Selective Catalytic Oxidation of Ammonia to Nitrogen on Atomic Oxygen Precovered Au(111)

Jinlong Gong, Rotimi A. Ojifinni, Tae S. Kim, John M. White, and C. Buddie Mullins*

*Department of Chemical Engineering, Materials Science and Engineering, and Chemistry,
Center for Nano- and Molecular Science and Technology, and Texas Materials Institute,
University of Texas at Austin, 1 University Station C0400, Austin, Texas 78712-0231*

Received April 14, 2006; E-mail: mullins@che.utexas.edu

Environmentally benign chemical processing and waste gas stream cleaning are becoming increasingly important. In this regard, ammonia removal is of great interest since it is an undesirable byproduct of industrial catalytic reactions. Selective catalytic oxidation (SCO) of ammonia to nitrogen and water is potentially an ideal technology for removing ammonia from oxygen-containing waste gases.[1,2] Adsorption and oxidation of NH_3 have been widely studied on Al,[3] Ir,[4−6] Pt,[7−9] Rh,[10] Ni,[11] Ru,[12] and Ag[13] single-crystal surfaces. The results show that Pt and Ir are very active for this reaction, but significant amounts of nitrous oxide or nitric oxide are produced.

Gold has received much attention as a catalyst for various reactions, especially for low-temperature CO oxidation,[14,15] the water−gas shift reaction,[16] and propylene epoxidation.[17] However, to the best of our knowledge, there have been no reports concerning ammonia oxidation on Au(111) single-crystal surfaces. Temperature-programmed desorption with simultaneous product analysis has been employed here to provide the first investigation of the selective catalytic oxidation of ammonia on Au(111) at temperatures between 77 and 600 K. The results demonstrate that, although NH_3 does not dissociate on clean Au(111), when precovered with atomic oxygen the surface exhibits a high selectivity toward the conversion of NH_3 to N_2 rather than NO_x.

The experiments were carried out in a molecular beam surface-scattering apparatus consisting of an ultra-high-vacuum (UHV) chamber (base pressure $< 2 \times 10^{-10}$ Torr) equipped with an Auger electron spectrometer (AES), low-energy electron diffraction optics (LEED), and quadrupole mass spectrometer (QMS).[14,15,18] The sample assembly consists of a Au(111) single crystal (11 mm in diameter, 1.5 mm thick) mounted on a tantalum support that is in thermal contact with a liquid nitrogen reservoir and can be resistively heated.[14] The surface temperature is monitored with a type K thermocouple, which is spot-welded to the backside of the tantalum plate. Atomic oxygen is dosed using a supersonic, radio frequency (rf)-generated plasma source from an 8 vol % O_2 in Ar gas mixture with ∼40% dissociation fraction, as determined via time-of-fight (TOF) measurements.[19] Research-purity NH_3, O_2, and Ar were used without further purification. The same apertures and nozzle were used for beams of NH_3 and the O-plasma to ensure that the dosed areas on the gold sample were coincident. The dosed area (∼7 mm^2) is smaller than the crystal face to enable precise and reproducible exposures without appreciable adsorption on surfaces other than Au(111). Standard cleaning methods[8,15] were used, and cleanliness was confirmed by AES and oxygen TPD. A trace amount of adsorbed molecular oxygen (<1% of total) is generated from exposure to the oxygen plasma but has an immeasurable effect on the experiments shown here. Thus, all experiments were carried out on surfaces that are predominately covered by O_{ad} with a very small amount of $O_{2,ad}$.
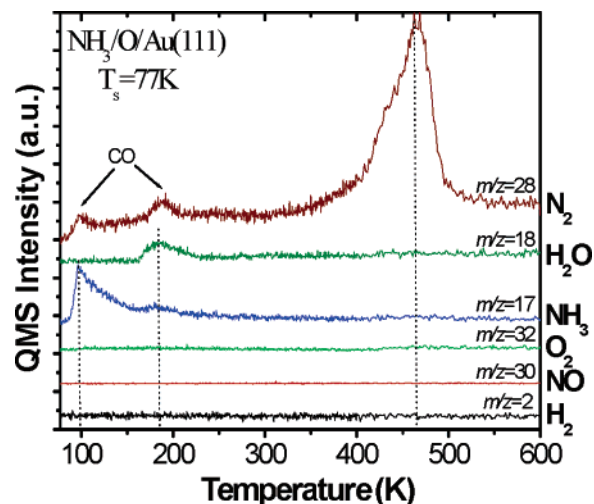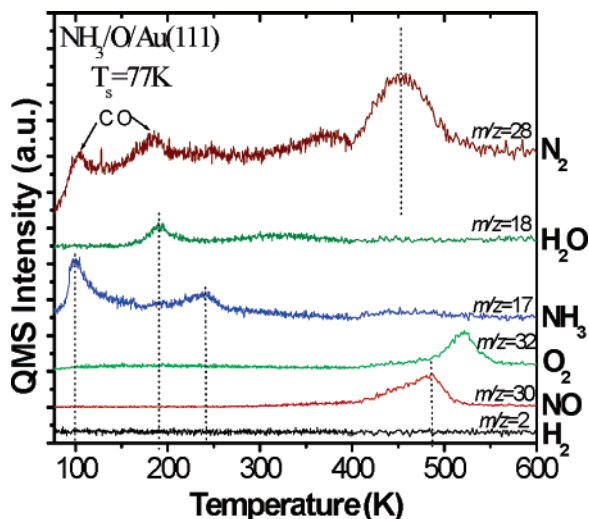

Figure 1. TPD spectra for H_2, NO, O_2, H_2O, and N_2 from the adsorption of 0.18 ML O atoms on Au(111) at 77 K followed by 0.23 ML NH_3 at 77K. The sample was heated with a rate of 1 K/s to 400K, then 3 K/s to 600 K.

