Role of Structural Fluctuation in a Surface Reaction Studied by Scanning Tunneling Microscopy: The CO + O → CO_2 Clean-Off Reaction on Ag(110)-(2 × 1)-O

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The kinetics of the clean-off reaction of O adatoms by CO on Ag(110)-(2 × 1)-O is investigated by scanning tunneling microscopy. The reaction is accelerated in the lower O coverage range where AgO chains with ($n \times 1$) ($n \geq 4$) configurations show significant structural fluctuation. Simulations based on the Ising model are used to provide a quantitative understanding of the acceleration, which originates from the dynamical formation of active O adatoms by fluctuation of AgO chains.

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The identification of "active sites" where reactions occur preferentially is crucial for an atomic-scale understanding of surface catalytic reactions. Defects such as steps, kinks, and vacancies are some examples of active sites [1]. The scanning tunneling microscopy (STM) study of Zambelli *et al.* [2] showed that the dissociation of NO on Ru(0001) takes place only at atomic step sites. In addition, the formation of ordered arrays of adsorbates affects surface reactions as shown in recent STM works [3–7], 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, one-dimensional (1D) systems have a propensity to be sensitive to these fluctuations as described by one of the maxims of condensed matter physics: *one chain does not make a crystal* [8]. 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 nanostructured compounds. Although STM has allowed us to observe such behavior during surface reactions, no clear evidence linking fluctuations to reactions has yet been obtained.

It is well known that the adsorption of O on (110) surfaces of fcc metals often results in the formation of quasi-1D structures accompanied by the mass transfer of substrate atoms [9]. The reactions of CO with O in such quasi-1D structures formed on Rh(110) [3] and Cu(110) [4] have been studied by STM, with O found to be highly reactive at the edges of these structures. However, these structures are so rigid that they are not good candidates for proving the above proposition. The -Ag-O-Ag- chains formed on Ag(110) are more promising. AgO chains arrange periodically to form ($n \times 1$) ($n = 2$–7) depending on the fractional O coverage, θ_O, due to repulsive interchain interactions [10–12]. While the chains appear as rigid straight lines in the (2 × 1) structure at room temperature (RT), the structures fluctuate to appear as segmented and sometimes "frizzy" chains in the ($n \times 1$) ($n \geq 4$) structures [12]. 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. Therefore, AgO chains on Ag(110) is a good system for investigating the effects of structural fluctuation on reactivity.

We focus on the clean-off reaction of O adatoms with CO on the Ag(110)-(2 × 1)-O surface. By directly monitoring reaction progress by STM, the time variation of θ_O is measured as a titration curve, and this is found to exhibit a drastic acceleration of the reaction in the lower θ_O range. Simulations based on the Ising model enable us to obtain a quantitative understanding of the acceleration, which originates from the dynamical formation of active sites by segmentation of AgO chains.

Experiments were performed in an ultrahigh vacuum chamber equipped with a variable-temperature STM (Omicron). A clean Ag(110) surface was prepared by standard procedures [13]. STM measurements were performed as titration measurements by first preparing the (2 × 1)-O structure and then removing O adatoms using CO at RT and 100 K. STM images of the same region were sequentially taken in the constant current mode using an electrochemically etched W tip under CO pressures. A high tunneling resistance of ≥ 1 GΩ was used to reduce tip-surface interactions. Observations for a C-containing surfaces ($\theta_C \sim 0.1$) were also made for comparison. Chains were found to bundle to form local (2 × 1)-O domains, even for low θ_O, in contrast to the behaviors on clean surfaces [14]. Oxidation of CO on O-covered Ag(110) proceeds according to the Langmuir-Hinshelwood mechanism [15,16], with CO adsorbates having enough mobility to migrate to the location of the tip. Thus, shadowing by the tip is not important in terms of relative reaction rates.

Structural changes in AgO chains over the course of the clean-off reaction at RT are substantially different on clean and C-containing surfaces, as can be seen in Fig. 1. The (2×1)-O phase prepared on the clean surface changes to (4×1) and (6×1) structures as the reaction progresses. This is the reverse of the structural changes occurring upon adsorption of O. Note that the AgO chains in the (6×1) structure were observed to bend and fluctuate as previously reported [12]. In contrast, local (2×1)-O domains remain on the C-containing surface throughout the reaction, while the space between domains increases as reaction progresses. The morphology of the step edges changes after the removal of O adatoms, indicating that the Ag adatoms that form on the terraces through the reaction migrate to the step edges.

