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Observation of an NH_3–NO Complex on the Pt(111) Surface

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The coadsorption of nitric oxide and ammonia has been studied on the Pt(111) surface using electron energy loss spectroscopy and thermal desorption spectroscopy to characterize the surface complex which forms between adsorbed molecular ammonia and adsorbed molecular nitric oxide. A stretching frequency of the surface complex occurs at 1280 cm^{-1} and is formed by the coalescence of the bridge-bonded nitric oxide stretching mode at 1490 cm^{-1} and the symmetric deformation mode of the low-coverage, high-temperature form of molecular ammonia at 1090 cm^{-1}. The thermal stabilities of some of the adsorbed nitric oxide and the low-coverage, high-temperature form of adsorbed molecular ammonia are increased as evidenced by the appearance of new high-temperature desorption peaks for both NO and NH_3 at 350 K. Thermal desorption experiments with coadsorbed nitric oxide and ammonia indicate that no nitrogen formation occurs directly from the surface complex. With heating, the NH_3–NO complex simply decomposes at 350 K, and desorption of molecular ammonia and nitric oxide occurs. Ammonia decomposition has been observed on this surface only above 400 K, and therefore it appears that NH_3 decomposition may be necessary to initiate the NO–NH_3 reaction on this surface.

INTRODUCTION

The coadsorption of ammonia and nitric oxide have been examined on the Pt(111) surface in order to characterize the interactions and reactions which occur between these chemisorbed species. These experiments are part of a program to characterize the surface chemistry of the nitrogen–hydrogen–oxygen system over platinum. Nitric oxide adsorption on platinum single-crystal surfaces has been studied recently by several authors (*1–8*). It is generally accepted that molecular nitric oxide adsorption predominates on platinum surfaces. Studies in this laboratory (*1, 2*) indicate that at low coverage, nitric oxide adsorbs primarily by bridge bonding; as coverage increases terminally bound nitric oxide forms from the bridge-bonded species, resulting in a surface dominated by terminally bound species at saturation. With increasing temperature (as NO desorption occurs), the adsorbed layer changes from a configuration containing primarily terminally bound species to an overlayer containing predominantly bridge-bound species at low coverage (*1, 2*).

Molecular adsorption of ammonia predominates on the Pt(111) surface below 400 K as indicated by several recent studies in this laboratory (*9–12*). Steady-state ammonia decomposition occurs above 400 K on the Pt(111) surface, indicating ammonia dissociation does occur at elevated temperature (*11*) even on the Pt(111) surface. The two forms of adsorbed molecular ammonia have been characterized using isotope-exchange thermal desorption (*11*), electron energy loss spectroscopy (*9, 10*), and ultraviolet photoemission spectroscopy (UPS) (*12*). These two forms of adsorbed molecular ammonia are distinguished by the descriptive names "low-coverage, high-temperature form" and "high-coverage, low-temperature form" throughout the discussion which follows. The low-coverage, high-temperature form of adsorbed molecular ammonia desorbs in a wide desorption peak in the 170 to 400 K temperature range and has a large oriented dipole moment as indicated by the 3.0-eV de-

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crease in work function observed (12). The high-coverage, low-temperature form of adsorbed molecular ammonia interacts with the Pt(111) less strongly as evidenced by the narrow desorption peak at 150 K and the lack of further work function change observed (12).

EXPERIMENTAL

These coadsorption studies were performed in two experimental systems which have been described in detail elsewhere (13, 14). The electron energy loss system (EELS) contains two 127° sector analyzers used for vibrational measurements, a single-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), a quadrupole mass spectrometer (QMS) for thermal desorption spectroscopy (TDS), and a low-energy electron diffraction system (LEED). The desorption system contains LEED, a single-pass CMA for AES, and a multiplexed QMS for TDS experiments.

Generally, ammonia was dosed onto the front surface of the Pt(111) samples through a stainless-steel microchannel plate. The front surfaces of the samples were uniformly exposed to gas flux since the dosing arrays are larger than the sample surface. During the desorption experiments which were run to determine the amounts of nitrogen produced, background ammonia exposures were used so that both sides of the Pt(111) sample were exposed uniformly.

The platinum single-crystal samples were polished using the usual metallographic techniques. They were cleaned using high-temperature oxygen treatment and high-temperature annealing *in vacuo* as described previously (13). Temperatures were measured using a 0.08-mm Chromel–Alumel thermocouple spot-welded to the edge of the sample. The desorption spectra shown were taken using a linear heating rate of 4.1°/s.

