Single-Molecule Reaction and Characterization by Vibrational Excitation

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Controlled chemical reaction of single *trans*-2-butene molecules on the Pd(110) surface was realized by dosing tunneling electrons from the tip of a scanning tunneling microscope at 4.7 K. The reaction product was identified as a 1,3-butadiene molecule by inelastic electron tunneling spectroscopy. Threshold voltage for the reaction is ~365 mV, which coincides with the vibrational excitation of the C-H stretching mode. The reaction was ascertained to be caused by C-H bond dissociation by multiple vibrational excitations of the C-H stretching mode via inelastic electron tunneling process.

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Mode-selective chemical processes have been widely utilized in photochemistry, photobiology, or laser micromachining [1]. Much attention has been paid to the desorption induced by multiple electron transition (DIMET) caused by a femtosecond laser, in which the excitation process of ladder climbing of vibrational states makes the nonlinear desorption rate on the photon flux of incident laser [2]. The vibrational excitation of adsorbates thus provides a promising prospect for mode-selective process, which enables the functional-group selective reaction. Scanning tunneling microscope (STM) is an ideal electron source for the mode-selective vibrational excitations of a single molecule through the inelastic electron tunneling process [3]. There have been reports which describe surface phenomena caused by vibrational excitation of a single molecule [4–10], but it is still challenging to realize a chemical reaction on a single molecule through vibrational excitation of a specified bond. A pioneering investigation of intramolecular bond dissociation via vibrational excitation with STM has been reported for O_2 molecules on a Pt(111) substrate [6]. Dissociation of the O_2 molecules has been explained on the basis of a vibrational-heating mechanism by a resonant inelastic electron tunneling process. Similar mechanisms have been proposed in the previous studies of Xe atom switching on Ni(110) [4] and Si-H bond dissociation at the Si(100)-(1×1) surface [5]. The threshold energy of the tunneling electrons for the reaction is the key information for the determination of the vibrational mode responsible for the bond dissociation. However, as far as we know, there has been no systematic finding of the threshold energy of the tunneling electrons for bond dissociation.

Here, we report a mode-selective, molecule-to-molecule chemical reaction by STM; a *trans*-2-butene molecule to a 1,3-butadiene molecule on Pd(110) surface. We propose a model for the reaction in which a multiple vibrational excitation of the molecule via inelastic electron tunneling process is a key process. Inelastic electron tunneling spectroscopy with STM (STM-IETS) [11] was used to chemically identify the reaction product.

All experiments were performed using a low-temperature STM (LT-STM, Omicron GmbH) with an electrochemically etched tungsten tip equipped in an ultrahigh vacuum chamber ($< 3 \times 10^{-11}$ Torr) [10]. The Pd(110) surface was maintained at 4.7 K during both imaging and measurement of IETS spectra, except gas dosing in which the sample temperature is estimated to be ~50 K. Topographic STM images of *trans*-2-butene (Fig. 1(a)) and 1,3-butadiene (Fig. 1(b)) on the Pd(110) surface are quite different from each other; the former appears as a dumbbell shape where two protrusions are aligned perpendicular to the Pd row. The latter appears as an elliptical protrusion whose long axis is parallel to the Pd row. We propose a model for the adsorption configuration

