JOURNAL OF CATALYSIS **68**, 349–354 (1981)

The Reduction of Nitric Oxide with Hydrogen on the Pt(111) Surface

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Received May 22, 1980; revised July 31, 1980

The reduction of nitric oxide with hydrogen was studied using steady-state reactivity measurements in the range 10^{-9} to 10^{-8} Torr on the Pt(111) surface over the temperature range 100 to 800 K. The reaction products observed were nitrogen, ammonia, and water. The platinum surface was characterized using low-energy electron diffraction, Auger electron spectroscopy, and thermal desorption. Adsorption and desorption of reactants and products were studied previously on the Pt(111) surface using thermal desorption spectroscopy and electron energy loss spectroscopy. Reduction of nitric oxide occurs rapidly above 400 K on this platinum surface. In excess nitric oxide the dominant product is molecular nitrogen. Below 550 K, in excess nitric oxide, the nitrogen product inhibits nitric oxide reduction. Above 550 K the dissociation of nitric oxide appears to limit both ammonia and nitrogen formation. In excess hydrogen, ammonia is the dominant product from 300 to 500 K; above about 500 K, nitrogen formation dominates the reaction. The formation of an ammonia–nitric oxide surface complex appears to inhibit ammonia formation in the region 300–400 K. Competition is observed between the two reaction branches in the 450- to 550-K regime suggesting a common precursor for both reaction pathways.

INTRODUCTION

The reduction of nitric oxide is an interesting reaction in terms of practical importance and fundamental interest. Steady-state kinetic studies concerning the reduction of nitric oxide with hydrogen over the Pt(111) surface are the primary results discussed in this report. These experiments are part of a program to characterize the surface chemistry of the nitrogen–hydrogen–oxygen system over noble metal surfaces. Studies of ammonia oxidation (*1*, *2*), and the ammonia–nitric oxide reaction (*2*, *3*) on single-crystal platinum surfaces have been previously reported. Studies concerning adsorption, desorption, and dissociation of nitric oxide (*4*, *5*), ammonia (*5*–*8*), water (*9*, *10*), and hydrogen (*11*) have been reported for the Pt(111) surface. Recent results concerning coadsorption of ammonia and nitric oxide on the Pt(111) surface (*12*) indicate that a stable NH_3–NO plays an important role in determining the thermal stability of adsorbed ammonia. Aspects of these studies relevant to our discussion of the reductions of nitric oxide are briefly reviewed under Results.

Pirug and Bonzel (*13*) studied the reduction of nitric oxide with hydrogen in the region 0.1 to 1 Torr over a wide range of temperatures. Using X-ray photoelectron spectroscopy coupled with thermal desorption and steady-state reactivity experiments, they concluded that NO dissociation plays a crucial role in determining reaction rates. Tret'yakov *et al.* (*14*) also studied nitric oxide reduction with hydrogen over platinum. They separated the reaction branches by manipulation of reactant pressures and proposed a mechanism to rationalize the kinetic expressions they observed (*14*).

The kinetic data we report here, as well as adsorption data reported previously (*4*–*12*), indicate that this reaction system is extremely complex. Unfortunately, this complexity, coupled with the experimental uncertainty in rate constant determination, makes assignment of elementary reaction steps extremely difficult.

EXPERIMENTAL

These steady-state reactivity experi-

0021-9517/81/040349-06$02.00/0

ments were performed in an ultrahigh vacuum system equipped with several gas inlets, a cylindrical mirror analyzer for Auger electron spectroscopy (AES), a low-energy electron diffraction unit (LEED), and a multiplexed mass spectrometer. The sample temperature could be programmed over the temperature range 100 to 1300 K. The rates reported in excess hydrogen (averages of three detrminations) were measured by decreasing the temperature in 50° steps. The temperature was held constant for 3 to 5 min at each step to ensure that the measured rates were steady-state rates. The rates reported in excess nitric oxide are the average of three determinations made by decreasing the temperature continuously at a rate of 36°/min from 875 to 100 K. Control experiments were run for the extreme reactant partial pressure ratios using the 50° step decrease method described above to ensure that the measured rates were steady-state rates. Background pressures for the reaction products were determined below 200 K, where no reactivity was observed. Reaction rates were estimated using the stirred-tank formulation for a flow reactor,