A noticeable difference is also observed in the titration curves for the clean surface compared to the C-containing surface [Fig. 1(h)]. Initially, the reaction proceeds gradually on both surfaces, but accelerates suddenly on the clean surface at $\theta_O \sim 0.2$. A similar change in the reaction rate has been observed previously [10,17,18]. Note that the segmented chains appear around this θ_O. In contrast, variations in the reaction rate are not remarkable for the C-containing surface. This suggests that the acceleration is caused by structural changes including fluctuations of the chains. Least-squares fits of the titration curves were made by assuming second-order kinetics, $-d\theta_O/dt = r\theta_O\theta_{CO} = r\Gamma P\theta_O(1 - \theta_O)$, where r, Γ, and P are the rate constant, CO sticking coefficient, and CO pressure, respectively. However, this is unable to reproduce both of the curves. Deviations in the clean surface are remarkable, especially in the low θ_O region where the reaction accelerates.

STM observations at low temperatures were able to clarify the location of active sites and the detail of the progress of the clean-off reaction. Figure 2 shows a sequence of STM images taken at 100 K where reactions were confirmed to have occurred by a thermal desorption study [13]. Exposing the (2×1)-O structure prepared on the clean surface to CO leads to the formation of 1D brighter stripes. The 1D stripes grow all the way across the terrace from one step edge to the other. As the heights of the stripes are almost the same as that of a single atomic step of Ag(110), these stripes are associated with aligned Ag adatoms that are left behind after the removal of O from the AgO chains. These results indicate that reactions occur only at the end of the chain and proceed one-dimensionally.

Higher reactivities at the ends of the chains can be explained by differences in the bonding configurations of O in the chain. If the chain terminates with O, this oxygen should be highly reactive because it is not sandwiched between two Ag adatoms and is directly exposed to CO. Thus, this reacts first, with the O adatom in the A site (denoted as O_A below) then remaining [Fig. 2(h)]. The Ag-O bonding configuration of O_A relaxes differently from that inside the chain because the Ag atom at the end of the chain is bonded only to the O_A. This may make the O_A slightly less bound and more reactive.

Let us consider a reaction scheme for explaining the acceleration observed at RT for a clean surface. The marked difference in AgO structure between the clean and C-containing surfaces is that the chain structures fluctuate in segments on the clean surface, in contrast

