

Chemisorbed Oxygen on Au(111) Produced by a Novel Route: Reaction in Condensed Films of $\text{NO}_2 + \text{H}_2\text{O}$

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We report a facile, low-temperature reaction between condensed-phase NO_2 and H_2O that leads ultimately to the formation of a large concentration ($\theta_0 = 0.42$ monolayers) of adsorbed oxygen adatoms on a Au(111) surface. This reaction represents a novel route to generate surface oxygen on Au that can be utilized in fundamental studies of oxidation catalysis over Au such as low-temperature CO oxidation and the operation of Au converter tubes used in redox chemiluminescence detectors for atmospheric NO_x . Also, this reaction may be relevant to heterogeneous processes occurring on ice particles in stratospheric clouds. This reaction is not specifically catalyzed by the Au(111) surface or by the defects present on the Au surface, and so this reaction may have some general utility for facile oxidation of unreactive surfaces.

Introduction

Some time ago, we reported that low-temperature coadsorption of H_2O and NO_2 on Au(111) led to new peaks in the thermal desorption spectra of these two molecules and led to the formation of oxygen adatoms at the surface.¹ We have carefully reinvestigated this chemistry, which we had found difficult to reliably reproduce earlier, in order to define the conditions for surface oxygen formation and to investigate the mechanism of such a reaction. This intriguing chemistry is of interest for a number of reasons. The interaction of oxygen with transition metal surfaces has received significant attention, particularly with regard to the role of chemisorbed oxygen in oxidation reactions catalyzed on these surfaces. Higher selectivity in oxidation catalysis might be achieved by using a less reactive metal catalyst, such as Au, if reactive oxygen can be made available on the gold surface. The adsorption and reactions of organic molecules such as methanol, formic acid, formaldehyde, acetylene, and ethylene have been studied on clean and oxidized Au(110)^{2,3} and Au(111).¹ In general, organic molecules show no reactivity on clean Au surfaces but can be oxidized when coadsorbed with oxygen adatoms. Outka et al.^{2,3} found that methanol was activated by 0.25 monolayers (ML) of oxygen adatoms and oxidized to form methyl formate, H_2O , H_2 , and CO_2 . Formaldehyde was oxidized to HCOOH , H_2O , and CO_2 . Formic acid and acetylene were oxidized to H_2O and CO_2 . Ethylene is the only one of these molecules that does not react with oxygen adatoms on Au(110). Also, recently, gold has been found to be an effective component in the Au/ TiO_2 catalyst for the water-gas shift reaction.⁴ However, fundamental studies on Au surfaces have long been hampered by the extremely small dissociative sticking coefficient of O_2 under UHV conditions; i.e., exposure of O_2 on the Au(111) surfaces does not result in chemisorption of any measurable amount of adsorbed oxygen.⁵

Previously, studies of O/Au(111) had to resort to high-pressure and high-temperature exposure to O_2 , conditions that are known to cause the segregation of impurities to the Au surface, to dosing O_2 in the presence of a hot filament,⁶ or to using O_3 ,⁷ which is clean but is potentially hazardous to use.

Therefore, it would be useful to discover a more convenient method to cleanly produce surface oxygen on Au under UHV conditions for use in fundamental studies of oxidation reactions on Au. In this Letter, we report on characterization of a novel reaction between coadsorbed NO_2 and H_2O , which conveniently and reliably generates surface atomic oxygen on Au(111) surfaces. For conditions described herein, oxygen coverages from 0 to ~ 0.42 ML oxygen adatoms can be produced. A more detailed report discussing the reaction mechanism involving the intermediates nitrite– N_2O_4 and nitrosonium nitrate (NO^+NO_3^-) will be published elsewhere.⁸

Experimental Method

These studies were carried out in a UHV chamber equipped with a double-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), reverse-view 4 grid optics for low-energy electron diffraction (LEED), a UTI 100C quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD), a Mattson Galaxy 6020 FTIR spectrometer for reflection–absorption infrared spectroscopy (RAIRS), an ion gun for sputtering, and gas, dosing facilities. The system base pressure was 2×10^{-10} Torr.

TPD measurements were made with the sample surface in line-of-sight to the QMS ionizer and using a low, linear heating rate of 3.5 K/s. A screen biased by -55 V was placed between the QMS ionizer and the sample to suppress low-energy electrons coming out of the QMS.⁹ AES was used to check the cleanliness of the surface and measure the coverage of atomic oxygen. Spectra were recorded using an incident beam energy of 3 kV and a modulation voltage of 6 V_{p-p} . A 0.2 μA beam current was used to minimize electron-induced desorption.

