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Effects of halogens on interactions between a reduced TiO₂ (110) surface and noble metal atoms: A DFT study



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ABSTRACT

Using DFT calculation, we investigate the effects of halogens on the interactions between rutile TiO₂ (110) and noble metal atoms (Au, Ag, Cu, Pt, and Pd). Fluorine, chlorine, and bromine atoms occupy the oxygen defect sites of TiO₂, decreasing the stability of noble metal atoms on the surface. This decrease occurs because the halogens inhibit electron transfer from TiO₂ to the noble metal atoms; the electron transfer from reduced TiO₂ to the noble metal atom stabilizes the noble metal atom adsorption. In contrast, iodine strengthens the interactions between TiO₂ and some noble metal atoms, namely Ag and Cu. This stabilization occurs because of the covalent interaction between iodine-doped TiO₂ and the noble metal atom. Therefore, the stabilization is explained well by chemical hardness. This result suggests that iodine-doping of a TiO₂ surface would be an effective method for the preparation of highly stabilized noble metal clusters.

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1. Introduction

Noble metal clusters and nanoparticles exhibit high catalytic activities for several catalytic reactions when deposited onto selected metal oxides. For example, catalysts used in exhaust gas cleaning rely on Pt, Pd, and Rh nanoparticles deposited onto Al₂O₃, CeO₂, Y-stabilized ZrO₂, and their complex oxides [1–10]. In addition, silver (Ag) and copper (Cu) clusters deposited onto Al₂O₃ have been studied to reduce the use of Pt, Pd, and Rh [3,5,11–14].

Some noble metal clusters possess unique chemical properties that are not observed in the bulk metals. One remarkable example is Au. In bulk, Au is inert and inactive, whereas Au clusters have high catalytic activities [15,16]. However, it is difficult to achieve highly disperse Au clusters onto metal oxides [15,17–19]. Special techniques are required for the preparation of highly dispersed Au clusters on metal oxides, such as the elimination of Cl by neutralization [20–22] or hydrogen reduction [23,24] and the use of special Cl-free Au precursors [25–27].

Experimental results indicate that the presence of Cl inhibits the dispersion of Au clusters onto metal oxides, i.e., Cl enhances the aggregation of nanoscale Au clusters on metal oxides [15,17–19]. No detailed mechanism for this inhibition was known before the mechanism we proposed in previous studies [28–30]. We have recently investigated the mechanism in detail and clarified the effect of the presence of Cl on the interactions between model nanoscale Au clusters and model rutile TiO₂ (110) surfaces using DFT (density functional theory) calculations [28–30]. The calculations confirmed that the presence of a Cl atom in an oxygen defect site on a reduced TiO₂ surface inhibits electron transfer from the TiO₂ surface to Au atoms and decreases the interaction strength between the Au atom and the TiO₂ surface.

Here, we used DFT calculations to investigate whether other halogens (F, Br, and I) show similar effects to that of Cl. We also investigated the effects of halogen addition on the other noble metals because it is advantageous to improve both their dispersion and interaction with metal oxide supports, with the aim of achieving further resource savings and durability improvements [5,6,9,10,31–36]. We considered noble metals including the coinage metals (Au, Ag, Cu), which are same group as Au, and the platinum group metals (Pt and Pd), which is neighbor group of coinage metals, and calculated the properties of each noble metal when co-located with halogens on a metal oxide surface.

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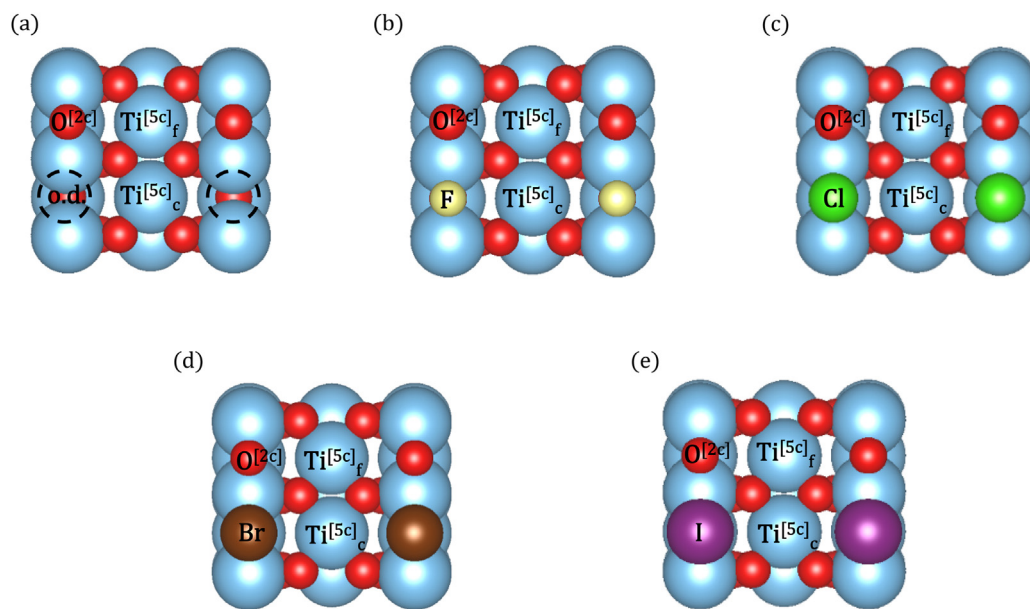


