Electronic state and particle size analyses of Cu nanoparticles on rutile TiO₂(110)

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Abstract

The electronic states and the particle size of Cu nanoparticles deposited on the rutile $TiO_2(110)$ surfaces have been investigated by synchrotron radiation photoelectron spectroscopy and high-resolution medium ion scattering (MEIS). We observed the photoelectron spectra of O 2*s* and Ti 3*p* lines and also measured the work functions for the reduced TiO₂ (R-TiO₂) and the oxygen rich TiO₂ (O-TiO₂). As the results, the all O 2*s* and Ti 3*p* lines for R-TiO₂ and O-TiO₂ show higher binding energy (E_B) shifts and the E_B shifts for O-TiO₂ are larger than those for R-TiO₂. The work functions for both surfaces decrease abruptly by a small amount of Cu deposition. This reveals that an electronic charge transfer takes place from Cu nanoparticles to the substrates. MEIS analysis reveals that the Cu nanoparticles are formed as both 2D and 3D islands on R-TiO₂.

1. Introduction

It is well known that Cu based catalysts, both pure and supported on metal-oxides, are used in reactions such as water gas-shift (WGS: $CO + H_2O \rightarrow CO_2 + H_2$), methanol oxidation, methanol synthesis, and others [1,2]. However, their performance is not fully understood and is highly dependent on the synthesis conditions or the nature of the oxide support. There are three candidates to explain the catalytic activity; [i] changes in the reactive surface area associated with nanoparticle formation, [ii] quantum size effect, [iii] charge transfer between nanoparticle and substrates.

In the previous study, we have found a reaction path that CO molecules react with the O adatoms (O_{ad}) atoms adsorbed on the 5-fold Ti rows at RT. This CO oxidation reaction is enhanced pronouncedly by the presence of Au nano-clusters on the O-TiO₂(110) surfaces, which were prepared by exposing reduced TiO₂ surfaces (R-TiO₂) to O₂ at almost room temperature (RT) [3]. Figure 1 illustrates the R- and O-TiO₂(110) surfaces with a ball and stick model. This strong activity is attributed to an electronic charge transfer from Au to the O-TiO₂ support to form an interface dipole and not to creation of a surface excess charge like a Ti³⁺ state. The interface dipole with a polarity of positive charge on the vacuum side, which is opposite to the O_{ad} on the 5-fold Ti rows induces an attractive interaction between them and thus lowers the potential barrier for the dissociative adsorption of O₂ on the 5-fold Ti rows. This interface dipole also generates an attractive force upon a polar CO molecule, which leads to trap of the CO near the perimeter interface of Au/O-TiO₂(110).



Figure 1. Ball and stick model for R- (left) and O-TiO₂(110) (right). Red balls represent oxygen and light blue and green balls denote 6-fold Ti and 5-fold Ti, respectively. Orange balls represent O_{ad} atoms and V_O is bridging O vacancy. Small dark blue ball denotes Ti interstitial acting as an *n*-type donor.

In this study, we analyze the electronic properties of Cu nanoparticles deposited on R- and O-TiO₂(110) surfaces by photo-electron and photon-induced secondary electrons emission spectroscopy using synchrotron-radiation (SR) light. We first determine the core level shifts of O 2*s* and Ti 3*p* by a hemispherical electrostatic analyzer as a function of Cu coverage. The work functions were measured by secondary electrons spectra from negatively biased Cu/TiO₂(110) samples, which are very sensitive to surface electronic states. We also checked the sizes of Cu nanoparticles on R-TiO₂ for Cu coverage of 0.5 ML.

2. Experimental

The experiment was carried out at Beam-line 8 connected to a storage ring named AURORA working at Ritsumeikan SR Center. This beam-line consists of photoelectron spectroscopy (PES), high-resolution medium energy ion scattering (MEIS) and molecular beam epitaxy (MBE) systems [4,5]. Two types of varied-space-plane gratings cover photon energy from 10 up to 700 eV and incident photon energy was calibrated precisely by measuring Au $4f_{5/2,7/2}$ spectra for incidence of primary and the 2nd harmonic waves. A hemispherical electro-static analyzer (ESA) detected emitted photoelectrons with an energy resolution better than 0.05 eV at a pass energy of 2.95 eV. The binding energy (E_B) of core levels was calibrated assuming the E_B value of 84.0 eV for Au $4f_{7/2}$ line emitted from bulk Au (in the previous analysis [6,7], we calibrated the E_B value by fitting the Fermi edge of Au 6*s* band). In the present MEIS analysis, we used 120 keV He⁺ ions and scattered He⁺ ions were energy-analyzed by a toroidal ESA with an excellent energy resolution ($\Delta E/E = 9 \times 10^{-4}$; FWHM), which makes it possible to determine the shape and size of metal nanoparticles [8].