The Au(111) sample (ca. 10 mm diameter \times 2 mm thickness) was mounted tightly under tension between two 0.015 in. tungsten wires that were imbedded in two grooves along the crystal edges. These two wires were spot-welded to thick Ta rods directly attached to a liquid N_2 -cooled Cu block. The sample could be cooled to 85 K and resistively heated to 1000 K. The temperature was measured by a chromel–alumel thermocouple firmly placed directly into a hole in the edge of

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the Au crystal. The Au(111) surface was cleaned by repeated sputtering–annealing cycles using Ar⁺ ion sputtering at room temperature (10 min, 500 V, 1 μ A) at an incident angle of 45° and annealing at 973 K for 10 min. The cleanliness and structure of the surface were checked by AES and LEED. Sharp spots characteristic of good ordering were always observed after annealing. Usually, a (1 \times 1) LEED pattern was seen, but sometimes a pattern due to a reconstructed surface structure, Au(111)-($\sqrt{3} \times 2$),¹⁰ was seen.

Deionized water (H₂O) was used after degassing via several freeze–pump–thaw cycles. NO₂ was used as received (Matheson, 99.9%). To minimize reactions of NO₂ in the doser gas lines, stainless steel and gold-plated gaskets were utilized, and the entire dosing manifold gas line was initially passivated at \sim 150 °C under NO₂ pressure for 30 min.

Results and Discussion

NO₂ adsorption on Au(111) single-crystal and polycrystalline gold surfaces is completely reversible, and no decomposition was detected in previous studies in our group.^{11–13} On Au(111), there are two NO₂ desorption states in TPD with peak desorption temperatures of 230 and 143 K. The high-temperature peak is due to the chemisorbed monolayer of NO₂, revealed by both HREELS¹¹ and FTIR¹³ to be mostly composed of chelating NO₂. The desorption activation energy for this species is 14 kcal/mol. As the exposure increases, the low desorption temperature peak grows in owing to the formation of a physisorbed multilayer of NO₂. This exists as a pure dimer of NO₂, N₂O₄. On Au (poly) surfaces, there is another NO₂ TPD peak at 325 K due to molecular adsorption at defect sites.¹²

H₂O adsorption on Au(111) has been studied previously¹⁴ and was also reinvestigated by us as a reference for subsequent coadsorption reactions. TPD spectra show only one desorption peak even after very high exposures, indicating that H₂O on Au(111) is very weakly held, nucleating clusters even in the “monolayer” regime, and it clearly shows zero-order desorption kinetics. H₂O desorption occurs over the range of 155–165 K, depending on the coverage of H₂O. These factors make a coverage determination of H₂O on Au(111) very difficult. To roughly estimate the H₂O concentration, TPD experiments were performed utilizing “background dosing” where the H₂O pressure could be measured with an ion gauge. Since the sticking probability of H₂O is unity on a cold surface at 86 K,^{14,15} we can use the H₂O pressure to determine the number of H₂O molecules adsorbed on the surface for a given background dose. We estimate that this result is within a factor of 3 of the correct value based on the typically encountered errors in determining the actual H₂O pressure at the Au(111) surface. The coverage of H₂O on the surface after exposures using a directed beam were obtained by comparison of the subsequent TPD area with that following TPD after background dosing. The monolayer equivalent coverage of H₂O on Au(111) was calculated to be one-half of the H₂O/Pt(111) bilayer coverage determined by XPS.¹⁶ This coverage on Au(111) could be obtained by a 1 L background exposure.

Even though the adsorption of NO₂ and H₂O are completely reversible when adsorbed separately on Au(111), coadsorption leads to reaction. We have previously reported that new NO₂ and H₂O peaks in TPD are observed,¹ and here we focus on the most interesting feature, the appearance of O₂ desorption.

