

Dissertation Abstract

Controlling chemical reactivity of ultrathin oxide film by interface manipulation

(酸化物超薄膜の界面操作による化学反応性の制御)

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How to precisely control the chemical reactivity is one of the longstanding issues in modern chemistry. In particular, in heterogeneous catalysis solid surface has served as a challenging playground of materials design to control chemical reactivity for a long period of time. The precise prediction of chemical reactivity as well as its stability is, of course, the prerequisite of rational materials design. In the progress of catalyst design, the computational method has successfully contributed to describe surface chemical reaction in detail and further to find the effective descriptor of catalytic activity from the accumulated atomic-scale insights.¹

Ultrathin oxide films grown on metal substrate has been the subject of great interest not only as supporting materials for chemically active nanoparticles but also as catalysts in the field of heterogeneous catalysis.² Ultrathin oxide films, such as MgO(100), Al₂O₃(0001), and FeO(111), on metal substrates provide a variety of opportunities to control the chemical and/or physical properties of adsorbates, such as geometric and electronic structures and adsorption energy. Such properties are to depend on (See Figure 1): (i) the charge transfer between adsorbates and oxide-metal interface,³ which is closely correlated with the electronic affinity of adsorbate and change in the work-function, (ii) the adhesion between oxide and metal layers underneath, which could results in strong polaronic distortion,^{4a} (iii) the film thickness,⁴ and (iv) the chemical composition of oxide surface⁵. In particular, the influence of the charge transfer (i) and the adhesion (ii) on the chemical reactivity of oxide film is strongly correlated with the film thickness (iii) and also the changes in electronic distribution and bonding character at the oxide-metal interface. Property of oxide-metal interface is the key to control the catalytic activity of ultrathin oxide film.

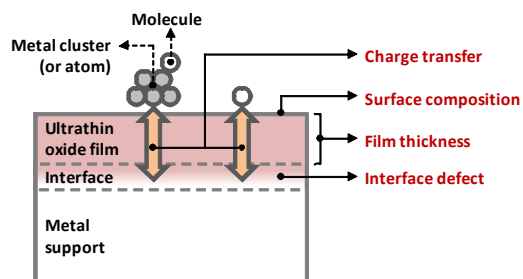


Figure 1. Schematic diagram for controlling the chemical reactivity of ultrathin oxide film supported by metal substrate.

In this study, I investigated water dissociation on ultrathin MgO film supported by Ag(100) substrate as a model reaction by means of first-principles calculation. MgO film can be epitaxially grown on the Ag(100) because of the small mismatch (2.7%) between their lattice constants, and has been considered as the prototype of ionic metal oxides due to its simple geometric and electronic properties.⁶ Water dissociation on the MgO(100) bulk surface has so far been observed to occur only if the dissociation products are stabilized by defects or neighboring water molecules.⁷ Compared with the MgO bulk surface, the chemical reactivity for water dissociation is remarkably enhanced on a single monolayer (ML) MgO film deposited on a Ag(100) surface.⁸ Although the superiority has been experimentally demonstrated, the details of the phenomenon such as how it depends on film thickness or the contribution of defect-free terrace sites as venues for chemical activity have not been clarified. In addition, water splitting for the hydrogen generation has recently been received an increasing level of attraction due to the necessary step of low-temperature water-gas shift (LT-WGS) reaction as well as fundamental scientific interest.

Controlling water dissociation on an ultrathin MgO film by tuning film thickness

Using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, I have demonstrated that the chemical reactivity for water dissociation on an ultrathin MgO film supported by the Ag(100)