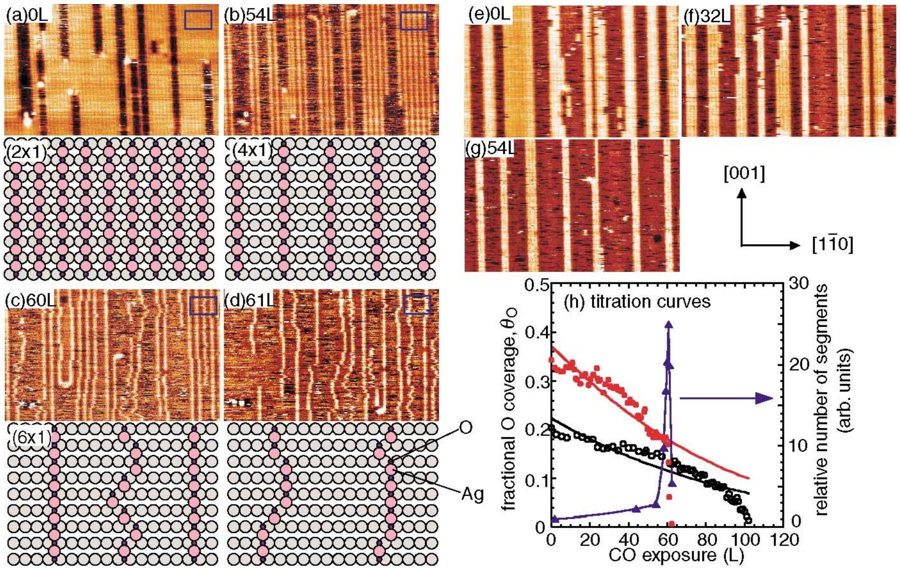

FIG. 1 (color). Two series of STM images of 37×27 nm^2 continuously taken at RT under a nominal CO pressure of 1×10^{-8} torr for clean [(a)–(d)] and C-containing [(e)–(g)] surfaces ($I_t = 0.2$ nA, $V_{tip} = 1.4$ V). 1 L = 1×10^{-6} torr s. Schematic models of the regions marked by blue rectangles are also shown for (a)–(d). (h) Titration curves obtained for both clean (red solid circles) and C-containing (empty circles) surfaces. Thick red and black curves are the least-squares fits obtained by assuming second-order kinetics. The relative number of segments for the clean surface is also plotted (blue triangles and curve).

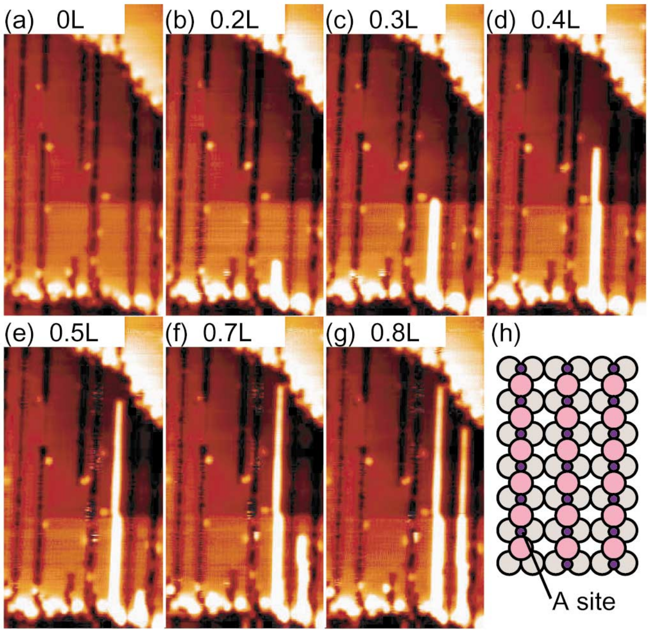

FIG. 2 (color). (a)–(g) A sequence of $20 \times 50\ \mathrm{nm}^2$ STM images taken at 100 K under a nominal CO pressure of 5×10^{-10} torr ($I_t = 0.2$ nA, $V_{\mathrm{tip}} = 1.4$ V). (h) A schematic model of site A.

with the straight bundled chains on the C-containing surface. In addition, the O adatom at the edge of the chain is highly reactive and the reaction front propagates one-dimensionally. The following reaction scheme thus emerges: Initially, the reaction occurs at the step edges and proceeds one-dimensionally. As θ_O decreases, rearrangement of the chains proceeds in parallel with the reaction and the surface structure changes from (2×1) to $(n \times 1)$. As the interchain separation becomes wider, the chains become more segmented. Since O adatoms at the ends of segments are reactive, segmentation of chains enhances the number of active O adatoms directly exposed to CO. As a result, the reaction accelerates as θ_O decreases. This scheme can be reinforced by comparing the variation in the number of segments over the course of the reaction with the titration curves. The relative number of segments can be roughly evaluated by superimposing a mesh consisting of (2×1) unit cells onto the STM images. The peak of the number of segments coincides with the sudden drop in the titration curve that can be seen in Fig. 1(h). Thus, the rate equation can be written as $-d\theta_O/dt = \chi\sigma_O(1 - \theta_O)$, where σ_O is the coverage of active O adatoms and $\chi = r\Gamma P$.

Quantitative features regarding the fluctuation of chains and σ_O can be obtained using the Ising model, as was originally proposed by Sasaki *et al.* [19]. Fluctuation is assumed to occur in thermal equilibrium. Although the chain shape and σ_O are time varying, the average chain shape in thermal equilibrium is calculated and then σ_O is estimated. It is not unreasonable to assume that the titration curve measured under the present experimental conditions (200 sec/image) reflects an ensemble average of σ_O over the thermal distribution of fluctuating chains rather than an instantaneous value of a fluctuating chain.

