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学 位 論 文 題 目 Chemical reactivity of oxygen induced one-dimensional  
sur f ace compounds on Ag(110) studied by variable  
temperature scanning microscopy

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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 and electronic states. 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. 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.

In this thesis, chemical reactivity of the novel quasi one-dimensional compounds formed on Ag(110) has been investigated by tracing the surface structural variation with variable-temperature STM(VT-STM) accompanied by the following thermal and photo-induced reactions: (1)the reaction of O adatoms in the 1D compounds with CO( $\text{CO}_{(\text{gas})} \rightarrow \text{CO}_{(\text{ad})}$ ,  $\text{CO}_{(\text{ad})} + \text{O}_{(\text{ad})} \rightarrow \text{CO}_{2(\text{gas})}$ ), (2)photo-induced elimination of O adatoms( $\text{O}_{(\text{ad})} + \text{photon} \rightarrow \text{O}^*_{(\text{ad})}$ ,  $\text{O}^*_{(\text{ad})} + \text{C}_{(\text{ad})} \rightarrow \text{CO}_{(\text{ad})}$ ,  $\text{CO}_{(\text{ad})} + \text{O}_{(\text{ad})} \rightarrow \text{CO}_{2(\text{gas})}$ ) and (3)the reaction of O adatoms in the 1D compounds with  $\text{H}_2\text{O}$ ( $\text{H}_2\text{O}_{(\text{gas})} \rightarrow \text{H}_2\text{O}_{(\text{ad})}$ ,  $\text{H}_2\text{O}_{(\text{ad})} + \text{O}_{(\text{ad})} \rightarrow 2\text{OH}_{(\text{ad})}$ ). We identified the active sites of these reactions where the reaction occurs preferentially and moreover elucidated the correlation between their microkinetics and the surface structural variation.

## 1. Microkinetics of CO oxidation on Ag (110) (2x1)-O: structural fluctuation and chemical reaction

The identification of active sites is crucial for an atomic-scale understanding of surface catalytic reactions. Defects such as steps, kinks and vacancies are some examples of active sites. In addition, the formation of ordered arrays of adsorbates affects surface reactions with some reactions occurring preferentially at the peripheries of these structures. The fluctuating configurations of these low-dimensional structures can be thermodynamically favorable at finite temperatures, because the energy gain overcomes the energy cost that accompanies local structural fluctuation. In particular, 1D systems have a propensity to be sensitive to these fluctuations. Thus, the dynamical formation of active species and sites by these fluctuations is a key factor in establishing a microscopic model for chemical reactions at surfaces and nano-structured materials such as metal clusters, macromolecules and proteins.

The dissociative adsorption of molecular oxygen on Ag (110) forms novel quasi 1D surface compounds of  $-\text{Ag}\cdot\text{O}\cdot\text{Ag}\cdot\text{O}\cdot$  running along the [001] direction. These AgO chains arrange periodically in the self-organized manner to form ordered structures of  $(7 \times 1)\cdot\text{O}$

to  $(2 \times 1)\text{-O}$  depending on the O coverage. The AgO chains show the structural fluctuation at low O coverage regions reflecting their quasi one-dimensionality. While the AgO chains appear as rigid straight lines in the  $(2 \times 1)\text{-O}$  structure at room temperature, the structure fluctuate to appear as segmented and sometimes “frizzy” chains in the  $(n \times 1)\text{-O}$  structures ( $n > 4$ ). Energetically-equivalent structures of different configurations of segments exist, reflecting the 1D nature of the chains. Thus, chains fluctuate between configurations rather than freezing into a single configuration, and consequently segmented or frizzy chains are observed. The AgO chain is a good system for investigating the effects of structural fluctuation on reactivity.

By using VT-STM, we have conducted systematic investigations about the temperature dependence of the structural fluctuation of chain, the identification of the active site for the reaction, and the influence of the structural fluctuation on the reaction. Major findings are as follows.

