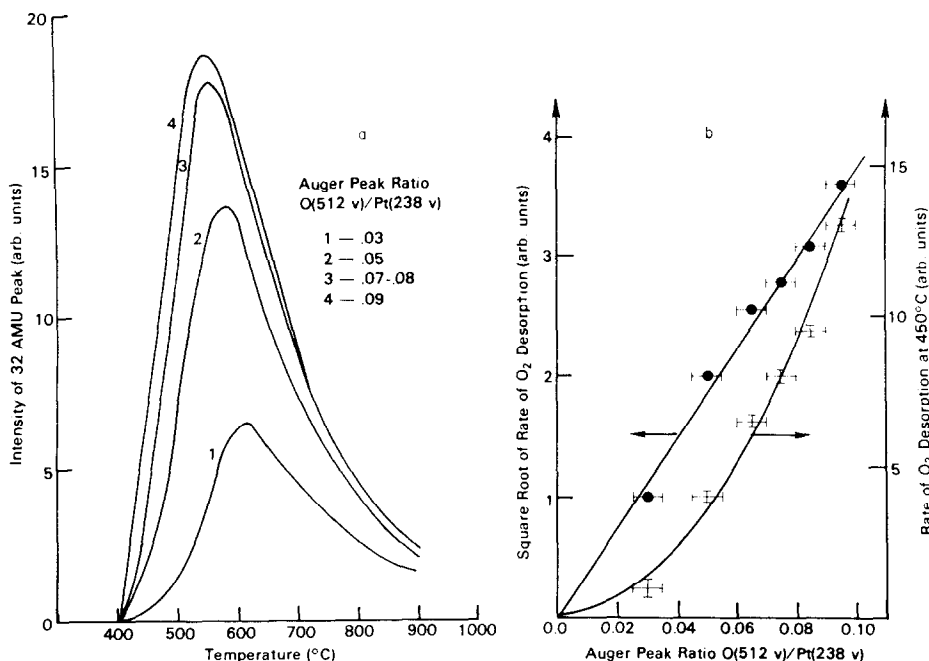

FIG. 10. (a) Oxygen thermal desorption spectra for a surface saturated during steady-state ammonia oxidation at 400°C. The reaction mixture contained excess oxygen; nitric oxide was being formed. (b) The rate of desorption at 450°C as a function of initial oxygen surface concentration shows the parabolic dependence of desorption rate on oxygen concentration expected for a second-order desorption process.
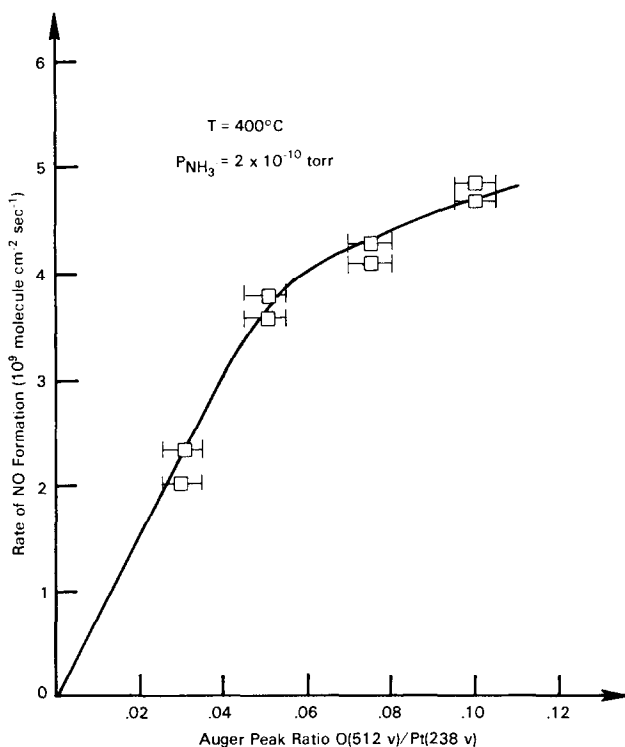
FIG. 11. Nitric oxide formation rate as a function of surface oxygen concentration measured by Auger electron spectroscopy.

