Project Title:
Theoretical study of interaction between tunneling electrons and individual molecules at surfaces

Name: Yousoo Kim, Emi Minamitani, Kenta Motobayashi, Jaehoon Jung, and Seiji Takemoto (Previous member: Hyung-Joon Shin)
Affiliation: Surface and Interface Science Laboratory, Advanced Science Institute, Wako Institute

1. Background and purpose of the project, relationship of the project with other projects.

During the past decade, computer simulations based on a quantum mechanics have developed an increasingly important impact on solid-state physics and chemistry and on materials science. In field of material science, the surface chemistry is fundamentally important to many areas, such as molecular electronics, heterogeneous catalyst, fuel cell, and so forth. The adsorption of molecules on to a surface is a necessary prerequisite to any surface mediated chemical process. Understanding the bonding nature between the molecule and the surface on the basis of the electronic structure is therefore one of the most important issues in this field. The computational methods like density functional theory (DFT) have played a prominent role to elucidate the interaction between the molecule and the surface.

From the theoretical investigation of the adsorbed molecule on surface in combination with STM experiment, we could expect the following research goals: 1) the deep understanding of the chemical/physical properties of an adsorbate on the surface, 2) the fine control of the chemistry on the surface.

2. Specific usage status of the system and calculation method

We have been studying the single molecule adsorption on the well-defined metal surface using computational method in combination with experimental method. In our studies, first-principles simulations have been carried out using the Vienna Ab-initio Simulation Package (VASP) code in the density functional level of theory. The Perdew-Wang exchange-correlation functional has been used and the inner electrons are replaced by projector augmented wave pseudopotentials (PAW). The climbing image nudged elastic band method (CI-NEB) was used to determine the minimum energy paths (MEPs) and the transition states were confirmed by imaginary frequency modes. The projected density of states (PDOS) analysis onto the molecular orbital of adsorbate has been performed in order to clarify the distribution of the molecular states near the Fermi level using the first-principles molecular dynamics program, STATE (Simulation Tool for Atom Technology). STM image simulations were performed using Tersoff-Hamann approach. The computational results have been compared with the available experimental result of our group, such as STM and STM-IETS.

3. Results

(1) State-selective Dissociation of a Single Water Molecule on an Ultrathin MgO Film & Controlling Water Dissociation on an Ultrathin MgO Film by Tuning Film Thickness

The interaction of water with oxide surfaces has drawn considerable interest, owing to its application to problems in diverse scientific fields. Atomic-scale
Insights into water molecules on the oxide surface have long been recognized as essential for fundamental understanding of the molecular processes occurring there. Here, we have performed the STM study of single water molecules on MgO(100)/Ag(100) combined with the first-principles density functional theory (DFT) calculation.

In the STM experiment, the water molecule is adsorbed at atop sites of the Ag(100) surface beneath the 2 ML MgO film, which correspond to Mg$_{2}^{+}$ sites of the MgO surface (Figure 1).

Figure 2 shows the vibrational induced dissociation of water molecule on the 2 ML MgO film. The dissociated products always sit at the bridge site of MgO (Figure 2b).

The existence of density of states (DOS) of an adsorbate near the Fermi energy ($E_F$) is essential for the resonant model of electron-vibration coupling induced by inelastically tunneled electrons (Figure 3).

Figure 4 shows the structures of adsorbates and the reaction energy for the dissociation of a single water molecule on the MgO($n$ ML)/Ag(100) ($n = 1, 2, \text{ and } 3$) and MgO(100) surfaces. The water molecule first adsorbs asymmetrically on top of the surface magnesium, where one hydrogen atom interacts with a neighboring surface oxygen atom via hydrogen
bonding, which is in good agreement with STM image (Figure 1). In addition, Figure 4 clearly indicates that the chemical activity of the ultrathin MgO film is sensitive to film thickness. This implies that catalytic activity on ultrathin MgO films can be controlled by film thickness.

The film thickness dependence of chemical reactivity for water dissociation is closely correlated with both the geometric and the electronic natures of the oxide-metal interface because of (1) the large interface distance allowing severe geometric distortion due to water dissociation (Figure 5) and (2) the strong hybridization of the interface electronic states stabilizing the highly distorted oxide film (Figure 6).

