

ethylene reductively coordinates to Rh(III)–H formed during the exchange procedure and inserts in the Rh–H bond to produce an ethyl ligand σ -bonded to Rh(II). Another C_2H_4 can then reductively coordinate to the Rh(II) species and insert between the Rh(II)–C bond of the ethyl ligand and form Rh(I)–butyl. Butene is then formed and displaced by coordination with additional ethylene. This scheme requires the active site to be located in the α -cage due to size considerations, and so the difference in activity between RhCa–X(A) and RhCa–X(C) is then explained as due to a greater amount of Rh accessible to ethylene in RhCa–X(A).

Conclusions

Adsorption of C_2H_4 onto RhCa–X zeolite is shown to produce a new species, E2, identified as an intermediate in the formation of an active site for dimerization within the zeolite. The origin of this species is a Rh(III) cation, which is reduced through coordination with ethylene, producing paramagnetic Rh(II) σ -bonded to ethylene, which was studied by ESR. ESEM measurements of this species formed with C_2D_4 support this assignment, in which only two deuteriums interact with the Rh nucleus at a distance of 0.28 nm. The interaction number and distance are not consistent with a π -bonded reaction intermediate such as those reported for ethylene dimerization by Pd–X and Ni/SiO₂ catalysts. The proximal ethylene carbon atom is suggested to

rehybridize to sp^3 and bond end-on to Rh. The subsequent decay of ESR signal E2 is explained as a further reduction to Rh(I) in order to form the active species for dimerization.

The difference in the rates of decay of species E1 and E2, and also in the amounts of products formed, is attributed to the location of Rh cations in the activated samples. In catalysts activated at ~ 673 K to form RhCa–X(A), Rh is more accessible to ethylene in the α -cage than in catalysts activated at ~ 773 K to form RhCa–X(C). Reduction of the catalysts removed the precursors to species E1 and E2, but the product yield did not decrease. Activation under vacuum produced less active catalysts, which is attributed to a decrease in the dispersion of Rh. Other major species, B1 and B2, appear simultaneously with the dimerization products.

On the basis of the structural information about the formation of the reaction intermediate species E2, it is suggested that ethylene dimerization occurs by a similar mechanism for both heterogeneous and homogeneous Rh catalysts involving successive reductive coordination steps. This mechanism is different from the ethylene dimerization mechanisms in Pd–X and Ni/SiO₂.

Acknowledgment. This research was supported by the National Science Foundation, the Robert A. Welch Foundation, and the Texas Advanced Research Technology Program.

Registry No. C_2H_4 , 74-85-1; Rh, 7440-16-6.

Coadsorption of Ethylene and Potassium on Pt(111). 2. Influence of Potassium on the Decomposition of Ethylene

Rebecca G. Windham and Bruce E. Koel*

Department of Chemistry and Biochemistry and the Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, Colorado 80309-0449 (Received: March 3, 1989; In Final Form: July 27, 1989)

The effect of preadsorbed potassium on the decomposition of ethylene on the Pt(111) single-crystal surface has been studied by temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). Potassium decreases the amount of ethylene decomposition and increases the activation energy for C–H bond cleavage. Low coverages of potassium ($\theta_K \approx 0.05$ monolayer) cause a 2–3 kcal mol^{–1} increase in the activation energy for C–H bond breaking, and hydrogen evolution at 310 K characteristic of the dehydrogenation of ethylene to ethylidyne (CCH₃) on Pt(111) is eliminated entirely. At 300 K and $\theta_K = 0.12$ monolayer, we observe a metastable intermediate in the decomposition of ethylene to form ethylidyne, which we propose to be ethylidene (CHCH₃). High potassium coverages ($\theta_K \geq 0.50$ monolayer) cause the activation energy for C–H bond breaking to increase by 13 kcal mol^{–1} (from 18 to 31 kcal mol^{–1}), resulting in ethylidene stabilization on the surface over the range 300–420 K. Complete dehydrogenation of ethylene occurs with an activation energy similar to that for breaking the first C–H bond, without forming a stable ethylidyne species. We suggest that the strong influence of potassium on the activation energies of these surface reactions, i.e. the inhibition of dehydrogenation of surface hydrocarbons, is due to the destabilization of carbon–metal σ bonds in the dehydrogenated hydrocarbon species due to charge transfer from potassium to platinum.

