investigations are in progress to acquire further insights regarding the nature of the intermediates under various reaction conditions.

Experimental Section

Methane decomposition was carried out for 4 h on pre-reduced samples of 10% Ni/SiO_2 and 10% Ru/Al_2O_3 at 250° and 325 °C in separate reactors. Each of these was subsequently quenched in a liquid-nitrogen bath. The reactors were then mounted in a closed-cycle refrigerator and INS spectra were collected at −253 °C on the filter difference spectrometer (FDS) instrument at the Lujan Center at Los Alamos National Laboratory. Data were treated by deconvolution of the instrumental resolution function[24] and subtraction of spectra of identical starting samples. Some of the experiments were repeated and an excellent reproducibility was observed.

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Real-time Observation of the H/D Exchange Reaction between Ethylene and Hydrogen on Pt(111)**

Chang Min Kim,* Chang-Hoon Hwang,
Chang-Woo Lee, and Heon Kang*

Adsorption and reactions of small hydrocarbon molecules on well-characterized metal single-crystal surfaces have been extensively studied to understand heterogeneous catalysis on a molecular level and design more effective catalysts.[1] Deuterated hydrocarbons are frequently used in surface-science studies of hydrocarbon reactions on metal and metal-oxide surfaces. Reaction mechanisms of surface reactions can be better understood by observing H/D reaction products and the kinetic isotope effect. The H/D exchange products on the surface have been analyzed using several different techniques including thermal desorption spectroscopy (TPD), laser induced desorption (LID), secondary ion mass spectroscopy (SIMS), and vibration spectroscopy. The H/D exchange product distribution is often difficult to determine reliably if a molecule undergoes multiple H/D substitution. The H/D substituted molecules are too similar in their spectroscopic features to identify accurately by using vibration spectroscopy. SIMS, TPD, and LID data are often very confusing because of the fragmentation of molecules on the surface or in a mass spectrometer. Fragmentation makes it difficult to quantitatively identify multiply deuterated hydrocarbon species on the surface.

We investigated the reaction of C_2D_4 and H on a Pt(111) surface using a Cs^+-ion reactive ion scattering (RIS) method. We successfully identified $C_2D_{4-x}H_x$ ($x = 0-4$) species on the surface and observed their concentration change in real time in the temperature range of 200–300 K.

The Cs^+ RIS technique was shown to be an effective method to monitor molecules on surfaces. The experimental details and operating principle for the RIS method can be found elsewhere.[2] Briefly, a Cs^+-ion beam of low energy (10–100 eV) is collided with the surface to be analyzed, and the Cs^+–molecule cluster ions emitted from the surface are analyzed by a mass spectrometer. The Cs^+–molecule cluster ions are formed as the Cs^+-ion projectiles pick up adsorbed

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[*] Prof. Dr. C. M. Kim
Department of Chemistry
Kyungpook National University
Taegu, 702-701 (South Korea)
Fax: (+82) 53-950-5330
E-mail: cmk@knu.ac.kr

Prof. Dr. H. Kang
School of Chemistry
Seoul National University
Kwanak-ku, Shinrim-dong
Seoul, 151-742 (South Korea)
Fax: (+82) 2-889-5719
E-mail: surfion@snu.ac

Dr. C.-H. Hwang, C.-W. Lee
Department of Chemistry
Pohang University of Science and Technology
Pohang, 790-784 (South Korea)

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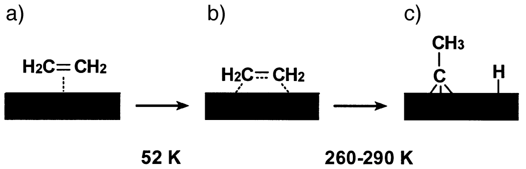
molecules (reactive scattering process). The greatest advantage of this technique is that molecules are identified in the neutral state and that fragmentation is minimized.

The chemistry of ethylene on Pt(111) has been extensively studied by a variety of surface analysis techniques including TPD,[3, 4] LID,[5, 6] SIMS,[7] near edge X-ray absorption fine structure (NEXAFS),[8] high-resolution electron energy loss spectroscopy (HREELS),[9] sum-frequency generation (SFG),[10] and reflection absorption infrared spectroscopy (RAIRS).[11] The surface reaction steps of ethylene on Pt(111) are shown in Scheme 1, the surface moieties shown have been clearly identified. However, the detailed mechanism for dehydrogenation of di-σ-bonded ethylene to ethylidyne has not been clearly resolved. In addition to the reactions shown in Scheme 1, H/D exchange reactions and desorption of ethylene and ethane take place in the temperature range 220–300 K.