On MgO films of 2 ML thickness, the dissociation barrier of water is 770 meV. Therefore, if vibrational excitation is a driving force for the dissociation of water, we expect that the energy of at least two electron processes is required to overcome the dissociation barrier by the excitation of the \( \nu_{\text{OH}} \) mode (448 meV). In addition, the computationally predicted dependence of chemical reactivity on the film thickness is in good agreement with the the experimental observation in which the water molecules on the 3 ML MgO film cannot be dissociated by the vibrational excitation.
When tunneling electrons flow directly into the LUMO level of water (Right panel of Figure 7), the OH bonds are weakened by the occupation of anti-bonding orbitals, leading ultimately to the dissociation of water. The calculated charge density for the LUMO of water shows that nodal planes are located at the OH bonds, which suggests that the LUMO is strongly involved in splitting a water molecule. The adsorption sites of available dissociation products have been also identified using DFT calculations (Figure 8).

In addition, we could also dissociate water by applying a bias corresponding to the lowest unoccupied molecular orbital (LUMO) energy. When we applied a sample bias voltage of 1.5 V to the water molecule, it splits into dissociated products, as shown in Figure 7.

In summary, two types of dissociation
pathways—vibrational excitation and electronic excitation—are selectively achieved by means of injecting tunneling electrons at the single molecule level, resulting in different dissociated products according to the reaction paths (Figure 9). These two different routes for the controlled dissociation of water molecules using an insulating film as a substrate presents an opportunity that is largely not feasible on metal surfaces. Also, based on our computational results, we propose that the film thickness and the adhesion strength between oxide and metal substrates are key factors in controlling the heterogeneous catalytic activity of an ultrathin oxide film supported by a metal substrate.

The (1×1) surface supercells were employed to describe Fe_{tet1} and Fe_{oct2} terminated Fe_{3}O_{4}(111) surfaces (See Figure 10(a)). Figure 10(b) shows the slab model used in the calculation, which are periodically separated by about 18 Å.

In the experiment, when the surface still contained a small portion of oxygen deficient area even after a cleaning cycle using annealing in O_{2} atmosphere, we also found another type of surface structure (B) right next to the region of the regular termination (A). Figure 11 shows STM images containing such an area. Region A corresponds to the regular termination. It appeared as a hexagonal lattice with any bias voltage in any tip condition. New region marked as B, on the other hand, appears either as a honeycomb structure (Figures 11(a) and 11(c)) or as a hexagonal lattice (Figures 11(b) and 11(d)) depending on the bias (comparison of (a) and (b)) and tip condition (comparison of (c) and (d)). Sites of protrusions in the region A are found to correspond
RICC Usage Report for Fiscal Year 2010

to three of six protrusions forming the honeycomb structure in the region B (Figure 11(a)), but does not correspond to the sites of protrusions of the hexagonal lattice in B (Figure 11(b)).

Figure 11. STM images ((a) and (b) 9 nm × 15 nm; (c) and (d) 10 nm × 10 nm) showing bias and tip dependence of the appearances of two regions. Region A corresponds to the regular termination. Appearance of the region B, either honeycomb or hexagonal lattice, depends both on the bias ((a) and (b)) and on the tip condition ((c) and (d)). Tunneling parameters: (a) $V_{bias} = +2.0\, V$ and $I_t = 0.2\, nA$; (b) $V_{bias} = -2.0\, V$ and $I_t = 0.2\, nA$; (c) and (d) $V_{bias} = -1.0\, V$ and $I_t = 0.2\, nA$.

To verify experimental STM images, we performed STM simulations of surfaces terminated by the Fe$_{tet1}$ and Fe$_{oct2}$ layers. Figure 12 shows the results of the bias voltage ±2 V. For the Fe$_{tet1}$ termination, protrusions at the Fe$_{tet1}$ sites (marked by blue triangles) form hexagonal lattice at both bias voltages. In contrast, for the Fe$_{oct2}$ termination, the Fe$_{oct2}$ sites (red circles) appear bright, forming hexagonal lattice at +2 V, whereas both Fe sites are bright resulting in a honeycomb structure at -2 V.

These results qualitatively agree well with the experimental observation, but only under certain tip conditions (e.g., the tip taking Figure 11(c)). The simple Tersoff-Hamann approach generates STM images using the local density of states (LDOS) of surface. However, because the Tersoff-Hamann approach does not include the tip information such as the chemical composition and the geometry, it is not surprising that the bias dependence is different (sometimes opposite) to the real STM images (e.g., Figures 11(a), 11(b) and 11(d)). The tip that produces different bias dependence from the simulation often yields clearer and sharper images, which is an implication of the chemical modification of the tip apex. Thus it is reasonable that the bias dependence is not completely reproduced by the simulation.