Fig. 1. Model surfaces and notation of atom species of the surfaces. (a) a reduced rutile TiO_2 (110) 1×2 surface, abbreviated as $r\text{TiO}_2$, (b) a fluorine adsorbed $r\text{TiO}_2$ (F- $r\text{TiO}_2$), (c) a chlorine adsorbed $r\text{TiO}_2$, adsorbed $r\text{TiO}_2$ (Cl- $r\text{TiO}_2$), (d) a bromine adsorbed $r\text{TiO}_2$ (Br- $r\text{TiO}_2$), and (e) an iodine adsorbed $r\text{TiO}_2$ (I- $r\text{TiO}_2$).

In this work, we considered the adsorption of noble metal atoms. It may seem that calculations of the adsorption of atoms are not relevant to investigations of the interactions between noble metal clusters and metal oxide supports. In fact, atomically dispersed noble metals are fundamentally different species than even the smallest metal clusters [37–39]; we also assume that distributions of spin and electrons in noble metal clusters cannot be represented by the noble metal atom. Additionally, we argued that the cluster size is crucial to investigations of the CO oxidation mechanism by Au/ TiO_2 catalyst [40]. Thus, the noble metal atom model is unsuitable for investigating the catalysis of the noble metal cluster. However, investigating the adsorption of noble metal atoms onto various sites on the metal oxide surface is important to gain an in-depth understanding of the stability and electronic structure of noble metal clusters on metal oxide surfaces, because the atom-surface interactions are consistent units of the cluster-surface interaction. Furthermore, the atom-surface interactions are important factors in the Ostwald ripening mechanism, which occurs during calcination in the synthesis of supported noble metal catalysts.

2. Computational procedures

2.1. Method

We used the Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation (GGA-PBE) exchange correlation functional [41]. Pure DFT calculations, such as those using GGA-PBE, are generally unsuitable for calculations involving the oxides of 3d metals because they underestimate the destabilization from electron exchange interactions between 3d electrons [42–45]. Despite this fact, GGA-level calculations have been widely used to investigate the Au/ TiO_2 system [12,15,28–30,36,40,46–62], and the calculated results for the adsorption of Au onto rutile TiO_2 correspond well with experimental results [28,55–62]. Therefore, we compared the results by GGA-PBE and GGA-PBE with a Hubbard +U term (known as a DFT+U approach [42], which can estimate the electron exchange interactions between 3d electrons more accurately than GGA). The considered U values for the Ti 3d orbital were

2.0 and 4.0 eV [43,44]. The results of these calculations are discussed in Section 3.1.

The projector-augmented wavefunction (PAW) method [63,64] was used order to describe core electrons. The numbers of valence electrons of Au, Ag, Cu, Pt, Pd, F, Cl, Br, I, Ti, and O were 11, 11, 11, 10, 10, 7, 7, 7, 7, 10, and 6, respectively. Energy cutoff for the wave function was 400 eV, and that of augmented charge was 2400 eV. A $4 \times 4 \times 1$ Monkhorst mesh [65] was used for k -point sampling. All electronic structures, total energies, and stable geometries were calculated by spin-polarized DFT. All DFT calculations were performed using VASP (Vienna Ab-initio Simulation Package), and all geometry visualizations were performed by the VESTA (Visualization Systems for Electronic Structural Analysis) program [66]. The charges on atoms were estimated by Bader charge analysis [67–70].

2.2. Models

Rutile TiO_2 is a common support for heterogeneous catalysts, especially supported Au cluster-based catalysts [15,17–19]. There are many experimental studies of the interface between the noble metal cluster and rutile TiO_2 [15,55–62,71–73], while few similar studies exist for anatase TiO_2 . We, therefore, assumed that the rutile TiO_2 model is more convenient than anatase TiO_2 for use in investigations of the interactions of noble metal clusters and comparison with experimental results. Additionally, the thermal stability of anatase TiO_2 is too low for it to be used as a three-way catalyst. However, rutile TiO_2 has higher thermal stability than anatase and thus may be used as a three-way catalyst. Therefore, we adopted rutile TiO_2 as the model surface in our investigations.

A slab model of the rutile TiO_2 (110) 1×2 surface with one oxygen defect was adopted as a model surface (abbreviated as $r\text{TiO}_2$; Fig. 1(a)); the vacuum region in the super cell is ~ 1.5 nm. There is little interaction between a noble metal atom and the noble metal atom of the neighboring unit cell, and the unit size dependency of the results for Au/ $r\text{TiO}_2$ and Au/Cl- $r\text{TiO}_2$ systems were confirmed in our previous work [28]. The $r\text{TiO}_2$ had 12 atomic layers, and the bottom 3 layers were fixed during geometry optimization to mimic the bulk structure. The halogen-adsorbed model surfaces had a halogen atom adsorbed onto the oxygen defect site; these model surfaces are shown in Fig. 1(b–e). We considered unsat-

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