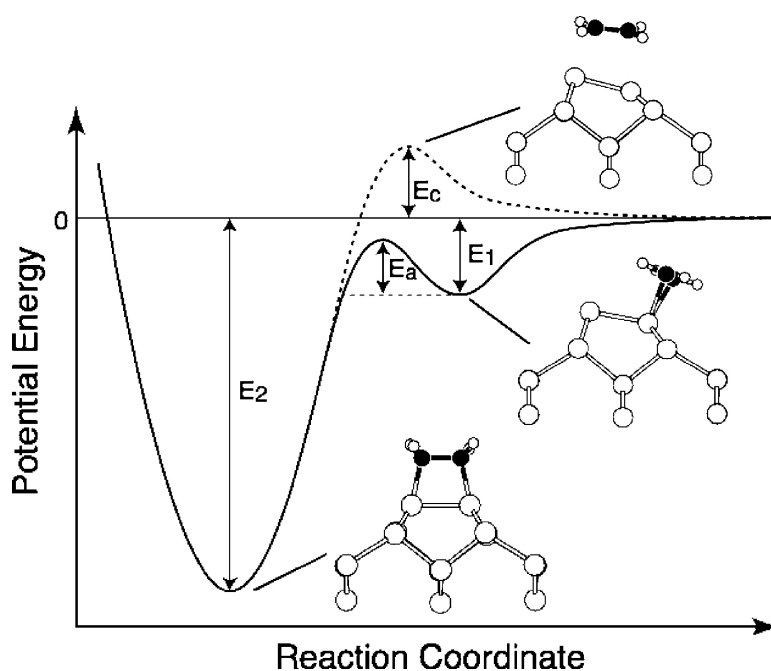


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*J. Am. Chem. Soc.*, **2004**, 126 (32), 9922-9923 • DOI: 10.1021/ja047426o • Publication Date (Web): 24 July 2004

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## Precursor Mediated Cycloaddition Reaction of Ethylene to the Si(100)c(4 × 2) Surface

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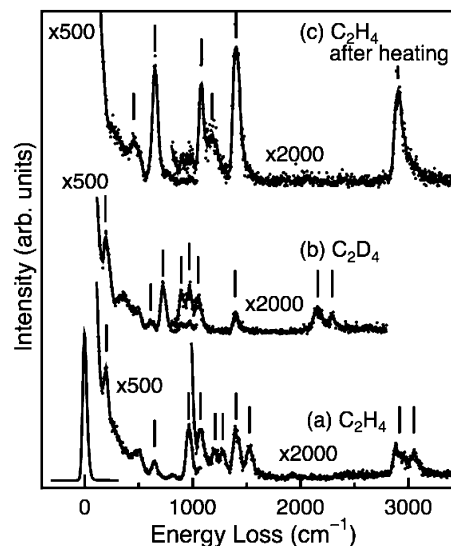
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The cycloaddition reaction of alkene to the Si(100) surface is one of the promising methods to link an organic molecule to the substrate via stable di- $\sigma$  SiC bonds.<sup>1,2</sup> Since the discovery of the di- $\sigma$ -bonded ethylene on Si(100),<sup>3</sup> many experimental and theoretical studies have been reported on the chemisorbed state. In addition, the reaction mechanism has been challenged because the frontier orbital theory states that the [2 + 2] cycloaddition reaction between ethylene and the symmetric dimer on Si(100) is apparently forbidden in thermal reaction. It has been predicted that the buckled dimer on Si(100) plays an important role in initiating the di- $\sigma$  bond formation. However, only a few studies have been reported on the reaction mechanism of di- $\sigma$  bond formation. Clemen et al. reported that the chemisorption of ethylene takes place via a mobile precursor state.<sup>4</sup> Liu and Hamers refined possible models for the di- $\sigma$  bond formation of ethylene on Si(100) using surface infrared spectroscopy.<sup>5</sup> The reaction pathways of ethylene adsorption on Si(100) have been investigated using ab initio cluster calculations<sup>6</sup> and the first-principles slab calculations;<sup>7</sup> they have predicted that the di- $\sigma$  bond formation occurs via a precursor that is weakly bonded to the down dimer atom.

In this communication, we report the direct observation of a precursor state for the di- $\sigma$  bond formation of ethylene on Si(100)c-(4 × 2) using high-resolution electron energy loss spectroscopy (HREELS) at low temperature, and the precursor state is identified as a weakly adsorbed  $\pi$ -complex type. From the vibrational spectra as a function of temperature, we estimate the activation energy from the precursor to the di- $\sigma$  species and the CC bond length.