substrate depends greatly on film thickness.⁴ The activation energy for water dissociation considerably decreases as the film thickness decreases; these are lower than that of the bulk MgO surface by 29% and 49% for the 2-ML and 1-ML MgO surfaces, respectively (See Figure 2). The thickness dependence, experimentally observed in the water dissociation on MgO film, is qualitatively in good agreement with the computational results, where water dissociation was achieved by vibrational excitation of molecule through inelastic electron tunneling process.^{4b} Also, the further stabilization of the dissociation products by hydrogen bonding between adsorbates would be expected as shown in the partial dissociation of water molecules on bulk MgO surface.^{7a} The enhanced chemical activity for water dissociation on MgO/Ag(100), compared to that achieved with their bulk counterpart, originates from the greater stability of dissociated products, which is due in turn to the strong hybridization of their electronic states at the oxide-metal interface. The geometric change of MgO/Ag(100) during water dissociation is especially interesting at the interface as well as at the surface. Whereas the density of states (DOS) feature, at the oxide-metal interface, for MgO did not change before (S) and after non-dissociative adsorption (A) of the water molecule, the tails of DOS plots broadened into the higher energy region after the water dissociation (D) for the 1-ML and 2-ML MgO films, (See Figure 3). This implies that the interaction between electronic states at the oxide-metal interface has increased for the dissociative adsorption state. It is revealed that the film thickness and the adhesion between oxide and metal substrates are key factors in controlling the heterogeneous catalysis of an ultrathin oxide film supported by a metal substrate.

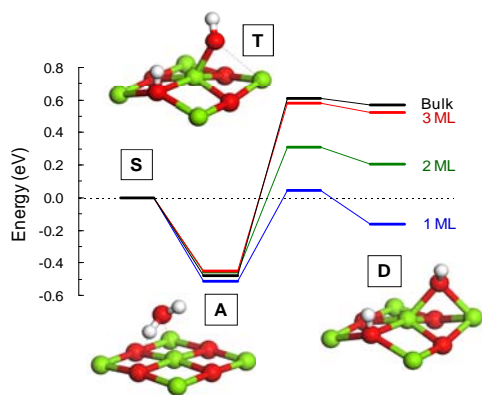


Figure 2. Reaction energy diagram for the dissociation of a single water molecule on MgO(*n* ML)/Ag(100) (*n* = 1, 2, and 3) and MgO(100) surfaces (H, white; Mg, green (grey); O, red (dark grey)).

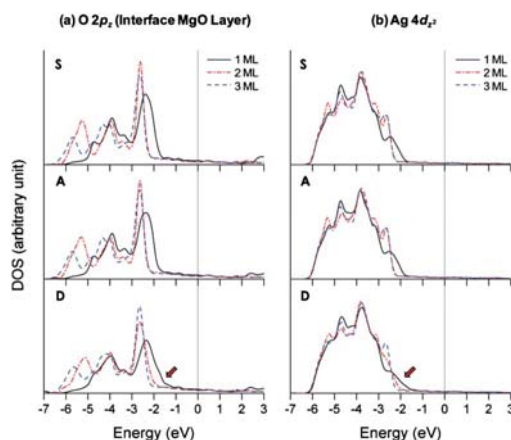


Figure 3. Projected DOS (PDOS) of the *z* component of (a) Ag 4*d* and (b) O 2*p* states for MgO/Ag(100) before water adsorption (S), at a non-dissociative adsorption state (A), and at a dissociative adsorption state (D). PDOS are plotted for the oxide-metal interface region (MgO 1 layer + Ag 2 layers). The Fermi level is set at 0 eV.

Activation of ultrathin oxide film by interface defect for chemical reaction

The interaction between the oxide and metal interface layers remarkably enhances the chemical reactivity of the ultrathin MgO film for water dissociation as compared to that achieved with their bulk counterpart. The manipulation of the local structure at the oxide-metal interface is expected to play a pivotal role in controlling the catalytic activity of oxide film. To fundamentally understand the structure-reactivity relationship concerning the oxide-metal interface, it is important to systematically study how the chemical reaction depends on the kind of irregular interface defects. I have succeeded to reveal that the existence of structural imperfections, such as an O vacancy (*int-O_{vac}*), an Mg impurity (*int-Mg_{imp}*) or an O impurity (*int-O_{imp}*), at the oxide-metal interface improves the chemical reactivity using spin-polarized periodic DFT calculations (See Figure 4).⁹ Figure 5 shows that the adsorption strength of water molecule and the further chemical reactivity of MgO films for water dissociation change as a consequence of the strong charge localization at the oxide-metal interface.

