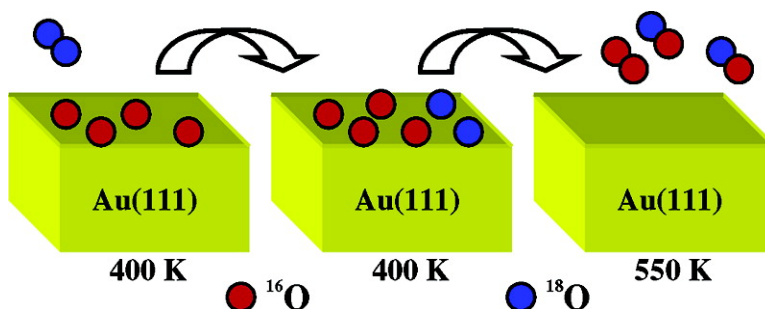


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Enhancement of O₂ Dissociation on Au(111) by Adsorbed Oxygen: Implications for Oxidation Catalysis

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Abstract: We show that the dissociation probability of O₂ on the reconstructed, Au(111)-herringbone surface is dramatically increased by the presence of some atomic oxygen on the surface. Specifically, at 400 K the dissociation probability of O₂ on oxygen precovered Au(111) is on the order of 10⁻³, whereas there is no measurable dissociation on clean Au(111), establishing an upper bound for the dissociation probability of 10⁻⁶. Atomic oxygen was deposited on the clean reconstructed Au(111)-herringbone surface using electron bombardment of condensed NO₂ at 100 K. The dissociation probability for dioxygen was measured by exposing the surface to ¹⁸O₂. Temperature programmed desorption (TPD) was used to quantify the amount of oxygen dissociation and to study the stability of the oxygen in all cases. Oxygen desorbs as O₂ in a peak centered at 550 K with pseudo-first-order kinetics; i.e., the desorption peak does not shift with coverage. Our interpretation is that the coverage dependence of the activation energy for dissociation (ΔE_{dis}) and/or preexponential factor (ν_a) may be responsible for the unusual desorption kinetics, implying a possible energy barrier for O₂ dissociation on Au(111). These results are discussed in the context of Au oxidation chemistry and the relationship to supported Au nanoparticles.

Introduction

The behavior of oxygen adsorbed on Au is a topic of considerable current interest because of the discovery that highly dispersed, small gold clusters on metal-oxide supports are active catalysts for low-temperature oxidation of CO and propylene.^{1–3} Studies of a range of materials, including Au clusters supported on metal oxides and Au single crystals, have been performed to determine the structure of the Au catalyst and the reaction mechanism relating to their activity.^{4–9} Although the structures of oxide supported Au catalysts are well-studied,^{4,6} there is still controversy regarding the mechanism for the enhanced reactivity. One barrier to understanding the oxidation chemistry is the ability to study the behavior of oxygen on the Au surface. The major obstacle is adsorption of sufficient oxygen on the surface to study reactivity since most sources of oxygen, e.g. O₂ or NO₂, do not thermally dissociate with a high enough rate to deposit significant amounts of oxygen on the surface.^{10–12} Indeed, the

dissociation of O₂ to yield oxygen is most likely the key, rate-limiting step in the oxidation of CO and hydrocarbons.

To date, several preparation methods of oxygen preadsorbed Au surface have been addressed. Most recently, Mullins and co-workers have deposited oxygen atoms on Au(111) using a supersonic beam of oxygen atoms produced from a radio frequency generated plasma source.¹³ Atomic oxygen has also been prepared on Au(111) by exposure of ozone,¹⁴ thermal dissociation of gaseous O₂ using hot filaments,¹⁵ O⁺ sputtering,¹⁶ and coadsorption of NO₂ and H₂O.¹⁷ In this study, we describe a new method for depositing atomic oxygen on Au(111) by electron bombardment of NO₂ condensed on the Au(111) surface.