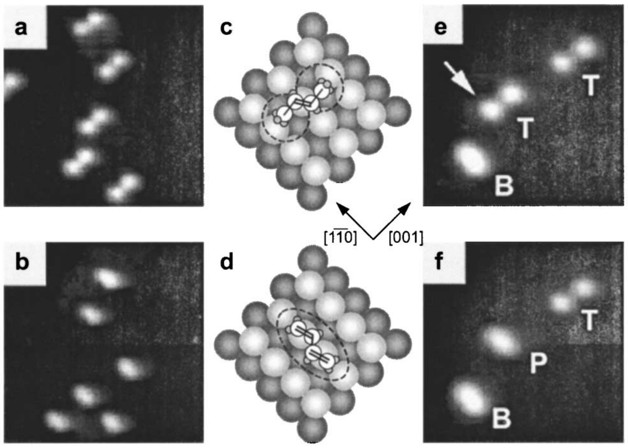

FIG. 1. STM images of (a) *trans*-2-butene and (b) 1,3-butadiene molecules (area = 45×45 Å^2, $V_s = -300$ mV, $I_t = 1.00$ nA). Schematic representation of the adsorption site of (c) *trans*-2-butene and (d) 1,3-butadiene molecule on Pd(110), respectively. STM images of coadsorbed surface (area = 20×20 Å^2, $V_s = -200$ mV, $I_t = 0.86$ nA) (e) before and (f) after dosing tunneling electrons on a target molecule of *trans*-2-butene marked with an arrow in (e). The *trans*-2-butene, reaction product, and 1,3-butadiene molecules are labeled *T*, *P*, and *B*, respectively, in (f).

of *trans*-2-butene and 1,3-butadiene molecules in Figs. 1(c) and 1(d), respectively. In both cases, C=C bonds are located at on-top sites. This shows good consistency with the adsorption sites and orientations determined from near-edge x-ray absorption fine structure (NEXAFS) and high-resolution electron energy-loss spectroscopy (HREELS) studies [12,13]. Figure 1(e) shows the surface on which molecules of *trans*-2-butene (labeled *T*) and 1,3-butadiene (labeled *B*) are coadsorbed. After taking this image, the STM tip is positioned over the *trans*-2-butene molecule, which is marked by an arrow in the figure, to dose tunneling electrons. The dosing condition is the tunneling current of 7 nA, the sample bias voltage of 450 mV and the dosing period of 1 sec with the feedback loop turned off. This causes a topological change of *trans*-2-butene molecules; *T* of Fig. 1(e) changes to *P* of Fig. 1(f). Because of the similarity of the STM images between a 1,3-butadiene molecule and the reaction product, we are tempted to consider that a *trans*-2-butene molecule is converted to a 1,3-butadiene molecule via dehydrogenation.

In order to identify the chemical specification of the reaction product, we performed the STM-IETS to obtain the vibrational information [11]. The STM-IETS measurement is carried out as follows: the STM tip is precisely positioned over a target molecule and the feedback loop is then turned off. Sinusoidal modulation of 397 Hz in frequency and 5.7–14.1 $\mathrm{mV_{rms}}$ in amplitude is superimposed on the sample bias voltage, V_s. The second harmonic of the modulation frequency was measured with a lock-in amplifier, which is proportional to d^2I/dV^2, which exhibits a peak-shaped signal at the threshold energy for excitation of the vibrational mode. The signals are collected and averaged after each bias scan.

Figure 2(a) represents the characteristic vibrational spectra obtained for *trans*-2-butene on a Pd(110) surface together with the spectrum obtained on Pd substrate. In a background-subtracted spectrum of the *trans*-2-butene molecule [Fig. 2(b)], the characteristic features at ±366 meV can be identified which is consistent with the vibrational energy of C-H stretching mode measured by HREELS [13]. The features corresponding to the C-H stretching mode are the most characteristic vibrational fingerprint of hydrocarbon molecules in STM-IETS spectra. Indeed, it has been observed for several hydrocarbons on various metal surfaces; ethylene (358 mV) [11], Cu(II) etioporphyrin (359 mV) [14], pyridine (377 mV) [15], tetrahydrothiopene (370 mV), and pyrrolidine (368 mV) [16] on Cu(100), and ethylene (357 mV) and acetylene (368 mV) on Ni(110) [17]. In the detection of the C-H stretching mode of a *trans*-2-butene molecule, we use considerably high gap resistance of 1 GΩ so as to avoid the dehydrogenation of the molecule during measurement. Deuteration of the molecule causes a spectral shift of this peak to 268 mV for *trans*-2-butene-d_8, which is in good agreement with previous STM-IETS results for the C-D stretching mode observed for other deuterated hydrocarbon species [11,15,17].

