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Titanium-promoted Au–Ti bimetallic nanoparticle catalysts for CO oxidation: A theoretical approach

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ABSTRACT

To solve the problems of deactivation of Au nanoparticle (NP) catalysts, we studied the catalytic activity of 10-atom Au–Ti bimetallic NPs on TiO_2 (1 1 0) supports for CO oxidation by means of density function theory (DFT) calculation with DFT + U method. The calculations showed that Au–Ti NPs were more strongly adsorbed on TiO_2 than Au monometallic NPs. The adsorption energy of O_2 was higher on Au–Ti NPs than on Au NPs, leading to low CO poisoning. The reaction barrier for CO oxidation reaction at interfacial site was lower in the Au–Ti NP system. These results suggest that Au–Ti NPs are a promising catalyst for CO oxidation.

1. Introduction

Unlike inert property of bulk gold, gold nanoparticles (NPs) with size of a few nanometers supported on metal oxide (MO_x) supports show high catalytic activity for the oxidation of small molecules such as CO, even at temperatures below room temperature [1,2]. Since the discovery of the high catalytic activity of gold NPs, numerous studies have been performed to explain this high catalytic activity of gold NPs [3–8]. Although it has not yet fully understood, the interaction between NPs and MO_x is thought to be one of the key factors in the catalytic activity of gold NPs [7,9].

However, the gold NP/MO_x catalyst system has several critical problems that prevent its use as catalysts in CO oxidation. One of these problems is deactivation. The active sites of the system are easily poisoned by CO because of the relatively high adsorption energy of CO than of O_2 [10]. Furthermore, the weak interaction between NP and MO_x supports leads to the agglomeration or detachment of NPs [11]. Both phenomena decrease the activity of the catalyst. In addition, the cost for Au NP catalyst is quite high; Au is as expensive as other noble metals such as Pt, Pd, and Ag.

One way to solve the above mentioned problems is to use bimetallic catalysts [12–15]. Here, we propose the use of Au–Ti bimetallic NPs on a TiO_2 support. We chose Ti as the bimetallic component for the following reasons. First, bimetallic Ti–Pt NP catalysts showed low CO adsorption energy [16,17], which is the main factor in CO poisoning. In addition Ti is more abundant and cheaper than Au. Thus, Au–Ti bimetallic catalysts would be less costly than Au monometallic catalysts.

In this report, we studied the catalytic activity of Au–Ti NP on TiO_2 support system for CO oxidation using density functional theory (DFT) calculations to establish whether the Au–Ti NPs are an applicable catalysts for CO oxidation catalysts. In Section 3.1, we performed DFT calculations on various structures of the NP/TiO_2 system and obtained the most stable structure. Using the final structure, we evaluated the adsorption properties of CO and O_2 molecules for CO oxidation in Section 3.2. Finally, we calculated the energy barrier of the reaction in Section 3.3. As a result, we evaluated the stability and catalytic activity of the Au–Ti bimetallic NP on TiO_2 support.

2. Computational details

Spin-polarized DFT calculations with plane-wave basis sets were carried out using the Vienna Ab initio Simulation package [18–20]. We used the generalized gradient approximation with the PW91 functional to describe the exchange-correlation energy of electrons [21]. Ionic cores were treated by the projector-augmented wave method [21,22]. The plane-wave cut-off was set to 400 eV and the convergence criteria for electronic structure and atomic geometry were 1.0×10^{-4} eV and 0.03 eV/Å, respectively.

To treat the highly localized Ti 3d orbitals, DFT + U method of Dudarev et al. [23] was applied. Using the scheme of Lutfalla's [24],

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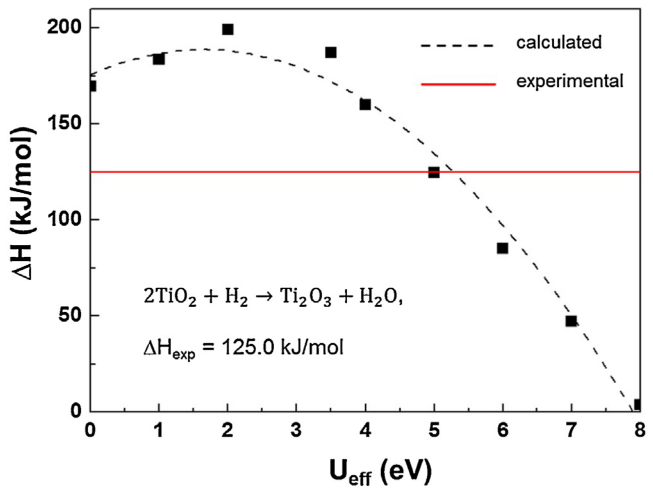

Fig. 1. The effect of U_{eff} on reduction energy of TiO_2 to Ti_2O_3. Black dot is calculated energy, and red line is experimental energy. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the effective U value (U_{eff}) for titanium was calibrated by fitting the energy for the following reduction reaction of rutile TiO_2:

$$2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O \qquad (1)$$

The rectangular unit cell of bulk rutile TiO_2 is composed of two Ti atoms and four O atoms, and the hexagonal unit cell of Ti_2O_3 is composed of 12 titanium atoms and 18 oxygen atoms. We did geometry optimization and calculated energy for bulk TiO_2 and bulk Ti_2O_3 with a $(4 \times 4 \times 4)$ Monkhorst-Pack grid and a $(2 \times 2 \times 2)$ Γ-centered grid, respectively. The experimental reduction energy, 125 kJ/mol [24], is mostly matched for U_{eff} = 5.0 eV, as shown in Fig. 1. This value was used as the optimal U_{eff} value in later calculations.

