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Dehydrogenation of a Single Acetylene Molecule on the Cu(111) Surface

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Dehydrogenation of acetylene molecules on metal surfaces is a crucial step in converting acetylene into carbon materials and other useful hydrocarbons for industrial applications. In this study, the dehydrogenation of a single acetylene molecule on a Cu(111) surface was investigated using scanning tunneling microscopy (STM) experiments and density functional theory (DFT) calculations. The dehydrogenation reaction, induced by applying a bias voltage pulse, transforms acetylene to C_2 without producing a detectable C_2H intermediate, in contrast to similar experiments on Cu(100) where a C_2H intermediate was detected. DFT calculations indicate that differences in molecule-surface interactions alter the reaction barrier for the two steps of dehydrogenation. The immediate reaction from acetylene to C_2 is driven by a lower reaction barrier for the second C–H bond dissociation compared to the first, along with the absence of an orientation change in the target molecule.

Unsaturated hydrocarbons have been widely used in industrial processes.[1] Conversion of acetylene (C_2H_2), the simplest unsaturated hydrocarbon, on transition metal surfaces has attracted significant attention, not only for industrial applications but also as a model reaction to understand the catalysis of more complex unsaturated hydrocarbons. To gain fundamental knowledge of acetylene conversion, the adsorption and reaction of acetylene molecules on various metal surfaces have been extensively studied both experimentally[2-4] and theoretically.[5-7] Among these, Cu is recognized as a prominent material that facilitates various reactions, including those initiated by dehydrogenation, such as the synthesis of carbon-based materials like graphene[8] and acetylene coupling reactions.[4] To achieve more precise control over the reaction of acetylene on Cu surfaces, it is essential to understand the elementary processes and the detailed mechanisms of acetylene dehydrogenation. Macroscopic analyses, including the evaluation of reaction products and kinetics, provide statistical insights into the activity of catalysts. In contrast, microscopic analyses at the single-atom/molecule level are invaluable for elucidating detailed reaction mechanisms, because the local geometric and electronic structure of the atomic-level active sites on solid catalyst surfaces critically influence the adsorption and reactivity of molecules. However, the previous studies of acetylene on Cu surfaces at the single-molecule level have primarily focused on molecular dynamics on surfaces,[9-12] and the elementary processes and reaction mechanisms have not been explored in detail. Therefore, elucidating the origin of the unique reactivity of acetylene on Cu surfaces requires the investigation of the adsorption and reactions on well-defined single-crystalline surfaces at the atomic and single-molecule levels.

Scanning tunneling microscopy (STM) is a technique that enables surface observation at the atomic level, as well as single-molecule spectroscopy and reaction analysis on surfaces.[9,13] To investigate the mechanism of acetylene adsorption and reaction on Cu surfaces, STM studies on low-index surfaces have been conducted.[9-12,14] On the Cu(100) surface, the adsorption structure[9] and the dehydrogenation reaction[14,15] have been studied at the single-molecule level. In contrast, on the Cu(111) surface, only the adsorption structure of a single molecule has been reported.[11] However, the reaction mechanisms on both surfaces are not yet fully understood. Therefore, further studies are needed to clarify the details of the reaction processes on Cu surfaces.

In this study, the adsorption structure and dehydrogenation process of acetylene adsorbed on Cu(111) were investigated at

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the single-molecule level using a combination of STM experiments and density functional theory (DFT) calculations. Dehydrogenation of acetylene on Cu(111) was induced by applying a bias voltage pulse from the STM tip. We found that a single acetylene molecule was immediately converted to C_2, which differs from the two-step dehydrogenation reaction observed on Cu(100).[14]

All experiments were performed using a low-temperature STM (LT-STM, Omicron GmbH) with a W tip under ultrahigh vacuum (UHV) conditions (< 3×10^{-10} Torr) at ~6 K. All voltages (V) refer to the sample bias. The single crystalline Cu(111) surface was cleaned by cycles of Ar^+ ion sputtering and annealing at 773 K. Acetylene molecules were adsorbed onto a clean Cu(111) surface at temperatures below 50 K. Figure 1a is a high-resolution STM image of three acetylene molecules adsorbed on Cu(111). The acetylene molecules, which have a dumbbell-like shape, are aligned along the three symmetrically equivalent Cu<1$\bar{1}$0> axes. The adsorption site of acetylene was identified as a bridge site, with the two carbons adsorbing in threefold hollow sites (Figure 1b). DFT calculations confirmed the bridge site as the most stable adsorption structure (Figure 1c). Previous studies have also shown that adsorption at the bridge site is the most stable configuration.[16,17]

To investigate the reaction behavior of acetylene molecules on Cu(111), the STM tip was positioned over the centre of a single acetylene molecule, and a voltage pulse was applied between the STM tip and the sample. After applying a bias voltage pulse of 3.0 V, the appearance of the molecule changed (Figure 2a,b). Note that neither rotation nor diffusion of the acetylene molecules was observed. Moreover, no further changes were observed even after applying additional voltage pulses of up to 5.0 V to the product molecule (Figure 2b). A previous study reported that applying bias voltage to acetylene molecules on Cu(100) induced dehydrogenation and the sequential formation of C_2H and C_2.[14] In contrast, only one kind of product was obtained on Cu(111).