Figure 1 shows several TPD spectra of O₂ after initially dosing 1 ML H₂O on Au(111) at 86 K followed by dosing NO₂ at the same temperature. As the NO₂ exposure was increased to more than 3.3 ML, desorption of O₂ was observed in a peak

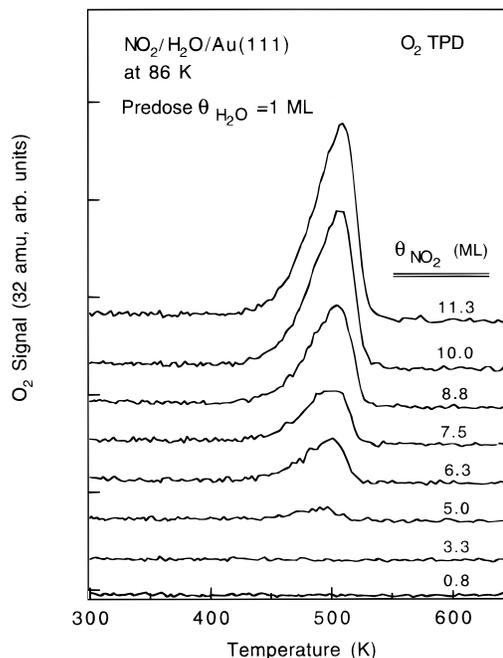


Figure 1. O₂ TPD spectra following NO₂ dosed on a Au(111) surface at 86 K precovered by 1 ML H₂O at the same temperature.

at 517 K. This peak saturated when the NO₂ coverage was more than 10 ML. In previous work, exposure of Au(111) to O₃ at 300 K generates an atomic oxygen adlayer that desorbs as molecular O₂ in TPD over the range of 515–545 K as the oxygen coverage increases.¹⁷ Thus, the oxygen species generated by coadsorption of NO₂ and H₂O can be identified as atomic oxygen by the desorption temperature of O₂ in Figure 1. The appearance of the O₂ TPD peak corresponds to the strongest interaction between N₂O₄ and H₂O, which is demonstrated by the formation of an additional high-temperature desorption peak at 214 K in the corresponding TPD spectra of H₂O.⁸ Tolbert et al.¹⁸ also observed a desorption peak at high temperature in the TPD of H₂O when they studied the reaction of N₂O₅ with ice surfaces. They attributed this high-temperature peak to hydrated N₂O₅. A strong interaction between N₂O₄ and H₂O appears to be a key factor in surface oxygen formation. For the monolayer of NO₂, a relatively weak interaction between water and nitrogen oxides was observed, which gives a desorption peak at 195 K in the water TPD spectra, and no surface oxygen was formed. We monitored a number of other QMS signals during TPD, and we also detected HNO₃ and HONO as desorbed products under all conditions.

Experiments were carried out to quantify the surface oxygen coverage using an initial dose of 1.5 ML H₂O on Au(111) at 86 K followed by NO₂ exposures on the surface at the same temperature. This coadsorbed layer was then heated to 435 K to remove weakly adsorbed species and decompose any precursors to get an oxygen-covered Au(111) surface. After the sample was cooled to 86 K, the O/Au ratio was measured by AES. Figure 2 shows these oxygen coverages generated by NO₂ + H₂O coadsorption. The left ordinate axis is the AES peak-to-peak height ratio of the O(KLL) 519 eV signal to the Au(MNN) 239 eV signal, and the right-hand axis is given as oxygen monolayers. These data are consistent with Figure 1 (even though the H₂O coverage is 1.5 ML), showing that there is no oxygen formed at NO₂ coverages below a thin multilayer (3.3 ML) and that oxygen formation reaches saturation at NO₂ exposures of more than 10 ML. This saturation coverage of atomic oxygen on Au(111), with an O/Au AES ratio of 0.47