Experiments were performed in an ultrahigh vacuum chamber equipped with a spectrometer for HREELS, a low-energy electron diffraction optics and a quadrupole mass spectrometer for gas analysis. For HREELS measurements, an energy resolution of 16 cm<sup>-1</sup> (direct mode) and an incidence angle of 60° with respect to the surface normal were used. The sample was cooled with liquid helium, the flow rate of which was controlled to keep a constant temperature. The experimental details have been described elsewhere.<sup>8</sup> First-principles slab calculations based on the density functional theory (DFT) with generalized gradient correction<sup>9</sup> were also performed to evaluate the energetics of this adsorption process, where the unit cell was Si(100)(2 × 4) and the thickness of the slab was five silicon layers (see the Supporting Information for details).

Figure 1a,b shows the HREELS spectra of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub> on Si(100)c(4 × 2) at 48 K, respectively. Figure 1c shows the EELS spectrum of C<sub>2</sub>H<sub>4</sub> on Si(100)c(4 × 2) after heating at 150 K, which is in good agreement with the previously reported spectra of di- $\sigma$  ethylene species on Si(100).<sup>3</sup>



**Figure 1.** HREELS spectra of (a) C<sub>2</sub>H<sub>4</sub> and (b) C<sub>2</sub>D<sub>4</sub> on Si(100)c(4 × 2) at 48 K. (c) After exposing C<sub>2</sub>H<sub>4</sub> on Si(100) at 48 K followed by heating at 150 K, the spectrum was measured at 48 K. All spectra were measured in the specular mode. The primary electron energy,  $E_p = 5.0$  eV.

**Table 1.** Assignments of Observed HREELS Peaks (cm<sup>-1</sup>) of Adsorbed C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub> Species on Si(100)c(4 × 2) at 48 K and Di- $\sigma$ -Bonded C<sub>2</sub>H<sub>4</sub> Species on Si(100)c(4 × 2)

mode	C <sub>2</sub> H <sub>4</sub> /Si(100) at 48 K	C <sub>2</sub> D <sub>4</sub> /Si(100) at 48 K	C <sub>2</sub> H <sub>4</sub> /Si(100) di- $\sigma$ species
hindered mode	200	194	—
$\nu_{\text{SiC}}$	642	611	452
CH <sub>2</sub> wag (sp <sup>2</sup> )	968	722	650
$\nu_{\text{C-C}}$ (sp <sup>3</sup> )	1064	893	—
CH <sub>2</sub> wag (sp <sup>3</sup> )	1207	—	1080
CH <sub>2</sub> rock (sp <sup>2</sup> )	1280	973	1182
CH <sub>2</sub> scis	1394	1053	—
$\nu_{\text{C=C}}$ (sp <sup>2</sup> )	1522	1396	1404
$\nu_{\text{CH}}$ (sp <sup>3</sup> )	2915	2160	—
$\nu_{\text{CH}}$ (sp <sup>2</sup> )	3051	2305	2905

In EELS spectra at 48 K, several new peaks are observed in addition to the vibrational peaks originating from the di- $\sigma$  ethylene species. The sharp peaks at 200 cm<sup>-1</sup> for C<sub>2</sub>H<sub>4</sub> and 194 cm<sup>-1</sup> for C<sub>2</sub>D<sub>4</sub> on Si(100)c(4 × 2) increase in intensity with increasing exposure until the multilayer starts to develop. We attribute these peaks to the hindered mode between ethylene and the substrate.<sup>8</sup> Other peaks are attributed to the internal vibrational modes, and the peak assignments are summarized in Table 1. Judging from the CH stretching (3051 cm<sup>-1</sup>) and the CC stretching (1522 cm<sup>-1</sup>) modes and the strong CH<sub>2</sub> wagging mode at 968 cm<sup>-1</sup>, we can

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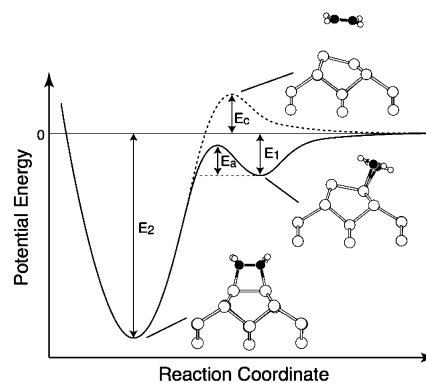
<sup>‡</sup> Department of Physics.

reasonably conclude that these peaks originate from a weakly adsorbed ethylene species. Note that in the ethylene multilayer the CC stretching mode is observed at  $1610\text{ cm}^{-1}$ . Thus, the internal bonds are slightly perturbed by the interaction between ethylene and the Si(100)c(4 × 2) surface. By comparing the vibrational spectra of chemisorbed ethylene with ethylene transition-metal complex, we conclude that this weakly adsorbed ethylene is a  $\pi$ -complex type.<sup>10,11</sup> Using the empirical relation between the CC stretching energy and the CC bond length for adsorbed ethylene species,<sup>10</sup> the CC bond length of this species is estimated to be  $1.38\text{ \AA}$ .