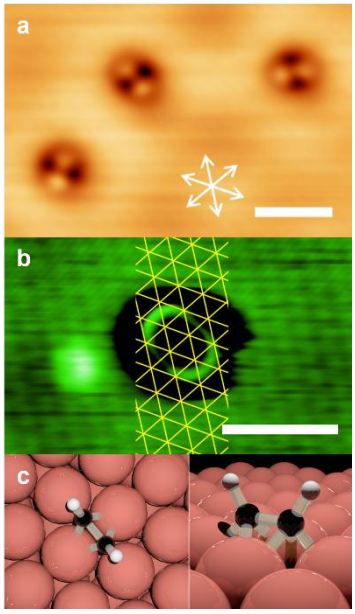

Figure 1. (a) Topographic STM image of acetylene molecules on Cu(111) (V = 0.1 V, I_t = 20 nA). White arrows indicate Cu<1$\bar{1}$0> axis. (b) Topographic STM image of an acetylene molecule on Cu(111), obtained using a molecular tip (V = 0.1 V, I_t = 25 nA). The superimposed grid indicates the positions of surface Cu atoms. Scale bars: 1 nm. (c) Optimized structure of an acetylene molecule on Cu(111) by DFT calculations.

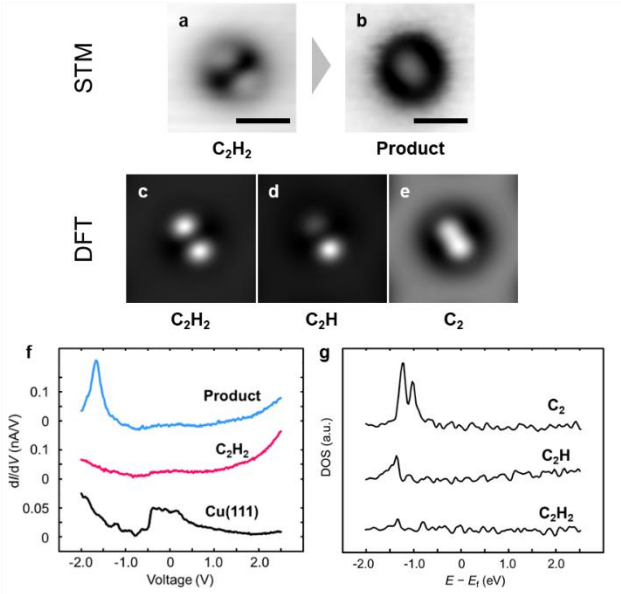

Figure 2. (a,b) Topographic STM images of (a) acetylene (V = 0.1 V, I_t = 5.0 nA) and (b) the product obtained from dehydrogenation of acetylene (V = 60 mV, I_t = 10 nA) on Cu(111). Scale bars: 5.0 Å. (c–e) Simulated STM images of (c) acetylene, (d) C_2H, (e) C_2 on Cu(111) ($E - E_f$ = 1.0 eV). (f) dI/dV spectra of the Cu(111) surface, acetylene and the dehydrogenated product measured by STM. Lock-in detection with a modulation voltage of 10 mV was used. The setpoint was 2.5 V and 1.0 nA. The tip was positioned above the centre of the target molecule. All spectra are averages of six measurements. (g) LDOS of acetylene, C_2H and C_2 on Cu(111) from DFT calculations.

To identify the reaction products, the electronic structures of Cu(111), acetylene molecules, and the product were investigated using scanning tunneling spectroscopy (STS) (Figure 2f). The STS spectrum for the product shows a peak around −1.6 V, indicating that the product has an electronic state different from that of the acetylene molecule. The local density of states (LDOS) from DFT calculations exhibit similar peaks for both C_2H and C_2 molecules adsorbed at the bridge site on Cu(111) (Figure 2g). In other words, it is difficult to identify whether the generated molecule was C_2H or C_2 based on a comparison between the STS spectrum and the calculated LDOS. However, we found clear differences in the symmetry and appearance of the simulated STM images, allowing us to identify the molecule based on the shape of the STM images. The simulated STM image of C_2H has an asymmetric shape (Figure 2c–e) and maintains this asymmetry near the Fermi level, from −2.0 to 2.0 eV (Figure S1). In contrast, the C_2 molecule has a symmetric shape, which it retains from −2.0 to 2.0 eV (Figure S1). The high-resolution STM image (Figure 2b) of the product, measured at a close tip-surface distance, exhibits a symmetric and elliptical sombrero-like structure, which is consistent with the simulation result for the C_2 molecule. STM measurements revealed that the elliptical sombrero-like structure shown in Figure 2b has the same adsorption orientation as the acetylene molecule in Figure 2a, suggesting that it is a linear molecule, C_2,

rather than a single carbon atom. Based on the STM and DFT results, we conclude that the product generated from dehydrogenation of acetylene on Cu(111) is C_2.