Introduction

Promoters enhance the rate and/or selectivity for many important catalytic reactions, such as Fischer–Tropsch synthesis. In order to provide a fundamental explanation of these effects, many studies have been made regarding the promotion of single-crystal metal surfaces which serve as well-defined, model catalysts. In particular, the effect of potassium on important reactants such as CO^{1,2} and H₂^{3,4} has been studied previously on

Pt(111). More recently, the influence of potassium on the adsorption of some possible hydrocarbon products of the Fischer–Tropsch reaction such as ethylene^{5–7} and benzene⁸ has been studied. At the high temperatures used in catalytic reactions, these hydrocarbon products can decompose on the catalyst surface to form various adsorbed hydrocarbon species. Also, intermediates in catalytic synthesis certainly involve adsorbed hydrocarbon species. Thus, for a complete understanding of promoted catalytic

(1) Garfunkel, E. L.; Crowell, J. E.; Somorjai, G. A. *J. Phys. Chem.* **1982**, *86*, 310.

(2) Crowell, J. E.; Garfunkel, E. L.; Somorjai, G. A. *Surf. Sci.* **1982**, *121*, 303.

(3) Zhou, X.-L.; White, J. M. *Surf. Sci.* **1987**, *185*, 450.

(4) Gebhard, S. C.; Windham, R. G.; Koel, B. E., submitted for publication in *Surf. Sci.*

(5) Windham, R. G.; Bartram, M. E.; Koel, B. E. *J. Vac. Sci. Technol.* **1987**, *A5*, 457.

(6) Windham, R. G.; Bartram, M. E.; Koel, B. E. *J. Phys. Chem.* **1988**, *92*, 2862.

(7) Zhou, X.-L.; Zhu, X.-Y.; White, J. M. *Surf. Sci.* **1988**, *193*, 387.

(8) Garfunkel, E. L.; Maj, J. J.; Frost, J. C.; Farias, M. H.; Somorjai, G. A. *J. Phys. Chem.* **1983**, *87*, 3629.

reactions, it is important to have additional studies that determine the effects of potassium on the hydrocarbon species that may be present on the metal catalyst surface during reaction.

In the course of the last 10 years, the chemical nature of the decomposition products of ethylene on clean, single-crystal metal surfaces has been determined, mainly by vibrational spectroscopy using high-resolution electron energy loss spectroscopy (HREELS). Various decomposition products have been identified, depending on the identity and surface structure of the metal. Hills et al.⁹ noted that ethylidyne (CCH_3) has been identified as one of the initial decomposition products, regardless of the molecular ethylene adsorption state, on the close-packed surfaces of 4d and 5d Group VIII metals, e.g. $\text{Pt}(111)$,¹⁰ $\text{Rh}(111)$,^{11,12} $\text{Pd}(111)$,¹³ and $\text{Ru}(001)$.^{9,14} The initial ethylene decomposition product on the $\text{Ni}(100)$ ¹⁵ and $\text{Pd}(100)$ ¹⁶ surfaces has been assigned as a vinyl species (CHCH_2). On $\text{Fe}(110)$,¹⁷ $\text{Ni}(111)$,¹⁸ and $\text{Ni}(110)$ ¹⁹ surfaces the intermediates proposed for the decomposition of ethylene are acetylene (C_2H_2) and ethynyl (CCH). On the $\text{Fe}(111)$ surface, no ethylene thermal decomposition intermediates have been observed.²⁰

Temperature programmed desorption (TPD) measurements give C:H stoichiometries for surface species and activation energies for C-H bond breaking reactions. On $\text{Pt}(111)$, the hydrogen produced from ethylene decomposition desorbs in sharp peaks at 310 and 510 K, with a broad shoulder above 550 K, for saturation coverages of chemisorbed ethylene.^{6,21} The first peak, at 310 K, is due to the dehydrogenation of ethylene to form ethylidyne (CCH_3). The second peak, at 510 K, can be attributed to the further decomposition of ethylidyne to form various C_nH species. The broad shoulder above 550 K represents the completion of dehydrogenation to form a graphitic carbon overlayer.

In this paper, we report new studies of the influence of potassium on the decomposition mechanism of ethylene and on the relative stabilities of hydrocarbon species on $\text{Pt}(111)$ above 300 K. These experiments involve adsorption of ethylene on the $\text{Pt}(111)$ surface at 100 K and subsequent heating to temperatures of 300–800 K. The sequential hydrogen evolution that accompanies ethylene decomposition was monitored by TPD, and the stable, adsorbed hydrocarbon species produced were identified by HREELS. The influence of potassium on ethylene chemisorption on $\text{Pt}(111)$ below 300 K has been presented by us previously.^{5,6} In that work, we observed several interesting effects: (1) the formation of a new, π -bonded state of ethylene; (2) a constant saturation coverage of ethylene over the range $\theta_K = 0.0$ –0.4; and (3) an increase by as much as 50% in the amount of reversibly adsorbed ethylene.