It is well-known that molecular adsorption of NH_3 on a clean surface results in a bond to the metal via the N atom.[20] Previous UHV studies have shown that ammonia binds weakly and without dissociation to clean Au(111).[21] The NH_3 spectra (Figure S1, Supporting Information) exhibit a submonolayer peak whose maximum shifts to lower temperature (135 → 105 K) with increasing coverage up to one monolayer. Higher NH_3 coverages give rise to a second peak at lower temperature (∼90 K). The NH_3 desorption spectrum from clean Au(111) is similar to but somewhat simpler than those on Ag,[13] Ru,[12] and Pt.[9]

To follow the surface reaction between adsorbed O adatoms and NH_3, a beam of NH_3 having a flux of ∼3 × 10^{13} molecules cm^{-2} s^{-1} was impinged on a 0.18 ML (1 ML = 1.387 × 10^{15} (molecules/atoms)/cm^2) atomic oxygen covered surface at 77 K. During the ammonia dose, no evolving gas-phase products were detected. TPD spectra (Figure 1) were obtained subsequently by heating the surface at 1 K/s up to 400 K and then at a rate of 3 K/s to 600 K. In contrast to what was found for the initially clean surface, $NH_{3\ ad}$ dissociates in the presence of O_{ad}, similar to what has been observed on other transition metals.[6,22,23] Water (mass 18) desorption produces a peak at ∼180 K, while the recombinative desorption of N_2 produces a peak at ∼470 K[24] (∼89% of the adsorbed ammonia is converted to N_2). The possibility of a signal at m/e = 28 from background CO was eliminated by monitoring the N_2 cracking fragment at 14 amu. No other desorbing products were observed (including O_2) in this particular experiment.

The O_{ad}/NH_3 ratio has a large effect on the selectivity of transition metal catalysts.[25] To further explore this phenomenon, similar

Figure 2. TPD spectra for H$_2$, NO, O$_2$, NH$_3$, H$_2$O, and N$_2$ from the adsorption of 0.64 ML O atoms on Au(111) at 77 K followed by 0.23 ML NH$_3$ at 77 K. The sample was heated with a rate of 1 K/s to 400K, then 3 K/s to 600K.

experiments with differing atomic oxygen coverages were employed. Figure 2 shows the spectra for H$_2$, NO, O$_2$, NH$_3$, H$_2$O, and N$_2$, following sequential adsorption at 77 K, of 0.64 ML O$_{ad}$ and 0.23 ML NH$_3$. Roughly 53% of the adsorbed ammonia reacts to form either N$_2$ or NO. The quantity of NO produced is ∼30% of the N$_2$ observed and is seen in a broad peak around 480 K. The NH$_3$ peak at ∼100 K is ascribed to physisorbed NH$_3$, unperturbed by O, and the ∼240 K peak to either enhanced binding of ammonia in the presence of O$_{ad}$[26] or the recombination of ammonia dissociation fragments (NH$_{x\,ad}$). The N$_2$ peak (∼460 K) is slightly broader, and its intensity is weaker than that shown in Figure 1. Also, as shown, some unreacted oxygen was detected via recombinative desorption. No other N-containing products were observed.

The initial step in the formation of either N$_2$ or NO is the dissociation of NH$_3$. We have recently shown that preadsorbed oxygen on Au(111) will abstract hydrogen from water at low temperature,[18] and we speculate that a similar abstraction of hydrogen from ammonia is the initial step in the surface decomposition of NH$_3$. Upon heating, much of the NH$_{x\,ad}$ left on the surface probably further decomposes by 300 K, leading to a surface partially populated by N$_{ad}$ and O$_{ad}$, since any NH$_{x\,ad}$ recombination would likely occur at ∼240 K. Thus, we propose that N$_{ad}$ and O$_{ad}$ species are the only direct participants in the formation of N$_2$ and NO. For initial O$_{ad}$ precoverages that are low (θ_O < 0.5 ML), it appears that N$_{ad}$ undergoes recombinative desorption between 400 and 500 K exclusively, while at higher O$_{ad}$ precoverages some NO is produced in addition to evolution of N$_2$, similar to what is observed in ammonia oxidation on Ir(111).[6] However, almost the same amount of NO$_{ad}$ was desorbed when the oxygen coverage was increased to 1.30 ML (not shown). It appears that N$_{ad}$ species involved in the decomposition of ammonia on O$_{ad}$ precovered Au(111) are predominantly consumed by recombination of N$_2$ rather

than formation of NO. We were unable to detect desorbing hydrogen or any hydrogen-containing species other than ammonia and water.