RESULTS

A series of vibrational spectra for adsorbed nitric oxide, adsorbed ammonia, and coadsorbed nitric oxide and ammonia are shown in Fig. 1. The presence of an ammonia–nitric oxide surface complex is clearly illustrated by these vibrational spectra. Nitric oxide adsorbed on the Pt(111) surface has two vibrational transitions at 1490 and 1710 cm^{-1} due to nitric oxide adsorbed in bridged and terminal configurations, respectively (1, 2), as shown in the lower panel of Fig. 1. A spectrum of the Pt(111) surface saturated with the low-coverage, high-temperature form of molecular ammonia (formed by heating a surface saturated at 100 to 173 K,

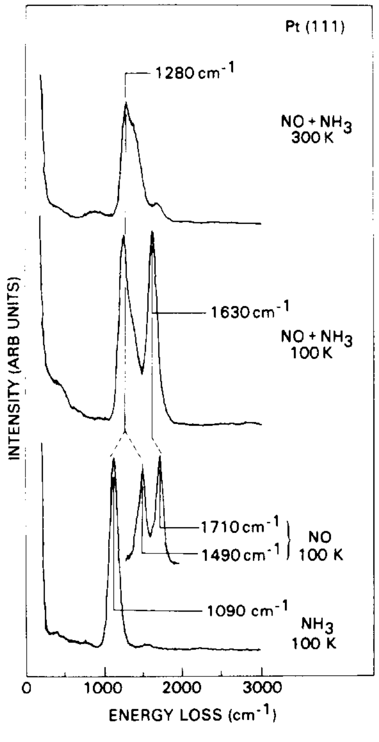

FIG. 1. Electron energy loss spectra illustrating the formation of an NH_3–NO complex formation on the Pt(111) surface. The lower spectra show reference spectra for the low-coverage form of ammonia and an intermediate coverage of nitric oxide. Postadsorption of nitric oxide onto low-coverage ammonia at 100 K yields the shifted spectrum labeled NH_3 + NO 100 K. Heating this layer of coabsorbed NH_3 and NO to 300 K yields the spectrum labeled NH_3 + NO 300 K whose primary transition is caused by a surface complex between ammonia and nitric oxide.

then cooling again to 100 K) is also shown in the lower panel of Fig. 1. The symmetric bending mode at 1090 cm^{-1} (*9, 10*) is the dominant vibrational mode observed. Saturation of such a surface with nitric oxide at 100 K yields the spectrum shown in the middle panel of Fig. 1. Both nitric oxide stretching modes are shifted down by about 80 cm^{-1} while the symmetric ammonia bending mode is shifted up by about 150 cm^{-1}. With heating to 300 K the shifted terminally bound NO stretching mode decreases in intensity as some nitric oxide desorbs. The single broad peak remaining at 1280 cm^{-1} is characteristic of the surface complex formed between nitric oxide and ammonia.

A series of thermal desorption spectra taken following adsorption of ammonia, adsorption of nitric oxide, and coadsorption of ammonia with nitric oxide are shown in Fig. 2. Desorption of ammonia from the Pt(111) surface saturated with ammonia at 100 K is shown in Fig. 2, spectrum a. The low-temperature, high-coverage state of chemisorbed molecular ammonia desorbs in a narrow peak at 150 K, while the high-temperature, low-coverage state desorbs in a broad peak in the 170 to 400 K range. Following ammonia saturation of the Pt(111) surface at 173 K, only the broad high-temperature peak characteristic of the low-coverage, high-temperature state of adsorbed ammonia is observed as shown in Fig. 2, spectrum b.

Ammonia desorption from a surface presaturated with ammonia at 173 K, then saturated with nitric oxide at 173 K is shown in spectrum c. Note that a complete monolayer of nitric oxide can be postadsorbed on this ammonia-saturated surface. The thermal stability of the low-coverage, high-temeperature form of adsorbed molecular ammonia has been enhanced considerably. Most of the ammonia now desorbs above 300 K in a peak centered at 350 K (Fig. 2, spectrum c) instead of desorbing fairly uniformly over the 170 to 400 K temperature range (as in spectrum b).

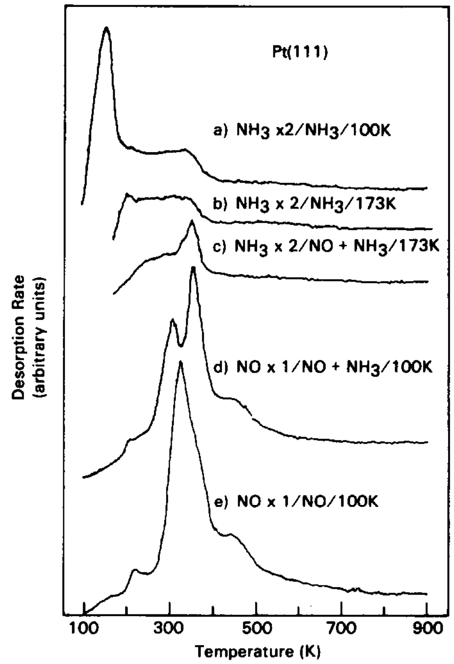

FIG. 2. A set of thermal desorption spectra illustrating the formation of an NH_3–NO complex on the Pt(111) surface (compare spectra b and c; also d and e). (a) NH_3 desorption following saturation of the surface at 100 K with NH_3. (b) NH_3 desorption following saturation of the surface at 173 K with NH_3. (c) NH_3 desorption following saturation of the surface at 173 K first with NH_3, then with NO. (d) NO desorption following saturation of the surface first with NH_3 at 173 K, then with NO at 100 K. (e) NO desorption following saturation of the surface at 100 K with NO.