We find that the oxygen exhibits unusual desorption behavior that may be important in determining the reactivity of oxygen on this surface. Specifically, the oxygen recombines to form gaseous O₂ with a peak temperature of 550 K in temperature programmed desorption. The O₂ desorption feature exhibits pseudo-first-order kinetics, indicating that it is not due to simple recombination of two oxygen atoms. Given that the production of O₂ is the reverse of dissociation, studies of this process provide further insight into a key step in the oxidation processes on Au.

We also find that the dissociation probability of O₂ is increased by more than 3 orders of magnitude when some atomic oxygen is present on the surface. The initial dissociation

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- (1) Haruta, M. *Catal. Today* **1997**, *36*, 153.
- (2) Bond, G. C.; Thompson, D. T. *Gold Bull.* **2000**, *33*, 41.
- (3) Haruta, A. *Chem. Rec.* **2003**, *3*, 75.
- (4) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647.
- (5) Haruta, M.; Date, M. *Appl. Catal. A* **2001**, *222*, 427–437.
- (6) Lopez, N.; Janssens, T. V. W.; Clausen, B. S.; Xu, Y.; Mavrikakis, M.; Bligaard, T.; Norskov, J. K. *J. Catal.* **2004**, *223*, 232.
- (7) Gottfried, J. M.; K. C. *Surf. Sci.* **2004**, *566–568*, 1112.
- (8) Kim, T. S.; Stiehl, J. D.; Reeves, C. T.; Meyer, R. J.; Mullins, C. B. *J. Am. Chem. Soc.* **2003**, *125*, 2018.
- (9) Davis, K. A.; Goodman, D. W. *J. Phys. Chem. B* **2000**, *104*, 8557.
- (10) Legare, P.; Hilaire, L.; Sotto, M.; Maire, G. *Surf. Sci.* **1980**, *91*, 175.
- (11) Pireaux, J. J.; Chtaib, M.; Delrue, J. P.; Thiry, P. A.; Liehr, M.; Caudano, R. *Surf. Sci.* **1984**, *141*, 211.
- (12) Bartram, M. E.; Koel, B. E. *Surf. Sci.* **1989**, *213*, 137.

- (13) Stiehl, J. D.; Kim, T. S.; McClure, S. M.; Mullins, C. B. *J. Am. Chem. Soc.* **2004**, *126*, 1606.
- (14) Saliba, N.; Parker, D. H.; Koel, B. E. *Surf. Sci.* **1998**, *410*, 270.
- (15) Canning, N. D. S.; Outka, D.; Madix, R. J. *Surf. Sci.* **1984**, *141*, 240.
- (16) Gottfried, J. M.; Elghobashi, N.; Schroeder, S. L. M.; Christmann, K. *Surf. Sci.* **2003**, *523*, 89.
- (17) Wang, J.; Voss, M. R.; Busse, H.; Koel, B. E. *J. Phys. Chem. B* **1998**, *102*, 4693.

probability of O_2 is less than 10^{-6} on the clean Au(111)-herringbone surface. Once some atomic oxygen is seeded on the surface, the dissociation probability is increased to on the order of 10^{-3} at a surface temperature of 400 K. This remarkable result in combination with imaging studies reported elsewhere¹⁸ indicates that O_2 dissociation is very sensitive to the structure of the surface and, in particular, the creation of small gold islands possibly formed by Au atoms released from the surface. It may also indicate that there are important changes in the electronic structure of the surface presented to an incoming O_2 molecule, as has been suggested by recent theoretical results.¹⁹

Experimental Section

All experiments were carried out in a stainless steel ultrahigh vacuum chamber described in detail elsewhere.²⁰ Briefly, the chamber has a base pressure of $\sim 6 \times 10^{-10}$ Torr and consists of an X-ray photoelectron spectrometer (PHI ESCA 5300) with a Mg anode X-ray source and a hemispherical electron energy analyzer, a quadrupole mass spectrometer (UTI 100c), and low-energy electron diffraction (LEED) optics.