Experimental Section

The experiments were performed in a two-level, ultrahigh-vacuum chamber that has been described previously.^{6,22} The system base pressure was 2×10^{-10} Torr. TPD measurements were made using a UTI quadrupole mass spectrometer in line-of-sight with the sample surface and using a linear heating rate of 10 – 19 K s^{-1} . TPD profiles for H_2 were made by monitoring

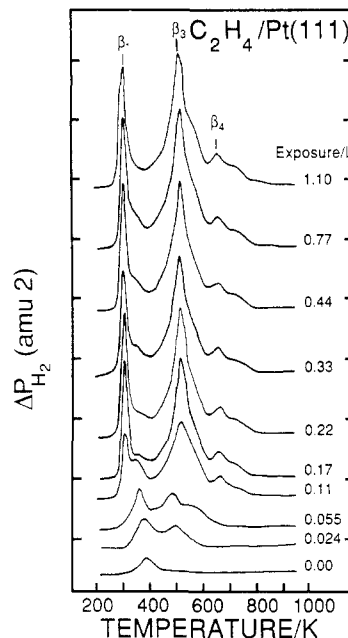


Figure 1. H_2 TPD spectra as a function of ethylene exposure on $\text{Pt}(111)$ at 100 K.

the 2-amu mass spectrometer signal. The crystal temperature was measured by a chromel–alumel thermocouple spot-welded to the side of the crystal. The HREELS spectrometer is constructed of single 127° cylindrical sectors in the monochromator and analyzer. For specular reflection, $\theta_{\text{in}} = \theta_{\text{out}} = 65^\circ$ from the surface normal. Off-specular measurements were made by rotation of the analyzer about an axis perpendicular to the scattering plane. Typical conditions for HREELS were as follows: incident energy, 0.35–1 eV; incident current, 1×10^{-10} A; resolution, 7 meV (56 cm^{-1}) fwhm; angular resolution, 4° fwhm. All HREELS spectra were taken for a Pt sample temperature of 100 K. All Auger electron spectroscopy (AES), TPD, and HREELS data were taken by using an IBM/XT computer with a Tecmar interface.

The $\text{Pt}(111)$ crystal was cleaned under vacuum by a combination of Ar^+ sputtering (1 kV, 6 μA), annealing at 1200 K under vacuum, and oxygen treatments (2×10^{-8} Torr, 800–1000 K). AES, low-energy electron diffraction (LEED), and HREELS were used to ensure that the surface was clean and well-ordered. Polymer grade ethylene (99.9%, SGP) and ethylene- d_4 (99%, CIL) were used without further purification. Ethylene saturation exposures were nominally 1.1 langmuirs (corrected for ion gauge sensitivity and for an enhancement of 50 by the multichannel array doser).

The potassium was deposited with a SAES getter source. The deposition procedure has been described previously.⁶ Briefly, this involved depositing a multilayer of potassium and then annealing the surface to achieve the desired coverage. The potassium coverages in this paper are defined relative to a potassium monolayer saturation coverage, $\theta_K \equiv 1$ monolayer corresponding to 5.01×10^{14} potassium atoms cm^{-2} , or 33% of the density of $\text{Pt}(111)$ surface atoms.²³

Results

1. Temperature Programmed Desorption (TPD) Studies. The thermal desorption profiles for H_2 resulting from ethylene decomposition following various ethylene exposures at 100 K on $\text{Pt}(111)$ are shown in Figure 1. Also shown for reference in the bottom desorption profile as 0.00-langmuir C_2H_4 exposure is the H_2 TPD spectrum due to adsorption of a trace amount of H_2 from the background. TPD and AES measurements indicate that 54% of the ethylene desorbs molecularly, while 44% decomposes on $\text{Pt}(111)$.^{6,24} We assume the total ethylene coverage to be 0.25

(9) Hills, M. M.; Parmeter, J. E.; Mullins, C. B.; Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 3554.

(10) Steininger, H.; Ibach, H.; Lehwald, S. *Surf. Sci.* **1982**, *117*, 685.

(11) Koestner, R. J.; Koestner, M. A.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1982**, *121*, 321.

(12) DuBois, L. H.; Castner, D. G.; Somorjai, G. A. *J. Chem. Phys.* **1980**, *72*, 5234.

(13) Gates, J. A.; Kesmodel, L. L. *Surf. Sci.* **1983**, *124*, 68.

(14) Barteau, M. A.; Broughton, J. Q.; Menzel, D. *Appl. Surf. Sci.* **1984**, *19*, 92.

