

## III-L In-Situ Observation of Surface Reactions by Variable Temperature Scanning Tunneling Microscopy

Chemical reaction at a well-defined single crystal surface has been intensively investigated as a prototype for heterogeneous catalytic reaction, electrochemical reaction and corrosion. The surface chemical reactions are heterogeneous in nature reflecting the structural and electronic imperfections relevant to steps, vacancies and impurities. In addition, the surface reactions are significantly influenced by the presence of reactants and products which often form ordered arrays. Therefore, in order to get better understanding of the surface reactions, it is vital to unravel the nature of these local properties which are closely linked to chemical reactivity of the surfaces reactions. Advent of scanning tunneling microscopy (STM) has enabled us to tackle the challenge with the ability to image the surface reactions in both real-time and real-space with atomic resolution. We investigate the reactivity of novel one-dimensional (1D)  $-Ag-O-Ag-O-$  compounds formed upon the dissociative adsorption of oxygen molecule on Ag(110) by the use of variable temperature scanning tunneling microscopy (VT-STM). The 1D compounds are arranged periodically to form  $(n \times 1)-O$  ( $n = 2-7$ ) reconstructed structures in which their mutual distance changes in self-organized manner depending on the O coverage. In addition, 1D compounds show structural fluctuation in the low O coverage regime reflecting the low dimensionality. These intriguing characteristics make them promising as a model system to explore physical and chemical properties of nano-structured materials.

### III-L-1 In-Situ Observation of Chemical Reaction of the 1D Compounds with CO on Ag(110)

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The reduction of O adatoms of the 1D compounds with CO was investigated by using VT-STM. STM measurements were performed as titration measurements by first preparing the  $(6 \times 1)-O$  surface and then reacting O adatom with CO to form  $CO_2$  that desorbs immediately after the reaction at constant temperatures at 180–208 K. STM images of the same region were sequentially taken in the constant current mode using an electrochemically etched W tip under the CO pressure of  $3 \times 10^{-8}$  mbar. In order to reduce tip-surface interactions, a high tunneling resistance of  $> 1$  G $\Omega$  was used. From sequential images, it is found that the reactivity of O adatoms at the ends of 1D compounds is so high that the reaction occurs only at the ends. Reflecting the specific reactivity of O adatoms at the ends of 1D compounds, the O coverage is decreased linearly with the progress of the reaction. From the temperature dependence of the slopes of the titration curves together with the reaction model, the activation barrier was estimated to be 39.2 kJ/mol.

### III-L-2 Real-Time Observation of the Spatial Propagation of Reaction Front with Atomic Resolution: $H_2O + O \rightarrow 2OH$ on Ag(110) $(6 \times 1)-O$

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Interaction of  $H_2O$  with solid surfaces is important in broad spectrum of scientific fields ranging from meteorology to heterogeneous catalysis. The adsorption of  $H_2O$  on  $(n \times 1)-O$  has been studied extensively, and various adsorbed states are reported such as chemisorbed  $H_2O$ , multilayers,  $(OH)(H_2O)_n$ ,  $(OH)_2H_2O$  and

OH species. However, the reaction kinetics and the influence of these species on the kinetics are unknown. STM measurements were made for the structural variation occurring over the course of the reaction of O adatoms in the 1D compounds with  $H_2O$  at 175 K. While chemisorbed  $H_2O$  molecules and hydrogen-bonded  $H_2O$  clusters exist transiently at 175 K, formed OH species remain on the surface stably and form  $(OH)(H_2O)_n$  and  $(OH)_2H_2O$  clusters as a nucleation center. STM images of the same regions were sequentially acquired in the constant current mode using an electrochemically etched W tip under the  $H_2O$  pressure of  $1 \times 10^{-9}$  mbar. Sequential STM images revealed that the reaction is highly nonlinear such that the reaction proceeds explosively with propagating reaction front after an induction period. In the induction period the reaction occurs only at the ends of 1D compounds similar to the reaction with CO. The reaction front propagates on the surface like a tidal wave irrespective of surface steps and impurity islands with the velocity of 1 nm/sec. The reaction model is proposed that the formed OH species play a role of catalyst as follows: OH species act as a nucleation center to form  $H_2O$  clusters. Clustering of  $H_2O$  increases the local coverage of  $H_2O$  by extending the residence time and enhances the reactivity of  $H_2O$  located at the periphery of the cluster as a proton donor.