The nitric oxide desorption spectrum is also modified by coadsorption with the low-coverage, high-temperature form of ammonia as illustrated by spectra d and e in Fig. 2. Nitric oxide desorption from the Pt(111) surface saturated with nitric oxide at 100 K is shown in spectrum e. The primary nitric oxide desorption peak occurs at 325 K.

Desorption of nitric oxide from a Pt(111) surface presaturated with ammonia at 173 K, then saturated with nitric oxide at 100 K is shown in Fig. 2, spectrum d. The primary nitric oxide peak at 325 K (spectrum e) has been split into two peaks at 300 and 350 K (spectrum d). That is, the thermal stability of some of the adsorbed nitric oxide has been increased by interaction with adsorbed molecular ammonia. Both the complexed nitric oxide (spectrum d) and the complexed ammonia (spectrum c) desorb at 350 K, indicating that their desorption rates at 350 K are being limited by the decomposition rate of the surface complex.

Taken together, the vibrational and thermal desorption results shown in Figs. 1 and 2 indicate that a complex is formed between adsorbed nitric oxide and ammonia. Details of the interactions are not yet clear. The large work function change observed for adsorption of the low-coverage, high-temperature form of ammonia indicates that the adsorbed ammonia is oriented and transfers substantial electron density into platinum. The decrease in the NO stretching frequencies observed may result from increased back-donation from the metal into the NO caused by electron donation on adjacent NH_3 molecules. Coadsorbed nitric oxide might also be polarized by direct interaction with the dipoles on adjacent ammonia molecules. This may result in coupling of the vibrational modes and enhancement of the low-frequency mode at the expense of the higher-frequency modes. We feel direct interaction probably plays an important role since the molecules must be fairly close together because of substantial coverage obtained during coadsorption experiments.

A series of experiments have been done to explore the decomposition of the nitric oxide–ammonia surface complex. Attention was focused particularly on the possibility of direct N_2 formation from the complex. No significant N_2 formation was observed from decomposition of the nitric oxide–ammonia complex. As illustrated in Fig. 3, similar amounts of nitrogen are formed independent of the presence of ammonia in the overlayer. The dashed spectra in Fig. 3 indicate the amount of NO (spectrum a) and N_2 (spectrum d) desorbing from this Pt(111) surface saturated with NO at 100 K. Nitric oxide desorption from a surface presaturated with NO at 100 K, then saturated with ammonia is shown in spectrum b of Fig. 3. Notice again the shifted NO peak at 350 K due to the formation of a surface complex with ammonia. Ammonia desorption from this same overlayer is shown in spectrum c. The background increases rapidly since the sample was exposed to ammonia from the background so that both sides of the sample would be covered with ammonia. Notice that the low-temperature ammonia peak is not shifted substantially, but the high-temperature state desorbs in a peak at 350 K as observed previously. The amount

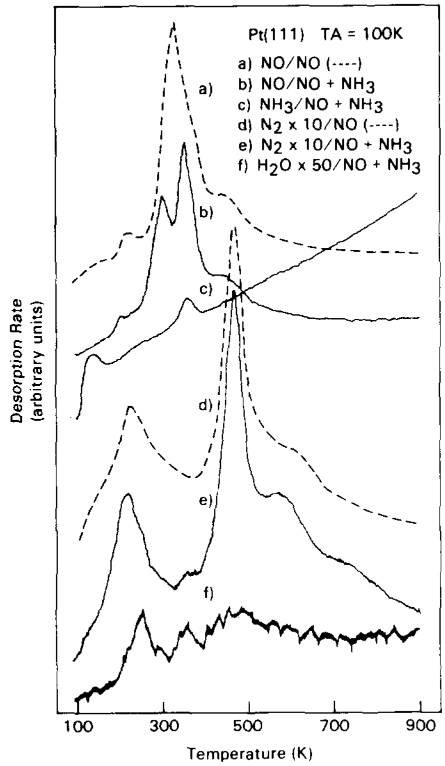

FIG. 3. A set of thermal desorption spectra illustrating that no significant amount of N_2 is formed from the NH_3–NO surface complex (compare spectra d and e). (a) NO desorption from the surface saturated with NO at 100 K. (b) NO desorption from a surface first saturated with NO, then with NH_3 at 100 K. (c) NH_3 desorption from a surface saturated with NO, then saturated with NH_3 at 100 K. The NH_3 background rises during desorption because the NH_3 exposure was done from background. (d) N_2 desorption from a surface saturated with NO at 100 K. (e) N_2 desorption from a surface first saturated with NO at 100 K, then saturated with NH_3 at 100 K. (f) H_2O desorption from a surface saturated with NO, then NH_3 at 100 K.

