

## LETTERS

### Selective Partial Hydrogenation of 1,3-Butadiene to Butene on Pd(110): Specification of Reactant Adsorption States and Product Stability

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Selective partial hydrogenation of 1,3-butadiene ( $C_4H_6$ ) to butene ( $C_4H_8$ ) on hydrogen-precovered Pd(110) has been investigated using temperature-programmed desorption (TPD), scanning tunneling microscopy (STM), and high-resolution electron energy loss spectroscopy (HREELS). Below room temperature,  $C_4H_6$  was molecularly chemisorbed on a hydrogen-precovered Pd(110) surface and was in the  $\pi$ -bonded chemisorption state. The hydrogenation of  $C_4H_6$  did not occur in the sparse domains of less than 0.25 ML. With increasing  $C_4H_6$  coverage,  $C_4H_6$  formed dense domains, and the  $\pi$  bond was weakened. Only the weakly  $\pi$  bonded  $C_4H_6$  was hydrogenated to  $C_4H_8$  at about 200 K. Because the stability of resultant  $C_4H_8$  was low on the surface at the reaction temperature,  $C_4H_8$  desorbed immediately after being produced or dehydrogenated to  $C_4H_6$  if even a part of the  $C_4H_8$  remained on the surface. We concluded that the balance between the hydrogenation reactivity of  $C_4H_6$  and the stability of  $C_4H_8$  leads to the partial hydrogenation on the Pd surface.

#### Introduction

Selective hydrogenation of complex alkenes, which contain more than two unsaturated bonds, is interesting and important from the viewpoint of industrial use.<sup>1</sup> It is known that 1,3-butadiene ( $C_4H_6$ ) on Pd surfaces is partially hydrogenated to butene ( $C_4H_8$ ), whereas on Pt surfaces, 1,3-butadiene is completely hydrogenated to butane ( $C_4H_{10}$ ).<sup>2,3</sup> The difference between the reaction on the Pt surface and that on the Pd surface has been attributed to the difference in the adsorption state of 1,3-butadiene, where it adsorbs via C=C double bonds, i.e., di- $\sigma$  bond on Pt and the  $\pi$  bond on Pd.<sup>2,3</sup> However, such a classification still neglects important factors for the occurrence of selective hydrogenation, because the Pd surface effects not

only the hydrogenation but also the decomposition of 1,3-butadiene even though it is in the  $\pi$ -bonded state. To clarify this point, more precise investigations of adsorption states and structure-specificity are required, such as the recent studies of bimetallic surface reactivity.<sup>4–6</sup> In addition, the examination of product stability is also important for understanding partial hydrogenation.

In this letter, the hydrogenation of 1,3-butadiene to butene on Pd(110) has been studied focusing on the details of the differences in the adsorption states and the product stability, using temperature-programmed desorption (TPD), scanning tunneling microscopy (STM), and high-resolution electron energy loss spectroscopy (HREELS). We could distinguish two types of chemisorbed  $C_4H_6$ , namely, strongly  $\pi$ -bonded  $C_4H_6$  in sparse domains and weakly  $\pi$ -bonded  $C_4H_6$  in compressed domains on hydrogen-preadsorbed Pd(110). Here, we discuss the coverage-dependent reactivity in terms of the chemisorbed states and local structures of  $C_4H_6$ . Finally, we examine the

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cause of partial hydrogenation on the Pd surface taking into consideration the stability of  $C_4H_8$ .

