

Application of In-Situ High Energy-Resolution Fluorescence Detection and Time-Resolved X-Ray Spectroscopy: Catalytic Activation of Oxygen over Supported Gold Catalysts

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Abstract. Life-time-broadening reduction in high-energy-resolution fluorescence detected XAS produced spectra of unprecedented detail. Au L₃ edge spectra of a Au/Al₂O₃ catalyst under various reaction conditions showed the interaction of oxygen with the gold particles on this catalyst. A reaction path on the gold particle in the oxidation of CO was established.

Keywords: Gold catalysis; XAS; HERFD XAS; High-energy resolution spectra; In-situ; Oxidation of CO;

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INTRODUCTION

Understanding structure-performance relationships in catalysis aids the design and construction of improved catalysts. Application of X-ray absorption spectroscopy has resulted in partial insight by determining the averaged structure of supported metal catalysts. It was shown that in-situ and time-resolved measurements are required to obtain insight into catalytically active structures, because the structure of catalysts are strong functions of temperature, pressure and reducing or oxidizing atmosphere. However, the structures of the catalytically active sites remain often unknown. Progress has been made in understanding the fine structure in the near-edge spectra of L₃ edges of supported metal catalysts and the mode of bonding of adsorbates and reaction intermediates can be determined [1]. The intrinsic lifetime broadening results in broad spectral features, and limits the information that can be obtained from the spectra. Spectral sharpening can be obtained by using high energy-resolution detection of fluorescence lines, which cause a decreased lifetime broadening and changes in spectral shape are detected with more detail. We applied high energy-resolution fluorescence detection spectroscopy to determine the activation of oxygen over gold catalysts and to reveal the active species in the oxidation of CO. The mechanism of this

reaction is strongly debated and the main unanswered question is how the oxygen molecule is activated. To date, no data were available on the reaction of oxygen on the gold particle [2]. The application of in-situ high energy-resolution fluorescence detection and time-resolved X-ray absorption spectroscopy in a true reactor combined with full multiple scattering calculations (FEFF8) shows how nanometer-sized gold particles activate the oxygen molecule. From the high-resolution data, we determined the bonding of reactants on the gold surface under various gas atmospheres and true reaction conditions. Recording time-resolved spectra after sudden changes of gas environment enabled us to propose a mechanism of how gold catalyzes the oxidation of CO.

EXPERIMENTAL

A 4 wt% Au/Al₂O₃ catalyst was synthesized. A solution of HAuCl₄ (2.1 x 10⁻³M) was prepared by dissolving HAuCl₄·3H₂O in deionized water (300 mL). The solution was heated to 353 K, and 3 g of γ-Al₂O₃ (Condea) and urea were added. The suspension was kept dark and stirred while maintaining the temperature at 353 K during 16 h. The solid was then centrifuged, washed three times with deionized water, and dried under vacuum at room temperature for 12

hours. A sieve fraction of 90–125 nm was introduced into the in situ reactor for X-ray absorption measurements. Transmission electron microscopy showed small gold particles of 1–3 nm. The catalysts were reduced in hydrogen at 423 K prior to exposure to He, H₂, 1% CO in He, and 20% O₂ in He. All measurements were performed under constant flow of gases over the catalyst. The measurements were performed using the third harmonic of two u35 undulators 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 monochromator was equipped with a pair of Si(220) single crystals and higher harmonics were rejected by two Cr-coated mirrors. A beam spot of 0.3 mm by 1 mm was used, with a total flux of about 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 α_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.

RESULTS AND DISCUSSION

Figure 1 compares the normal fluorescence XAS spectrum of a reduced Au/Al₂O₃ catalyst to the

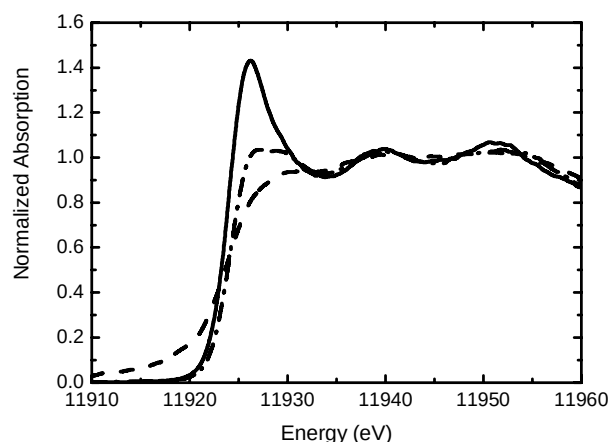


FIGURE 1. Au L₃ edges of reduced Au/Al₂O₃ in normal detection mode (dashed line) and in HERFD mode (dashed dotted line) and of Au/Al₂O₃ under 20% O₂ in He in HERFD mode (solid line).