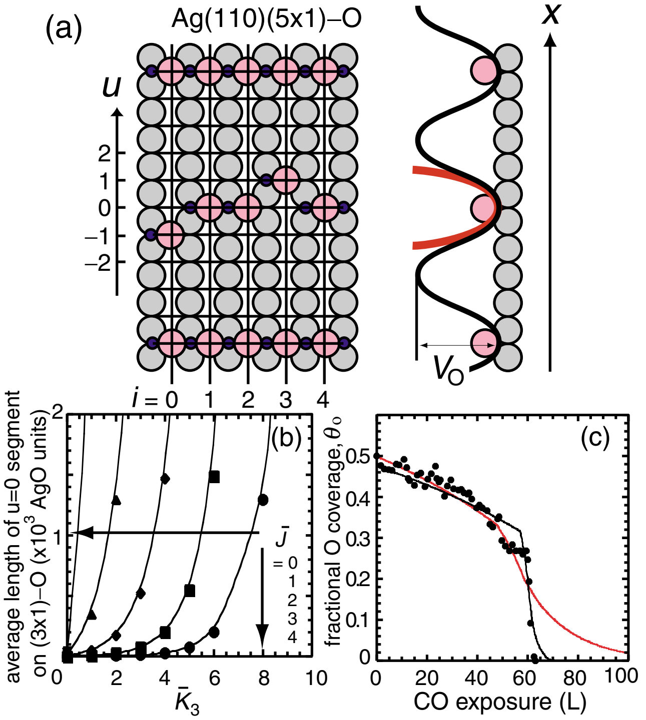

FIG. 3 (color). (a) Schematic of a fluctuating chain. The displacement of the ith AgO unit, u_i, is shown graphically. The model potential is illustrated by the approximated parabola. (b) Plot of the average length of $u = 0$ segments in the (3×1) structure as a function of $\bar{K}_3$ for various $\bar{J}$. (c) Comparison of experimental (black solid circles) and theoretical titration curves [$(\bar{J}, \bar{K}_3) = (1, 2)$ (red) and $(1, 4)$ (black)]. Experimental results are corrected so that the initial θ_O is 0.5 for comparison.

An AgO chain is first defined as a string of AgO units moving across the (1×1) lattice points only in the $[1\bar{1}0]$ direction. With the displacement of the ith AgO unit, u_i, defined as shown in Fig. 3, each fluctuating chain is then described by a set of u_i [20]. Each AgO unit feels attractive intrachain and repulsive interchain interactions as mentioned earlier. The nearest neighbor interaction energy, $W(u_i, u_{i+1})$, and the potential energy, $V(u_i)$, are then treated as intrachain and interchain interaction energies, respectively. Thus, the total energy of a chain in the $(n \times 1)$ structure, $E_{\mathrm{total}}(n)$, is given by $E_{\mathrm{total}}(n) = \sum_i [W(u_i, u_{i+1}) + V_n(u_i)]$. The energy $W(u_i, u_{i+1})$ varies as 0 and J for $|u_i - u_{i+1}| = 0$ and 1, respectively, where J is the excitation energy needed to create the $|u_i - u_{i+1}| = 1$ configuration. Since the STM images reveal that no AgO segments in the fluctuating chains are displaced by $|u_i - u_{i+1}| > 1$, $W(u_i, u_{i+1})$ is taken as infinity for $|u_i - u_{i+1}| > 1$. A mean-field potential of $V_n(x) = V_0[1 - \cos(2\pi/n)x]/2$ is assumed for $V(u_i)$, which is further expanded around the minimum to $V_n(u_i) = K_n u_i^2$ $[K_n = V_0/4(2\pi/n)^2]$ as shown in Fig. 3.

Using the transfer matrix technique, the distribution of displacements and average length of displaced segments u can be estimated using the periodic boundary condition [19]. Figure 3(b) shows the average length of a segment at $u = 0$ for the (3×1) structure as a function of $(\bar{J}, \bar{K}_3) = (J/k_BT, K_3/k_BT)$, where k_B is the Boltzmann constant. The larger values of $(\bar{J}, \bar{K}_3)$ result in longer chains. Since typical terrace widths of 100–200 nm are observed by STM, calculations are performed only for $(\bar{J}, \bar{K}_3)$ sets that produce segments shorter than 500 AgO units (~ 200 nm). Fitting was conducted by adjusting χ as a fitting parameter. The experimental results are reproduced reasonably well for $(1, 4)$, as shown in Fig. 3(c). The value of $\bar{J}$ is consistent with the work of Sasaki *et al.*, in which $\bar{J}$ of 1.5 was used. Thus, at $T = 300$ K, J is estimated to be 25 meV, which implies that the AgO chains fluctuate easily at RT, as observed by STM.

