

Characteristic Configuration of Cis-2-butene Molecule on Pd(110) Determined by Scanning Tunneling Microscopy

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Adsorption of cis-2-butene molecules on the Pd (110) surface was studied by scanning tunneling microscopy (STM) at 4.7 K for the first time. In contrast to the fact in the previous work that trans-2-butene molecules are adsorbed at the on-top site of the Pd(110) surface with its C=C double bond being almost parallel to the $[1\bar{1}0]$ axis, cis-2-butene molecules were found to be adsorbed slightly off the on-top site. In addition, the C=C bond was not parallel to the $[1\bar{1}0]$ axis, but to four directions equivalent to the structure of the Pd(110) surface. Furthermore, at high bias voltages for the STM measurement, the cis-2-butene molecule became unstable and moved in two different manners around the palladium atom to which the molecule was bonded, suggesting the existence of two different mechanisms underlying the motion on the surface. [DOI: 10.1143/JJAP.41.4976]

KEYWORDS: scanning tunneling microscopy, Pd(110), hydrocarbon, adsorption

1. Introduction

One of the most attractive targets in recent surface science is the identification of the adsorbed isomeric molecules on the surface, and the clarification of how the chemical reactions of molecules depend on their configurations on the surface. In addition to the isomeric structures, their adsorption configuration on material surfaces, in terms of factors such as adsorption site and molecular orientation, plays an important role in chemical reactions, such as catalysis, corrosion and etching. For example, during catalytic processes, the hydrogenation reaction of hydrocarbons is strongly influenced by the configurations of the related molecules on the surface.^{1,2} Therefore, in order to understand and control the molecular reactions on material surfaces, it is extremely important to analyze the adsorption structures of isomeric molecules at the single molecular level.

Scanning tunneling microscopy (STM) is known to have powerful potential in this field. Namely, instead of information averaged over various molecules, it can provide us information for individual molecules. Since electronic structures are probed by STM measurement, the molecular configuration can be analyzed in detail. In fact, recently, the adsorption configuration of the trans-2-butene molecule and its chemical reaction into the 1, 3-butadiene molecule induced by inelastic tunneling was studied by STM at the single molecular level.³ Configurations of the two molecules were clearly discriminated and determined.

As is well known, the 2-butene molecule is a kind of hydrocarbon and has trans-2- and cis-2- isomeric structures (Fig. 1). Therefore, when the configuration of the another one, cis-2-butene, is determined, this material becomes an intriguing candidate for the study described above. In this paper, we present our recent STM results for the configurations of the adsorbed cis-2-butene molecules on Pd(110) at 4.7 K. A completely different adsorption characteristic from that of trans-2-buten was observed for cis-2-butene.

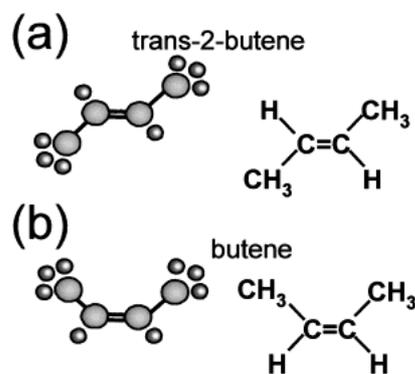


Fig. 1. Schematics of (a) trans-2- and (b) cis-2-butene molecules.

2. Experimental

Experiments were performed using a low-temperature STM system (LT-STM, Omicron GmbH) with double thermal shield cups equipped in an ultrahigh vacuum (UHV) chamber. In general, since the activation barriers for surface diffusion or rotation for molecules are below 100 meV, their mean residence time at 77 K is below 10^{-7} s.⁴ Therefore, a high-coverage molecular surface is prepared for STM imaging of the surface in order to reduce molecular motions. However, this method is not suitable in this case because it becomes difficult to analyze the characteristic of the isomers at the single molecular level. In addition, in the case of hydrocarbons on the catalysis surface, there exists a process of thermal dehydrogenation.^{2,4} Therefore, all measurements were performed at 4.7 K.

