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State-sensitive monitoring of gold nanoparticle sites on titania and the interaction of the positive Au site with O_2 by Au Lα_1-selecting X-ray absorption fine structure [☆]

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Dedicated to Edward Solomon.

Abstract

The heterogeneity of gold sites in various Au/TiO_2 catalysts was studied by means of state-sensitive Au L_3-edge X-ray absorption fine structure (XAFS) combined with high energy-resolution X-ray fluorescence spectrometry. A series of Au/TiO_2 catalysts were prepared via deposition-precipitation method on anatase-type or mesoporous (amorphous) TiO_2 added with NaOH (lower Au loading) or urea (higher Au loading). The mean Au particle size ranged between 29 and 87 Å based on high-resolution TEM (transmission electron microscope) measurements. The Au Lα_1 emission peak energy for Au/mesoporous–TiO_2 in air and Au/anatase–TiO_2 in CO (5%) corresponded to Au^0 state. The emission peak energy for Au/anatase–TiO_2 in air shifted toward that of Au^I state. For relatively greater Au particles (average 87 Å) dispersed on mesporous TiO_2, the major valence state discriminated by Au Lα_1-selecting XANES (X-ray absorption near-edge structure) spectrum tuned to Au Lα_1 emission peak top was Au^0, but the $Au^{\delta-}$ state could be successfully monitored by Au Lα_1-selecting XANES tuned to the emission energy at 9707.6 eV, of which population was relatively small compared to the case of smaller Au particles (average 29 Å) on anatase-type TiO_2. On the other hand, negative charge transfer from Au 5d to support was demonstrated in $Au^{\delta+}$-state sensitive XANES tuned to 9718.3–9718.7 eV. The $Au^{\delta+}$-state sensitive XANES spectra resembled theoretically generated XANES for interface $Au^{\delta+}$ sites model on TiO_2 in contact with surface Ti sites. Further charge transfer was demonstrated from Au to adsorbed O_2 for Au/anatase–TiO_2 catalyst.

Keywords: Gold; Titanium oxide; X-ray absorption fine structure; Fluorescence spectrometry; Chemical state

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1. Introduction

Gold is chemically inert, however, it was found to become active when dispersed as nano-particles of size 30 Å or smaller in low temperature CO oxidation [1,2]. Various possibilities have been proposed as the active sites: anionic Au cluster site, perimeter site, and lower-coordination step-edge site [1,2]. However, it is difficult to observe each site one by one among Au nano-particles dispersed over porous, complex surface of TiO_2.

In order to overcome the heterogeneity problem of Au sites, we applied state-sensitive XAFS spectroscopy [3,4] to a series of Au/TiO_2 samples. Due to the differences of deposition-precipitation (DP) conditions of Au compound with NaOH or urea, reaction time of DP, and crystalline

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phase of TiO_2 support (anatase/rutile or amorphous), particle size and loading amount of Au were systematically controlled. Catalytically active Au nano-particle sites populated in narrow size distribution centered at 29 Å were monitored state-sensitively in CO or O_2 atmosphere to extract activation sites for the low-temperature oxidation reaction.

In this spectroscopic method, better-resolved, steeper XANES spectra were obtained to remove the core-hole lifetime width (Γ) of K levels for Cu [4,5] and Sn [4] and L_3 levels for Dy [6], Pt [7], and Pb [4,8] by selecting the $K\alpha_1$ and $L\alpha_1$ emission, respectively.

2. Experimental

2.1. Samples

$K^+[Au^I(CN)_2]^-$ (Wako) was thoroughly mixed with boron nitride (BN) to be 1.0 wt% Au and pressed into a disk of 20 mm in diameter. Au metal foil was controlled to be the thickness of 6 μm and powders of $Au^ICl[P(C_6H_5)_3]$ (>99.9%, Aldrich), $Au^{III}(OH)_3$ (Wako), and $Au_2^{III}O_3$ (Wako) were thoroughly mixed with BN and pressed into a disk of 20 mm in diameter, to make the Au L_3 absorption edge jump to be 1.