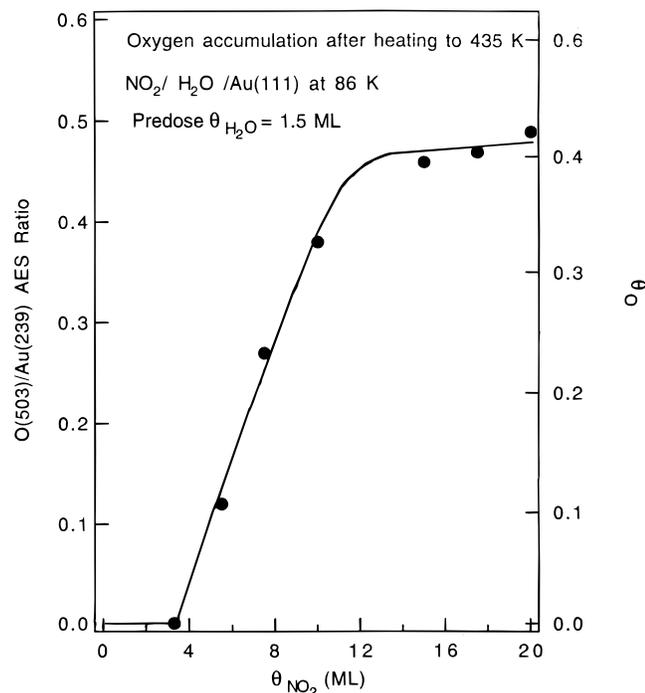


Figure 2. Surface oxygen coverage determined by AES using the peak-to-peak height ratio of the O (519 eV) signal to the Au (239 eV) signal. The initial dose of H₂O was 1.5 ML in all cases with increasing subsequent NO₂ exposures. The relationship between the O/Au AES ratio and the oxygen coverage was determined by studies of O₃/Au(111).¹⁷

corresponds to $\theta_0 = 0.42$ ML. The coverage was determined by calibration of the O/Au ratio with that of atomic oxygen formed by O₃ decomposition on Au(111),¹⁷ and it is also consistent with the O/Au ratio of a chelating NO₂ monolayer on Au(111) with $\theta_{\text{NO}_2} = 0.4$ ML.¹¹

To further characterize this reaction, we also carried out TPD studies after predosing NO₂ and then postdosing H₂O on Au(111) at 86 K. Figure 3a–d shows that for submonolayer and monolayer NO₂ precoverages, independent of the amount of H₂O dosed, there was no O₂ desorption detected in TPD. In contrast, a substantial amount of O₂ desorption was observed after dosing H₂O on top of an NO₂ multilayer, as shown in Figure 3e,f. The independence of the reactivity on the dosing sequence and unique reaction selectivity for multilayer NO₂ indicates that oxygen formation reactions (or formation of oxygen-generating precursors) occur at the interface between the N₂O₄ and H₂O clusters and have little to do with the Au(111) surface.

To further probe effects of the Au(111) surface on oxygen formation, we conducted reactions on a Au(111) single crystal with a high concentration of defects as characterized by desorption of NO₂ in TPD at 325 K. No oxygen was desorbed in TPD when we dosed multilayer H₂O and NO₂ on this defective surface at 110 K. Surprisingly, TPD of H₂O still showed just one H₂O desorption peak at the same temperature as the desorption of H₂O from defect-free Au(111). This result indicates that defects on Au(111) do not promote oxygen formation. These experiments also led us to see that the dosing temperature was an important parameter.

The crucial influence of dosing temperature on oxygen generation is shown by the TPD experiments in Figure 4. Figure 4d shows that a substantial amount of O₂ was produced in TPD when we predosed 1 ML H₂O on Au(111) at 86 K followed by dosing 7.5 ML NO₂ at the same temperature. However, when

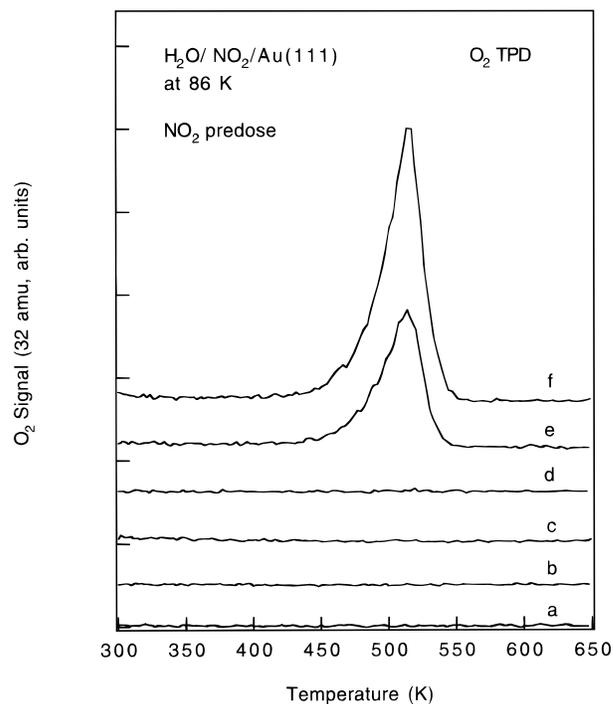


Figure 3. O₂ TPD spectra after predosing NO₂ on Au(111) at 86 K followed by H₂O exposure at the same temperature. (a) 1 ML H₂O dose after 0.5 ML NO₂, (b) 6 ML H₂O dose after 0.5 ML NO₂, (c) 0.5 ML H₂O dose after 1 ML NO₂, (d) 6 ML H₂O dose after 1 ML NO₂, (e) 1 ML H₂O dose after 7.5 ML NO₂, and (f) 4.5 ML H₂O dose after 7.5 ML NO₂.