## Experimental Section

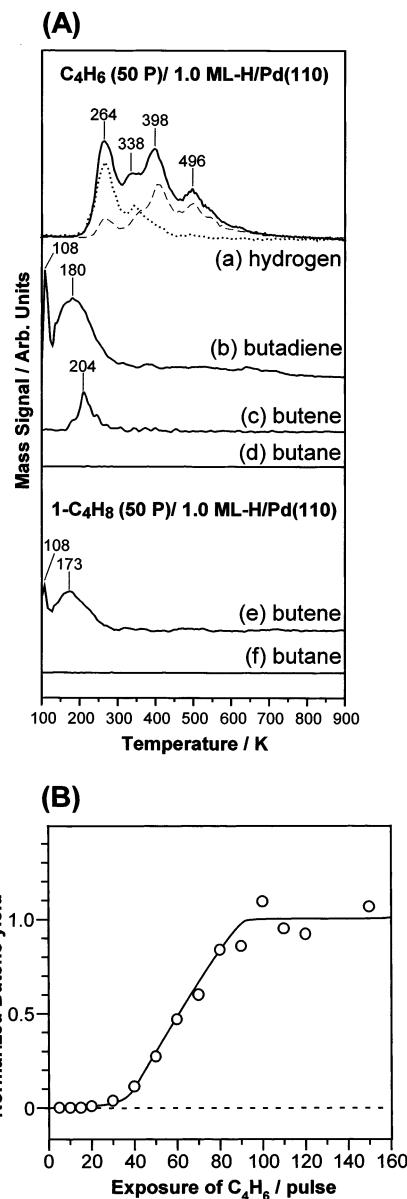
All experiments were carried out in ultrahigh vacuum (UHV) chambers at the base pressure of  $1 \times 10^{-10}$  Torr. The Pd(110) surface was cleaned by repeating argon ion sputtering, annealing to 1100 K and  $O_2$  treatment at 850 K. The cleanliness of the surface was checked by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). Gaseous molecules were introduced into the UHV chamber using a pulsed gas doser. The coverage of the chemisorbed layer was controlled by changing the number of shots of the pulsed gas dosing system. All TPD measurements were carried out at the heating rate of 6 K/s. The desorptions of hydrogen, 1,3-butadiene, butene, and butane were monitored by measuring the parent species, the mass numbers of which are  $m/e = 2, 56, 58$ , and 60, respectively, using a quadrupole mass spectrometer. The STM images were obtained using the Beetle-type STM (Besocke Delta Phi GmbH) with an electrochemically etched W tip, equipped in the UHV chamber. STM images were acquired in the constant-current mode. A set of a double-path monochromator and a single-path energy analyzer (Specs: DELTA 0.5) were used in the HREELS experiment. The electron beam was input to the surface at the angle of  $60^\circ$ , and the HREELS spectrum was obtained at the scatter angle of  $60^\circ$  from the surface normal in the scattering plane along  $[1\bar{1}0]$ . The resolution of all HREELS spectra was 3.4 meV ( $27\text{ cm}^{-1}$ ).

## Results and Discussion

A set of TPD results obtained from  $C_4H_6$  dosed for 50 pulses on 1.0-ML-H preadsorbed Pd(110) at 100 K is shown in Figure 1A(a–d) (1 ML =  $9.35 \times 10^{14}\text{ cm}^{-2}$ ). Figure 1A(b) shows  $C_4H_6$  desorption, and the peaks at 108 and 180 K are attributed to the multilayer and first  $C_4H_6$  layer. The desorption of  $C_4H_8$  is observed at 204 K, as shown in Figure 1A(c), whereas  $C_4H_{10}$  was not detected (Figure 1A(d)). Here, we can confirm that the Pd surface acts as a partial hydrogenation system under our experimental conditions.

Hydrogen desorption signals also include important information concerning butadiene reactions. Four distinct peaks are observed in the  $H_2$  TPD spectrum, as shown in Figure 1A(a). Dotted and dashed lines in Figure 1A(a) are  $H_2$  and  $D_2$  desorption spectra, respectively, obtained from that of deuteride 1,3-butadiene ( $C_4D_6$ ) on 1.0 ML-H/Pd(110). Two peaks at 264 and 338 K are assigned to the recombination of preadsorbed hydrogen because of the large  $H_2$  peak denoted by the dotted line. Because the desorption temperature of surface hydrogen on clean Pd(110) is 300 K,<sup>7</sup> the observed different temperatures suggest that the preadsorbed hydrogen is displaced from the surface to subsurface or bulk sites upon the  $C_4H_6$  adsorption. HREELS results show that the peaks assigned to surface hydrogen decreased with increasing coverage of 1,3-butadiene and disappeared when the surface was covered with  $c(4 \times 2)$  of 1,3-butadiene.<sup>8</sup> Such adsorption site displacement has been reported in the cases of  $CO$ <sup>7</sup> and ethylene<sup>9</sup> adsorption on hydrogen-preadsorbed Pd(110). Furthermore, it is noteworthy that subsurface hydrogen is considered to be active in the hydrogenation of ethylene and acetylene, as pointed out by Ceyer's group.<sup>10–12</sup>