(1) The structural fluctuation is very susceptible to temperature as expected. The degree of fluctuation is reduced with the decrease of temperature and is frozen below 250K because of the decreased contribution from the entropic term.

(2) From the titration measurements of the CO reaction carried out at 180~208K where the fluctuating chain is frozen into straight chain, it was found that the reaction occurs only at the ends of the chains and follows the 0th order reaction kinetics. These indicate that the O adatom at the site is highly reactive. The activation barrier and the pre-exponential factor were estimated to be 41kJ/mol and  $1.7 \times 10^3 \text{cm}^2 \text{s}^{-1}$ , respectively.

(3) The reaction kinetics at room temperature show strong nonlinearity in contrast to the reaction at 180~208K. The in-situ STM measurements were performed as titration measurements by first preparing the  $(2 \times 1)\text{-O}$  structure and then removing O as  $\text{CO}_2$  using CO at room temperature. We found that the reaction kinetics show strong nonlinearity that the reaction rate measured is accelerated in the lower O coverage range where fluctuating AgO chains appear. In addition, the reaction rate is almost constant on the C-containing surface where the chains are bundled to appear as rigid paired ones even at very low O coverage where fluctuating chains are observed on the clean surface. Combined with the Ising model calculations, the kinetics of this reaction are explained by the dynamical formation of active O adatoms in the fluctuating AgO chains. It is an old idea on surface reactions that the rate of a reaction should increase in the range of fluctuations, but so far there have been no direct proof for this proposition. By tracing reaction rate of CO oxidation on Ag (110)  $(2 \times 1)\text{-O}$  combined with the simulation based on the Ising model, we have given the direct and convincing proof for this proposition for the first time.

## 2. Photo-induced oxygen elimination reaction

The surface photochemical events are closely connected with lifetimes of photo-excited states in adsorbate-surface complex. In general, the compounds strongly interacting with

electronic and lattice systems of the substrate likely have shorter lifelines. It is interesting to investigate the photochemical reactions of strong interacting surface compounds such as the 1D AgO chain. Recently, the systematic investigation of photo-induced oxygen elimination revealed the property of this reaction as follows.

(1) the reaction does not take place on a clean Ag (110) surface, i.e., carbidic C adatoms identified by AES are necessary for the photochemistry. (2) O adatoms are removed as CO<sub>2</sub>. (3) the reaction proceeds via substrate-mediated excitation. However, the active site for the reaction is unclear. The STM observation provides complementary information which help construct microscopic model for the photo elimination reaction.

STM observation revealed that the ultra-violet irradiation leads the conversion of (2x1)-O to (4x1)-O and (6x1)-O with the fragmentation of the chains. Based on these results, we have made a microscopic model of the photo elimination as follows: an O adatoms is excited by the substrate absorption of UV photon and then reacts with a neighboring carbidic C adatom CO that is further oxidized to desorb as CO<sub>2</sub>.

### 3. The reaction of H<sub>2</sub>O with O atom in AgO chain: autocatalytic process and the propagation of the reaction front

The surface structural change during the reaction of H<sub>2</sub>O with the AgO chains was measured at 175K by the use of VT-STM. Initially, the reaction proceeds slowly reflecting that the reaction occurs only at the ends of the chains. After this induction period, the OH formation proceeds in the autocatalytic manner with a reaction front that propagates like a tidal wave irrespective of surface steps and impurity islands. We proposed that the reaction model involving the process where produced OH species play as a catalyst as follows: (1) The OH species make clusters of H<sub>2</sub>O as nucleus center of longer residence time to increase the H<sub>2</sub>O coverage. (2) Clustering enhances the reactivity as a proton donor of H<sub>2</sub>O in the transition state via hydrogen bonding interaction between OH and H<sub>2</sub>O.