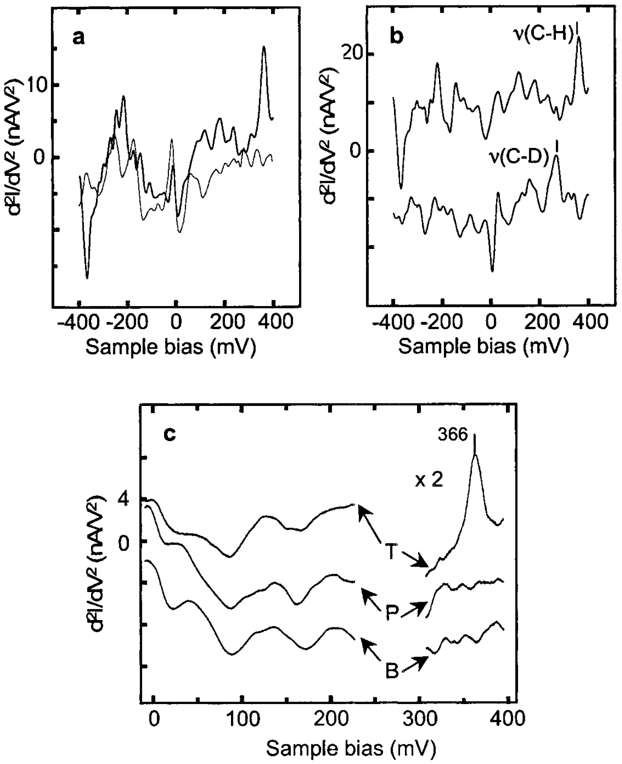

FIG. 2. (a) Vibrational spectra obtained for the clean Pd(110) surface (dashed line) and *trans*-2-butene (solid line) by STM-IETS taken at a gap resistance of 1 GΩ with a 14.1 $\mathrm{mV_{rms}}$ ac modulation at 397 Hz. The spectra are averages of four scans from −400 to +400 mV. (b) Vibrational spectra for *trans*-2-buten (upper line) and *trans*-2-buten-d_8 (lower line) after background subtraction. The change in conductance for the peaks at ±366 mV (268 mV) is 6% (5%) at positive sample bias, and 7% (3%) at negative sample bias, for the C-H (C-D) stretching mode of *trans*-2-butene (*trans*-2-butene-d_8). (c) Vibrational spectra for *trans*-2-butene (curve *T*), reaction product (curve *P*), and 1,3-butadiene (curve *B*) shown in Fig. 1(f), respectively. The spectra were taken at a gap resistance of 200 MΩ within the range of 0 and 230 mV, in the region where the dehydrogenation does not occur, and 1.5 GΩ within the range of 300 and 400 mV.

For the purpose of identifying the reaction product, STM-IETS measurement was performed on *trans*-2-butene (*T*), reaction product (*P*), and 1,3-butadiene (*B*) shown in Fig. 1(f). In Fig. 2(c), the spectrum of *trans*-2-butene (curve *T*) is dominated by a strong C-H stretching peak at 366 meV, while no peak is observed in the C-H stretch region both for reaction product (curve *P*) and for 1,3-butadiene (curve *B*). Adsorption geometry can affect inelastic vibrational excitation mechanisms and the related selection rules in STM-IET spectroscopy [16,18,19]. In the present system, the geometry of σ(C-H) in *trans*-2-butene is quite different from 1,3-butadiene on Pd(110) surface. NEXAFS study reveals that the σ(C-H) resonance of *trans*-2-butene is enhanced on $E//[110]$ [13] and that of 1,3-butadiene is enhanced on $E//[001]$ [12]. This means that the C-H in $-\mathrm{CH_3}$ groups (sp^3 symmetry) of *trans*-2-butene are lifted toward the vacuum, yet the C-H in $\mathrm{CH_2}$ groups (sp^2 symmetry) of 1,3-butadiene are parallel to the surface. Indeed, Lauhon *et al.* have reported that the C-H stretching mode has a surface normal component, but is not observed for a benzene molecule on Cu(100) where the benzene ring is flat and the C-H stretching mode has no surface normal component [15]. A similar result was also observed for thiophene and pyrrole on Cu(100) [16]. As a result, the lack of a C-H stretching mode of 1,3-butadiene and reaction product provides spectroscopic evidence for the conversion of a *trans*-2-butene molecule into a 1,3-butadiene molecule. In the lower frequency region, on the other hand, the vibrational spectra show weak and broad shapes. Although we cannot assign all peaks perfectly, it is obvious that the vibrational spectrum of the reaction product shows a great resemblance to that of 1,3-butadiene, which also permits us to identify the reaction product as 1,3-butadiene.

