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Room-Temperature Reaction of Oxygen with Gold: An In situ Ambient-Pressure X-ray Photoelectron Spectroscopy Investigation

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Gold is commonly regarded as the most inert element.[1] However, the discovery of the exceptional catalytic properties of gold nanoparticles (NPs) for low temperature CO oxidation[2] initiated great interest due to its promising applications and spawned a large number of studies devoted to the understanding of the reaction mechanism.[3−6] Nevertheless, no consistent and conclusive picture has arisen.[7−13]

One of the most important and controversial issues is the activation mechanism of O_2 on Au.[9,14−19] For instance, on the basis of the experimental observation that a bilayer Au structure, which completely wets the oxide support, exhibits extraordinary catalytic activity, Goodman et al. proposed that Au can be directly involved in the activation of O_2.[9] In contrast, more recently, Behm et al. found that the amount of active oxygen species on the Au/TiO_2 surface has a linear relationship with the number of perimeter sites at the interface between the oxide support and the Au NPs, indicating that the support-Au interface plays a dominating role in the oxygen activation.[19] Furthermore, on the basis of theoretical calculations, under-coordinated Au atoms were proposed to have the capability to adsorb and even dissociate O_2.[14] Using high-intensity in situ X-ray absorption near-edge structure (XANES), van Bokhoven and co-workers observed an increased white line intensity at the Au L_3 edge for Au NPs supported on Al_2O_3 and TiO_2 substrates during treatment in O_2, indicating that Au NPs can be oxidized by molecular oxygen.[17,18] However, Liu et al. calculated that the dissociation barrier is larger than 2 eV on nonsupported Au and even at the Au/TiO_2 interface the dissociation barrier is still 0.52 eV,[15] which means that O_2 has a very weak interaction with Au, and thus spontaneous dissociation of molecular oxygen on the Au surface is not energetically favorable.

To reconcile these controversial observations and proposals we investigated the reactivity of O_2 with bulk Au foil and Au NPs supported on $TiO_2(110)$ surface using in situ ambient pressure X-ray photoelectron spectroscopy (AP-XPS) at O_2 pressures of up to 1 Torr.[20,21] Our data demonstrate that molecular oxygen does not have a strong interaction with Au surfaces at room temperature. However, we observed that molecular oxygen can be activated on both types of samples by X-ray irradiation to produce oxidic Au. We further investigated and compared the stability of oxidized Au on both model systems.

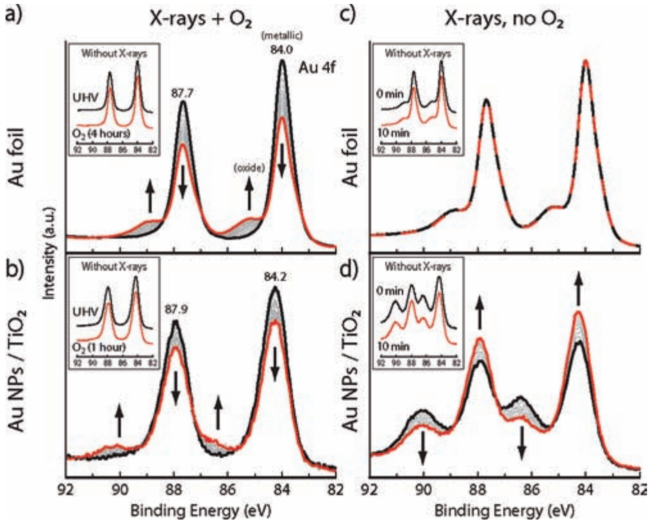

Figure 1. Time evolution of the XPS spectra of Au 4f under X-ray irradiation at room temperature. (a) Au foil and (b) Au NPs on TiO_2 support in the presence of 1 Torr O_2. (c) Oxidized Au foil and (d) oxidized Au NPs on TiO_2 support in UHV. The peaks on the higher energy binding side of the metallic $4f_{7/2}$ and $4f_{5/2}$ peaks are due to oxidized gold. The bold black and red curves correspond to the first and the last spectrum, respectively. The arrows indicate the direction of the intensity changes. The insets show the Au 4f spectra from the test experiments under similar condition, but without X-ray irradiation for the specified time.