$$r_i = \Delta P_i S_i / R T_g A,$$

where r_i is the 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" caused by reaction on the catalyst sample, S_i is the pumping speed for species "i", R is the gas constant, T_g is the gas temperature, and A is the catalyst area. The catalyst area was 2.0 cm^2 and a gas temperature of 300 K was used for calculation of the rates. Pumping speeds were estimated from the exponential decay of pressure following the introduction of a pulse of gas under reaction conditions. The mass spectrometer was calibrated against the ion gauge for reactants and products of this reaction system. Internal comparisons of this data should be fairly accurate; however, the reliability of the absolute rates may not be high.

RESULTS

Nitric oxide and hydrogen interact with the Pt(111) surface in a complex manner as illustrated by the multiple desorption peaks for both species shown in Fig. 1. Dissociatively adsorbed nitric oxide, which recombines and desorbs as a shoulder near 450 K, is the most stable form of adsorbed nitric oxide (*4*). The recombination of nitrogen from dissociatively adsorbed nitric oxide yields a largely desorption limited nitrogen peak which occurs near 450 K (*4*), as illustrated in Fig. 1. Nitric oxide adsorbs easily at 100 K on a Pt(111) surface previously saturated with hydrogen at 100 K as shown in the lower panel of Fig. 1. However, the thermal stability of hydrogen on the Pt(111) surface is decreased substan-

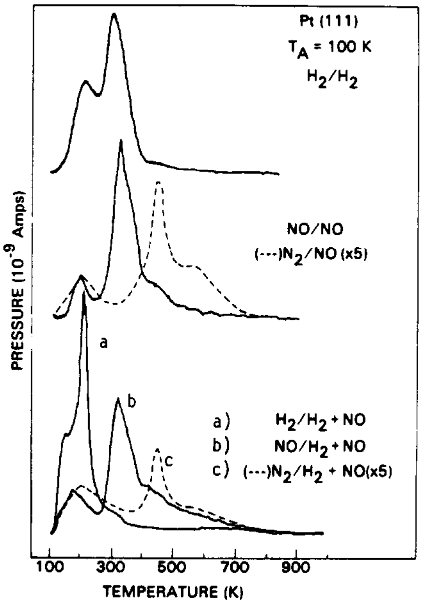

FIG. 1. A series of thermal desorption spectra taken following saturation of the Pt(111) surface at 100 K. A hydrogen desorption spectrum from a hydrogen-saturated surface is labeled H_2/H_2. Nitric oxide and nitrogen desorption spectra from a nitric oxide-saturated surface are labeled NO/NO and N_2/NO, respectively. Hydrogen, nitric oxide, and nitrogen desorption spectra from a hydrogen-saturated surface postsaturated with nitric oxide are labeled H_2/H_2 + NO, NO/H_2 + NO, and N_2/H_2 + NO, respectively. The heating rate was 4.7°/sec.

tially when hydrogen is coadsorbed with nitric oxide, as indicated by the marked decrease in desorption temperature for hydrogen in the presence of adsorbed nitric oxide. Similar sequential adsorption experiments run on a surface presaturated with nitric oxide indicate that only small amounts of hydrogen adsorb. These results suggest that large coverages of nitric oxide might inhibit the reaction by blocking hydrogen adsorption or by decreasing the thermal stability of surface hydrogen.

Water produced in this reaction desorbs rapidly since the water has a binding energy of 40 kJ/mol and desorbs near 150 K (*9*, *10*). Steady-state water formation rates were measured during these experiments. Qualitatively they were simply the sum of the nitrogen and ammonia formation curves with appropriate multiplicative constants to account for reaction stoichiometries, mass spectrometer sensitivity, and pumping speed. Unfortunately, the water pumping speeds varied fairly widely during the course of our experiments making quantitative interpretation of the water results impossible.