The reaction yield per incident electron as a function of the sample bias voltage at a constant tunneling is shown in Fig. 3(a), both for *trans*-2-butene and for *trans*-2-butene-d_8. We also show its slope in the same graph. The variation of the reaction yield shows a rapid increase at the threshold voltages of $\sim$365 and $\sim$275 mV for a normal *trans*-2-butene molecule and a *trans*-2-butene-d_8 molecule, respectively. The bias voltages correspond exactly to the C-H and C-D vibrational stretching modes observed in STM-IETS spectra (see Fig. 2(b)). This obviously indicates that the C-H (C-D) stretching mode is a "doorway" to the C-H (C-D) bond dissociation.

A single-electronic transition process, via which a tunneling electron occupies an antibonding state of a C-H bond to invoke C-H dissociation [5], is not a suitable mechanism for the present reaction. This is because the unoccupied antibonding state of C-H bond is more than $\sim$3 eV above the Fermi level [20], and that the electronic excitation generally does not show an isotope shift in threshold energy [21]. In addition, as is described below, this phenomenon is not a single-electron process. Instead, we consider vibrational heating as a plausible mechanism where the C-H (C-D) stretching mode is excited to higher quanta in a ladder-climbing manner, such as the DIMET process.

A feature commonly observed for the vibrational-heating mechanism is a nonlinear power-law dependence of reaction rate per electron (R) on tunneling current (I), $R \propto I^n$, where n is the order of the reaction [4–6]. Figures 3(b) and 3(c) show typical R-I curves obtained on *trans*-2-butene molecules and *trans*-2-butene-d_8 molecules, respectively. For *trans*-2-butene, the estimated n is $\sim$2 in the bias voltage region between 370 and 600 mV and is $\sim$1 with the bias above 800 mV. The results for *trans*-2-butene-d_8, on the other hand, show that $n \sim 3$ for $V_s < 400$ mV, $n \sim 2$ for 600 mV$<V_s<$ 800 mV, and $n \sim 1$ for $V_s > 1000$ mV. The abrupt change of the reaction order with the energy of the tunneling electrons is clear evidence of the involvement of multiple excitation processes in the dehydrogenation.