The mesoporous TiO_2 sample was synthesized in aqueous solution using dodecylamine [9] given by Professor H. Yoshitake at Yokohama National University. The specific surface area (SA) was 1000 $m^2\,g^{-1}$ and wormhole-like pore size distributed in narrow range centered at 30 Å. The Au/TiO_2 catalyst was prepared by mixing 1 g of TiO_2 (Degussa P25; anatase 70% and rutile 30%) or mesoporous TiO_2 with 50 ml of aqueous solution of $HAu^{III}Cl_4 \cdot 4H_2O$ (Wako, 1.3 mM) (Table 1a–c). The mixture was stirred at 328 K for 4.5–7 h. The pH of the solution was maintained at 8 by adequately adding NaOH [10]. The powder was filtered and washed several times with de-ionized, distilled water. Dried powders were calcined at 523–673 K in air. The Au/TiO_2 catalyst was also prepared by mixing 1 g of TiO_2 (P25) with 100 ml of aqueous solution of $HAuCl_4 \cdot 4H_2O$ (4.2 or 0.51 mM) by adding 42 or 5.1 mM of urea, respectively. The mixture was stirred at 353 K for 4–16 h in the absence of light [11]. Then, the filtered powder was processed similar to the preparation using NaOH and finally calcined at 573 K in air (Table 1d–g). Thus, the obtained Au/TiO_2 catalysts are denoted "Au/(type of TiO_2)-(alkaline used)-(DP time)-(calcined temperature)", e.g. Au/P25-urea-16-573.

The Au/TiO_2 sample disks were sealed in on-reaction cell for X-ray measurements purged with dry air or with the mixture of CO (5%) and argon (95%). The window was polyethylene naphthalate film of 16 μm in thickness (Q51-16, Teijin).

2.2. Characterization

Transmission electron microscope images were measured using field-emission-type TEM (JEM-2010F, JEOL) with an accelerating voltage of 200 kV at the Center of Advanced Materials Analysis, Tokyo Institute of Technology (Dr. A. Genseki). The powder was dispersed in carbon tetrachloride using ultrasonic and mounted on carbon-coated Cu grid.

The X-ray measurements were performed at 290 K at the undulator beamline 37XU of SPring-8 (Sayo, Japan). The storage ring energy was 8.0 GeV operated in top-up mode at the ring current of 99–97 mA. A Si(1 1 1) monochromator and Rh-coated mirror were used. The undulator gap value was optimized to maximize the X-ray beam flux at each data point. To stabilize the X-ray beam position on the surface of the sample, a feedback mechanism using MOSTAB (monochromator stabilization) [12] was applied. No position change was detected within the range of 50 μm throughout the beamtime.

A homemade Rowland-type fluorescence spectrometer was used to analyze Au $L\alpha_1$ emission equipped with Johansson-type Ge(5 5 5) crystal ($d = 0.65321$ Å, Saint Gobain). The detail of the spectrometer was described in Refs. [4,13,14]. An ionization chamber was purged with the mixture of nitrogen (30%) and helium (70%) in front of the sample. The opening of slit **0** in front of the ionization chamber was 0.25–0.5 mm (horizontal) × 0.5–1 mm (vertical). The sample was placed in a plane near horizontal. The plane was tilted by 6° toward the incident X-ray

Table 1
Preparation conditions via deposition-precipitation (DP) method and the property of various Au/TiO_2 samples[a]

Entry	Alkaline	TiO_2	pH	DP reaction temperature (K)	DP reaction time (h)	Calcined temperature (K)	Au loading (wt%)[b]	Average Au particle size (Å)
a	NaOH	mesoporous	8	328	7	523	0.21	87 ± 23
b	NaOH	mesoporous	8	328	4.5	673	0.21	78 ± 30
c	NaOH	P25	8	328	7	673	0.09	32 ± 21
d	urea	P25	3 → 8	353	4	573	7.1	37 ± 10
e	urea	P25	3 → 8	353	16	573	6.8	35 ± 19
f	urea	P25	4 → 8	353	4	573	0.97	29 ± 10
g	urea	P25	4 → 8	353	16	573	0.93	29 ± 18

[a] Gold precursor was $HAuCl_4 \cdot 4H_2O$.

[b] Evaluated based on the Au $L\alpha_1$ emission and Au L_3 absorption edge intensity.