We prepared the O-TiO₂(110) surfaces by exposure of O₂(5N) onto the R-TiO₂(110), which were formed by sputtering with 0.75 keV Ar⁺ followed by annealing at 870 K for 10 min in UHV. The above O₂ exposure was carried out starting from a temperature of ~325 K and down to RT under O₂ pressure of 4×10^{-4} Pa.

Cu was then deposited on the clean surfaces at RT with a Knudsen cell at a rate of 0.08 ML/min under UHV condition. Here, 1 ML means 1.77×10^{15} atoms/cm², corresponding to the areal density of Cu(111). The average size and shape [two-dimensional (2D) and three-dimensional (3D)] were determined by high-resolution MEIS [8]. Here, the 2D clusters were defined by the height below two atomic layers and the 3D shape was approximated by a partial sphere with a diameter d and height h. Note that the MEIS and UPS analyses were made at RT and all the experiments were performed *in situ* under UHV condition ($\leq 2 \times 10^{-8}$ Pa).

3. Results and Discussion

The O 2*s* and Ti 3*p* spectra for the R-TiO₂ as a function of Cu coverage are shown in Figure 2. It is seen that the E_B values of both O 2*s* and Ti 3*p* lines shift toward a higher energy side with increasing Cu coverage. Shown in Figure 3 are the E_B shifts of O 2*s* and Ti 3*p* lines for the R-TiO₂(110) substrates, as a function of Cu coverage.



Figure 2. O 2s (a) and Ti 3p (b) spectra for R-TiO₂(110) as a function of Cu coverage.



Figure 3. Binding energy shifts of O 2s (blue circles) and Ti 3p (black triangles) observed for Cu on R-TiO₂(110) as a function of Cu coverage.

The higher E_B shifts take place for both O 2*s* and Ti 3*p* lines even though very small and the E_B shifts of O 2*s* are larger than those of Ti 3*p*.

The electric dipole induced by an electron charge transfer at an Cu/support interface should change the work function Φ . Figure 4 shows the secondary electrons spectra measured for clean R-TiO₂(110) and Cu/R-TiO(110) at several Cu coverage. By measuring the on set of the kinetic energy of secondary electrons E_{kin} , we can deduce the work function Φ experimentally.

$$\Phi = \Phi_{SP} + \mathcal{E}_{kin} + eV \tag{1}$$

where Φ_{SP} is the work function of the spectrometer employed and V is the applied bias voltage and e is electron charge (-1.6×10⁻¹⁹ C).



Figure 4. Secondary electrons spectra measured at photon energy of 120 eV for clean R-TiO₂(110) and several Cu coverage on R-TiO₂(110). Samples were negatively biased at -3.0 V against the ground.

The work functions determined here are indicated in Figure 5, as a function of Cu coverage. The Φ value decreases drastically at low Cu coverage and then gradually approaches that of bulk Cu. This drastic decrease in work function is ascribed to the electronic charge transfer from Cu to R-TiO₂(110) substrate. Indeed, the slightly higher E_B shifts of Ti 3*p* and O 2*s* are probably due to strengthening of the downward band bending as the result of the electronic charge transfer.



Figure 5. Work functions measured from secondary electrons emission spectra for Cu/R-TiO₂(110) as a function of Cu coverage. Dash line denotes the work function of bulk Cu(111)

Next, as a function of Cu coverage on the O-TiO₂(110) substrate, we show Ti 3*p* and O 2*s* spectra (Figure 6), the E_B shifts of O 2*s* and Ti 3*p* (Figure 7), secondary electrons spectra (Figure 8), and the change of work function (Figure 9). The O 2*s* and Ti 3*p* lines shift toward higher energy side and work function decreases in a quite similar manner but larger than those for R-TiO₂. These results indicate the electronic charge transfer presented here may relax the initial upward band bending with increasing Cu coverage. Indeed, the E_B values of both O 2*s* and Ti 3*p* lines for the O-TiO₂(110) substrate was lower than those for the R-TiO₂(110) substrate (Figures 2 and 6).