The reconstructed clean Au(111) surface was prepared by cycles of Ar^+ sputtering (1000 eV, 1.3 μA) at 300 K followed by annealing at 900 K for 5 min and 700 K for 1 h. This procedure was repeated until no impurities were detected using X-ray photoelectron spectroscopy (XPS). In addition, the consistent surface structure of Au(111) was confirmed by the presence of satellites in LEED due to the herringbone reconstruction on the Au(111) surface.

Atomic oxygen deposited on Au(111) was prepared by exposure of NO_2 followed by electron bombardment. Specifically, NO_2 (Matheson, anhydrous grade) was exposed directly on Au(111) at 100 K with a pressure rise of 1×10^{-10} Torr for 1 min resulting in multilayer NO_2 on the Au(111) surface. Subsequently, the Au(111) surface with multilayer NO_2 was biased to +100 V and exposed to an electron source (UTI 100c mass spectrometer filament with an emission current of 2 mA) for 1 min. The integrated current flux on the surface was 7 μA .

$^{18}O_2$ (Matheson, 99 at. %) was exposed on clean or oxygen precovered Au(111) with a pressure rise of 1×10^{-7} Torr using background dosing for 1 min while maintaining the surface temperature at 400 K. The $^{18}O_2$ flux was estimated via the equation: $N_{inc} = Pt / (2\pi mk_B T)^{1/2}$, where P , m , and T are pressure, mass, and temperature of $^{18}O_2$, respectively, and t is the exposure time. The number of $^{18}O_2$ that dissociated (N_{ads}) was estimated by measuring the amount of $^{18}O^{16}O$ produced in TPD relative to the amount of $^{16}O_2$ at saturation coverage (0.4 monolayer) and assuming a Au(111) surface density of 1.3×10^{15} atoms/cm². The $^{18}O_2$ dissociation probability was then calculated from the ratio, N_{ads}/N_{inc} . It should be noted that the absolute value of dissociation probability may not quantitatively accurate due to the uncalibrated ion gauge; however, the quantitative aspect of our measurement does not affect our final conclusions. Analogous experiments were performed using directed dosing—i.e. with an effusive source directed toward the crystal surface such that the background pressure rise was small. These experiments qualitatively reproduced our result of $^{18}O_2$ dissociation; however, the flux could not be as accurately determined in the directed-dosing geometry. We also performed analogous experiments in a separate vacuum chamber with a base pressure of $< 3 \times 10^{-10}$ Torr and using a separate Au(111) crystal to rule out artifacts in the data shown.

All TPD data were taken by UTI 100c mass spectrometer with an average heating rate of 10 K/s, as described in detail previously.²¹ All TPD experiments were performed with the crystal biased at -100 V to avoid electron-induced reaction from the mass spectrometer filament.

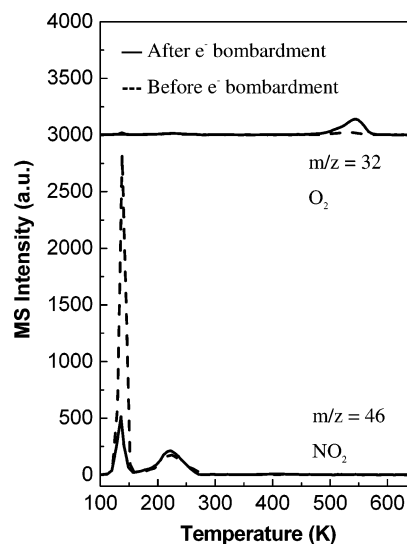


Figure 1. Temperature programmed desorption of NO_2 and O_2 from the Au(111): after (solid line) and before (dashed line) electron bombardment of condensed NO_2 . No O_2 desorption peak was detected before electron bombardment (dashed line). Electron bombardment of the NO_2 condensed surface for 10 s (7 μA integrated current flux, 100 eV energy) leads to a dramatic decrease of the NO_2 multilayer peak and an apparent O_2 desorption peak evolved at 550 K (solid line), indicating the dissociation of NO_2 and deposition of oxygen. The heating rate used in these experiments was ~ 10 K/s.