3. Results and Discussion

A clean and flat Pd(110) surface, with a 20-nm-wide terrace, was prepared by a standard polishing technique, Ar⁺ sputtering and annealing cycles. Base pressure was $< 3 \times 10^{-11}$. The butene molecules (99% purity for both trans-2- and cis-2-butene molecules) were introduced onto the surface through a variable leak valve ($< 2.2 \times 10^{-10}$ Torr). A

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mechanically sharpened and field emitted tungsten wire was used as a STM tip. Sometimes the STM tip can be modified with molecules in order to be able to observe the adsorbed molecules and substrate more clearly.^{3,5)} However, in the case of *cis*-2-butene, adsorbed molecules became unstable with the modified STM tip. Therefore, in order to minimize the interaction between tip and sample for the precise determination of the adsorbed molecular configurations, all images were obtained with a nonmolecular terminated bare tip in this study.

Figures 2(a) and 2(b) show a typical STM image of *trans*-2-butene and *cis*-2-butene molecules adsorbed on the Pd(110) surface and a magnified image of the surface. Here, both the 2- and *cis*-2-butene molecules are co-adsorbed. A *trans*-2-butene (labeled “T”) is known to be imaged by STM as having a dumbbell-like pair of protrusions.³⁾ It is adsorbed at the on-top site on the Pd(110) surface with the C=C bond being

almost parallel to the $[1\bar{1}0]$ axis, and two CH₃ related parts are considered to be imaged brightly, and to have a dumbbell-like structure. On the other hand, *cis*-2-butene (labeled “C”) was observed in completely different shape. Namely, it has an asymmetric gourd-like shape, and one side on the long-axis is brighter than the other one. This assignment was confirmed by the observation of the surface with the adsorption of the pure *cis*-2-butene molecules. In this paper, we call the brighter side the “head” of the molecule. Another remarkable point is that the *cis*-2-butene molecules appeared with their long-axes in the four different directions on the same surface as indicated by the schematic in Fig. 2(c). The single small spots in Fig. 2(a) are possibly considered to be impurities.

Regarding the structures of *trans*-2- and *cis*-2-butene molecules, it is difficult to explain the observed differences described above by only the geometric difference in the molecular structures. A possible explanation is that the molecular orbitals are modulated by the interaction between CH₃ groups in the molecules and the substrate. In order to clarify this point, let us first determine the adsorption site.

If it were possible to image both the adsorbed molecules and the atomic structure of the substrate together, the details of the adsorption site could be determined easily. However, corrugation of the molecules is about 0.1 nm, while the corrugation associated with the close-packed metal surface is of the order of 0.0001–0.001 nm.⁶⁾ Thus, it is difficult to visualize both the adsorbed molecules and the substrate atomic structure together. There are two useful techniques for determining the adsorbed sites. One is to estimate the positions of molecules by comparing them with a grid mesh of the clean substrate surface obtained for the same size area. In this case, adsorption sites of the *trans*-2-butene molecules can be used as the reference. Namely, as mentioned above, *trans*-2-butene molecules are adsorbed at the on-top site of the substrate.³⁾ However, distortion of the STM image due to the piezo creep during scanning may affect the results obtained with this method. Another method is digital filtering with the Fourier transfer conversion technique.^{6,7)} This is a very simple technique for enhancing periodic structures such as substrate atoms. However, it also highlights some noise frequency components around the periodic structure. Therefore, in order to determine the adsorption site of the *cis*-2-butene and its configuration precisely, we applied these two independent techniques simultaneously, i.e., we performed double checking to determine the relative positions of adsorbed molecules and substrate atoms.

Figure 3(a) shows an STM image of a clean Pd(110) surface. Each atom of the surface can be clearly observed. Figure 3(b) is an STM image with the adsorbed molecules after treatment by Fourier transfer conversion technique. The substrate periodic structure is enhanced, and is in good agreement with that in Fig. 3(a). After comparison of Figs. 3(a) and 3(b), the grid mesh of the clean substrate surface is drawn over Fig. 3(b), which is shown in Fig. 3(c). In Fig. 3(c), each cross of the mesh indicates the Pd atomic position, on-top site. For example, the center of a *trans*-2-butene molecule indicated by T is on an on-top site.