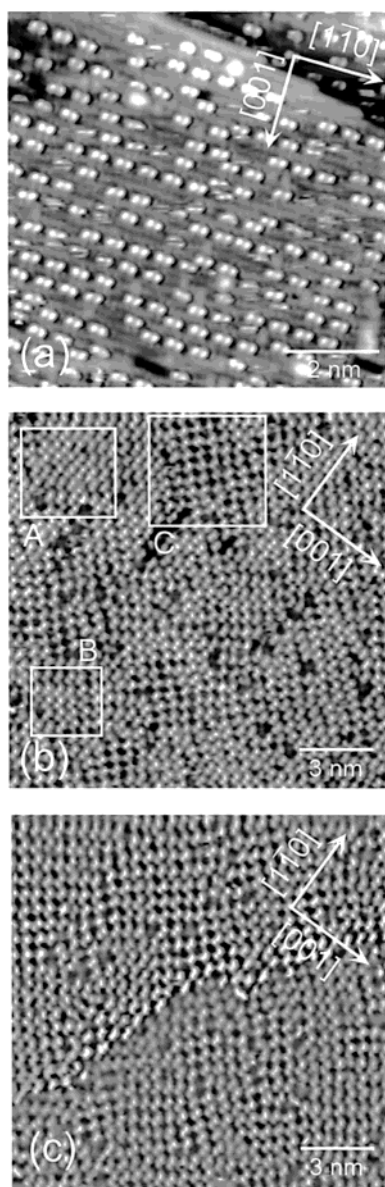
On the other hand,  $D_2$  desorption peaks at 398 and 496 K indicate decomposition of adsorbed 1,3-butadiene ( $C_4D_6$ ) on Pd(110), as denoted by the dashed line in Figure 1A(a). Small  $D_2$  desorption peaks at 264 and 338 K are attributed to the



**Figure 1.** (A) TPD spectra of (a)  $H_2$ , (b)  $C_4H_6$ , (c)  $C_4H_8$ , and (d)  $C_4H_{10}$  obtained from the 1,3-butadiene ( $C_4H_6$ : 50 pulses)/1.0-ML-H/Pd(110) surface. Dotted and dashed curves inserted in part a are the TPD spectra of  $H_2$  and  $D_2$ , respectively, obtained from the 1,3-butadiene- $d_6$  ( $C_4D_6$ : 50 pulses)/1.0-ML-H/Pd(110) surface. TPD spectra of (e)  $C_4H_8$  and (f)  $C_4H_{10}$  obtained from 1-butene ( $C_4H_8$ : 50 pulses)/1.0-ML-H/Pd(110) surface. All spectra were obtained at the heating rate of 6 K/s. (B) The plots of butene ( $C_4H_8$ ) yield against  $C_4H_6$  exposure. The  $C_4H_8$  yield was estimated by integrating the TPD peak of butene shown in Figure 1A(c).

exchange reaction between preadsorbed hydrogen and molecular  $C_4H_6$ .<sup>8</sup> These assignments are consistent with previous HREELS measurements,<sup>13</sup> in which it was confirmed that  $C_4H_6$  is molecularly adsorbed on Pd(110), at least, at temperatures below room temperature. Note that, although  $C_4H_6$  is still present on the surface, hydrogenation terminates at the end of  $C_4H_6$  desorption in TPD.

Desorption yield of  $C_4H_8$  as a function of the  $C_4H_6$  exposure is shown in Figure 1B. The desorption yields were estimated by integrating the TPD peak of  $C_4H_8$ . With a low  $C_4H_6$  exposure of less than 20 pulses, no hydrogenated species were detected. When the  $C_4H_6$  exposure exceeded 20 pulses, hydrogenation began. The amount of  $C_4H_8$  desorption increased