Results and Discussions

There is no detectable thermal dissociation of NO_2 on Au(111) based on TPD experiments (Figure 1). NO_2 is the only species evolved from the surface, based on a quantitative analysis of mass spectrometer fragmentation patterns. Specifically, there is no O_2 (32 amu) detected (Figure 1, dashed line). There are two NO_2 desorption peaks centered at 136 and 220 K, which are assigned to sublimation of NO_2 multilayers and desorption of NO_2 adsorbed directly on the surface. The multilayer peak grows indefinitely with exposure. These desorption temperatures are close to the previous TPD study of NO_2 on Au(111), where multilayer and monolayer NO_2 were found to desorb at 143 and 230 K, respectively.^{12,17} The lack of NO_2 dissociation on clean Au(111) is also consistent with previous studies.¹²

NO_2 exposure (1×10^{-10} Torr pressure rise for 1 min) followed by electron bombardment (integrated current flux of 7 μA with 100 eV energy) leads to a decrease of the NO_2 (46 amu) peak and an increase of the O_2 (32 amu) peak, as shown in Figure 1 (solid line). Specifically, 10 s of electron bombardment results in a dramatic decrease of multilayer NO_2 , while monolayer NO_2 remains intact. Simultaneously, an O_2 desorption peak was detected at 550 K. Comparing with other studies,¹⁴ this O_2 desorption feature is readily assigned to the recombination of atomic oxygen on the surface, indicating that atomic oxygen was deposited via the electron-induced dissociation of NO_2 . No evidence for deposition of nitrogen was found in the experiments, based on the absence of N_2 production in our desorption data. The only other species detected in our temperature programmed desorption experiments were NO and NO_2 . We also found that deposition of atomic oxygen through electron bombardment competes with electron induced desorption of NO_2 , yielding the depletion of NO_2 and thereby limiting the coverage of atomic oxygen.

(18) Min, B. K.; Deng, X.; Pinnaduwa, D.; Friend, C. M. Submitted for publication.

(19) Mills, G.; Gordon, M. S.; Metiu, H. *J. Chem. Phys.* **2003**, *118*, 4198.

(20) Xu, X. P.; Friend, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 6779.

(21) Deiner, L. J.; Serafin, J. G.; Friend, C. M.; Weller, S. G.; Levinson, J. A.; Palmer, R. E. *J. Am. Chem. Soc.* **2003**, *125*, 13252.

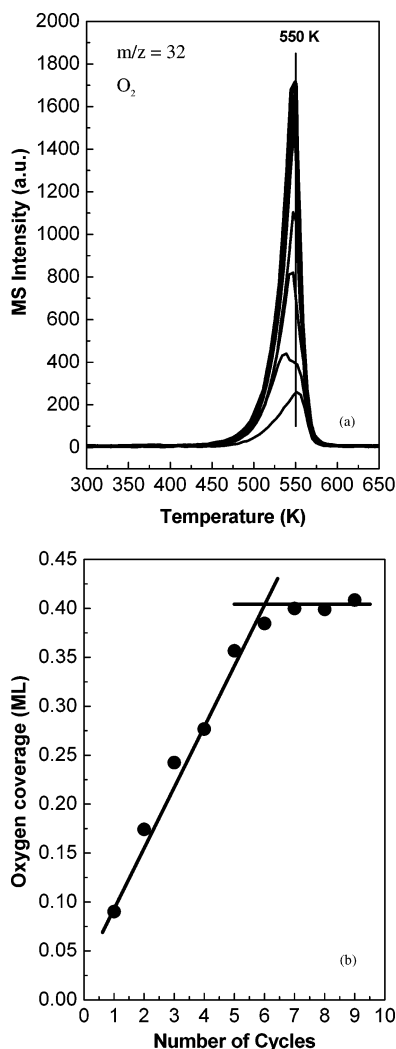


Figure 2. (a) Temperature programmed desorption of O₂ from Au(111) through the recombination of atomic oxygen for various initial coverages of O and (b) the corresponding absolute atomic oxygen coverage as a function of the number of cycles of NO₂ exposure and electron bombardment (note: the linear lines are fits by the program). The absolute coverage is estimated using O(1s) X-ray photoelectron spectra (data not shown). The heating rate used in all TPD experiments was ~ 10 K/s.