The experiments were performed at beamline 11.0.2 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.[20,21] This system consists of a preparation chamber and an AP-XPS analysis chamber with base pressure of 3×10^{-10} Torr. The Au foil and the $TiO_2(110)$ single crystal samples were cleaned by several cycles of Ar^+ sputtering and annealing. Au NPs were obtained by thermal evaporation of Au onto the $TiO_2(110)$ surface at 320 K, following a procedure described in the literature.[22] The amount of deposited Au was calibrated by the ratio between Au 4f and Ti 2p peaks. O_2 gas was dosed through a leak valve. A photon energy of 690 eV was used to acquire all the spectra. The binding energy scale was calibrated by using the metallic Au $4f_{7/2}$ (binding energy 84.0 eV) peak and the Fermi edge of Au foil as references. The photon flux density was approximately 4×10^{12} photons mm^{-2} s^{-1}.

The insets in Figure 1a,b show the Au 4f spectra obtained from the gold foil and from a 0.3 ML (monolayer) of Au on TiO_2 under UHV and under 1 Torr of O_2, respectively. In comparison with

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bulk Au foil (84.0 eV), the Au $4f_{7/2}$ peak of the submonolayer deposit shifts to a higher binding energy (84.2 eV), due to a combination of initial and final state effects.[23,24] After exposure to O_2 at 1 Torr for several hours in the absence of X-rays, both peak position and width remain the same. These results demonstrate that O_2 does not have a strong interaction with Au, both in bulk form and in the form of NPs, under the above conditions. This observation is consistent with the known inertness of Au, which originates from the filled d-band structure.[1]

However, we observed that under X-ray irradiation in the presence of oxygen gas, the Au surfaces could be oxidized. Figure 1 panels a and b show the time evolution of the Au 4f region under irradiation of X-rays in the presence of 1 Torr of O_2 over 15 min. On the foil the intensity of the metallic Au 4f peaks (Au $4f_{7/2}$ 84.0 eV and Au $4f_{5/2}$ 87.7 eV) decreases with time, while at the same time two additional peaks appear, which are shifted by 1.3 eV to higher binding energies relative to the metallic Au 4f peaks. Previous studies have reported similar peak shifts for oxidized Au surfaces prepared using different oxidation methods.[25−28] On the Au NPs formed by evaporation on the TiO_2 crystal, two additional peaks develop also at the higher binding energy side that can be attributed to oxide as well. It is noteworthy to mention that both the oxidation rate and the chemical shift of the oxide peaks depend strongly on the size of NPs,[28−30] which is still under further investigation.

X-ray induced formation of chemisorbed oxygen species have been reported previously.[31,32] However, these measurements were carried out under ultrahigh vacuum at temperatures below 30 K, where chemisorbed oxygen is produced from physisorbed molecular oxygen. Therefore, both the experiment conditions and the activation process are dramatically different from the ambient conditions in this communication.

The stability of the oxidic Au species formed in this way was subsequently investigated also under X-ray irradiation. We found that the two samples show different behaviors. While the oxidic Au in the NPs on $TiO_2(110)$ could be readily reduced under X-ray irradiation, the oxidic Au film formed at the surface of the foil was resistant to X-ray irradiation. This is shown in Figure 1c,d, where the spectra were recorded sequentially during 10 min. The difference in reduction behavior lends support to the oxygen spillover model proposed by Ono and Cuenya,[33] based on the well-known facile reducibility of the TiO_2 support. Under X-ray irradiation, oxygen vacancies can be generated on the TiO_2 surface.[34] For the NP sample oxygen can spill from the oxidized Au NP to the reducible TiO_2 substrate, while this reduction channel is not available for bulk gold. The different reduction behavior makes it difficult to compare the oxidation rate of the two samples during X-ray induced oxidation because for Au NPs the oxidation and reduction processes induced by X-rays take place simultaneously. To exclude any effect related to the UHV condition alone, we have investigated the stability of the oxidic species under UHV without X-ray irradiation. As shown in the insets of Figure 1c,d, both samples are stable after 10 min under UHV in the absence of the X-ray beam.

In summary, using AP-XPS we have demonstrated that molecular oxygen does not oxidize Au at room temperature, either in the form of supported NPs on $TiO_2(110)$ or in bulk (foil) form at pressures of up to 1 Torr. These observations indicate that the proposed gold-only activation mechanism of O_2 is unlikely under these reaction conditions.[8,13,15,16,19] With the help of X-ray irradiation, however, both surfaces can be effectively oxidized under 1 Torr of O_2. Therefore, our observations demonstrate that X-rays play a critical dual role during in situ measurements and that extreme care must be taken to carry out experiments and interpret spectra, especially when using intense synchrotron radiation.

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