The first remarkable point is that the *cis*-2-butene molecular STM image is located off from the on-top site of the palladium atom. In addition, the long-axis of the image is not parallel to the atomic row ($[1\bar{1}0]$ axis), in contrast to the case of

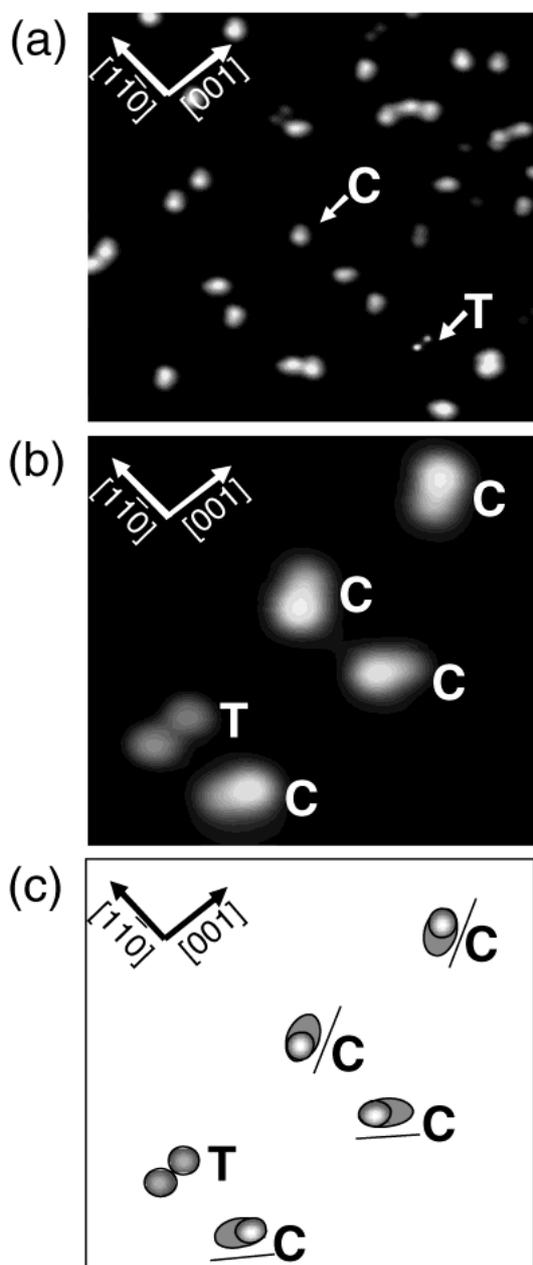


Fig. 2. (a) STM image of *trans*- (T) and *cis*- (C) 2-butene molecules ($V_s = -20$ mV, $I_t = 1.0$ nA). (b) A magnification of (a). (c) Schematics of the molecular arrangement in (b).