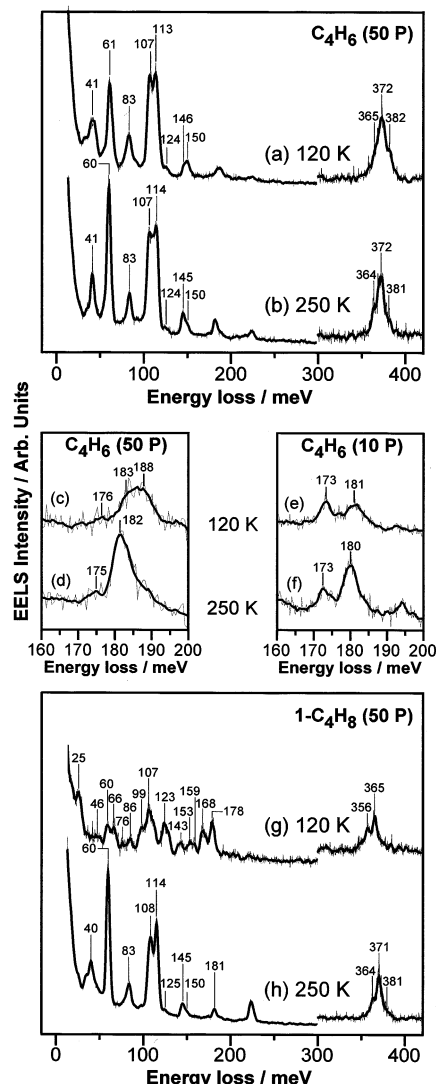


**Figure 2.** (a) STM image of low-coverage 1,3-butadiene ( $\text{C}_4\text{H}_6$ : 10 pulses) on 1.0-ML-H/Pd(110) at 214 K. STM images of high-coverage 1,3-butadiene ( $\text{C}_4\text{H}_6$ : 50 pulses) on 1.0-ML-H/Pd(110) obtained at (b) 180 and (c) 250 K. All STM images were obtained at the sample bias of  $-100$  mV and tunneling current of  $0.9$  nA.

considerably on increasing  $\text{C}_4\text{H}_6$  exposure from 30 to 90 pulses and saturated at 90 pulses.

Figure 2a shows the STM image of  $\text{C}_4\text{H}_6$  dosed with 10 pulses on 1.0-ML-H preadsorbed Pd(110), where hydrogenation did not take place. Individual  $\text{C}_4\text{H}_6$  molecules are imaged as a pair of protrusions. Each protrusion is located at the on-top site of Pd(110) corresponding to the  $\text{C}=\text{C}$  bond in  $\text{C}_4\text{H}_6$ . A previous study revealed that  $\text{C}_4\text{H}_6$  is  $\pi$ -bonded and the molecular plane is parallel to the surface, in which the  $\text{C}-\text{C}$  single bond in  $\text{C}_4\text{H}_6$  is aligned along  $[1\bar{1}0]$ .<sup>13</sup> The  $\text{C}_4\text{H}_6$  molecule was ordered with 4 times the lattice constant ( $2.76$  Å) along  $[1\bar{1}0]$ ,  $1\text{D}-(4 \times n)$ , and the  $p(4 \times 2)$  structure was also formed partially at the surface.

Three types of ordered structures were observed at the  $\text{C}_4\text{H}_6$  exposure of 50 pulses below the hydrogenation temperature ( $180$  K), i.e.,  $1\text{D}-(2 \times n)$ ,  $1\text{D}-(3 \times n)$ , and  $c(4 \times 2)$  areas marked A, B, and C in Figure 2b, respectively. On annealing the sample above the hydrogenation-termination temperature ( $250$  K), the



**Figure 3.** HREELS spectra of 1,3-butadiene ( $\text{C}_4\text{H}_6$ : 50 pulses) on 1.0-ML-H/Pd(110) at (a) 120 and (b) 250 K. All spectra were measured at  $90$  K. (c and d) Expansion of the HREELS spectra in the  $\text{C}=\text{C}$  stretching region of parts a and b, respectively. HREELS spectra in the  $\text{C}=\text{C}$  stretching region obtained for the low-exposure 1,3-butadiene ( $\text{C}_4\text{H}_6$ : 10 pulses) on 1.0-ML-H/Pd(110) at (e) 120 and (f) 250 K. The peak at  $173$ – $176$  meV is assigned to the  $\text{CH}_2$  scissoring mode of  $\text{C}_4\text{H}_6$ . HREELS spectra of 1-butene ( $\text{C}_4\text{H}_8$ : 50 pulses) on Pd(110) at (g) 120 and (h) 250 K. All spectra were obtained in the specular mode, except for that in the region of  $300$ – $420$  meV ( $18^\circ$  off-specular).

