A Theoretical Insight into the Enhanced Catalytic Activity of Au by Multiple Twin Nanoparticles

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It is well known that gold exhibits high catalytic activity for CO oxidation when deposited as nanoparticles (NPs) on base metal oxides and the performance of Au NPs depends on their size [1]. Recently, we have reported CO oxidation is influenced by the morphology of Au NPs [2]. In this study, we have investigated CO adsorption on Au NPs with the variation of size and morphology. CO adsorption is a kind of key factor for the catalytic activity because it is influenced by the electronic structure of the adsorption sites.

Spin-polarized DFT calculations were carried out. The Perdew-Burke-Ernzehof (PBE) functional and ultrasoft Vanderbilt pseudo-potentials were adopted. A kinetic-energy cutoff for the plane-wave basis is 30 Ry. Adsorption energy in eV is defined as E_{ad} = E[adsorbed system] – E[isolated NP] – E[adsorbate], thus a negative E_{ad} means stable adsorption.

Figure 1 shows model structures for Au NPs. Octahedron (O_h) was adopted for single crystal NPs and Decahedrons (D_{3h}, D_{5h}) were used for single and multiple twin morphology. Three generations of the NP size were constructed by adding atoms on the periphery of NPs. The number of atoms in the D_{5h} structure is even or odd, depending on the size. Therefore, five atoms marked in Fig.1(c) are removed in order to keep spin states in the size generations.

Size dependence of CO adsorption energy is shown in Fig. 2. CO is adsorbed on vertices of all NP models. For the single crystal and the simple twin NPs, the size dependence is small and the morphology of their structures has little effect on the adsorption energies. Their energies range from –0.85 to –0.91 eV. On the other hand, strong size dependence is found for the CO adsorption on the D_{5h} structure. Especially, the size of Au_{49} and Au_{54} NPs for each spin state gives more stable adsorption of CO than that on the single crystal and the single twin NPs. The strong CO adsorption on the small multiple twin NPs comes from the instability of the NP structure. Upon CO adsorption, deformation of the twin NP structure is larger than that of other structures. CO binding energy on Au NPs was reported to be relevant to the CO oxidation reaction [3]. Thus, it is suggested that the multiple twin NPs with the size of less than 2 nm (=Au_{176} or Au_{181}) shows higher catalytic performance for CO oxidation than the single crystal NPs of all sizes.

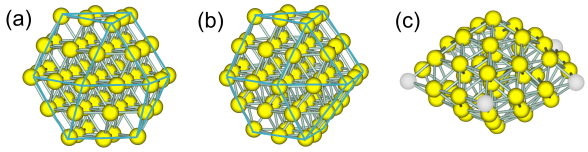

Fig. 1 Model structures for (a) single crystal [O_h], (b) single twin [D_{3h}], and (c) multiple twin [D_{5h}] Au nanoparticles.

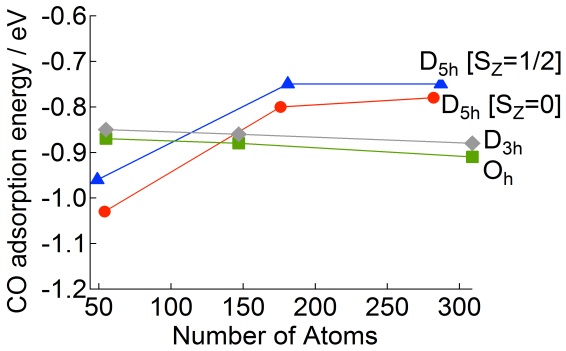

Fig. 2 Size dependence of CO adsorption energy. O_h: single crystal, D_{3h}: single twin (vertex site on grain boundary), D_{5h} [S_z=0 or 1/2]: multiple twin.

The computations were performed using Research Center for Computational Science, Okazaki, Japan.

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