Iterative NO₂ exposing and electron bombardment were carried out to prepare higher coverages of atomic oxygen on Au(111) surface until saturation coverage was reached. Briefly, NO₂ was directly exposed at a pressure rise of 1×10^{-10} Torr at 100 K, followed by the electron bombardment (integrated current flux of $7 \mu\text{A}$ with 100 eV energy) for 1 min, leading to atomic oxygen deposition from NO₂. Repetition of these processes resulted in an increase in the oxygen coverage. Figure 2a shows O₂ TPD data with respect to the number of repetitive cycles mentioned above. The intensity of the O₂ desorption peak increases as the number of cycles is increased and becomes constant after seven cycles.

The absolute coverage of atomic oxygen deposited on Au(111) was estimated by comparing the XPS intensity ratio (O(1s)/Au(4f)) of saturated oxygen atoms with that measured for chemisorbed NO₂ (data not shown). The coverage of the first layer NO₂ on Au(111) surface has been previously estimated by Koel and co-workers to be 0.4 monolayer.¹⁴ Based on their calibration, the maximum coverage of oxygen atoms deposited using our method was calculated to be ~ 0.4 mono-

layer. This value is close to the saturation coverage of atomic oxygen deposited from the reaction of NO₂ and H₂O ($\theta_{\text{O}} = 0.42$ monolayer),¹⁷ but less than that obtained from ozone exposure ($\theta_{\text{O}} = 1.2$ monolayer).¹⁴ The absolute coverage for different dosing and bombarding cycles has been determined from the ratio of the integrated area under the O₂ TPD peaks to that of the saturation coverage. Figure 2b shows that the increase of atomic oxygen coverage is nearly linear with repetitive cycles up to 7, at which point there is no further increase.

The peak temperature for O₂ evolution is 550 K, independent of oxygen coverage, implying pseudo-first-order kinetics of oxygen desorption. The apparent activation energy of desorption calculated assuming a preexponential factor of $1 \times 10^{13} \text{ s}^{-1}$ and first-order kinetics²² is ~ 33 kcal/mol, consistent with previous estimates of 31.7–33.6 kcal/mol.^{9,14}

We attribute the pseudo-first-order kinetics of O₂ desorption peaks on Au(111) to a restructuring of the surface, based on LEED and STM data (described elsewhere¹⁸). Since the surface structure changes when oxygen is deposited from electron bombardment of NO₂, we propose that the activation energy and/or preexponential factor for desorption of O₂ are dependent on surface structure. This conclusion also raised the possibility that specific surface structures are required for O₂ dissociation and that the kinetics for O₂ dissociation may be dependent on the method used for oxygen deposition. Alternative explanations for the observed pseudo-first-order kinetics are that the rate-limiting step for the O₂ desorption on Au(111) is the conversion of an oxidic oxygen species to chemisorbed oxygen¹⁴ or that attractive interactions control the rate, as proposed for Ni(110) where pseudo-first-order kinetics are observed when H₂ forms from one-dimensional chains of H atoms.²⁴ Our explanation is most similar to the latter case of attractive interactions because both resemble a surface phase transition.

Since atomic oxygen recombination and desorption is the microscopic reverse of O₂ dissociation and adsorption, the surface restructuring observed after O deposition from electron bombardment of NO₂ may indicate a coverage-dependent enthalpy (ΔE_{dis}) and/or entropy (ν_{d}) change. Likewise, there may be a dependence in the kinetic barriers for O₂ dissociation and adsorption on oxygen coverage which lead to the dependence of O₂ dissociation probability on oxygen atom coverage. Thus, we studied the effect of oxygen pre-coverage on the dissociation probability of O₂ by performing studies of ¹⁸O₂ at a surface temperature of 400 K.