Next, to understand the reaction in more detail, the threshold energy for dehydrogenation of acetylene was investigated. Figure 3a shows the dependence of the reaction probability on the applied voltage. The reaction probability is defined as the ratio of molecules that underwent the reaction to the total number of molecules. All trials were conducted at 1.0 nA for 3.0 seconds, and it became evident that the reaction occurred when a voltage pulse of ≥ 2.7 V was applied. The reaction probability increased monotonically with increasing voltage for voltages ≥ 2.7 V, reaching 100% at ≥ 3.4 V. Thus, the threshold energy for the reaction on Cu(111) is determined to be ~2.7 eV, which is nearly the same as that on Cu(100).[14] Additionally, although we applied negative bias voltages at up to −5.0 V, no reaction was observed, indicating that the reaction depends on the polarity of the bias voltage. Therefore, it can be concluded that the reaction occurs through a resonance mechanism induced by injecting tunneling electrons from the STM tip to the molecule. Furthermore, when a voltage above the reaction threshold was applied, the molecule just under the tip reacted and no changes were observed in adjacent molecules, suggesting the field effects were negligible in this reaction (Figure S2).

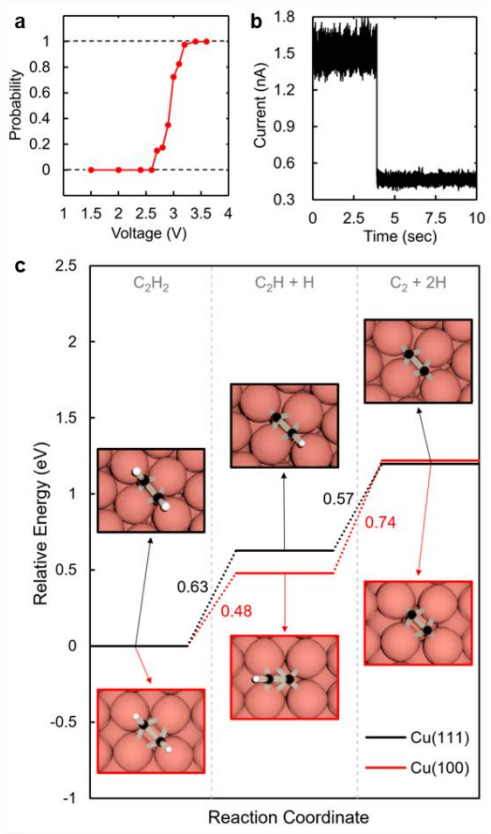

Figure 3. (a) Reaction probabilities of acetylene to the dehydrogenated product (C_2) on Cu(111) as a function of the energy of the applied bias voltage. The probability is derived from the ratio of the number of reacted acetylene molecules to the total number (40 molecules) of trials at each voltage, with the tunneling current set to 1.0 nA and pulse duration fixed at 3.0 s, with the feedback loop off. (b) Current trace measured on an acetylene molecule during a voltage pulse (V = 2.7 V, I_t = 1.5 nA) with the feedback loop off. (c) DFT-calculated energy diagram of the dehydrogenation process (starting from acetylene, through C_2H, to C_2) on Cu(111) (black line) and Cu(100) (red line), with the corresponding optimized structures for each step. The total energy for each step is given by: $E_{Tot}(Cu + M + xH) = E_{Tot}(Cu + M) + xE_{Tot}(Cu + H) - xE_{Tot}(Cu)$, where $E_{Tot}(Cu + M)$ is the total energy of M (= acetylene, C_2H, C_2) adsorbed on the Cu slab, $E_{Tot}(Cu + H)$ is the total energy of a H atom adsorbed on Cu, and $E_{Tot}(Cu)$ is the total energy of clean Cu. x is the number of generated H atoms.

Figure 3b shows the typical change in the tunneling current trace measurement during a bias voltage pulse of ≥ 2.7 V. The tunneling current is sensitive to changes in the gap distance between the STM tip and the sample. The drastic decrease in current observed in Figure 3b indicates a change in the molecule under the tip. This one-step change, which was also observed at ≥ 2.7 V and at any other current, reflects the dehydrogenation of acetylene to C_2 through the dissociation of two hydrogen atoms, either simultaneously or within a very short time. In contrast to acetylene on Cu(111), a two-step change of current was observed in the tunneling current trace measurement for acetylene on Cu(100),[14] suggesting the presence of the intermediate species, C_2H, for a certain period. Furthermore, the selective formation of C_2H achieved by applying a bias voltage pulse near the threshold energy was confirmed in the STM images on Cu(100).[14] This difference originates from variations in the interfacial interactions between the surface and the molecules, depending on the specific facets.