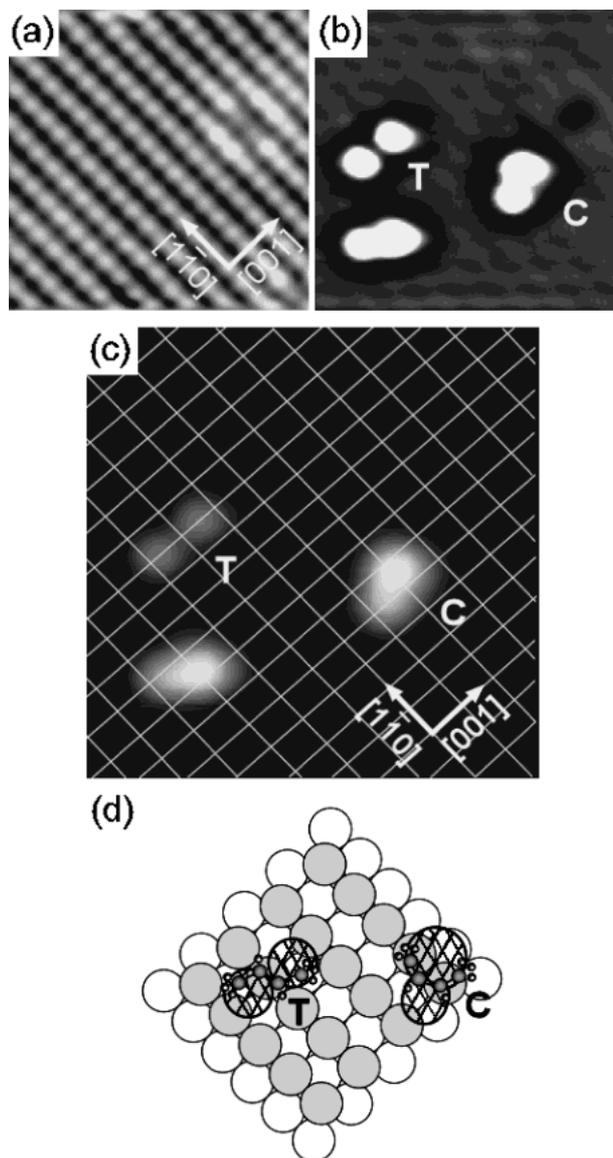


Fig. 3. (a) STM image of a clean Pd(110) surface. (b) STM image with adsorbed molecules after treatment by Fourier transfer conversion technique. (c) STM image of trans- (T) and cis-(C) 2-butene molecules with a grid mesh indicating the Pd(110) substrate surface lattice. (d) Schematics of the molecular configurations. Hatched areas drawn on the molecules correspond to the STM images in (c). STM conditions are $V_s = -20$ mV, $I_t = 0.50$ nA.

the trans-2-buten molecule. The orientation of the long-axis of the two cis-2-buten molecules shows two equivalent directions as compared to the crystal axis of the Pd(110) surface, resulting in the four equivalent orientations in Fig. 2(b).

Since the paired protrusions of the trans-2-butene cannot be explained by the model of observing the single C=C double bond, the dumbbell-like STM image of the trans-2-butene is related to the electronic structure of the two CH₃ parts in a molecule.^{3,8)} On the other hand, as is shown in Fig. 1(b), in a cis-2-butene molecule, two CH₃ parts exist on the same side of the C=C double bond axis. Therefore, overlap of the two CH₃ related orbitals in a molecule may form the gourd-like shape in the STM image. A schematic of the proposed adsorption model is shown in Fig. 3(d). The hatched structures of Fig. 3(d) correspond to the molecular STM images in Fig. 3(c). For trans-2-butene, the adsorption model in ref. 3 is

