Single Molecule Chemistry on an Ultrathin Oxide Film Surface

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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. We 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 and be enhanced compared to that achieved with their bulk counterpart using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations [1]. The change of chemical reactivity of ultrathin MgO film depending on the film thickness can be explained by the strengthening of the interaction between the oxide and metal interface layers [2]. This result implies that the artificial 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. We have also examined and compared the water dissociation on three model systems with defects at the oxide-metal interface of the 2-ML MgO/Ag(100) – an O vacancy (Fig. 1a), an Mg impurity or an O impurity – with the case of on the MgO film without defects using periodic DFT calculations [2]. Our results clearly show that such structural imperfections at the interface can improve the chemical reactivity of the MgO film supported by an Ag substrate. This is closely correlated with the accompanied change of charge distribution of the oxide surface due to the accumulation of transferred charge density at the interface (Fig. 1b). In addition, the chemical reactions on the ultrathin oxide film surface can be tuned by interface defects regardless of the charging of adsorbates.

In this talk, a recent result of coupling between molecular vibration and surface phonon in the CO hopping process on MgO/Ag(100) with tunneling electrons will also be introduced [3].

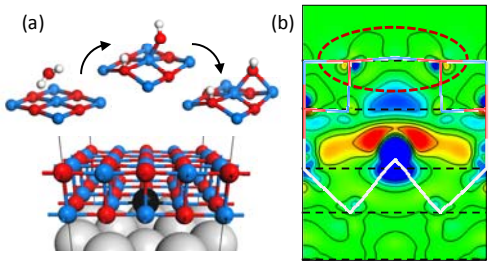

Figure 1. (a) Water dissociation on MgO/Ag(100) with interface O vacancy and (b) charge density difference map.

[1]. H.-J. Shin, J. Jung, K. Motobayashi, S. Yanagisawa, Y. Morikawa, Y. Kim, and M. Kawai, *Nat. Mater.* **9**, 442 (2010).
[2]. J. Jung, H.-J. Shin, Y. Kim, and M. Kawai, *Phys. Rev. B* **82**, 085413 (2010); *J. Am. Chem. Soc.* **133**, 6142 (2011); *J. Am. Chem. Soc.* **134**, 10554 (2012).
[3]. H.-J. Shin, J. Jung, M. Kawai, and Y. Kim, submitted.