Scheme 1. Surface reaction of ethylene on Pt(111); a) π-bonded ethylene, b) di-σ-bonded ethylene, c) ethylidyne.

We concentrated on the H/D exchange reaction between C_2D_4 and H on the surface. Figure 1 shows typical mass spectra of the Cs$^+$RIS products produced from a Pt(111) surface co-adsorbed with H and C_2D_4 at two different temperatures. Ethylene is adsorbed molecularly on Pt(111) at 200 K (Scheme 1). The only mass peak observed was 165 amu. This peak correspons to the $[CsC_2D_4]^+$ ion formed by pickup of C_2D_4 from the surface. The absence of fragmented peaks reveals the desorption of intact ethylene. At 270 K, the spectrum shows CsC_2D_3H (164 amu), $CsC_2D_2H_2$ (163 amu), CsC_2DH_3 (162 amu) species. The intensity of CsC_2H_4 (161 amu) peak is low but well above the noise level. The intensity distribution truly reflects the relative amounts of corresponding deuterated ethylene on the surface. Note that the ionizer of the mass spectrometer was turned off when we measured Cs$^+$–molecule cluster ions. Thus, we could detect desorbing molecules without cracking by mass spectrometry.

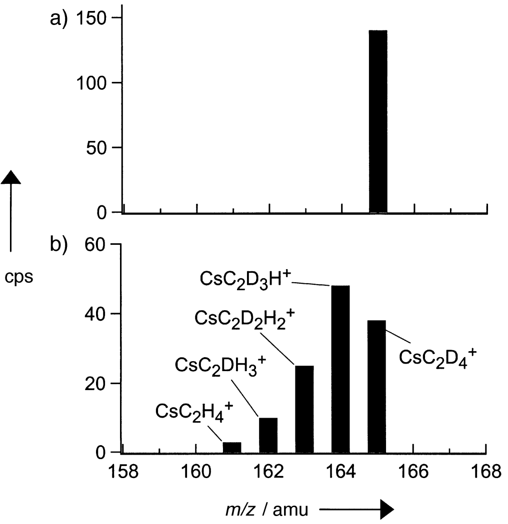


Figure 1. Mass spectra of the RIS products from the Pt(111) surface exposed to H_2 (5 L) and of C_2D_4 (0.5 L) at 200 K. The sample temperature was 200 K (a) and 270 K (b).

We monitored the change of the intensities of $C_2D_{4-x}H_x$ ($x = 0-3$) species while increasing the surface temperature from 220 K to 295 K (Figure 2). The data show that H/D exchange between ethylene and surface hydrogen takes place even below 230 K. They also show that accumulation of C_2D_3H is necessary to form $C_2D_2H_2$. It is the same for the formation of C_2DH_3. This result implies that the H/D exchange reaction takes place sequentially.

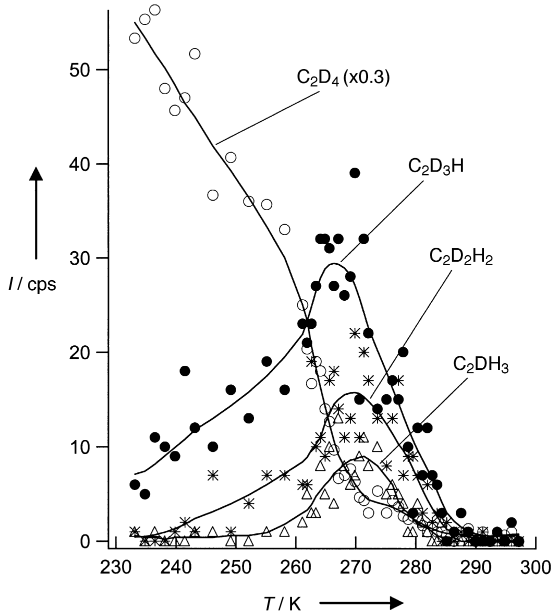


Figure 2. Real-time monitoring of the signal intensities for C_2D_4 (○), C_2D_3H (●), $C_2D_2H_2$ (*), and C_2DH_3 (△) on Pt(111) during temperature increase. The sample surface was prepared by dosing with H_2 (5 L) then C_2D_4 (0.5 L) at 200 K. The heating rate was 0.3 K s^{-1}. Lines drawn to aid the eye.

The intensity of C_2D_4 decreased sharply at temperatures higher than 265 K and all of the ethylene species disappeared completely when temperature reached 290 K. This observation reflects decomposition of ethylene to ethylidyne. Notice that the total amount of $C_2D_{4-x}H_x$ ($x = 1-4$) formed is less than the decrease in the amount of C_2D_4; this is a result of desorption as ethylene and ethane and decomposition to ethylidyne. The amount of surface species removed by the Cs$^+$-ion beam itself was estimated to be less than 0.1 % of the total adsorbed species in the whole data collection period.