HERFD spectrum. The intensities of all features in the

HERFD spectrum are much sharper, especially the whiteline, which shows the benefit of applying lifetime broadening reduction. The first feature in the spectrum is the whiteline, which represents the amount of holes in the gold d band. The whiteline in gold arises from hybridization of the bands that are formed in bulk gold of s, p, and d orbitals. The resulting electron occupation is $6sp^{1+x}5d^{10-x}$ [3]. Because the number of atoms that contribute to the s, p, and d bands is much smaller in nano-particles, these bands are narrower and show less overlap, and therefore hybridize less. The number of holes in the d band in small particles is therefore smaller than in bulk [4]. The whiteline in the spectrum of the reduced Au/Al₂O₃ catalyst represents this number.

The third line in the spectrum is the HERFD spectrum of Au/Al₂O₃ under 20% O₂ in helium. A much higher whiteline is observed, which is indicative of a decreased number of d-electrons. Oxygen is adsorbed on the surface of the small gold particles and charge transfer from gold particle to oxygen molecule occurs. This clearly is evidence of activation of the oxygen molecule over the gold particle. The exact

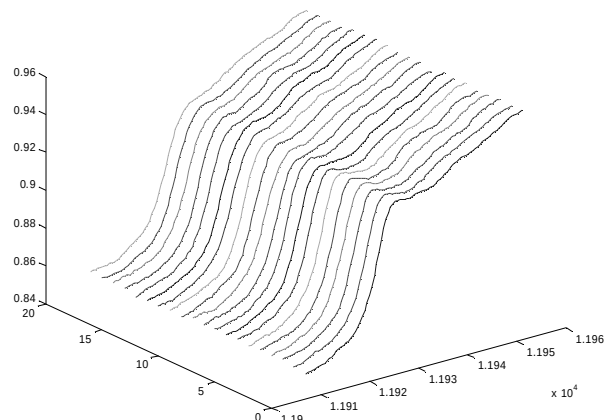


FIGURE 2. Au L₃ spectra of Au/Al₂O₃ after a switch of 20% O₂ to 1% CO in He, showing a decrease in intensity of the whiteline. One scan is taken every 2 s.

structure of the activated oxygen molecule remains unknown; it may be activated in the form of O₂^{δ-}, or via dissociation of the oxygen molecule and the formation of cationic gold. Theoretical predictions suggested that dissociation of oxygen on small gold particles does not occur [5]. As the exact nature of the gold - oxygen species is unknown, we refer to these species as partially oxidized gold.

Figure 2 shows the Au L₃ XANES spectra in normal fluorescence mode that are measured directly after switching the flow of 20% O₂ in He to 1% CO in He. A spectrum is recorded every two seconds. The small whiteline visible in the spectrum under 20% O₂

decreases in intensity over time. At the same time, the mass of CO₂ is observed in the mass spectrometer, which indicates the reaction of CO to oxygen on the gold surface. CO reacts with oxygen that is activated on the surface of gold nano-particles. Finally, measuring gold L₃ spectra of Au/Al₂O₃ under mixtures of CO and O₂ showed that small amounts of CO are adsorbed on the surface of the gold nano-particles [6].

When oxygen is admitted to gold nano-particles on a non-reducible support (Al₂O₃), it reacts with the gold surface and is activated. As soon as CO is admitted, a reaction occurs and CO₂ is formed. When both molecules are present, the interaction of oxygen with the catalyst is not observed; CO₂ is formed at high rates. Any oxygen molecule that interacts with the gold nano-particle and is activated will directly react with CO to form CO₂ [7].

CONCLUSIONS

The electronic and geometric structure of supported metal catalysts can be determined in more detail using high-energy-resolution fluorescence detection. The lifetime-broadening-reduced data are a potentially powerful tool for studying structure performance relations in heterogeneous catalysis.

The activation of oxygen over the gold particles in a Au/Al₂O₃ catalyst was observed by increased intensity of the whiteline. The activated oxygen is able to react with CO forming CO₂. In the oxidation of CO, there is a reaction path that occurs on the gold particle.

REFERENCES

1. M. K. Oudenhuijzen, J. A., van Bokhoven, J. T. Miller, D. E. Ramaker, D. C. Koningsberger, *J. Am. Chem. Soc.* **127** 1530-1540 (2005).
2. G. C. Bond, D. T. Thompson, *Gold Bull.* **33**, 41 (2000).
3. L. F. Mattheiss, R. E. Dietz, *Phys. Rev. B* **22**, 1663 (1980); M. G. Mason, *Phys. Rev. B* **27**, 748 (1983).
4. J. A. van Bokhoven, J. T. Miller, submitted.
5. I. N. Remediakis, N. Lopez, J. K. Nørskov, *Angew. Chem.* **117**, 1858 (2005); *Angew. Chem. Int. Ed.* **44**, 1824 (2005).
6. N. Weiher, E. Bus, R. Prins, L. Delannoy, C. Louis, D. E. Ramaker, J. T. Miller, J. A. van Bokhoven, *J. Catal.* **240**, 100-107 (2006).
7. J. A. van Bokhoven, C. Louis, J. T. Miller, M. Tromp, O. V. Safonova, P. Glatzel, *Angew. Chem. Int. Ed.* **45** 1-5 (2006).