$1\text{D}-(2 \times n)$  area disappeared, the  $1\text{D}-(3 \times n)$  area decreased, and the  $c(4 \times 2)$  area became dominant, as shown in Figure 2c. During this annealing procedure, some  $\text{C}_4\text{H}_6$  molecules were hydrogenated to  $\text{C}_4\text{H}_8$  and desorbed molecularly (Figure 1A). Therefore, we conclude that desorption and hydrogenation of  $\text{C}_4\text{H}_6$  at around  $200$  K occur in the dense phases, i.e.,  $1\text{D}-(2 \times n)$  and  $1\text{D}-(3 \times n)$  areas.

Figure 3, parts a and b, shows the HREEL spectra of  $\text{C}_4\text{H}_6$  dosed for 50 pulses on 1.0-ML-H preadsorbed Pd(110) at  $100$  K followed by annealing at  $120$  and  $250$  K, respectively. The assignments of the observed peaks have been reported previously.<sup>13</sup> The spectral features of observed vibrational bands at  $120$  K are similar to those at  $250$  K. However, a slight difference between parts a and b of Figure 3 is discerned at the  $\text{C}=\text{C}$  stretching region ( $182$ – $188$  meV). The peak of the  $\text{C}=\text{C}$  stretching mode is higher in energy and broader in width at  $120$  K than at  $250$  K as shown in Figure 3, parts c and d. In the HREEL spectra, the broadening of the peak of the  $\text{C}=\text{C}$

stretching mode at 120 K is interpreted as the mixture of the different domains at the surface. In comparison with the results of STM,  $C_4H_6$  having a higher energy  $C=C$  stretching mode corresponds to that in dense phases. The peak position of the  $C=C$  stretching mode represents the strength of the  $\pi$  bond between the  $C=C$  double bond and the metal substrate. When the interaction between the  $C=C$  bond and the substrate is strong, the  $C=C$  double bond in  $C_4H_6$  is weakened and the peak position of the  $C=C$  stretching mode is shifted to a low energy. Thus, we conclude that  $C_4H_6$  in dense domains is a weakly  $\pi$ -bonded species on Pd(110) and that it is the species hydrogenated to butene.

The HREEL spectra obtained for a low  $C_4H_6$  exposure (10 pulses) shows that the  $C=C$  stretching peak was positioned in a lower energy region, i.e., 180–181 meV at both 120 and 250 K, as shown in parts e and f of Figure 3. The strongly  $\pi$ -bonded  $C_4H_6$  at low coverage and that after annealing at 250 K have a common feature in the STM images; the strongly  $\pi$ -bonded  $C_4H_6$  occupies sparse domains, i.e.,  $c(4 \times 2)$ ,  $p(4 \times 2)$ , and  $1D-(4 \times n)$ , as shown in Figure 2, parts a and c. According to the coverage-dependent TPD measurement (Figure 1B), the strongly  $\pi$ -bonded low-coverage  $C_4H_6$  is not hydrogenated. Of course, the strongly  $\pi$ -bonded  $C_4H_6$  after annealing at 250 K is also not hydrogenated. Only weakly  $\pi$ -bonded  $C_4H_6$  in the dense domains is reactive in the hydrogenation to butene. This reactive tendency is in good agreement with a recent sum-frequency generation (SFG) study of ethylene hydrogenation.<sup>14</sup>

On the other hand, the stability of butene is important to partial hydrogenation. The HREEL spectrum of 1-butene on the 1.0 ML-H/Pd(110) surface is completely different from that of 1,3-butadiene on Pd(110) at 120 K, as shown in Figure 3g. Peaks at 178 and 355 meV are assigned to  $CH_3$  deformation and  $C-H$  stretching modes, respectively, that originate from the  $sp^3$  configuration. This indicates that 1-butene is molecularly chemisorbed on the surface at 120 K. After annealing the surface, the adsorbed 1-butene molecule starts to dehydrogenate to 1,3-butadiene at 170 K (not shown), and the spectrum finally becomes the same as that of 1,3-butadiene adsorption in Figure 3h. Other butene isomers show behavior similar to that of 1-butene on Pd(110). In addition, Figure 1A(e,f) shows a set of TPD results for 1-butene dosed on 1.0-ML-H preadsorbed Pd(110) at 100 K, in which the peak of  $C_4H_8$  desorption was observed at 108 and 173 K without  $C_4H_{10}$  desorption. These butene adsorption experiments reveal that when  $C_4H_8$  is produced from  $C_4H_6$  at 200 K it desorbs immediately after being produced or dehydrogenates and reverts to  $C_4H_6$ . Therefore,

butenes cannot be stabilized on Pd(110) above 200 K, which results in the selective partial hydrogenation of  $C_4H_6$  to  $C_4H_8$  on the Pd surface.