In addition, the calculated work-function for defective MgO films with *int-O_{vac}* is reduced by 0.17 eV compared to ND MgO/Ag(100). While the amount of charge transfer from substrate to adsorbates, i.e., O₂ and H₂O with high and low electron affinities, respectively, does not depend on the existence of *int-O_{vac}*, the non-dissociative

adsorption energy depends strongly on interface defect due to the abovementioned change of charge distribution on the oxide surface. This result implies that the chemical reactions on the ultrathin oxide film surface can be controlled by defects located at the oxide-metal interface, no matter whether the molecules are not activated by the charge transfer from the substrate.

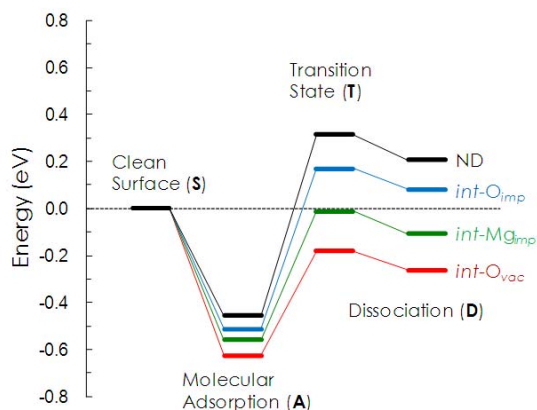


Figure 4. Reaction energy diagram (in eV) for the dissociation of a single water molecule on the non-defective (ND) and the defective MgO/Ag(100) surfaces; $int-O_{vac}$, $int-Mg_{imp}$, and $int-O_{imp}$.

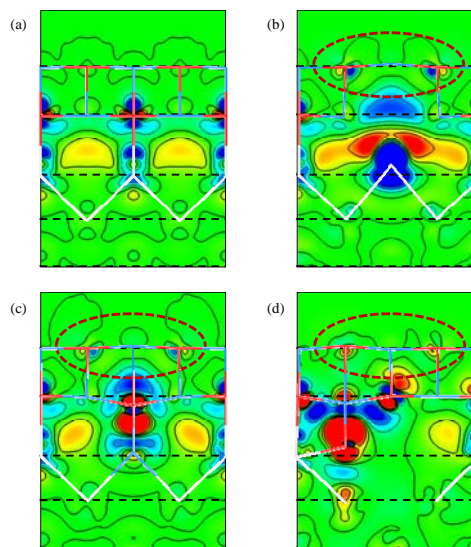


Figure 5. Charge density difference maps for non-defective and defective MgO/Ag(100) models; (a) non-defective (ND), (b) $int-O_{vac}$, (c) $int-Mg_{imp}$, and (d) $int-O_{imp}$. The atomic layers are indicated by black dashed lines.

Finally, in order to find a systematic way for controlling chemical reactivity, I concentrated on the oxide-metal interface with the impurity of the first row transition metal elements (Sc ~ Zn) in the periodic table (See Figure 6). Surface doping or surface alloy technique has been considered as the promising solution to adjust the catalytic properties of the single crystal surface. It is revealed that the single impurity of the metal at the interface is effectively stabilized by the existence of oxide film through the interaction between impurity atom and oxygen, and thus the reactivity can be predicted by the use of crystal (or ligand) field theory (CFT or LFT).¹⁰

In summary, it is revealed that the film thickness and the adhesion between oxide and metal substrates are key factors in tuning the heterogeneous catalysis of an ultrathin oxide film supported by a metal substrate. Defects at the buried interface are also found to play an important role in controlling the chemical reactions. This study not only reveals an ultrathin oxide film as a potential heterogeneous catalyst but also opens a new perspective for the development of techniques for the control and measurement of the interfacial structure of oxide film deposited on a metal substrate.

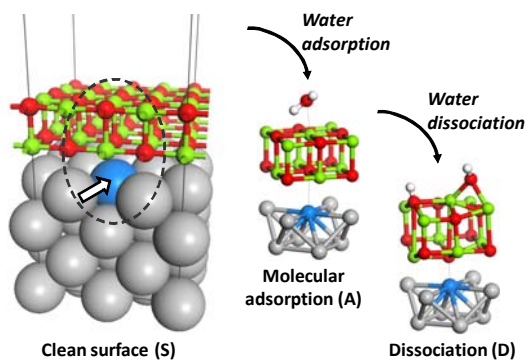


Figure 6. Impurity doping at oxide-metal interface of MgO/Ag(100). (H, white; Mg, grey; O, dark grey)

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