

Growth Mode Analysis of Metal Nanoparticles on Rutile TiO₂(110)

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Up to now, metal nanoparticles grown on oxides supports have attracted much attention as heterogeneous catalyst [1]. Metal nanoparticles have different growth modes depending on their constituent elements. It has been shown that the smaller the particle size, the stronger the catalytic activities [2,3]. Therefore, it is important to understand distribution of particle size. In this study, we have measured the areal occupation ratios of two-dimensional (2D) and three-dimensional (3D) Cu and Au islands formed on reduced TiO₂ (R-TiO₂) by medium energy ion scattering (MEIS). Here, the 2D island is defined as that with a height of one atomic layer. The shape of 3D islands is well approximated by a partial sphere with diameter and height.

Figure 1 shows the MEIS spectrum observed for Cu (1.0 ML) / R-TiO₂(110) at an incident angle of 45° and emergent angles of 45°. The observed MEIS spectrum is reproduced well assuming the following fitting parameters: d (diameter) = 5.1 nm, h (height) = 1.55 nm, σ_{3D} (areal occupation ratios of 3D-islands) = 100% and δ (standard deviation in size) = 10%. Figure 2(a) and (b) show the distribution of diameter of Cu and Au nanoparticles determined by MEIS and FE-SEM, respectively. The both MEIS results assuming $\delta = 10\%$ for Cu and 20% for Au are well coincident with the FE-SEM image. Interestingly, δ and the ratio of h/d for Cu are smaller than those for Au. According to DFT calculations [4, 5], deposited Au grows on steps and defects of TiO₂(110) because the Au cluster is weakly bound and essentially can move freely on the oxide surface. The presence of O vacancies on TiO₂(110) drastically increases the adsorption energy of Au. On the other hand, the Cu atom was preferentially adsorbed on two bridging oxygens with a bonding energy of -1.76 eV [6] and Cu/TiO₂ interactions are much stronger than Au/TiO₂ interactions. Furthermore, Au prefers to bind to bridging O vacancy but this is not the case for Cu. Thus, Cu is quite different from Au in metal/oxide interactions, which affect the size, dispersion, and surface position of the metal particles.

References

- [1] H.J. Freund, *Surf. Sci.*, **2002**, 500, 271.
 [2] M. Haruta, *Catal. Today*, **1997**, 36, 153.
 [3] M. Valden, X. Lai, and D.W. Goodman, *Science* **1998**, 281, 1647.

- [4] J. Graciani, A. Nambu, J. Evans, J. A. Rodriguez, and J. F. Sanz, *J. Am. Chem. Soc.*, **2008**, 130, 12056.
 [5] I. N. Remediakis, N. Lopez, and J. K. Nørskov, *Angew. Chem. Int. Ed.*, **2005**, 44, 1824.
 [6] J. A. Rodriguez, J. Evans, J. Graciani, J.B. Park, P. Liu, J. Hrbek, and J. F. Sanz, *J. Phys. Chem. C*, **2009**, 113, 7364.

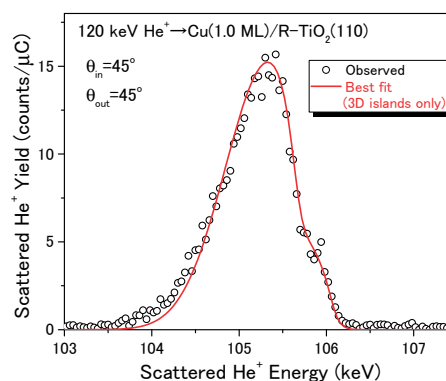


Fig. 1 MEIS spectrum observed for 120 keV He⁺ ions scattered from Cu(1.0 ML)/R-TiO₂(110) at $\theta_{in} = 45^\circ$ and $\theta_{out} = 45^\circ$.

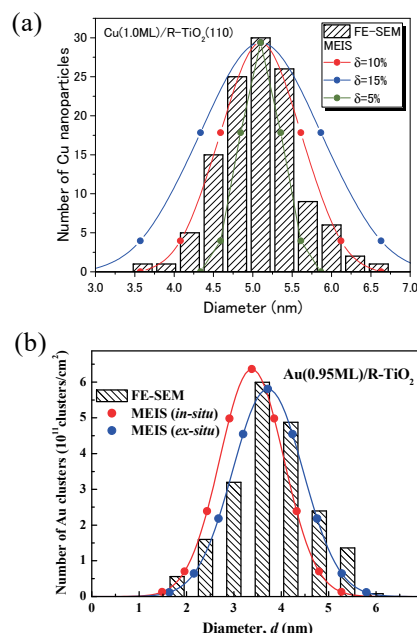


Fig. 2 Fluctuation of cluster size (diameter) determined (a) Cu and Au (b) by MEIS and FE-SEM