

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

Chemical reactions 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 catalytic activity. The 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) using variable temperature STM (VT-STM). The 1D compounds are arranged periodically to form  $(n \times 1)$  ( $n = 2-7$ ) reconstructed structures. In addition, the 1D compounds show structural fluctuation in low O coverage regime reflecting the low dimensionality. These characteristics make them promising as a model system to explore physical and chemical properties of nano-structured materials.

### III-I-1 In-Situ Observation of CO Oxidation on Ag(110)(2x1)-O by Scanning Tunneling Microscopy: Structural Fluctuation and Catalytic Activity

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On the added-row reconstructed Ag(110)( $n \times 1$ )-O surfaces where one-dimensional –Ag–O–Ag–O– chains arrange periodically, the clean-off reaction of O adatoms by CO was investigated using variable temperature scanning tunneling microscopy (VT-STM). Based on the *in-situ* STM observations of the surface structure variation in the course of the reaction at various temperatures, we found that the reaction kinetics are significantly affected by the structural transition of AgO chains from a solid straight line configuration to dynamically fluctuating configurations. Below 230 K where the chains are straight, the reaction takes place only at the end of the chains, so that the reaction progresses in the zeroth order kinetics with the reaction front propagating along the chain. The temperature dependence of the reaction rates yields the activation barrier of 41 kJ/mol and the pre-exponential factor of  $1.7 \times 10^3 \text{ cm}^{-2}\text{s}^{-1}$ . At room temperature, the reaction rate is drastically accelerated when almost half of O adatoms are eliminated and the chains start fluctuating. The dynamic formation of active sites equivalent to the end of chains upon the chain fluctuation results in the nonlinear increase of the reaction rate.

### III-I-2 Propagation of Reaction Front in the Disproportionate Reaction of H<sub>2</sub>O on Ag(110)(5x1)-O Surface: Role of Hydrogen Bonding Interaction

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The structural evolution in the course of the disproportionation of H<sub>2</sub>O with O adatoms in the added-row reconstructed Ag(110)-O surfaces was investigated by variable temperature scanning tunneling microscopy. Initially, the reaction takes place only at the ends of the added-rows, and then, after the induction period, the reaction progresses explosively with the reaction front propagating at the rate of 1 nm/s. The strong non-linearity can be explained by the autocatalytic reaction model where clustering of H<sub>2</sub>O by the hydration of OH makes both H<sub>2</sub>O coverage and reactivity of H<sub>2</sub>O sufficiently high that a new reaction pathway opens to drive the reaction front.