There are two possible reasons why the current change was observed in a single step on Cu(111): either the two C–H bonds were dissociated simultaneously, or the bonds were dissociated sequentially but could not be individually detected. In the former case, a one-step current change is reasonable because the electronic structure changes instantaneously due to the immediate reaction from acetylene to C_2. Furthermore, the reaction time would generally depend on the magnitude of the current, as the number of electrons flowing directly affects the frequency of reaction. Assuming a single excitation, the reaction time should decrease monotonically with increasing current. However, the measured reaction rate showed no clear correlation with the applied current and displayed a large deviation for a given current (Figure S3). When the two C–H bonds dissociate as two independent sequential steps, the reaction requires two excitations. Thus, if the two-step process occurs within a short time beyond the detection limit, or if the electronic changes associated with one of the steps are too subtle to produce a measurable current change, it is impossible to discriminate the reaction time for the first and second steps. This leads to greater variation in reaction time at a given current as shown in Figure S3. Therefore, we conclude that the two C–H bonds dissociate sequentially rather than simultaneously.

The reaction pathway was investigated using DFT calculations to understand why the current change is measured as a single step, leading to C_2 as the product. Figure 3c shows the energy diagram for the dehydrogenation process from acetylene to C_2 via C_2H on Cu(111) and Cu(100), highlighting the differences caused by molecule-surface interactions. The calculated pathways are relevant to both the tip-induced dissociation as well as to thermal decomposition, with the latter directly related to catalytic reactions. The most stable

structures of both C_2H and C_2 are for adsorption at the bridge site on Cu(111) and the hollow site on Cu(100), respectively, which is consistent with the adsorption behavior of acetylene molecules (Figure S4). Since H atoms generated from dehydrogenation were not visualized in the STM images, calculations were conducted under the assumption that H atoms were adsorbed far from the C_2 and C_2H species. As shown in previous studies, H atoms are most stable at the fcc hollow site on Cu(111)[18] and the hollow site on Cu(100)[19] (Figure S5). DFT calculations revealed a significant difference in the reaction pathways of the intermediate species on Cu(111) and Cu(100). The intermediate C_2H adsorbed at the bridge site on Cu(111) maintains the same orientation as acetylene and C_2. In contrast, C_2H adsorbs on Cu(100) with the long axis parallel to the $<1\bar{1}0>$ direction, which requires rotation from the original orientation of acetylene, as reported in the previous studies.[14,15] Considering the Hammond postulate, the geometry of the transition state for the first and second dehydrogenation steps is closer to the intermediate and product, respectively. Thus, the reaction pathway is expected to be more complex on Cu(100) than on Cu(111) due to the required rotation. Additionally, assuming that the energy differences before and after the dehydrogenation directly correlate with the reaction barrier heights, the second step is considered as the rate-determining step on Cu(100), whereas, on Cu(111), the first step is the rate-determining step. Moreover, the current change reflecting the generation of intermediates is more easily detectable on Cu(100) than on Cu(111), due to the involvement of the rotation in the reaction pathway only on Cu(100). Overall, the immediate reaction from acetylene to C_2 on Cu(111) can be interpreted by the lower reaction barrier for the second dissociation and the absence of an orientation change during the reaction.

In conclusion, we revealed the sequential dehydrogenation process of acetylene on the Cu(111) surface at the single-molecule level and found the immediate conversion from acetylene to C_2. The energy diagrams for dehydrogenation show that the immediate reaction from acetylene to C_2 on Cu(111) occurs because the reaction barrier for the second dissociation is lower than that for the first dissociation. Furthermore, the absence of an orientation change during the reaction facilitates the first and second dissociation compared to the observed sequential reaction on Cu(100). Our single-molecule study, combining STM experiments and DFT calculations, demonstrated a significant difference in the reaction pathways on Cu(111) and Cu(100) due to differences in molecule-surface interactions. These findings provide fundamental insights into the dehydrogenation of acetylene and the activation process of the C–H bonds, contributing to the understanding of acetylene conversion reactions and the production of various chemicals.

S. T. carried out all experiments. S. T. and M. L. carried out the density functional theory calculations. All authors contributed to the interpretation of the results and wrote the manuscript. M. L., E. K., and Y. K. planned and supervised the project.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information.

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Data Availability Statements

Data is available within the article and supporting this article have been included as part of the Supplementary Information.