## Conclusion

The selective partial hydrogenation of 1,3-butadiene to butenes on Pd(110) has been investigated using TPD, STM, and HREELS. The hydrogenation of 1,3-butadiene does not take place in the sparse domains of less than 0.25 ML, i.e.,  $c(4 \times 2)$ ,  $p(4 \times 2)$ , and  $1D-(4 \times n)$ , in which  $C_4H_6$  is in a strongly  $\pi$ -bonded state. On increasing the  $C_4H_6$  coverage,  $C_4H_6$  forms dense domains, i.e.,  $1D-(2 \times n)$  and  $1D-(3 \times n)$ , and turns into a weakly  $\pi$ -bonded state in these dense domains. Only the weakly  $\pi$ -bonded  $C_4H_6$  is hydrogenated to  $C_4H_8$  at about 200 K. On the other hand, 1-butene adsorption measurements clarify that the produced  $C_4H_8$  is not stabilized on the surface above 200 K because  $C_4H_8$  prefers to desorb at the temperature it is produced or is dehydrogenated to  $C_4H_6$  if any part of the  $C_4H_8$  remains on the Pd surface. We conclude that the effective partial hydrogenation of  $C_4H_6$  on the Pd(110) surface is realized because of the high hydrogenation activity of weakly  $\pi$ -bonded  $C_4H_6$  combined with the instability of  $C_4H_8$  produced at the reaction temperature.

## References and Notes

- (1) Ertl, G.; Knözinger, H.; Weitkamp, J. *Handbook of Heterogeneous Catalysis*; Wiley-VCH: Weinheim, Germany, 1997; Vol. 5.
- (2) Bertolini, J. C.; Cassuto, A.; Jugnet, Y.; Massardier, J.; Tardy, B.; Tourillon G. *Surf. Sci.* **1996**, *349*, 88.
- (3) Tourillon, G.; Cassuto, A.; Jugnet, Y.; Massardier, J.; Bertolini, J. C. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4835.
- (4) Hermann, P.; Guigner, J. M.; Tardy, B.; Jugnet, Y.; Simon, D.; Bertolini, J. C. *J. Catal.* **1996**, *163*, 169.
- (5) Hermann, P.; Tardy, B.; Simon, D.; Guigner, J. M.; Bigot, B.; Bertolini, J. C. *Surf. Sci.* **1994**, *307–309*, 422.
- (6) Bertolini, J. C.; Miegge, P.; Hermann, P.; Rousset, J. L.; Tardy, B. *Surf. Sci.* **1995**, *331–333*, 651.
- (7) Behm, R. J.; Penka, V.; Cattania, M.-G.; Christmann, K.; Ertl, G. *J. Chem. Phys.* **1983**, *78*, 7486.
- (8) Katano, S.; Kato, H. S.; Kawai, M.; Domen, K. In preparation.
- (9) Ichihara, S.; Okuyama, H.; Kato, H.; Kawai, M.; Domen, K. *Chem. Lett.* **2000**, 112.
- (10) Johnson, A. D.; Daley, S. P.; Utz, A. L.; Ceyer, S. T. *Science* **1992**, *257*, 223.
- (11) Daley, S. P.; Utz, A. L.; Trautman, T. R.; Ceyer, S. T. *J. Am. Chem. Soc.* **1994**, *116*, 6001.
- (12) Haug, K. L.; Burgi, T.; Trautman, T. R.; Ceyer, S. T. *J. Am. Chem. Soc.* **1998**, *120*, 8885.
- (13) Katano, S.; Ichihara, S.; Ogasawara, H.; Kato, H. S.; Komeda, T.; Kawai, M.; Domen, K. *Surf. Sci.* **2002**, *502–503*, 164.
- (14) Cremer, P. S.; Su, X.; Shen, Y. R.; Somorjai, G. A. *J. Am. Chem. Soc.* **1996**, *118*, 2942.