In summary, we demonstrate that ammonia does not dissociate on the clean Au(111) surface but that adsorbed O atoms, O$_{ad}$, facilitate NH$_{3\,ad}$ decomposition. The selectivity of the catalytic oxidation of ammonia to N$_2$ or NO on Au(111) is tunable by the amount of atomic oxygen precovering the surface. Both N$_2$ and NO are likely formed via simple recombination reactions (N$_{ad}$ + N$_{ad}$ and N$_{ad}$ + O$_{ad}$). At low oxygen coverages (θ_O < 0.5 ML), adsorbed ammonia is stripped to NH$_{x\,ad}$, which decomposes to form gaseous N$_2$. At high O$_{ad}$ coverages, NO is formed in a surface reaction between N$_{ad}$ and O$_{ad}$, but most surface N species involved recombine to form N$_2$, which desorbs with a peak at ∼460 K. Higher yields of N$_2$ can be obtained if the O$_2$/NH$_3$ mix is kept NH$_3$ rich.

Supporting Information Available: Details for TPD spectra for ammonia molecularly adsorbed on Au(111). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Il'chenko, N. I. *Russ. Chem. Rev.* **1976**, *45*, 1119.
(2) Olofssona, G.; Wallenbergb, L. R.; Andersson, A. *J. Catal.* **2005**, *230*, 1.
(3) Davis, P. R.; Newton N. G. *Surf. Sci.* **2003**, *546*, 149.
(4) Santra, A. K.; Min, B. K.; Yi, C. W.; Luo K.; Choudhary T. V.; Goodman, D. W. *J. Phys. Chem. B* **2002**, *106*, 340.
(5) Chen, W.; Ermanoski, I.; Madey T. E. *J. Am. Chem. Soc.* **2005**, *127*, 5014.
(6) Weststrate, C. J.; Bakker, J. W.; Rienks, E. D. L.; Martinez, J. R.; Vinod, C. P.; Lizzit, S.; Petaccia, L.; Baraldi, A.; Nieuwenhuys, B. E. *J. Catal.* **2005**, *235*, 92.
(7) Bradley, J. M.; Hopkinson, A.; King, D. A. *J. Phys. Chem.* **1995**, *99*, 17032.
(8) Kim, M.; Pratt, S. J.; King, D. A. *J. Am. Chem. Soc.* **2000**, *122*, 2409.
(9) Gland, J. L.; Kollin, E. B. *Surf. Sci.* **1981**, *104*, 478.
(10) Van Hardeveld, R. M.; Van Santen, R. A.; Niemantsverdriet, J. W. *Surf. Sci.* **1996**, *369*, 23.
(11) Lescop, B.; Galtayries, A.; Fanjoux, G. *J. Phys. Chem. B* **2004**, *108*, 13711.
(12) Parmeter, J. E.; Wang, Y.; Mullins, C. B.; Weinberg, W. H. *J. Chem. Phys.* **1988**, *88*, 5225.
(13) Ceyer, S. T.; Yates, J. T., Jr. *Surf. Sci.* **1985**, *155*, 584.
(14) Kim, T. S.; Stiehl, J. D.; Reeves, C. T.; Meyer, R. J.; Mullins, C. B. *J. Am. Chem. Soc.* **2003**, *125*, 2018.
(15) Stiehl, J. D.; Kim, T. S.; McClure, S. M.; Mullins, C. B. *J. Am. Chem. Soc.* **2004**, *126*, 1606.
(16) Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. *Science* **2003**, *301*, 935.
(17) Chou, J.; McFarland, E. W. *Chem. Commun.* **2004**, *14*, 1648.
(18) Kim, S. T.; Gong, J. L.; Ojifinni, R. A.; White, J. M.; Mullins, C. B. *J. Am. Chem. Soc.* **2006**, *128* 6282.
(19) Wheeler, M. C.; Seets, D. C.; Mullins, C. B. *J. Chem. Phys.* **1997**, *107*, 1672.
(20) Billic, A.; Reimers, J. R.; Hush, N. S.; Hafner, J. *J. Chem. Phys.* **2002**, *116*, 8981.
(21) Kay, B. D.; Lykke, K. R.; Creighton, J. R.; Ward, S. J. *J. Chem. Phys.* **1989**, *91*, 5120.
(22) Guo, H.; Chrysostomou, D.; Flowers, J.; Zaera, F. *J. Phys. Chem. B* **2003**, *107*, 502.
(23) Thornburg, D. M.; Madix, R. J. *Surf. Sci.* **1989**, *220*, 268.
(24) Song, Z.; Cai, T.; Hanson, J. C.; Rodriguez, J. A.; Hrbek, J. *J. Am. Chem. Soc.* **2004**, *126*, 8576.
(25) Gang, L.; Anderson, B. G.; van Grondelle, J.; van Santen, R. A. *Catal. Today* **2000**, *61*, 179.
(26) Benndorf, C.; Madey, T. E. *Chem. Phys. Lett.* **1983**, *101*, 59.

JA062624W