Even though Figure 2 gives clear indication for progressive H/D exchange, the investigation of the exchange kinetics is complicated because molecular desorption of ethylene and ethane takes place in the temperature range of 240–280 K. To compare their relative amounts exempt from the desorption effect, we plotted the ratio of C_2D_3H to C_2D_4, and $C_2D_2H_2$ to

C_2D_3H (Figure 3). Figure 3 shows clearly that the H/D exchange-reaction rate increases abruptly when the surface temperature reaches 260 K. The rate increase for the first H/D exchange ($C_2D_4 \rightarrow C_2D_3H$) is much greater than that for the second one ($C_2D_3H \rightarrow C_2D_2H_2$). The peculiar features of Figure 3 evoke an interpretation that new reaction channels may become operative at 260 K.

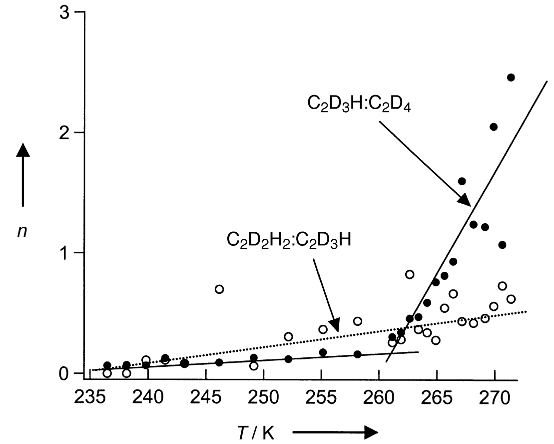
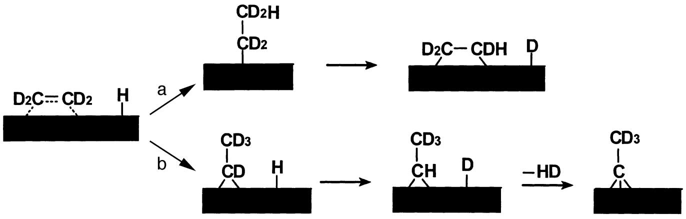


Figure 3. Relative amounts of C_2D_4, C_2D_3H, and $C_2D_2H_2$ on Pt(111) in the H/D exchange process; n = relative amount. The experimental conditions are the same as those in Figure 2.

Based on our observations and the information available in the literature, we propose the mechanism for the H/D exchange reaction of ethylene on Pt(111) as summarized in Scheme 2. At temperatures lower than 260 K, the reaction proceeds via ethyl intermediate (reaction a). When the surface temperature reaches 265 K, ethylidene species is formed and C_2D_3H is produced alternatively by α-hydrogen exchange (reaction b). Ethylidene finally decomposes to ethylidyne at higher temperatures.



Scheme 2. Proposed reaction mechanisms for the H/D exchange reaction of ethylene on Pt(111); a ⩽ 265 K; b ⩾ 265 K

It is generally accepted that the ethyl species is the common intermediate for the H/D exchange reaction and hydrogenation of ethylene on Pt(111).[4, 6, 12] The ethyl species is believed to be in fast equilibrium with ethylene on the surface and the equilibrium is shifted towards the ethylene side.

The presence of ethylidene in the temperature range of 260–290 K during ethylene reaction on Pt(111) has been reported by several groups.[10, 13, 14] We investigated the presence of ethylidene on the surface using the Cs^+ RIS technique. Because ethylidene and ethylene have the same mass, they cannot be identified by simple mass analysis of scattered Cs^+–molecule ions. To resolve this problem, we investigated the change of the $[CsC_2H_4]^+$ ion signal as a function of Cs^+-ion impact energy in our separate set of experiments. We have found that the yield of the $[CsC_2H_4]^+$ ion at 280 K requires a Cs^+-ion impact energy higher than that at 220 K, which implies that the C_2H_4 species is more strongly bound at 280 K than at 220 K. The strongly bound C_2H_4 species was assigned as ethylidene moiety.[15]

In conclusion, we have directly identified that H/D substituted ethylene molecules exist on the Pt(111) surface during the reaction between C_2D_4 and H. The relative populations for $C_2D_{4-x}H_x$ ($x = 0-4$) species were determined and their variation with temperature was measured in real time. Based on quantitative analysis of $C_2D_{4-x}H_x$ species on the surface, we proposed two different channels for the H/D exchange reaction on the surface. The capability of the Cs^+ RIS technique is ideally suited for the kinetic study of surface reactions especially when similar molecules are present on the surface.

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