As anticipated, there is no detectable dissociation of ¹⁸O₂ on the clean Au(111)-herringbone surface after exposure to a background pressure of 1×10^{-7} Torr of ¹⁸O₂ for 1 min, based on the absence of the signal for any isotope of dioxygen in TPD experiments (Figure 3, dashed lines). Specifically, there was no detectable 34 (¹⁶O¹⁸O) and 36 (¹⁸O₂) evolution in TPD data obtained after exposing clean Au(111) to ¹⁸O₂.

Dissociation of ¹⁸O₂ is detected after exposure of Au(111) precovered with atomic oxygen. Specifically, there is a clearly defined mass 34 (¹⁶O¹⁸O) peak at 550 K detected after exposing ¹⁸O₂ to Au(111) containing some ¹⁶O formed from NO₂ dissociation (Figure 3, solid lines). A peak associated with formation of ¹⁶O₂ (32 amu) is observed coincident with the

(22) Redhead, P. A. *Vacuum* **1962**, *12*, 203.

(23) King, D. A. *Surf. Sci.* **1975**, *47*, 384.

(24) Christmann, K.; Schöber, O.; Ertl, G.; Neumann, M. *J. Chem. Phys.* **1974**, *60*, 4528.

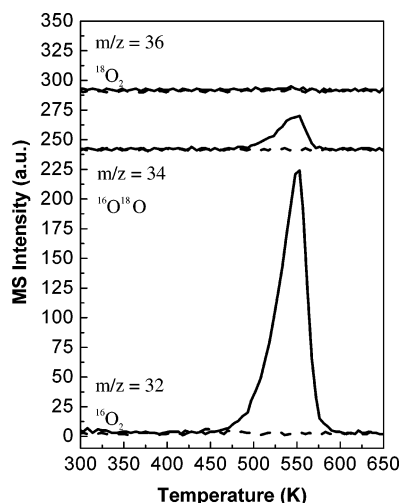


Figure 3. Temperature programmed desorption of $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$ from Au(111). A small amount of atomic oxygen (0.1 monolayer) is deposited on Au(111) by 1 cycle of NO_2 dosing and electron bombardment before dosing $^{18}\text{O}_2$ at 400 K. Note that $^{18}\text{O}_2$ was dosed using background dosing with a pressure of 1×10^{-7} Torr for 1 min. The appearance of desorption peak at 550 K with $m/z = 34$ indicates the dissociation of $^{18}\text{O}_2$ on atomic oxygen covered Au(111) (solid lines). $^{18}\text{O}_2$ was also dosed on clean Au(111) under the same conditions, in which case no apparent dissociation was observed (dashed lines).

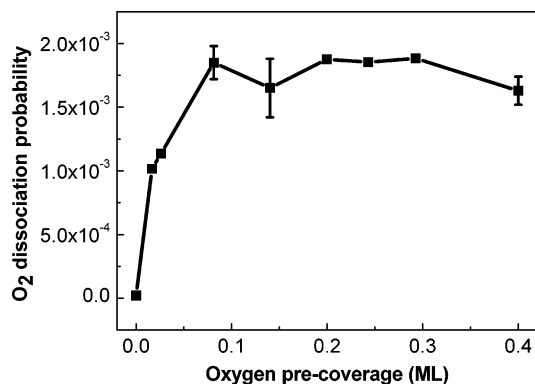


Figure 4. Dissociation probability of $^{18}\text{O}_2$ on a Au(111) as a function of oxygen precoverage. The oxygen precovered Au(111) was prepared via electron bombardment of condensed NO_2 , and $^{18}\text{O}_2$ was exposed at 400 K using background dosing with a pressure of 1×10^{-7} Torr for 1 min for all experiments. The dissociation probability is estimated from the temperature programmed desorption experiments, as described in the experimental section.

