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Activation of Oxygen on Gold/Alumina Catalysts: In Situ High-Energy-Resolution Fluorescence and Time-Resolved X-ray Spectroscopy**

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Catalysis by gold has received considerable attention in recent years. Particles of gold that are unsupported or supported on oxidic carriers have been reported to be very active in various oxidation reactions. Examples include the oxidation of CO in the presence or absence of hydrogen,[1] the water gas shift reaction,[2] and the oxidation of hydrocarbons.[3] The particle size greatly influences the catalytic activity of gold particles, and with decreasing particle size the activity increases. Moreover, the type of support also affects the catalytic activity: reducible supports lead to more active catalysts than nonreducible ones,[4] however, deviations from this trend have been reported.[5] Addition of reducible oxides to gold catalysts increased the catalytic activity of small gold particles considerably.[6] Correlated to this observation may be the enhanced stability of gold particles after the addition of transition-metal oxides.[7]

The origin of the high catalytic activity of gold catalysts has been strongly debated and various models have been presented. Goodman and co-workers[1b] suggested that the

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catalytic activity of small gold particles is paralleled by the loss of metallic character. Moreover, a double layer of gold atoms on a planar titania support was shown to be much more active than thicker layers of gold.[1c] Various authors proposed oxidic gold or a combination of reduced and oxidic gold as the active species in oxidation reactions by gold.[8] In addition, negatively charge gold atoms have been proposed to be the active centers.[9]

Initial theoretical calculations on the mechanism indicated that the support interface is responsible for the oxidation of CO.[10] Recently, however, a reaction path that only takes place on a gold particle was proposed.[11,1c] The major question that remains is the activation of the oxygen molecule which has been suggested to take place on the support.[12] The mechanism proposed by Bond and Thompson[8] involves the adsorption of CO on the gold particle at a low-coordinated gold atom. A hydroxy group from the support moves to a Au^{III} cation, meanwhile creating an anionic vacancy. These two species react to form a carboxylate group. The anionic vacancy on the support activates an oxygen molecule as O_2^-, which then is responsible for abstraction of a hydrogen atom, and CO_2 is formed. The hydroperoxide ion reacts with a second carboxylate species to form another CO_2 molecule and restores two hydroxy groups on the support.

Herein, we introduce in situ time-resolved and high-energy-resolution fluorescence-detected (HERFD) X-ray spectroscopy at the Au L_3 edge to determine the activation of oxygen on the gold particle. We studied gold supported on a nonreducible support, Al_2O_3. X-ray absorption near-edge structure (XANES) studies probe the local geometry and the oxidation state of the absorption atom. XANES is sensitive to adsorbates on the surface of metallic particles, and the spectral shape is affected by the mode of bonding.[13] The intensity of the first feature in the L_3 edge spectrum, which is called whiteline, reveals the number of holes in the d band and therefore reflects charge transfer after adsorption of molecules. Application of high-energy-resolution emission spectroscopy greatly enhances the resolution in the spectra.[14] Selective detection of a fluorescence channel with an instrumental broadening below the core hole lifetime greatly enhances the spectral resolution,[15] thus resulting in much sharper features in the X-ray absorption spectra. In addition to high-energy-resolution XAS, a time resolution of seconds can be achieved using normal fluorescence detection at beamline ID26 at the ESRF (Grenoble). The response of the system to changes in the gas composition, from oxidizing to reducing and back, can be determined.

The enhancement in spectral resolution when using high-energy-resolution fluorescence detection is illustrated in Figure 1a, which shows the X-ray absorption spectrum of gold foil measured simultaneously in normal transmission mode and with the high-energy-resolution fluorescence detector. A small whiteline at 11929 eV is visible in the transmission spectrum. The whiteline is very prominent in the spectrum that was recorded with the high-resolution fluorescence detector. Furthermore, all other features are much more pronounced. Any changes that occur after the adsorption of reactants, in the oxidation state of the gold or in its coordination, will be detected with much higher accuracy in the high-resolution data. Although the electron configuration of a gold atom is Xe4f^{14}5d^{10}6s^{1}, in bulk gold the s, p, and d orbitals overlap, which causes orbital hybridization and results in a 5d^{10-x}6sp^{1+x} electron configuration. The whiteline reflects this hole in the d band. Theoretically simulated spectra using the FEFF8 code are shown in Figure 1b. Spectra of bulk gold using the full L_3 core hole lifetime and reduced by 1.6 eV showed all the features that were experimentally observed, though the exact positions and relative intensities of the features varied. Theory predicted a double whiteline in the high-energy-resolution data which is observed as a slight asymmetry in the experimental whiteline.