When the Si surface exposed to ethylene at 48 K was annealed at 150 K, the peaks originating from the  $\pi$ -complex species disappeared and the peaks originating from the di- $\sigma$  bond species were increased in intensity. Therefore, the  $\pi$ -complex adsorbed species is a precursor state for the di- $\sigma$  chemisorption. It should be noted that the  $\pi$ -complex precursor and the di- $\sigma$  species coexist at low temperature (even at lower coverage) and the reaction from the precursor to the di- $\sigma$  species does not proceed at 48 K. This suggests that when gaseous ethylene molecules enter the adsorption potential on Si(100)c(4 × 2), some molecules are trapped in the intrinsic precursor state, but the other molecules can proceed to the di- $\sigma$  bond formation; the adsorption dynamics including a collision site, the orientation of an incoming molecule, etc. may control the branching ratio.

The EELS peaks of the precursor species did not change in intensity at 55 K within 1500 s. On the other hand, after dosing ethylene at 70 K, the precursor species were not observed; the reaction from the precursor to the di- $\sigma$  bond formation was completed before HREELS measurements. From these limited experimental results the reaction rates are estimated; more than  $2.2 \times 10^{-2}\text{ s}^{-1}$  at 70 K and less than  $1.1 \times 10^{-5}\text{ s}^{-1}$  at 55 K. Assuming the pre-exponential factor of  $10^{13}\text{ s}^{-1}$ , the activation energy  $E_a$  is roughly estimated to be 0.2 eV using the Arrhenius formula. The previous experimental study reported that the desorption energy of the di- $\sigma$  species ( $E_2$ ) is 1.64 eV and the activation energy difference for desorption and chemisorption from the precursor ( $E_1 - E_a$ ) is 0.13 eV.<sup>4</sup> Using these experimental results, a potential energy diagram for the cycloaddition reaction (di- $\sigma$  bond formation) of ethylene to Si(100)c(4 × 2) can be depicted (Figure 2).

We also performed first-principles calculation of ethylene on a Si(100) slab model;  $E_1 = 0.50\text{ eV}$ ,  $E_2 = 2.08\text{ eV}$ , and  $E_a = 0.04\text{ eV}$  were obtained by DFT. The  $\pi$ -complex precursor ethylene is adsorbed at the down dimer atom of the buckled Si-Si dimer where the CC bond length is  $1.41\text{ \AA}$ ,  $\nu_{\text{C=C}} = 1467\text{ cm}^{-1}$ , and the CC bond is nearly perpendicular to the Si-Si dimer (Figure 2). Since DFT calculation often underestimates activation barriers, we consider that the present calculation is consistent with the experiment and strongly supports the experimental finding of the  $\pi$ -complex precursor state. It is also consistent with the recent DFT calculation by Cho and Kleinman except that the CC bond and the Si-Si dimer are almost parallel in their precursor geometry.<sup>7</sup> We have found that, when ethylene approaches the Si-Si dimer with its CC bond being parallel to the dimer, there exists an activation barrier of  $E_c = 0.24\text{ eV}$  (see Figure 2). On the other hand, our



**Figure 2.** Potential energy diagram for the chemisorption of ethylene on Si(100)c(4 × 2).  $E_a$ ,  $E_1$ , and  $E_2$  represent the activation energy for the di- $\sigma$  formation, the adsorption energy of the precursor state, and that of the di- $\sigma$  chemisorption state, respectively. See the text for the definition of  $E_c$ .

precursor geometry is reached from gas phase without any activation barrier. Thus, the geometry of an incoming molecule may affect the adsorption dynamics. The diradical intermediate previously reported by the DFT cluster model calculation<sup>6</sup> turned out to be unstable within the present slab-model calculation.

In conclusion, we investigated the adsorption process of ethylene on Si(100) at low temperature using HREELS. The chemisorption of ethylene on Si(100) occurs via a precursor state. The  $\pi$ -complex precursor is evidenced as a stable intermediate state by the vibrational spectra. The activation barrier from the  $\pi$ -complex precursor to the di- $\sigma$  chemisorbed state is experimentally estimated to be 0.2 eV. The present first-principles calculations strongly support the  $\pi$ -complex precursor-mediated cycloaddition reaction of ethylene on Si(100)c(4 × 2).

**Acknowledgment.** This work was partly supported by a JSPS Grand-in-Aid for Scientific Research and a grant from the Toray Science Foundation.

**Supporting Information Available:** Details of first-principles slab calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA047426O