To study catalytic properties, a rutile TiO_2 (1 1 0) support was modeled by a (4×2) surface unit cell with three tri-layers (O–Ti–O) and 20 Å of vacuum layers as shown in Fig. 2(a and b). The upper two tri-layers were fully relaxed by geometry optimization. Metal NP was prepared on the TiO_2 surface using 10 atoms of Au and Ti: Au_{10}, Au_9Ti_1, Au_8Ti_2, and Au_7Ti_3. A $(2 \times 2 \times 1)$ Monkhorst-Pack grid k-point sampling was used to calculate the total energies of the systems.

The adsorption energy (E_{ads}) of adsorbate A on adsorbent B was calculated by following equation:

$$E_{ads} = E_{A-B} - E_A - E_B \qquad (2)$$

where E_{A-B} is the total energy of the system where A is adsorbed on B, and E_A and E_B are the total energies of A and B each. The transition states (TS) of a CO oxidation reaction were determined with the climbing image nudged elastic band method [25,26].

3. Results and discussion

3.1. Structural stability and electric properties of Au–Ti NPs on TiO_2 support

To identify the stable structures of Au and Au–Ti NPs, we first attached various Au_{10} NP structures on TiO_2 support and relaxed using geometry optimization. We have tested pyramid-like, hemisphere-like, and cage-like initial structures, and the most stable structure was found to be the cage-like structure (Figs. Fig. 2 and 3(a)). From the stable Au_{10} structure, we substituted one of the Au atoms with Ti and again relaxed the structure to obtain the stable Au_9Ti_1 NP structure. The structures of Au_8Ti_2 and Au_7Ti_3 NPs were obtained in a similar fashion. The resulting structures were also cage-like structure, similar to that of the Au_{10} NP (Fig. 3(c and d)). For Au_9Ti_1 NPs, the substitution of Au with Ti in the second and third layers was more unstable than the substitution in the first layer by 1.57 eV and 3.14 eV, respectively. It implies that Ti tends to be close to TiO_2 and interacts strongly with it.

The tendency of interaction can be also seen from the adsorption energy of NPs on the TiO_2 support, as plotted in Fig. 3(b). As the number of Ti atoms in the NP increased, the adsorption energy of the NP became stronger due to the large interaction between Ti and TiO_2. These strong adsorption energies of Au–Ti bimetallic NPs would reduce the degrees of sintering or detachment of NPs from the support [27,28]; thus, Au–Ti NPs would have higher stability than Au monometallic NPs.

We performed Bader charge analysis [28,29] for metal NPs and TiO_2 support (Table 1). The upper two layers of bare TiO_2 support

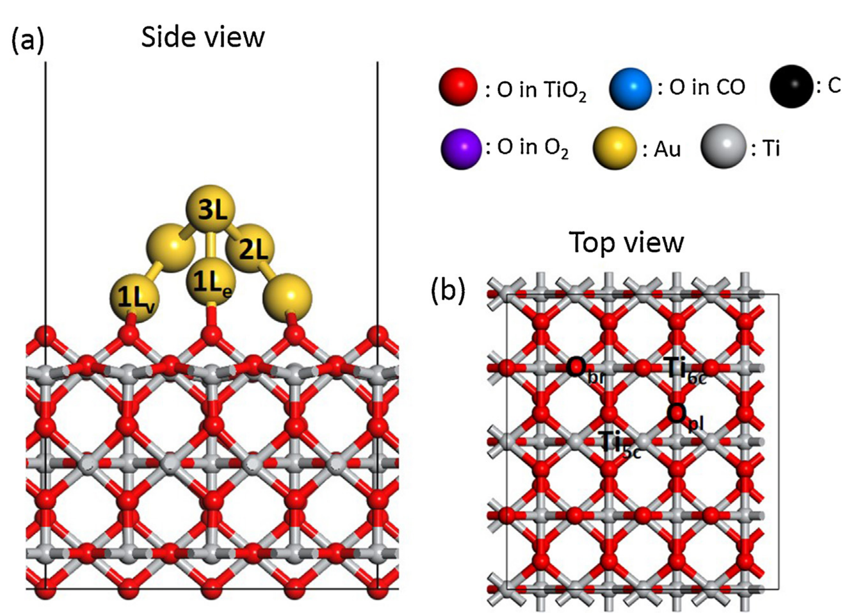

Fig. 2. (a) Side view of our cage-like NP/TiO_2 model and (b) top view of TiO_2 (1 1 0) support. $1L_v$, $1L_e$, 2L, and 3L denote Au atom of 1st layer vertex, 1st layer edge site, 2nd layer, and 3rd layer in metal NP, respectively. Ti_{5c}, Ti_{6c}, O_{br}, and O_{pl} denote fivefold coordinated Ti, sixfold coordinated Ti, bridging O, and in-plane O, respectively.