of nitrogen desorbing following coadsorption of nitric oxide and ammonia is shown in spectrum e (note that nitrogen sensitivity is ten times the nitric oxide sensitivity). Approximately the same amount of nitrogen is formed during the desorption of an equivalent overlayer of nitric oxide as illustrated in spectrum d (again multiplied by ten). The observation that no significant amounts of nitrogen are formed directly from the ammonia–nitric oxide complex is further supported by the insignificant amount of water formed during decomposition of the NH_3–NO complex as illustrated in spectrum f. Note that the water sensitivity has been increased to 50 times the NO sensitivity.

A series of coadsorption experiments have also been done with various initial coverages of ^{15}NO and $^{14}NH_3$ in order to search for $^{14}N^{15}N$ which might result from direct formation of N_2 from the $^{14}NH_3$–^{15}NO complex. As expected, ^{15}NO and $^{14}NH_3$ were the dominant desorption products; little N_2 formation occurred (as indicated previously by Fig. 3). The small amount of N_2 which did form near 475 K was primarily $^{15}N^{15}N$, apparently arising from decomposition of ^{15}NO. Less than 10% of the nitrogen desorbing at 475 K is $^{15}N^{14}N$, giving further indication that significant amounts of N_2 are *not* formed directly from the NH_3–NO complex.

The NH_3–NO reaction proceeds rapidly on the Pt(111) surface only above 400 K (*15*). Recent results also indicate ammonia decomposition only occurs above 400 K on the Pt(111) surface (*11*). The preceding discussion indicates that the NH_3–NO complex which forms below 350 K does not lead to the direct formation of N_2. Taken together all these results indicate that on the Pt(111) surface the NH_3–NO reaction may be initiated by decomposition of ammonia on the surface.

CONCLUSION

Coadsorption of ammonia and nitric oxide below 350 K on the Pt(111) surface results in the formation of a surface complex between adsorbed molecular nitric oxide and the low-coverage, high-temperature form of adsorbed molecular ammonia. Complex formation alters both the vibrational spectrum and the thermal desorption spectra of coadsorbed NH_3 and NO. The primary vibrational transition of the NH_3–NO complex occurs at 1280 cm^{-1} and is formed by coalescence of the bridge-bonded NO transition at 1490 cm^{-1} and the symmetric deformation mode of the low-coverage, high-temperature state of adsorbed ammonia at 1090 cm^{-1}. The thermal stabilities of some of the adsorbed nitric oxide and the low-coverage, high-temperature form of adsorbed NH_3 are increased, as evidenced by the appearance of a new high-temperature desorption peak for both species at 350 K. Thermal desorption experiments indicate that no N_2 formation occurs directly from the NH_3–NO surface complex. With heating, the complex simply decomposes at 350 K and desorption of NH_3 and NO occurs.

REFERENCES

1. Gland, J. L., and Sexton, B. A., *Surface Sci.* **94,** 355 (1980).
2. Gorte, R. J., Schmidt, L. D., and Gland, J. L., in preparation.
3. Pirug, G., Bonzel, H. P., Hopster, H., and Ibach, H., *J. Chem. Phys.,* in press.
4. Ibach, H., and Lehwald, S., *Surface Sci.* **76,** 1 (1978).
5. Gland, J. L., *Surface Sci.* **71,** 327 (1978).
6. Bonzel, H. P., Broden, G., and Pirug, G., *J. Catal.* **53,** 96 (1978).
7. Bonzel, H. P., and Pirug, G., *Surface Sci.* **62,** 45 (1977).
8. Bonzel, H. P., and Fisher, T. E., *Surface Sci.* **51,** 213 (1975).
9. Sexton, B. A., and Mitchell, G. E., *Surface Sci.* **99,** 523 (1980).
10. Sexton, B. A., and Mitchell, G. E., *Surface Sci.* **99,** 539 (1980).
11. Gland, J. L., and Kollin, E. B., *Surface Sci.,* accepted.
12. Fisher, G. B., *Chem. Phys. Letters,* (1981).
13. Gland, J. L., *Surface Sci.* **93,** 487 (1980).
14. Sexton, B. A., *J. Vacuum Sci. Technol.* **16,** 1033 (1979).
15. Gland, J. L., Woodard, G. C., and Korchak, V. N., *J. Catal.* **61,** 543 (1980).