Ammonia desorption from the Pt(111) surface is illustrated in the lower panel of Fig. 2. Two forms of adsorbed molecular ammonia are observed as indicated by isotope exchange thermal desorption experiments (*7*), vibrational studies (*6*), and photoelectron spectroscopy (*8*). Adsorption of ammonia above about 170 K yields a surface containing only the low-coverage form (*6*), as illustrated by the desorption spectrum labeled "NH_3/NH_3/173 K" in the upper panel of Fig. 2. Postsaturation of such a surface with nitric oxide increases the thermal stability of adsorbed ammonia substantially as indicated by the desorption spectrum labeled "NH_3/NH_3 + NO/173 K" in the upper panel of Fig. 2. The total amount of ammonia on the surface is the same for the two spectra mentioned above; in the presence of adsorbed nitric oxide a larger fraction of the ammonia remains on the surface until higher temperature. A more complete discussion of this complex is given by Gland and Sexton (*12*). Ammonia formed by reaction of coadsorbed nitric oxide and hydrogen has a desorption spectrum characteristic of ammonia desorbing from an ammonia–nitric oxide complex as illustrated by the desorption spectrum labeled "NH_3/H_2 + NO/100 K" in the upper panel of Fig. 2.

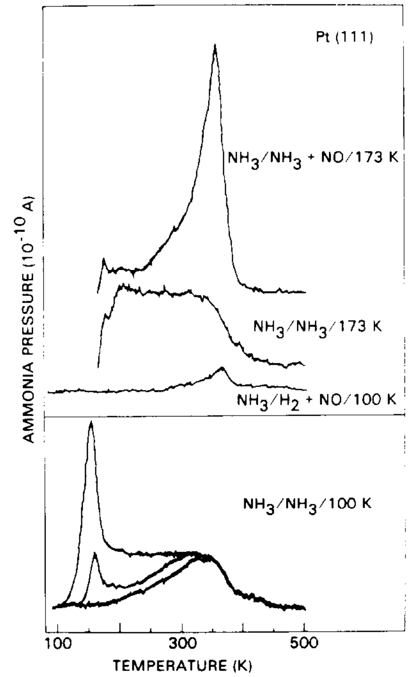

FIG. 2. A series of thermal desorption spectra taken from the Pt(111) surface at a heating rate of 10°/sec. An ammonia desorption spectrum from a surface saturated with ammonia at 173 K and postsaturated with nitric oxide at 173 K is labeled NH_3/NH_3 + NO/173 K. An ammonia desorption spectrum from a surface saturated with ammonia at 173 K is labeled NH_3/NH_3/173 K. An ammonia desorption spectrum from a surface saturated with hydrogen then postsaturated with NO at 100 K is labeled NH_3/H_2 + NO/100 K. Ammonia desorption spectra generated following exposure of this surface to 0.5, 1.0, and 3.0 L of ammonia at 100 K are labeled NH_3/NH_3/100 K. (1.0 L = 1.0×10^{-6} Torr sec.)

Figures 4 through 7 relate the results of steady-state reactivity experiments over the temperature range 100 to 800 K. Reactivity experiments in excess nitric oxide (Figs. 4 and 5) reveal that nitrogen is the dominant reaction product above the reac-

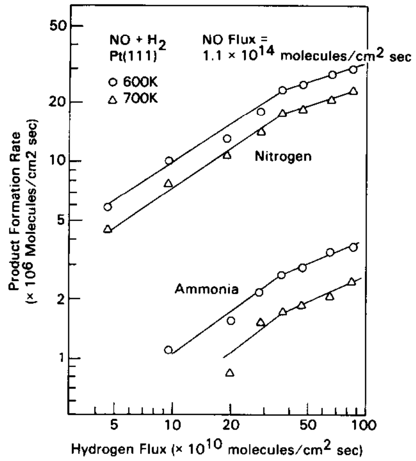

FIG. 3. Steady-state nitrogen and ammonia formation rates as a function of hydrogen flux in excess nitric oxide. This data are taken from the complete reactivity set represented in Fig. 4.