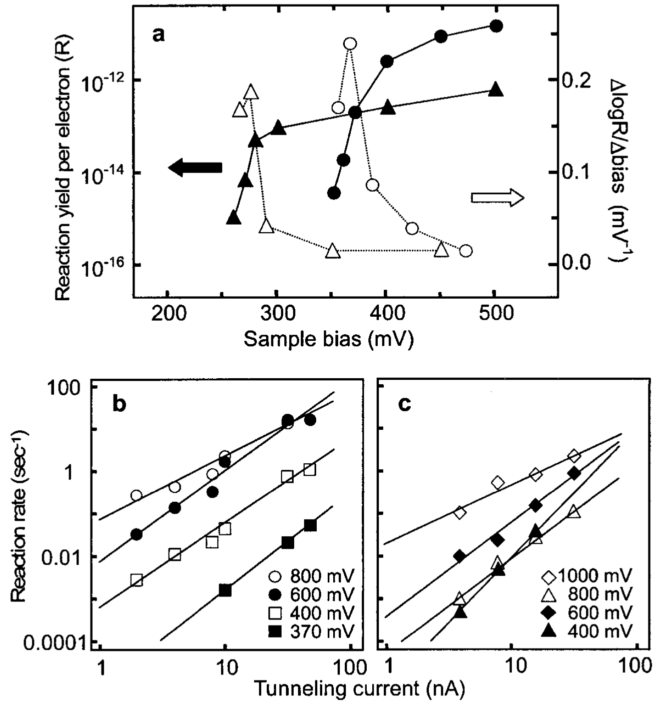

FIG. 3. (a) Reaction yield per electron for *trans*-2-butene and *trans*-2-butene-d_8 as a function of sample bias voltage under constant tunneling current of 32 nA. Dotted lines represent the slopes of the data. Reaction rate (R) as a function of tunneling current (I) for various applied sample bias voltages for (b) *trans*-2-butene and (c) *trans*-2-butene-d_8. Solid lines are the results of least squares fits to the data, whose slopes for applied bias voltages correspond to powers (n) in nonlinear power-law dependence, $R \propto I^n$. In (b), $n = 2.23$, 1.96, 2.09, and 1.45 for 370, 400, 600, and 800 mV, respectively. In (c), $n = 3.06$, 2.19, 2.21, and 1.36 for 400, 600, 800, and 1000 mV, respectively.

The microscopic dynamics of the dehydrogenation can be described with a potential curve that is schematically shown in Fig. 4. The system is initially at its ground state. It is excited into the states with higher vibrational quanta by injecting inelastically tunneled electrons in a ladder-climbing manner, and finally overcomes the activation barrier for the dehydrogenation [22,23]. This model has successfully explained the breaking of the adsorbate-surface bond by femtosecond laser irradiation [22] and the single-molecule dissociation of O_2 on Pt(111) by tunneling electrons [6]. The potential curve for the dehydrogenation should be constructed using the C-H (C-D) stretching coordinate and a truncated harmonic oscillator with a vibrational energy of 366 meV (268 meV) that is obtained from the STM-IETS spectrum (Fig. 2(a)). Based on the estimated reaction order on the tunneling current, the number of the vibrational bound state is considered to be two (three) for C-H (C-D). The harmonic oscillator model allows us to determine the effective barrier height for dehydrogenation in the range of 487 to 722 meV for *trans*-2-butene and of 536 to 781 meV for *trans*-2-butene-d_8.

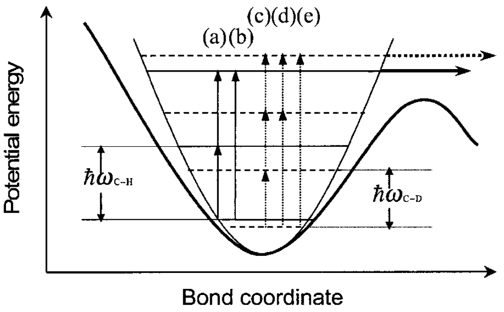

FIG. 4. Schematic representation of vibrational heating and dehydrogenation using a truncated one-dimensional harmonic oscillator. The potential well includes two C-H and three C-D vibrational states following the reaction orders determined from the experimental results (Figs. 3(b) and 3(c)). Representative types of vibrational transition for applied basis are considered as follows: (a) 370, 400, 600 mV and (b) 800 mV for C-H, (c) 400 mV, (d) 600, 800 mV, and (e) 1000 mV for C-D.