Figure 12. Simulated constant height STM images using GGA and GGA+U ($U = 5\, V$ and $J = 1\, V$) methods. Four images on the left correspond to Fe$_{tet1}$ termination and four images on the right correspond to Fe$_{oct2}$ termination. Sample bias voltages are set to +2V (upper row) and -2V (lower row). Rhombus in each image corresponds to the unit cell. Blue triangle and red circle indicate the Fe$_{tet1}$ and Fe$_{oct2}$ sites, respectively.

Therefore, we have concluded that the regular surface is terminated by a layer of Fe$_{tet1}$ whereas Fe$_{oct2}$ termination appears only in oxygen poor conditions by combined study of STM and first-principles simulations.
4. Conclusion

We have tried to examine the behaviors of single molecules on the metal supported insulating metal oxide surface and the regular termination of transition metal oxide surface using the first principles calculations. First, the vibrational excited dissociation of water molecule on the ultrathin MgO film supported Ag substrate has been successfully explained. Based on the computational results, we have proposed the two factors – the well-defined film thickness and the adhesion energy between oxide film and metal substrate – to design heterogeneous catalyst for water dissociation using a metal-supported oxide film. Second, the regular termination of Fe₃O₄(111) has been confirmed by the STM simulation using the Tersoff-Hanmann method. Our computational study combined with STM experiment shows the benefits of the computational approach to clarify the experimental results and to give a light for further experiments, especially, at the single molecule regime on the surface and at the surface structure verifications.

5. Schedule and prospect for the future

Ultrathin oxide film grown on metal substrate has been a subject of great interest not only as a supporting material for chemically active nanoparticles but also as a catalyst in the field of heterogeneous catalysis, where it provides various ways to control the properties of adsorbates via following factors (See Figure 13): (i) charge transfer between adsorbates and oxide-metal interface, which is closely correlated with the electronic affinity of adsorbate and workfunction reduction, (ii) adhesion between oxide and metal layers with strong polaronic distortion, (iii) film thickness, and (iv) the chemical composition of oxide surface.

Therefore, we will continue our work to find the way for controlling the chemical reactivity using theoretical and experimental studies. From the previous result, we expect that the chemical and physical modification at the oxide-metal interface can open the new way to control the chemical activity of oxide film.

6. If you wish to extend your account, provide usage situation (how far you have achieved, what calculation you have completed and what is yet to be done) and what you will do specifically in the next usage term.

- Completed researches

(The members registered as the user of RICC system in FY2010 are indicated by underline.)

(1) State-selective Dissociation of a Single Water Molecule on an Ultrathin MgO Film (H.-J. Shin, J. Jung, K. Motobayashi, S. Yanagisawa, Y. Morikawa, Y. Kim, and M. Kawai)

(2) Controlling Water Dissociation on an Ultrathin MgO Film by Tuning Film Thickness (J. Jung, H.-J. Shin, Y. Kim, and M. Kawai)

(3) Termination and surface species of the
magnetite (111) surface studied by scanning tunneling microscopy (T. K. Shimizu, J. Jung, H. S. Kato, Y. Kim, and M. Kawai)

- Research plan for FY2010

1. Doping effect on water dissociation on the metal supported oxide film surface.
2. Role of oxide-metal interface on the behavior of water film on the MgO/Ag(100) surface.
3. Hoping of CO molecule on MgO/Ag(100) surfaces.
4. Electron states of Phthalocyanine molecules on Au(111) surface.
5. Analysis of Kondo effect in adsorbed molecules.
6. DFT-based STM simulation using NEGF method.
7. Electronic structure of CNT/Metallic surface.
8. Electronic structure of graphene system.

7. If you have a “General User” account and could not complete your allocated computation time, specify the reason.

We have used about 50% of the assigned CPU resources to us. This was partly because of the overestimation of computational time, but mostly because of the reconsideration of research plans according to the publication process and corresponding experimental schedule during the fiscal year. For example, the study about the adsorption properties of benzene derivatives on Cu surface was cancelled due to the change of research environment, such as the report of other research group. Therefore, we will adjust both the computation time per one project and the number of project per one member for FY2011 based on more detailed research planning.
Fiscal Year 2010 List of Publications Resulting from the Use of RICC

* The members registered as the user of RICC system in FY2010 are indicated by underline.

[Publication]


[Oral presentation at an international symposium]