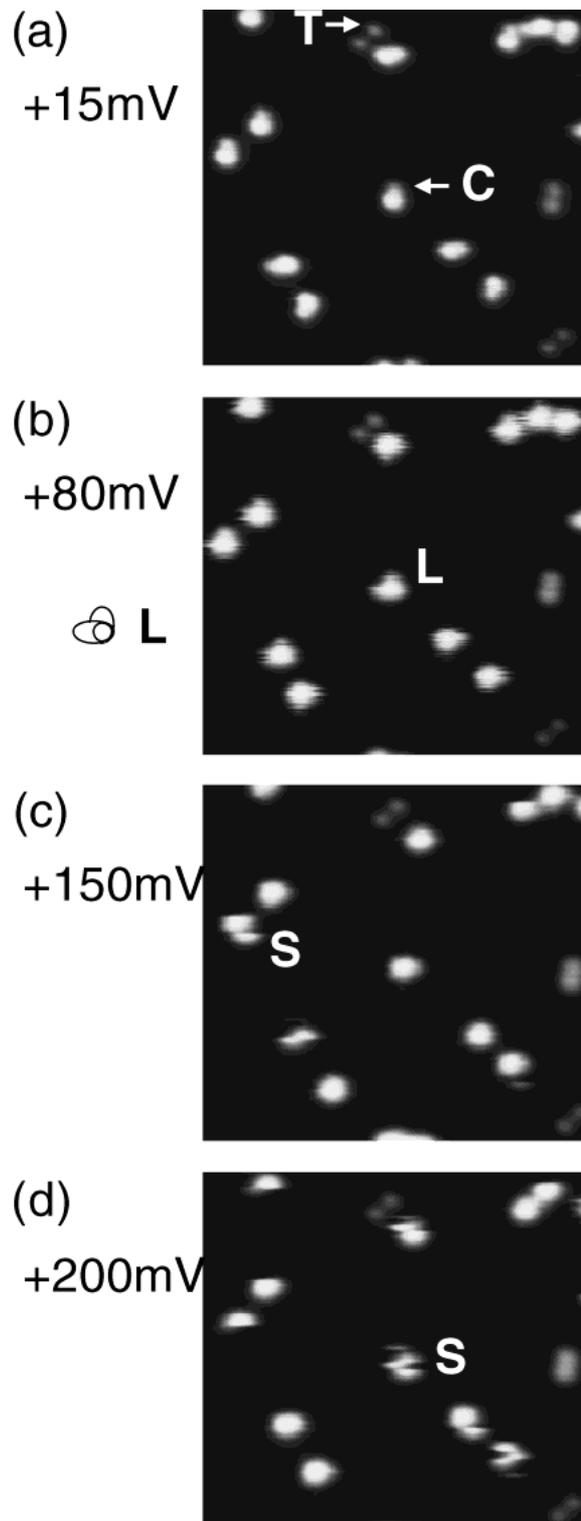


Fig. 4. Bias dependent STM images of trans- (T) and cis-(C) 2-butene molecules adsorbed on Pd(110). (a) $V_s = +15$ mV, $I_t = 1.0$ nA. (b) $V_s = +80$ mV, $I_t = 1.0$ nA. (c) $V_s = +150$ mV, $I_t = 1.0$ nA. (d) $V_s = +200$ mV, $I_t = 1.0$ nA.

shown. Theoretical calculation is necessary to further clarify the configuration of the cis-2-butene molecule.

Next, we studied the difference in the interaction between the adsorbed molecules and the substrate for trans-2- and cis-2-butene. Figure 4 shows a series of bias dependent STM images of the coadsorbed trans-2- and cis-2-butene isomers (tunneling current: 1.0 nA, ~ 6.4 nm²). The asymmetric gourd-

shape labeled “C” and the dumbbell-like shape labeled “T” represent *cis*-2-butene and *trans*-2butene molecules, respectively, similar to those in Fig. 2.

At low bias voltages, all adsorbed molecules were stable and could be observed clearly (Fig. 4(a)). However, when the bias voltage was raised to $V_{\text{bias}} = 80$ mV, the contours of almost all the *cis*-2-butene molecules became fuzzy and some of them exhibited an L-like shape as indicated by arrows “L” in Fig. 4(b) with a schematic model. Furthermore, at $V_{\text{bias}} = 150$ mV (Fig. 4(c)) and $V_{\text{bias}} = 200$ mV (Fig. 4(d)), strangely modulated structures appeared as indicated by arrows “S”. These phenomena are not caused by the contact between the STM tip and molecules because the tunneling current was fixed in these measurements. Namely, for the same tunneling current, the tip-sample distance increases with an increase in the bias voltage. Thus, the observed changes in the molecule images are considered to be due to the motion of the molecules under the STM tip during the scan. In fact, the STM scan was started from the bottom left and continued along the horizontal axis (from left to right then low to high), and the observed change appeared during one of the scans. *Trans*-2-butene molecules remained stable throughout this experiment.

Regarding of the observed molecular change, there exist at least two steps with the increase in bias voltage. In the first one shown in Fig. 4(b), the *cis*-2-buten molecule becomes unstable and exhibits an L-like shape. However, since the “head” of the molecule is kept on the same on-top site, this motion seems to be a type of rotation with the head position being the axis; however, in the second one shown in Figs. 4(c) and 4(d), the “head” part changes its position, suggesting a kind

of hopping process in this case. These results suggest the existence of two different energy transfer mechanisms for the case of *cis*-2-butene. A detailed study of these motions is now in progress and will be published elsewhere.⁹⁾

4. Conclusions

In conclusion, the adsorption of *cis*-2-butene molecules on the Pd (110) surface was studied by STM at 4.7 K for the first time. Completely different molecular configurations from those of *trans*-2-buten molecules were observed. In addition, at high bias voltages for the STM measurement, the *cis*-2-butene molecule became unstable and moved in two different manners around the palladium atom to which the molecule was bonded, suggesting the existence of two different mechanisms of the motion on the surface.

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