Finally, let us discuss the involvement of low-frequency vibrational modes, such as a hindered-translational mode or a hindered-rotational mode, into the dehydrogenation process. It has been reported that various motions of adsorbate such as rotation [8] and hopping [10] can be induced by exciting high-frequency vibrational mode with tunneling electrons, where the coupling between the high- and low-frequency modes is interpreted as the mechanism of the motion of the molecules. A special interesting case can be seen for the system of O_2 on Pt(111), where rotation of a O_2 molecule is induced by the excitation of O-O stretching mode which is followed by eventual dissociation of the O_2 molecule [6,7]. This result implies that the rotation of the O_2 molecule is a precursor state of the O_2 dissociation. In the current study, the molecule of the reaction product is rotated and translated from the original molecule in the adsorption configuration. However, unless the dehydrogenation occurs, there have been no signs of the motion of the *trans*-2-butene molecule either in the tunneling current or in the STM images even if tunneling electrons with sufficient energy to excite C-H mode are injected. Apparently this is a different situation from the case of O_2/Pt(111), and we do not consider this as a case where the energy of the high-frequency mode is transferred into the low-frequency mode followed by dehydrogenation. We believe that the rotation of the molecule occurs in the transition state of dehydrogenation or after the reaction is completed.

In conclusion, we have shown "molecule-to-molecule" conversion of a *trans*-2-butene molecule into a 1,3-butadiene molecule on the Pd(110) surface using a low-temperature STM. The reaction product is chemically identified with STM-IETS. We have revealed that the reaction is induced by multiple excitations of a vibrational mode in a ladder-climbing manner. In addition, we have identified the vibrational mode to be a C-H stretching mode which forms the ladder for the reaction by detecting threshold energy of the tunneling electron for the reaction. We believe that this is the first example that both the vibration-induced chemical reaction and the detection of the responsible vibrational mode are demonstrated simultaneously. Our study reveals that the controlled excitation of vibrational modes can be a powerful tool for tailoring chemical bonds into molecular systems, permitting the synthesis of new molecular systems that are inaccessible by conventional chemistry.

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[1] S. K. Sarkar and J. P. Mittal, Mater. Sci. Forum **301**, 1 (1999).
[2] J. A. Prybyla *et al.*, Phys. Rev. Lett. **64**, 1537 (1990).
[3] G. Binnig, N. Garcia, and H. Rohrer, Phys. Rev. B **32**, 1336 (1985).
[4] D. M. Eigler, C. P. Lutz, and W. E. Rudge, Nature (London) **352**, 600 (1991).
[5] T.-C. Shen *et al.*, Science **268**, 1590 (1995).
[6] B. C. Stipe *et al.*, Phys. Rev. Lett. **78**, 4410 (1997).
[7] B. C. Stipe, M. A. Rezaei, and W. Ho, Science **279**, 1907 (1998).
[8] B. C. Stipe, M. A. Rezaei, and W. Ho, Phys. Rev. Lett. **81**, 1263 (1998).
[9] S.-W. Hla, L. Barrels, G. Meyer, and K.-H. Rieder, Phys. Rev. Lett. **85**, 2777 (2000).
[10] T. Komeda *et al.*, Science **295**, 2055 (2002).
[11] B. C. Stipe, M. A. Rezaei, and W. Ho, Science **280**, 1732 (1998).
[12] S. Katano *et al.*, Surf. Sci. **502–503**, 164 (2002).
[13] S. Katano *et al.*, Jpn. J. Appl. Phys. **41**, 4911 (2002).
[14] T. M. Wallis, X. Chen, and W. Ho, J. Chem. Phys. **113**, 4837 (2000).
[15] L. J. Lauhon and W. Ho, J. Phys. Chem. A **104**, 2463 (2000).
[16] J. Gaudioso and W. Ho, J. Am. Chem. Soc. **123**, 10 095 (2001).
[17] J. Gaudioso, H. J. Lee, and W. Ho, J. Am. Chem. Soc. **121**, 8479 (1999).
[18] L. J. Lauhon and W. Ho, J. Phys. Chem. A **104**, 2463 (2000).
[19] J. I. Pascual *et al.*, Phys. Rev. Lett. **86**, 1050 (2001).
[20] J. C. Bertolini *et al.*, Surf. Sci. **349**, 88 (1996).
[21] Ph. Avouris *et al.*, Chem. Phys. Lett. **257**, 148 (1996).
[22] S. Gao, D. G. Busch, and W. Ho, Surf. Sci. **344**, L1252 (1995).
[23] S. Gao, Phys. Rev. B **55**, 1876 (1997).