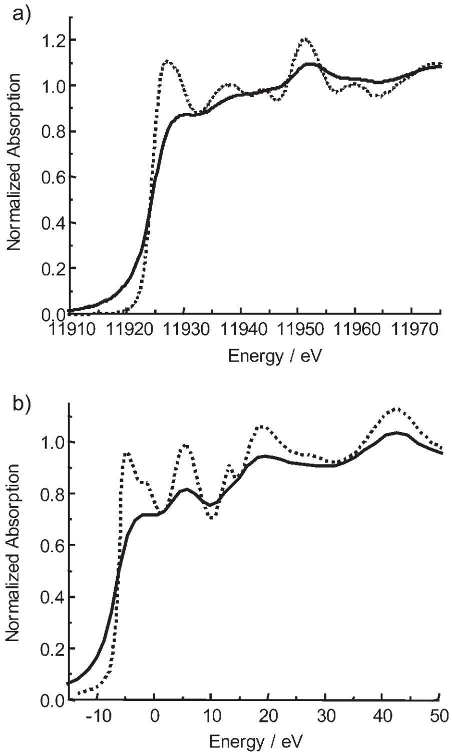

Figure 1. a) Experimental and b) theoretically simulated L_3 XANES of Au foil detected in transmission mode (——) and by using high-energy-resolution fluorescence detection (-----).

The Au L_3 near-edge spectra of Au/Al_2O_3 measured in various gas atmospheres using high-energy-resolution emission detection is shown in Figure 2a. The size of the gold particles is 1–3 nm as determined by scanning transmission electron microscopy (see Supporting Information). The XANES spectrum of the catalyst recorded at room temperature under helium after reduction shows the typical features of a fully reduced gold particle: a small whiteline and further features at similar positions as those in the spectrum of bulk gold. All these features have much less pronounced intensity compared to those in the spectrum of bulk gold (Figure 1). The whiteline has lower intensity than that in the spectrum of bulk gold because of the more atomic-like character in the small particles and the reduced s p d hybridization, as the band widths are smaller and show less overlap.

The spectrum of the Au/Al_2O_3 catalyst measured under 20% oxygen in helium shows an increased whiteline intensity

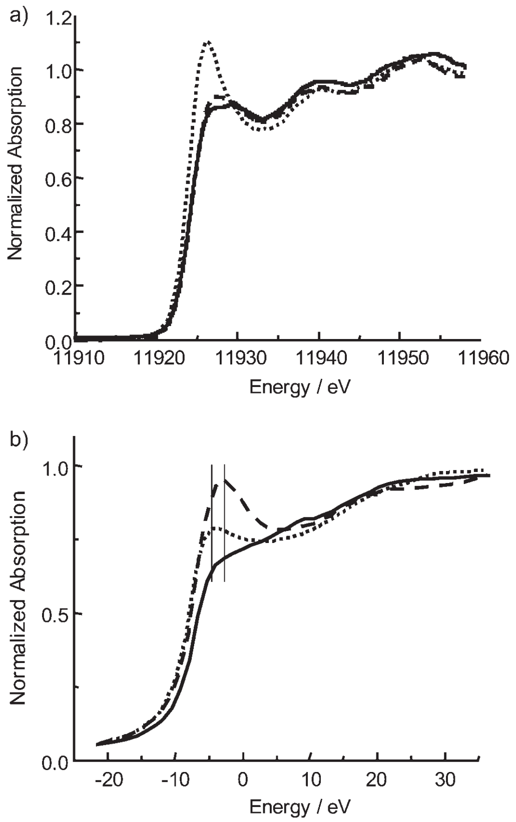

Figure 2. a) High-resolution Au L_3 XANES of 4% Au/Al_2O_3 in various atmospheres applied subsequently: He (——); 20% O_2 in He (-----); and 1% CO in He (–––). b) FEFF8-calculated Au L_3 XANES of gold clusters (——) with adsorbed oxygen (-----) or CO (–––).

