

Why Gold Becomes Active When in Form of Dispersed 3 nm Particles? Reaction Intermediate Detected at SPring-8*

Since ancient times, gold has been a symbol of wealth and power because of its eternal brightness due to its poor chemical reactivity. However, Au becomes chemically active when it is in the form of dispersed 3 nm particles, e.g., for the catalysis of low-temperature CO oxidation [1]. The reason for the contrasting reactivity of Au between the nanometer and centimeter scales is not yet known.

Various possibilities have been proposed as the active site of Au nanoparticles: anionic Au cluster sites, the interface sites between Au and the supporting metal oxide, and lower-coordination step-edge sites [1]. It is difficult to determine the active site because the site structure of Au nanoparticles cannot be determined individually from the various chemical states of Au.

X-ray diffraction (XRD) is insensitive to 3 nm particles because there is insufficient repetition of lattices of Au particles. Also, XRD does not discriminate between different chemical states. In contrast, X-ray photoelectron spectroscopy (XPS) can be used to monitor chemical states and provides the population of each state near the surface of the sample. However, XPS does not give structural information. X-ray absorption fine structure (XAFS) provides local structural information. However, the information is in the form of a statistical average if more than two chemical states are present in the element in the sample. A heterogeneous catalyst is a typical example of such a mixture of chemical states for the active element, particularly during catalysis.

To determine each Au site structure in Au nanoparticles on a porous, complex surface of TiO₂, we applied state-sensitive XAFS spectroscopy [2]. State-sensitive XAFS, which is an evolved version of general XAFS spectroscopy [3]. The statistical disadvantage of XAFS that it gives average information is not applicable to state-sensitive XAFS because the chemical states of Au can be distinguished by high-energy-resolution X-ray fluorescence spectrometry. XAFS data for each chemical state of Au was obtained by selecting X-ray fluorescence signals originating from anionic, neutral, and cationic Au sites independently [2].

A homemade Rowland-type fluorescence spectrometer [3] was set in the undulator beamline **BL37XU**. With the excitation energy set to 11943 eV, the Au $L\alpha_1$ emission from the sample was analyzed

using a Johansson-type Ge(555) crystal. The Rowland radius was 220 mm. The measured energy resolution of this fluorescence spectrometer was 2.9 eV at 9.7 keV including the contribution of the beamline.

The fluorescence spectrometer was tuned to each emission energy and the Au L_3 -edge XANES (X-ray absorption near-edge structure) spectra were measured. By tuning the energy to 9713.3 eV (peak of emission spectrum, Fig. 1, inset), Au $L\alpha_1$ -selecting Au L_3 -edge XANES spectra were measured for Au metal (Fig. 1, solid red line). The absorption edge at 11921.2 eV was steeper and the peaks at 11923.3, 11935.3, 11941.3, and 11948 eV were sharper and more resolved than those in the corresponding spectrum measured in transmission mode (Fig. 1, dotted blue line). This sharpening effect is derived from identical rationale used to discriminate between chemical states in XANES combined with high-energy-resolution fluorescence spectrometry [4].

The particle size of Au nanoclusters on TiO₂ was controlled between 2.9 and 8.7 nm by changing the deposition-precipitation synthesis conditions of the catalyst: the pH (NaOH or urea), the surface area of TiO₂ (60 - 1200 m²g⁻¹), the reaction temperature, and the duration of the deposition-precipitation reaction [2]. The Au particle size distribution was very narrow (standard deviation ≈26%).

The reason why there is critical difference in low-temperature CO oxidation reactivity depending on the

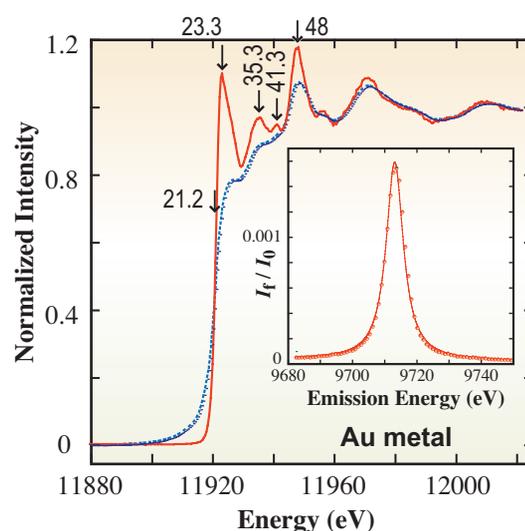


Fig. 1. Au $L\alpha_1$ -selecting Au L_3 -edge XANES spectrum tuned to Au $L\alpha_1$ peak (solid red line) and XANES spectrum measured in transmission mode (dotted blue line). (Inset) Au $L\alpha_1$ emission spectrum.

*Part 27 in the series.