The spontaneous formation of periodic stripe pattern was observed at room temperature under the dynamic equilibrium between the surface and gas phases through the formation and recombinative desorption of OH ( $\text{H}_2\text{O}_{(g)} + \text{O}_{(ad)} \rightleftharpoons 2\text{OH}_{(ad)}$ ). The (2×1)-O and OH phases self-assemble alternatively to form the stripe pattern. In general, the boundary increases the surface energy and the stripe pattern considering of alternating domains is unfavorable. It was proposed that the difference in the surface of both phases is likely responsible for formation.

## 論文審査結果の要旨

固体表面における化学反応は典型的な不均一反応であり、表面反応の理解には反応の活性点や反応に伴う表面構造の時間発展を原子レベルで調べる必要がある。これまで表面欠陥、ステップ、吸着した原子・分子集団が構成する特殊な反応場、などが活性点の候補として提案されてきた。しかしながら、このような局所構造と反応の相関が明らかになってきたのでここ数年のことである。出願者は、このような背景の下に、原子分解能を有する走査トンネル顕微鏡(STM)を用いて Ag(110)表面に酸素分子が解離吸着して生じる 1次元鎖化合物と CO 及び水との反応を観察し、反応活性点の道程、熱揺らぎによる活性点の動的生成が反応速度に与える影響の解明、反応端が化学波となって表面上に伝播していく様子の観察、などを行った。6 勝からなる審査請求論文は、以上の実験的研究成果をまとめたもので、主な実験結果は 3 章～5 章に述べられている。

3 章では、1次元鎖の酸素原子が CO と反応して CO<sub>2</sub> を生成する反応についてまとめられている。反応の進行に伴う表面構造変化を STM により追跡し、(1)1次元鎖内部の酸素原子に比べて、鎖の端に位置する酸素原子の反応活性が圧倒的に高く、熱構造揺らぎが抑えられる低温では反応が 0 次で進行すること、(2)室温では、熱構造揺らぎにより反応活性点である鎖の端の酸素原子が動的に生成し反応速度が増大すること、などを見出した。また、1次元鎖内及び鎖間の相互エネルギーを取り込んだイジングモデルを用いて、揺らいだ鎖の平均構造を導出し、反応速度と比較することで 1次元鎖を特徴付ける相互作用エネルギーを見積もっている。特に、(2)の結果は、イジングモデルによる解析と併せ、熱構造揺らぎにより反応活性点が動的に作り出され反応に大きな影響を与えることを具体的に示した初めての例であり、表面反応だけでなく、有限温度で構造揺らぎが頻繁に起こるクラスターや生体マクロ分子などの少数多体系における反応を考える上でも重要な成果として高く評価される。

4 章では、炭素不純物を微量に含む表面における 1次元鎖光誘起消失反応を STM で観察した結果がまとめられている。反応の進行により、1次元鎖がぶつ切りになる様子が観察され、炭素原子近傍の光励起された酸素原子が炭素と反応して CO を生成し、CO は近傍の酸素原子と反応し CO<sub>2</sub> となり鎖が消失するモデルを提案した。

5 章では、1次元鎖の酸素原子と水から水酸基が生成する反応を STM で観察した結果が述べられている。CO との反応と同様に鎖の端の酸素原子が活性点であることを明らかにした。これを加えて、反応が誘導期の後、爆発的に進行することを見出した。未反応の領域と反応した領域の境界が、波のように表面上を伝播する様子を観察することに成功した。反応の急激な進行と反応端の表面伝播は、生成した水酸基が殻になって水のクラスターが生成し、単独の水分子に比べてクラスター内の反応活性が水素結合により増大したためであるとし、生成物である水酸基が触媒として働いていることを述べている。原子レベルで反応端の伝播を捉えた例は、本研究を含めて 2 例しかなく、また、生成物が反応速度に与える影響を示した例としても非常に重要な成果といえる。

本論文は、従来得られなかった新規性の高い重要な発見を行っており、その現象の解析についても詳しい議論がなされている。したがって、そのオリジナリティは高く、博士論文として十分な質を備えたものと判断した。