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Surface Diffusion and Interaction of Metastable Formate on Ni(110) Investigated by Low-temperature Scanning Tunneling Microscopy

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An atomic scale analysis of the surface diffusion and interaction of formate adsorbed on Ni(110) has been performed using scanning tunneling microscopy (STM) at low temperatures. Our results revealed that formate adsorbed at long-bridged site is in a metastable adsorption state and diffuses along the trough of Ni(110). We found that the diffusion barrier of L-formate decreased when it interacted with the neighboring formate molecule.

Adsorption of formate ($HCOO^-$) on metal surfaces has been studied intensively as a prototype of catalytic reactions, i.e., methanol synthesis and water shift reaction.[1–6] Past infrared spectroscopic studies demonstrated that the cleavage of the O–H bond in formic acid (HCOOH) leads to the formation of the formate on metal and metal oxide surfaces.[1,5] The bridging configuration is know as the stable adsorption structure of formate. It is interesting to note that decomposition of formate depends on the kinds of metals and the surface structures, i.e., dehydrogenation on Cu and Pt surfaces and dehydration and dehydrogenation on Ni, Fe, and Ru surfaces.[6] The formate adsorbed on Ni surface is an interesting subject for elucidating such selectivity in reaction.

An atomic scale analysis using scanning tunneling microscopy (STM) provides a noble way to understanding heterogeneous phenomena in microscopic scale. Our previous study demonstrated that two types of formate form at short-bridged (S-formate) and at long-bridged (L-formate) sites when exposing the Ni(110) to formic acid at 50 K.[7] We found that the L-formate is in a metastable adsorption state and involved precursor diffusion because it was observed only at low temperature (below 120 K). Although the statistic behavior of adsorbed formate was clarified, the molecular diffusion of formate has not been examined yet. Real time monitoring of nanoscale areas using STM gives a new insight into the atomic scale understanding of molecular motion and diffusion under the influences of adjacent molecules, defects and impurities,[8–11] which cannot be obtained from the conventional techniques.[12,13]

In this letter, we present a time-elapsed STM study of the surface diffusion and interaction of L-formate adsorbed on Ni(110) at cryogenic temperatures. We carried out a detailed analysis of the formate diffusion by means of sequential STM imaging and found that the L-formates tend to diffuse along the trough of Ni(110) at low temperatures, whereas the S-formate is stable and immobile. In addition, STM analysis revealed that the diffusion barrier of the L-formate is decreased when it interacts with the neighboring S-formate.

All experiments were performed in an ultrahigh vacuum (UHV) chamber under a base pressure of 4×10^{-11} Torr. The Ni(110) surface was cleaned by repeating Ar^+ sputtering and annealing at 1000 K, until the cleanness was confirmed by STM imaging. The clean Ni(110) surface was exposed to formic acid at about 50 K through a dosing tube located near the substrate. All STM images shown here are obtained in the constant height mode by use of a low-temperature STM system (LT-STM, Omicron GmbH).

The STM image of formate molecules at 20 K obtained after exposing Ni(110) to formic acid at 50 K is shown in Figure 1a. The adsorbed formate molecules were resolved as protrusions with two depressions that always aligned along [1$\bar{1}$0] or [001] directions. The former is assigned to formate molecules adsorbed at S-formate sites and the latter is at L-formate sites.[7] Note that L-formate molecules transformed to S-formate when the substrate was heated to 120 K, indicating L-formate is in a metastable adsorption state.[7]

Although both of the formate species were immobile at 4.7 K, we found that the L-formate diffused with increased substrate temperature. The rescanning of the same area of Figure 1a revealed that a number of L-formate molecules diffused along the trough of Ni(110) row at 20 K (Figure 1b). The STM image taken at 50 K shows line structures and scratches due to the fast diffusion of L-formate (Figure 1c).

The molecule denoted L′ in Figure 1a is L-formate interacting with S-formate. Likewise the diffusion of the isolated L-formate (Figure 2a), L′-formate also moved along the trough, but their motion was confined to the sites nearby adjacent S-formate

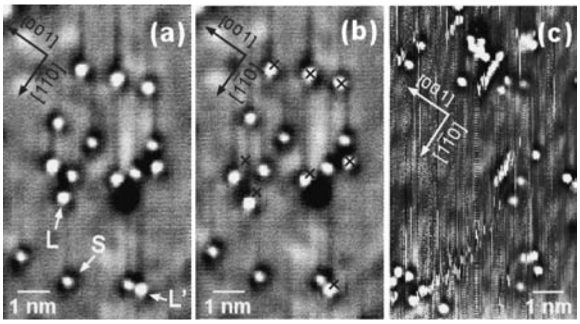

Figure 1. (a) An STM image of formate ($HCOO^-$) on Ni(110) at 20 K. The formate adsorbed at the long-bridged and the short-bridged sites are indicated by L and S, respectively. (b) An STM image obtained at the same area of (a) after 52 s. The L-formate interacted with S-formate is indicated by L′. The notation "×" in (b) is the position of L-formate shown in (a). (c) An STM image of formate on Ni(110) obtained at 50 K. The line structures and scratched noises in the image are due to the fast diffusion of L-formate. All STM images were taken with a sample bias of 20 mV and tunneling current of 1.0 nA.