second-order kinetics and an assumed pre-exponential factor of 10^{-3} sec^{-1} (10). Adsorption of oxygen at 400°C populates only this high-temperature form which corresponds to adsorption of atomic oxygen on the step edge sites (10). Desorption of oxygen adsorbed at 400°C during steady-state oxidation of ammonia indicates that this oxygen is also adsorbed in the same high-temperature state. These results indicate that the oxygen adsorbed during ammonia oxidation is adsorbed on the step edge sites. Figure 11 shows the nitric oxide formation rate as a function of surface oxygen concentration; these data were taken by varying oxygen pressure for a fixed ammonia pressure. The rate of NO formation increases rapidly as the surface oxygen concentration increases up to an Auger ratio of about 0.05; above this level the specific rate of nitric oxide formation as a function of surface oxygen concentration increases more slowly until the surface

becomes "saturated" with an oxygen Auger ratio of about 0.10. Several attempts with higher oxygen pressures have failed to increase the surface oxygen concentration above the 0.10 oxygen Auger ratio level during steady-state ammonia oxidation. Earlier studies of oxygen adsorption on this surface indicated that the apparent sticking coefficient for oxygen declines precipitiously above Auger ratios of 0.08 to 0.10 as the step edge sites become saturated. The fact that the rate of nitric oxide formation increases as the oxygen surface concentration increases does not prove that we are measuring the surface concentration of reactive species. However, in these studies the high reaction rates observed argue against the presence of inactive surface species. With a surface oxygen concentration of about 3×10^{13} oxygen atoms/cm^2 (RO = 0.05) approximately half the collisions of gas-phase ammonia molecules must be reactive if we

consider only collisions of gaseous ammonia molecules with adsorbed oxygen atoms. If adsorbed ammonia is reacting with adsorbed oxygen, the reaction probability per collision could decrease by up to a factor of 10 due to increased ammonia residence time on the surface. In either case, large concentrations of inactive surface oxygen seem unlikely. The observation that all of the adsorbed oxygen is in the same adsorbed state lends further credence to the contention that all of the atomic oxygen on the surface is participating in the reaction since all the oxygen is apparently the same. The observation that the specific rate of nitric oxide formation in terms of surface oxygen does not increase linearly can be rationalized in several ways. Vacant surface sites may play an important role in the rate-limiting step. The possibility that several types of adsorbed oxygen atoms may be present on the surface cannot be completely eliminated; however, the hypothesis that vacant surface sites are important for the reaction seems more reasonable at the present time.

CONCLUSIONS

The oxidation of ammonia proceeds rapidly above 150°C on the Pt(S) − 12(111) × (111) surface. The only nitrogen-containing products observed are nitric oxide and molecular nitrogen. The rate-limiting reaction for molecular nitrogen formation occurs between an adsorbed nitrogen-containing species derived from ammonia and either weakly adsorbed or gas-phase molecular oxygen. The rate-limiting reaction for the nitric oxide formation branch of this reaction network occurs between atomic oxygen adsorbed on the step edge sites and either weakly adsorbed or gas-phase molecular ammonia. The selectivity of the reaction network is correlated with the surface composition as measured by Auger electron spectroscopy during steady-state reactions. A surface covered with primarily nitrogen-containing species indicates that nitrogen formation is

the primary reaction occurring. Coverage of the surface with chemisorbed oxygen atoms indicates that nitric oxide formation is the primary reaction occurring. The observation that the reaction rates saturate for both branches of this reaction network with respect to increasing reactant pressure as the step edge sites become saturated indicates that the step edge sites are the most active surface sites for both reaction branches. This conclusion has been verified by recent preliminary experiments comparing the catalytic activity of the Pt(111) surface with the Pt(S) − 12(111) × (111) surface. The catalytic activity for both branches of the reaction is higher on the Pt(S) − 12(111) × (111) surface in the same temperature and pressure range.

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