tion initiation temperature of about 400 K. Both the nitrogen and ammonia formation rates increase with increasing hydrogen partial pressure as indicated in Fig. 3. The reaction orders for both nitrogen formation

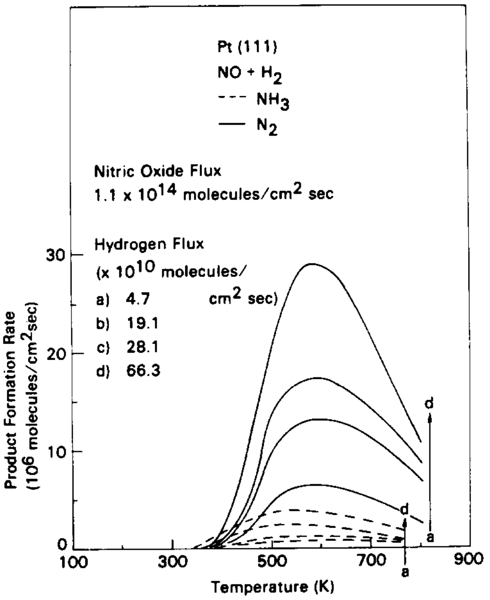

FIG. 4. Steady-state ammonia and nitrogen formation curves for a group of reaction mixtures with various hydrogen fluxes and constant excess nitric oxide flux as a function of temperature.

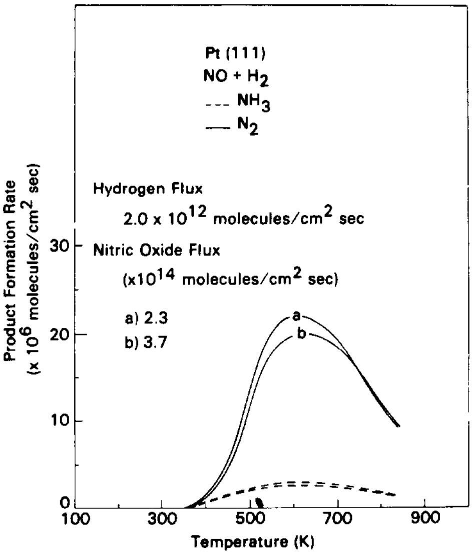

FIG. 5. Steady-state ammonia and nitrogen formation curves for two reaction mixtures with two excess nitric oxide fluxes and constant hydrogen flux as a function of temperature.

and ammonia formation are remarkably similar yet vary significantly over the temperature and pressure ranges indicated in Fig. 3. The reaction orders in excess NO range from approximately first order for the smaller hydrogen partial pressures to half order for the larger hydrogen partial presures over the temperature range studied as indicated in Fig. 3. This result suggests that the mechanisms of the two reaction branches are coupled. Similar reaction temperature profiles (Fig. 4) observed for the ammonia and nitrogen formation further support our contention that the reaction branches are coupled. Figure 5 further suggests that neither the nitrogen nor ammonia formation rate is significantly influenced by nitric oxide partial pressure variations in excess nitric oxide. This lack of nitric oxide inhibition contrasts with the low-temperature adsorption results discussed previously (see Fig. 1). The reaction results suggest, therefore, that the nitric oxide surface coverage may not be high under these reaction conditions. The thermal desorption results shown in the middle panel of Fig. 1 also suggest that surface nitrogen is more thermally stable than most adsorbed nitric oxide. Thermal desorption experiments were also run after exposure of the surface to reaction mixtures in the region 200 to 450 K in order to characterize species on the surface. Desorbing nitric oxide and nitrogen dominated the spectra. Taken together these results in excess nitric oxide suggest that the primary coupling mode for temperatures below 500 K may be inhibition of the reaction by the product nitrogen. The observation that the reaction initiation temperature correlates well with the temperature of nitrogen recombination and desorption lends further credence to this proposal.