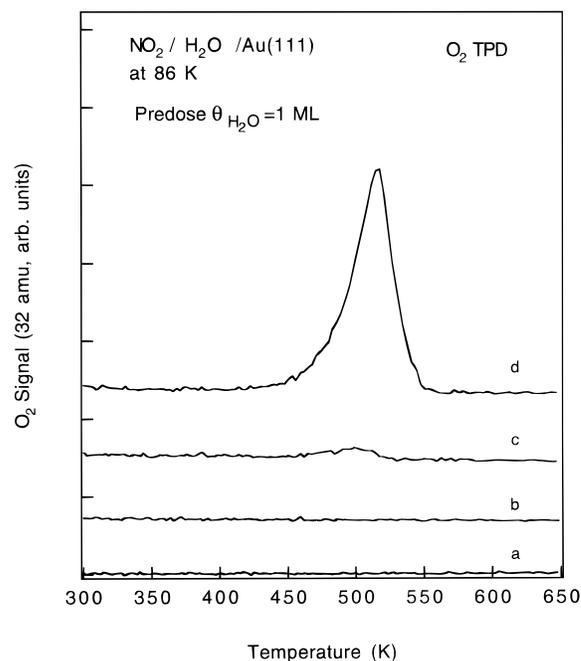


Figure 4. O₂ TPD spectra after several experiments to probe the requirements for generating surface oxygen. (a) 0.03 L of (NO₂ + H₂O) premixed in the gas line at room temperature and dosed on Au(111) at 86 K; (b) 7.5 ML NO₂ dosed at 110 K that was precovered by 1 ML H₂O dosed at the same temperature; (c) identical to that in (b) except that the dosing temperature was 86 K and the predosed H₂O layer was annealed to 115 K prior to NO₂ dosing. (d) 7.5 ML NO₂ dosed on Au(111) at 86 K that was precovered by 1 ML H₂O at the same temperature.

we exposed the same amount of NO₂ on a surface that was formed by dosing 1 ML H₂O on Au(111) at 86 K, followed by annealing the surface to 113 K, only a tiny amount of O₂ was

produced (Figure 4c). Furthermore, no O₂ desorption was detected when we dosed 1 ML H₂O on Au(111) at 110 K and then exposed 7.5 ML NO₂ at the same temperature (Figure 4b). These results demonstrate that the physical state of the H₂O plays a key role in the eventual formation of surface oxygen, and amorphous ice clusters formed at these low temperatures could be an active phase associated with surface oxygen formation. Amorphous ice, characterized by "free OH" species, has been demonstrated to be more reactive than crystalline ice for acetone adsorption, along with HCl and ClONO₂ decomposition, by Roberts and co-workers.^{19,20} In addition, when we dosed 0.03 L of a premixed (H₂O + NO₂) gas using a directed beam doser to Au(111) at 86 K, no oxygen was found as shown in Figure 4a. This indicates that oxygen formation does not depend on HNO₂ or HNO₃ intermediates because both HNO₂ and HNO₃ should have been dosed on the Au(111) surface. It is well-known that HNO₂ and HNO₃ are formed when gaseous NO₂ and H₂O are mixed at room temperature.

The results of other related experiments, including FTIR studies and a discussion of the reaction mechanism, will be reported elsewhere.⁸ Briefly, we concluded that N₂O₄ in thick films in the presence of free OH groups of amorphous ice isomerize to the nitrite (ONO-NO₂) isomer, which converts to nitrosonium nitrate (NO⁺NO₃⁻). This species decomposes below 400 K to generate atomic oxygen on the surface.

Conclusions

Even though H₂O and NO₂ do not react on Au(111) under UHV conditions when adsorbed separately, coadsorption leads to reaction. Under certain conditions, reaction leads eventually to the formation of oxygen adatoms. We have found that surface concentrations of atomic oxygen up to 0.42 ML can be readily produced on Au(111) surfaces by a reaction of coadsorbed H₂O and NO₂ at dosing temperatures below 100 K. The

requirements for surface oxygen formation are dosing temperatures below 100 K and NO₂ multilayers. The dosing sequence (either NO₂ or H₂O first) and defects on the Au(111) surface do not appreciatively affect the oxygen yield, indicating that this reaction probably occurs at the interface between amorphous ice and N₂O₄.

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