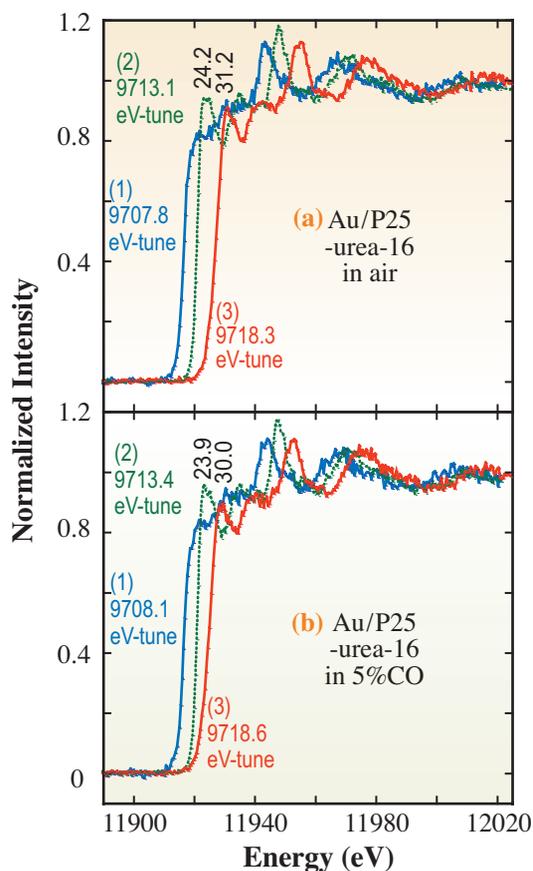


Fig. 2. Au $L\alpha_1$ -selecting Au L_3 -edge XANES spectra measured for Au/TiO₂(P25) of 2.9 nm nanoclusters synthesized at 353 K using urea in air (a) and in 5% CO (balance gas: Ar) (b). 0.93 wt% Au. The energies were tuned to 9707.8, 9713.1, and 9718.3 eV (a) and 9708.1, 9713.4 and 9718.6 eV (b).

Au particle size [1] was clarified on the basis of the Au $L\alpha_1$ -selecting Au L_3 -edge XANES spectra obtained by tuning the fluorescence spectrometer to 9708, 9713 and 9718 eV. The measured sample was a Au/TiO₂ catalyst of 2.9 nm nanoparticles synthesized using urea at 353 K for 16 h on TiO₂ (Degussa P25) in air and in CO(5%)/Ar.

The Au L_3 -edge energy and spectral pattern of XANES tuned to 9713 eV (Figs. 2(a-2) and 2(b-2)) resembled those for XANES measured for Au metal (Fig. 1, solid red line). Thus, the neutral Au⁰ site located on upper side of Au nanoparticles on TiO₂ was selected at 9713 eV (Fig. 3). When the energy was tuned to 9708 eV on the lower-energy side of Au $L\alpha_1$ emission, the Au L_3 -edge energy shifted by -4.6 to -4.7 eV toward the lower-energy side. The first intense peak became a weak shoulder at 11922 eV (Figs. 2(a-1) and 2(b-1)). These trends indicated greater Au 5d occupation [5]. Thus, the formation of the anionic Au^{δ-} site was suggested (Fig. 3(b)). The population of Au^{δ-} site was greater for Au

nanoparticles of 2.9 nm than for those with average size of 8.7 nm. However, this Au^{δ-} site was not affected whether in air or in 5% CO.

Finally, the fluorescence spectrometer was tuned to 9718 eV on the higher-energy side of Au $L\alpha_1$ emission. The Au L_3 -edge energy shift was +6.8 eV for Au/TiO₂(P25)-urea-16 of nanoparticles of 2.9 nm in air (Fig. 2(a-3)), greater than that in 5% CO (+3.9 eV, Fig. 2(b-3)) and that of nanoparticles of 8.7 nm (average) in air (+3.7 eV) [2]. Thus, it is suggested that O₂ molecules are activated on the cationic Au^{δ+} site, probably near the interface with the TiO₂ surface terminated with Ti atoms (the so called SMSI effect; Fig. 3(a)) by the further negative charge transfer from Au^{δ+} to the adsorbed O₂. The charge donation observed in Fig. 2(a-3) is a snapshot of the reaction intermediate of CO oxidation that proceeds on Au nanoparticles of 2.9 nm, but does not occur on larger Au nanoparticles [1].

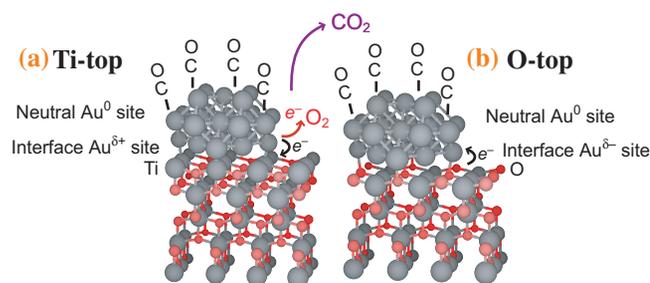


Fig. 3. Au₂₆ cluster models on anatase-type TiO₂(001) surface terminated with Ti atoms (a) and O atoms (b).

Yasuo Izumi

Graduate School of Science, Chiba University

E-mail: yizumi@faculty.chiba-u.jp

References

- [1] A. Cho: Science **299** (2003) 1684.
- [2] Y. Izumi, D.M. Obaid, K. Konishi, D. Masih, M. Takagaki, Y. Terada, H. Tanida and T. Uruga: Inorg. Chim. Acta **361**(4) (2008) 1149.
- [3] Y. Izumi *et al.*: J. Electron Spectrosc. Relat. Phenom. **119** (2001) 193.
- [4] Y. Izumi *et al.*: Anal. Chem. **77** (21) (2005) 6969.
- [5] N. Weiher *et al.*: J. Am. Chem. Soc. **129** (8) (2007) 2240.