Two alternative mechanisms can be used to rationalize the coupling of the two reaction branches above 500 K. Electron energy loss and temperature-programmed isotope exchange experiments (*5*) indicate that only the small desorption shoulder of nitric oxide, which desorbs near 350 to 400 K, corresponds to dissociatively absorbed nitric oxide. Since dissociation of nitric oxide does not occur easily on this platinum surface the common rate limitation for both ammonia and nitrogen formation may be dissociation of adsorbed nitric oxide. Some of the coupling might also occur by sequential formation of nitrogen since the ammonia produced by the reaction may react further with nitric oxide to yield nitrogen (*2*, *3*). Although both processes may be contributing, we feel the dominant coupling mode is probably furnished by a common rate-limiting step, dissociation of nitric oxide.

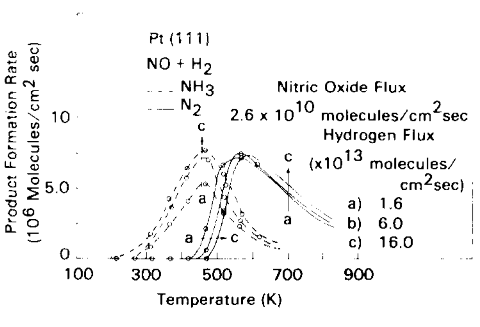

FIG. 6. Steady-state ammonia and nitrogen formation rates for a group of reaction mixtures with various excess hydrogen fluxes with constant nitric oxide flux as a function of temperature.

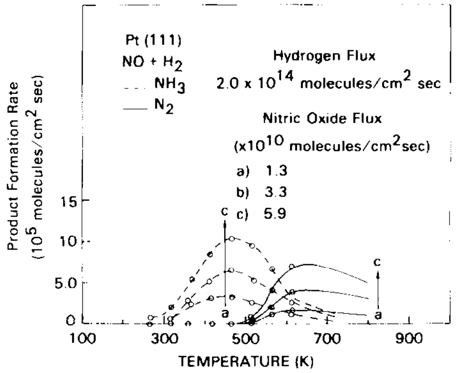

FIG. 7. Steady-state ammonia and nitrogen formation rates for a group of reaction mixtures with various nitric oxide fluxes and constant excess hydrogen flux as a function of temperature.

Generally, Figs. 6 and 7 both indicate that in excess hydrogen, ammonia formation begins near 300 K and is the dominant product up to about 500 K, where nitrogen formation begins to dominate. The initiation temperature for ammonia formation may be characteristic of decomposition of an ammonia–nitric oxide surface complex or a rapid increase in surface hydrogen coverage caused by nitric oxide desorption. Thermal desorption results discussed previously (see Fig. 2) suggest that surface complex dissociation is the more reasonable explanation.

Increasing the hydrogen partial pressure causes the initiation temperature for the nitrogen formation reaction to increase as the ammonia formation rate increases (Fig. 6). Competition between the reaction branches for nitrogen-containing species is apparently the cause of this synergistic effect. Ammonia formation dominates in the low-temperature region, where surface hydrogen has a substantial lifetime. As the hydrogen coverage decreases with increasing temperature, the recombination of nitrogen atoms becomes the dominant process. In excess hydrogen both the reaction branches are basically first order with respect to nitric oxide partial pressure as indicated in Fig. 7. This observation can be rationalized either by an arrival rate limited reaction, or a first-order surface rate limitation (e.g., dissociation of nitric oxide).

CONCLUSIONS

Nitric oxide and hydrogen react readily above 400 K to form nitrogen, ammonia, and water. In excess nitric oxide nitrogen formation predominates. Below 500 K nitric oxide reduction is inhibited by adsorbed nitrogen product. Above 500 K dissociation of nitric oxide may play a dominant role in both reaction branches. In excess hydrogen, ammonia is the dominant product below 500 K; above 500 K nitrogen formation dominates. The decomposition of an ammonia–nitric oxide surface complex may determine the initiation temperature for steady-state ammonia formation. Competition between ammonia formation and nitrogen formation increases the initiation temperature for nitrogen formation as hydrogen partial pressure is increased, suggesting that a common surface species plays a key role in both processes.

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