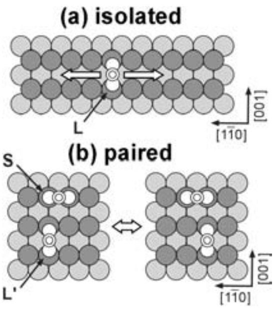

Figure 2. Schematic model of the surface diffusion of L-formate on Ni(110). The isolated L-formate diffuses along the trough of Ni(110) row (a) while the L-formate interacting with S-formate (L′) diffuses near S-formate (b).

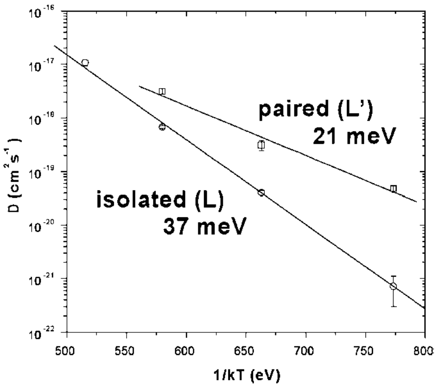

Figure 3. An Arrhenius plot of the thermal diffusion of L-formate (open circle) and L′-formate (open square) on Ni(110) by the analysis of the sequential STM images.

(Figure 2b). This suggests that the attractive adsorbate–adsorbate interaction stabilizes the L′–S dimer configuration.

In order to elucidate the diffusion mechanism, kinetic analysis was carried out in a temperature range between 15.0 and 22.5 K. To determine the diffusion rate, we recorded a series of STM images with a tunneling current of 0.5–1.0 nA and a sample bias of 20 mV. Under these conditions, we confirmed that the effect of the STM tip on the observed hopping motion is negligible, by changing scan rate. In addition, the diffusion rate increased when the sample bias was set to over 110 meV. The increase in the diffusion rate was caused by the excitation of specific molecular vibrational modes by the tunneling electrons.[14]

In Figure 3, we display an Arrhenius plot of the surface diffusion rates of L-formate as a function of sample temperature. The diffusion rate, $D(T)$, is described by an Arrhenius equation $D(T) = D_0 \exp(-E_{\mathrm{diff}}/k_{\mathrm{B}}T)$, where D_0 is the pre-exponential factor, E_{diff} is the activation energy of the diffusion, and k_{B} is the Boltzmann constant.[15,16] By fitting the plot, E_{diff} of the isolated L-formate was measured to be 37 meV and D_0 was $1.67 \times 10^{-9}\,\mathrm{cm^2\,s^{-1}}$. It is noteworthy that the L′-formate diffuses more frequently in comparison with the isolated L-formate as shown in Figure 3. The Arrhenius plot shows the decrease in both the activation energy (21 meV) and the diffusivity ($1.30 \times 10^{-11}\,\mathrm{cm^2\,s^{-1}}$) for L′-formate.

The changes in E_{diff} and D_0 stem from the interaction with S-formate. The decrease in the E_{diff} of L′-formate is probably caused by the local perturbation of the diffusion potential modified by the nearest neighbor S-formate. The charge density perturbation resulting from the substrate-mediated intermolecular interaction has been reported for CO on Cu(110).[15] In our previous STM study, we observed the chain structures of formate obtained after annealing the surface at 120 K. The weak modulation of the surface potential by the adsorbate traps the precursor intermediate (L′-formate), which would allow formation of self-assembled chain structures.[7] The short distance of L′-formate diffusion accounts for the decrease of D_0. As the substrate was heated, the diffusion distance increased for L-formate (three or four atomic sites) while L′-formate remained near S-formate. In addition, the curvature of the diffusion potential should also affect D_0.[17] The curvature of the diffusion potential with the higher barrier is larger at the bottom of the potential well. Formate in a well with a high curvature vibrates faster, and thus the D_0 of L-formate is larger.

In summary, we investigated the surface diffusion and interaction of metastable formate on Ni(110). While the S-formate molecules are immobile, the L-formate molecules tend to diffuse along the trough of Ni(110) at low-temperature regions. The diffusion barrier and pre-exponential factor of the L-formate is decreased when it interacts with the neighboring S-formate. These results suggest that the substrate-mediated intermolecular interaction modifies the surface potential.

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