which reflects charge transfer from the d band to the $2\pi^*$ orbital of oxygen, decreasing the gold d-orbital electron count and activating the oxygen molecule. This result agrees with previously reported partial oxidation of small gold particles in air.[16] On the basis of the intensity of the whiteline, the fraction of oxidized gold is about 15%, which is very similar to the amount reported by Miller et al.[16] Oxygen reacts with the surface of the small gold particles to form a surface oxide. Subsequent exposure of the partially oxidized catalyst to 1% CO in helium resulted in a decreased whiteline intensity. However, the whiteline intensity was higher than that measured in He and the energy of the maximum intensity was shifted to higher energy relative to the spectrum measured under oxygen. This behavior is ascribed to the bonding of CO on the surface of reduced gold particles.[17,13d] Simulation of spectra using the full multiple scattering code FEFF8 (Figure 2b) indicated that CO adsorption causes enhanced intensity of the whiteline at a higher energy than adsorbed oxygen (the clusters are taken from Reference [11]). Electron back-donation into the antibonding orbitals of CO is responsible for the charge transfer.

The evolution of the spectra, measured in conventional fluorescence mode, after switching the gas flow from 20% oxygen in helium to 1% CO in He is shown in Figure 3. Spectra were recorded every 2 s. The reduction is very fast and was complete after 14 s (seven scans). Meanwhile, small amounts of CO_2 were observed in the mass spectrometer. The reduction of partially oxidized gold catalysts is much faster than their oxidation, which took over 5 min to complete (spectra not shown).

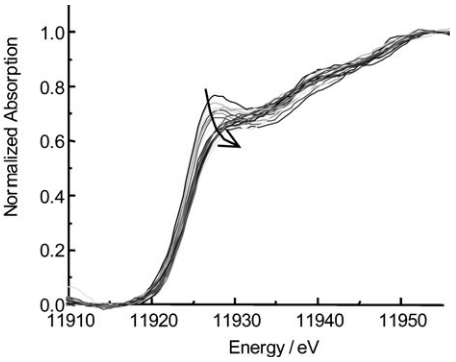

Figure 3. Kinetics of re-reduction in CO: Time-resolved XANES spectra measured in normal fluorescence mode.

One of the main questions regarding the mechanism is how oxygen is activated on the catalyst.[5,12] Various reports suggest that the metal–support interface plays a role and that the support activates oxygen and serves as a supply of oxygen that recombines with CO on the gold particle to form CO_2. Our in situ XANES study clearly showed that charge transfer from small gold particles to oxygen occurs when exposed to oxygen, along with partial depletion of the Au d band. A fraction of the surface atoms react with oxygen. Small gold particles on a nonreducible oxidic support activate oxygen, meanwhile forming partially oxidized gold: $Au^0 + O_2 \rightarrow Au_yO_x$. Miller et al. observed oxidation of gold by air with Au/Al_2O_3 catalysts by changes in the near-edge structure, which was confirmed by a decrease in the Au–Au coordination number and an increase in the Au–O contribution in a full EXAFS analysis.[16] The partially oxidized gold is reduced very quickly by CO to form CO_2 (Figure 3), showing that the partially oxidized gold particles readily react with CO to form CO_2, thus closing a catalytic cycle: $Au_yO_x + CO \rightarrow Au^0 + CO_2$. After the full reduction, adsorbed CO is observed on the surface by the broadening of the whiteline (Figure 2).[17,13d] Clearly, the reduction is much faster than the reoxidation and the rate-limiting step is the activation of oxygen on the gold surface.[8] In a mixed O_2/CO gas environment, fully reduced gold is expected,[18] probably with adsorbed CO on its surface.[17] In this mechanism, partially oxidized gold is formed upon reaction with oxygen and is present as a short-lived species under catalytic conditions.