Figure 6. O 2s (a) and Ti 3p (b) spectra for O-TiO₂(110) as a function of Cu coverage.

Figure 7. Binding energy shifts of O 2s (circles) and Ti 3p (triangles) observed for Cu on O-TiO₂(110) as a function of Cu coverage.

Figure 8. Secondary electrons spectra measured at photon energy of 120 eV for clean O-TiO₂(110) and several Cu coverage on O-TiO₂(110). Samples were negatively biased at -3.0 V against the ground.

Figure 9. Work functions measured from secondary electrons emission spectra for Cu/R-TiO₂(110) as a function of Cu coverage.

Finally, we determined the average size for Cu(0.5 ML)/R-TiO₂(110) by high-resolution MEIS. For measuring size of Cu nanoparticles, it needs He⁺ fractions of scattered from Cu [9-12]. Figure 10(a) and (b), respectively show the MEIS spectra for 122.67 keV and 114.09 keV He⁺ ions incident along the [110]-axis and scattered to 45° and 80° for Cu(001). Best-fits were obtained assuming the stopping power value of 1.8 and 1.1 times the Ziegler's data

and $\eta^+ = 0.56$ and 0.34, respectively for the emerging angles of 45 and 80°. We measured He⁺ fractions dependent on emerging angle for scattering component from the top layer atoms of Cu(001), as shown in Figure 11. Here, the emerging energy is fixed to 108 keV. The He⁺ fractions for Cu(001) are decreased slowly with increasing emerging angle and saturated above 75° (η bulk). He⁺ fractions dependent on exit path length is shown in Figure 12. The approximate curve was derived by

$$\eta_{short} = A_1 D$$

$$\eta_{long} = A_2 D \exp[-A_3 \cdot D] + \eta_{bulk}$$
(2)
$$\frac{1}{\eta} = \frac{1}{\eta_{short}} + \frac{1}{\eta_{long}}$$

where D is exit path length (atoms/cm²), $A_1 - A_3$ are fitting parameters. We used this approximate curve for nanoparticle size analysis.

Figure 10. MEIS spectra of Cu(001) observed for He⁺ ions incident along [110]-axis. Blue curves (thick) indicate best-fitted spectra and green and orange curves (thin) denote scattering component from top-layer Cu and those from deeper layer Cu, respectively. (a) (b) 122.67 keV and 114.09 keV are He⁺ ions scattered to 45 ° and 80° with respect to the surface normal, respectively.

Figure 11. He⁺ fractions determined for Cu(001) as a function of emerging angles. Emerging energy was fixed to 108 keV.

Figure 12. He⁺ fractions determined for Cu(001) as a function of exit path length. Red solid line denotes the approximate curve.

Figure 13(a) and (b), respectively show the MEIS spectra for for 120 keV He⁺ ions incident to 45° and scattered to 45° and 70° for Cu(0.5ML)/R-TiO₂. The best-fit spectra were obtained assuming a two size distribution of Cu clusters, which include 2D islands and 3D islands (d = 2.0 nm, h = 1.3 nm). This result differs from Au/R-TiO₂ [8].

Figure 13. MEIS spectra observed for 120 keV He⁺ ions incident on Cu(0.5 ML)/R-TiO₂(110). Incident and detection angles are -45° and 45° (a) and 70° (b) with respect to the surface normal.

4. Conclusions

In this study, we have studied electronic states and particle size of Cu nanoparticles deposited on the rutile $TiO_2(110)$ surfaces. We observed the photoelectron spectra of O 2*s* and Ti 3*p* lines and also measured the work functions for R-TiO₂ and O-TiO₂. As the results, the all O 2*s* and Ti 3*p* lines for R-TiO₂ and O-TiO₂ show higher binding energy (E_B) shifts and the E_B shifts for O-TiO₂ are larger than those for R-TiO₂. The work function for both surfaces decreases abruptly by a small amount of Cu deposition. This reveals that an electronic charge transfer takes place from Cu nanoparticles to the substrates. MEIS analysis reveals that the Cu nanoparticles are formed as both 2D and 3D islands on R-TiO₂.

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