$^{16}\text{O}^{18}\text{O}$. No 36 ($^{18}\text{O}_2$) is detected, which is consistent with the large amount of ^{16}O present on the surface, based on the ratio of the 32 amu/34 amu signal that indicates an abundance of ^{16}O relative to ^{18}O , yielding an estimate of $^{18}\text{O}:^{16}\text{O} < 1:20$. Analogous experiments were also performed in a separate vacuum chamber with a base pressure of $< 3 \times 10^{-10}$ Torr and using a separate Au(111) crystal. The qualitatively reproduced $^{18}\text{O}_2$ dissociation results rule out artifacts in the data shown.

The $^{18}\text{O}_2$ dissociation probability on Au(111) as a function of oxygen precoverage was estimated using quantitative analysis of the TPD experiments (Figure 4). Specifically, $^{18}\text{O}_2$ dissociation probability on clean Au(111) is less than 10^{-6} (estimated from the noise level of the mass spectrometer). When predepositing small amount of atomic oxygen (0.02 monolayer), the $^{18}\text{O}_2$ dissociation probability significantly increases to 10^{-3} . The $^{18}\text{O}_2$ dissociation probability increases at low oxygen precoverages (up to 0.1 monolayer). At higher oxygen precoverages,

the dissociation probability becomes nearly constant, reaching a value of 2×10^{-3} for oxygen precoverages in the range of 0.1–0.4 monolayer.

The significant enhancement of O_2 dissociation on the oxygen precovered Au(111) surface may be due to the release of Au atoms from the herringbone reconstructed Au(111). In a companion paper, we show that adsorption of atomic oxygen using electron-induced dissociation of NO_2 induces restructuring of the surface and release of Au atoms from the surface.¹⁸ Indeed, theoretical studies by Mills et al. showed small Au clusters on Au(111) have a higher binding energy with O_2 compared to a Au(111) surface,¹⁹ as a result of having a large number of low-coordinated Au atoms which facilitate orbital overlapping between Au and O_2 . Our recent STM study of oxygen deposition on Au(111) shows restructuring of Au(111)-herringbone structure accompanied by the formation of small gold island and/or serrated step edge due to the release of gold atoms at the expense of herringbone elbow sites (dislocation sites).¹⁸ These results support the possibility that the creation of low-coordinated gold atoms is responsible for the enhancement of O_2 dissociation.

Accordingly, the high activity of small Au clusters on metal-oxide supports for CO oxidation might originate from the enhanced O_2 dissociation due to the large number of low-coordinated Au atoms. Considering that O_2 dissociation is most likely the key, rate-limiting step in catalytic oxidation processes (as supported by the fact that Au(111) or Au(110) can also serve as oxidation catalysts once oxygen is deposited on these surfaces^{7,9}), it is not surprising that small Au clusters, which can enhance O_2 dissociation, show high catalytic activity in oxidation. Introducing Au atoms on a Au surface via physical vapor deposition (PVD) may provide more compelling evidence for all the discussions above, and these studies are currently under investigation in our lab.

Conclusions

The dissociation probability of O_2 on Au(111) at 400 K significantly increases up to 10^{-3} when a small amount of atomic oxygen is present on the surface. The enhancement of O_2 dissociation is possibly due to the release of Au atoms from the surface restructuring induced by atomic oxygen deposition. Atomic oxygen is deposited by electron induced NO_2 dissociation on the surface at 100 K. A saturation coverage is attained by the repetition of NO_2 dosing and electron bombardment. Desorption of O_2 , coming from recombination of atomic oxygen on Au(111), occurs at 550 K and does not shift with coverage, indicating pseudo-first-order kinetics. We attribute this unusual kinetics to the surface restructuring by oxygen deposition, which leads to a coverage-dependent enthalpy (ΔE_{dis}) and/or entropy (ν_{d}). In addition, the surface restructuring and the coverage-dependent enthalpy (ΔE_{dis}) and/or entropy (ν_{d}) may also serve as a kinetic barrier for O_2 dissociation on Au(111), resulting in an extremely low dissociation probability of O_2 on clean Au(111) (less than 10^{-6}).

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