In situ high-energy-resolution and time-resolved X-ray spectroscopy identified a possible reaction mechanism for the oxidation of CO over the gold particles in supported gold catalysts. On Au/Al_2O_3, there is a reaction channel that has partially oxidized gold as reaction intermediate. Charge transfer from a reduced gold particle to oxygen activates the oxygen molecule. The thermodynamic redox behavior of small gold particles is distinctly different from that of bulk gold, which is inert and unreactive.[19] The difference likely originates from the different electronic properties of the small gold particles, which have more d electrons at a different energy to those in bulk gold and which contain a large fraction of corners and edges. Exposure of the activated oxygen to CO rapidly leads to formation of CO_2 and fully reduced gold. We propose that reduced gold and its ability to transfer charge to oxygen are essential for high catalytic activity in the oxidation of CO.

In situ HERFD X-ray spectroscopy is likely to become a valuable tool in determining the structures of catalysts under catalytically relevant conditions. High-energy-resolution data with time-resolution and the possibility of in situ measurement in combination with mass spectrometry at synchrotrons makes it a promising tool in determining the structures of catalytically active sites.

Experimental Section

A solution of $HAuCl_4$ (2.1×10^{-3} M) was prepared by dissolving the appropriate amount of $HAuCl_4\cdot3H_2O$ in deionized water (300 mL). The solution was warmed to 353 K, and 3 g each of support γ-Al_2O_3 (Condea) and urea (0.21 M) were added. The suspension was kept away from light and stirred during 16 h while maintaining the temperature at 353 K. The suspension was then centrifuged, and the solid was isolated, washed three times with deionized water, and dried under vacuum at room temperature overnight. The fraction of powder containing particles of 90–125 µm was separated and introduced into the in situ reactor for X-ray absorption measurements. Transmission electron microscopy showed small gold particles of 1–3 nm.

The experimental setup consists of a reactor, which is a quartz tube with a diameter of 5 mm and a wall thickness of 100 µm, and a blower, which was used as a heater. The gas atmosphere in the reactor was controlled by five mass-flow controllers (Bronkhorst). Highly pure He, H_2, 1% CO in He, and 20% O_2 in He (Air Liquide) were used as the initial gas mixtures. The exhaust of the reactor was connected to a mass spectrometer (Pfeiffer QMS200). After reduction of the catalyst in H_2 at 423 K, the reactor was purged with He and cooled down to room temperature. The catalyst was put in contact with different CO- and O_2-containing gas mixtures at 298 K. All X-ray spectroscopic measurements were performed in situ under constant flux (10 mL min^{-1}) of a particular gas atmosphere through the reactor. The studies were performed at the high-brilliance XAFS-XES beamline ID26 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The electron energy was 6.0 GeV, and the ring current varied between 50 and 90 mA. The measurements were performed using the third harmonic of two u35 undulators. The monochromator was equipped with a pair of Si(220) single crystals. Higher harmonics were suppressed by two Cr-coated mirrors operating at 3 mrad relative to the incident beam. The X-ray beam measured 0.3 mm horizontal and 1 mm vertical, with a total flux on the order of 5×10^{12} photons s^{-1} on the sample. The energy was calibrated using a gold foil. The high-energy-resolution fluorescence detection was performed using a horizontal-plane Rowland circle spectrometer and an avalanche photodiode (APD, Perkin Elmer) as detector. The spectrometer was tuned to the Au $L\alpha_1$ (9713 eV) fluorescence line by using the (660) Bragg reflection of one spherically bent Ge wafer with $R = 1$ m and a diameter of 89 mm. The energy resolution of the spectrometer was 0.6 eV. A Canberra Si photodiode was mounted to measure the total fluorescence yield simultaneously. During XANES scans, the undulators were kept at a fixed gap and only the monochromator angle was changed. To measure fast kinetics, conventional XANES spectra were recorded every 2 s between 11900 at 11960 eV with energy steps of 0.5 eV. The statistics were insufficient to perform these measurements in the high-energy-resolution fluorescence detection mode. The XANES spectra in high-resolution mode were measured after the catalyst had reached steady-state conditions. The corresponding spectra were measured during 30 s from 11880 to 11980 eV with steps of 0.1 eV and averaging of 60 scans. Full XAS spectra over a 1000 eV range were also measured under steady-state conditions and used to normalize the XANES data.

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