The Ag-O bonding is basically characterized by three pairs of bonding/antibonding states formed by the hybridization of O $2p$ orbitals with Ag $4d$ bands. There are two occupied antibonding states below the Fermi level (E_F) and one partially occupied antibonding state crossing E_F [21,22]. Thus, electron filling of the antibonding states may be an origin of the small value of J. This qualitative explanation is reinforced by comparison of the electronic structure and flexibility of the 1D chains between Ag(110)-(2 × 1)-O and Cu(110)-(2 × 1)-O. Although two antibonding states are fully occupied in Cu(110)-(2 × 1)-O similar to those in Ag(110)-(2 × 1)-O, one antibonding state is located above E_F [23]. As a result, 1D Cu-O chains appear as rigid straight lines and do not bend or fluctuate during the clean-off reaction with CO [4]. The clearly different behavior of added-row chains on both Ag(110) and Cu(110) surfaces stems from the different population of electrons in the antibonding states.

In summary, we have investigated the clean-off reaction of O adatoms by CO on Ag(110) using a combination of STM observations and Ising model calculations. The kinetics of this reaction are explained by the dynamical formation of active O adatoms in the fluctuating AgO chains. Although the dynamical formation of active sites by thermal fluctuation is a fundamental concept common to chemical reactions on heterogeneous catalysts and nanostructured compounds, the formation of these active sites has not yet been explicitly demonstrated. Clear evidence of the influence of thermal fluctuations on reaction rates was demonstrated for the first time, to the best of our knowledge, by studying the quasi-1D system.

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[1] G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (Wiley, New York, 1994).
[2] T. Zambelli *et al.*, Science **273**, 1688 (1996).
[3] F. M. Leibsle *et al.*, Nature (London) **363**, 706 (1993).
[4] W. W. Crew and R. J. Madix, Surf. Sci. **349**, 275 (1996).
[5] J. Wintterlin *et al.*, Science **278**, 1931 (1997).
[6] S. Völkening and J. Wintterlin, J. Chem. Phys. **114**, 6382 (2001).
[7] N. Hartmann and R. J. Madix, Surf. Sci. **516**, 230 (2002).
[8] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, 1972).
[9] M. Kiskinova, Chem. Rev. (Washington, D.C.) **96**, 1431 (1996).
[10] H. A. Engelhardt and D. Menzel, Surf. Sci. **57**, 591 (1976).
[11] M. Taniguchi *et al.*, Surf. Sci. **262**, L123 (1992).
[12] W. W. Pai and J. E. Reutt-Robey, Phys. Rev. B **53**, 15 997 (1996).
[13] M. Ohta *et al.*, J. Phys. Chem. B **105**, 8170 (2001).
[14] O. Nakagoe *et al.*, Surf. Sci. **528**, 144 (2003).
[15] M. Bowker *et al.*, Surf. Sci. **92**, 528 (1980).
[16] U. Burghas and H. Conrad, Surf. Sci. **370**, 17 (1997).
[17] H. Albers *et al.*, Surf. Sci. **77**, 1 (1978).
[18] C. Backx *et al.*, Surf. Sci. **128**, 81 (1983).
[19] K. Sasaki *et al.*, Surf. Sci. **337**, 33 (1995).
[20] The value of u_i is restricted to vary from $-(n-1)/2$ to $(n-1)/2$; this prohibits collision between the AgO units of the nearest neighbor chains. The calculation was done only for odd n's.
[21] L. H. Tjeng *et al.*, Surf. Sci. **236**, 341 (1990).
[22] R. Courths *et al.*, Surf. Sci. **376**, 43 (1997).
[23] R. Courths *et al.*, Solid State Commun. **63**, 619 (1987).