(15) Zaera, F.; Hall, R. B. *Surf. Sci.* **1987**, *180*, 1.

(16) Stuve, E. M.; Madix, R. J.; Brundle, C. R. *Surf. Sci.* **1985**, *152/153*, 532.

(17) Erley, W.; Baró, A. M.; McBreen, P.; Ibach, H. *Surf. Sci.* **1982**, *120*, 273.

(18) Lehwald, S.; Ibach, H. *Surf. Sci.* **1979**, *89*, 425.

(19) Strosio, J. A.; Bare, S. R.; Ho, W. *Surf. Sci.* **1984**, *148*, 499.

(20) Seip, U.; Tsai, M.-C.; Küppers, J.; Ertl, G. *Surf. Sci.* **1984**, *147*, 65.

(21) Salmeron, M.; Somorjai, G. A. *J. Phys. Chem.* **1982**, *86*, 341.

(22) Bartram, M. E.; Windham, R. G.; Koel, B. E. *Surf. Sci.* **1987**, *184*, 57.

(23) Pirug, G.; Winkler, A.; Bonzel, H. P. *Surf. Sci.* **1985**, *163*, 153.

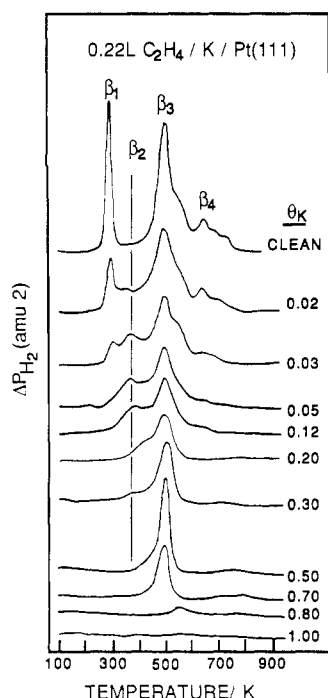


Figure 2. H₂ TPD spectra of 0.22-langmuir ethylene exposure on clean and potassium-covered Pt(111) at 100 K.

monolayer on Pt(111) at 100 K.^{6,25}

At low coverages (0.024 langmuir), only two desorption states, β_1 and β_3 , are observed. The β_1 peak shifts from 380 to 350 K with increasing coverage, prior to development of the sharp β_1 state at 310 K. At these low coverages, H₂ desorption in the β_1 state initially is desorption-rate-limited, with ethylene decomposition occurring below 300 K, as shown in a TPD/TPSSIMS study by Creighton and White.²⁶ As the ethylene exposure is increased above 0.11 langmuir, we observe the development of sharp β_1 state at 310 K. At these higher coverages, the H₂ desorption in the β_1 state is rate-limited by ethylene decomposition.²⁶ The hydrogen resulting from ethylene decomposition at these higher ethylene coverages desorbs in sharp peaks at 310 and 510 K, with a broad shoulder beginning at 550 K. The first peak at 310 K, denoted β_1 , is due to the decomposition of ethylene to form ethynylidyne, CCH₃. The second desorption peak at 510 K, denoted β_3 , is due to the further decomposition of ethynylidyne to C_nH fragments. The broad shoulder starting at 550 K, denoted β_4 , represents the complete dehydrogenation of surface hydrocarbons to form a graphitic overlayer on Pt(111). These results are consistent with previous work.^{6,21,26} The apparent activation energies for each sequential decomposition step, calculated by assuming a reaction-rate-limited unimolecular decomposition and a preexponential factor of 10^{13} s^{-1} , are as follows: β_1 , $E_a = 18 \text{ kcal mol}^{-1}$; β_3 , $E_a = 31 \text{ kcal mol}^{-1}$; and β_4 , $E_a = 33\text{--}49 \text{ kcal mol}^{-1}$.

A 1.1-langmuir C₂H₄ exposure is necessary to completely saturate the surface for all molecular ethylene adsorption.⁶ However, as seen in Figure 1, 0.22 langmuir of C₂H₄ is sufficient to saturate the amount of irreversibly adsorbed ethylene which decomposes upon heating in TPD. The thermal desorption traces for H₂ resulting from ethylene decomposition following 0.22 langmuir of C₂H₄ at 100 K are shown in Figure 2 for increasing potassium precoverages on the Pt(111) surface. Exposures larger than 0.22 langmuir cause increasing background effects, due to desorption from the supports and sides of the crystal, that mask some important features in the spectra. However, the H₂ TPD results for 1.1-langmuir C₂H₄ exposures (not shown here) are entirely consistent with those presented in Figure 2.

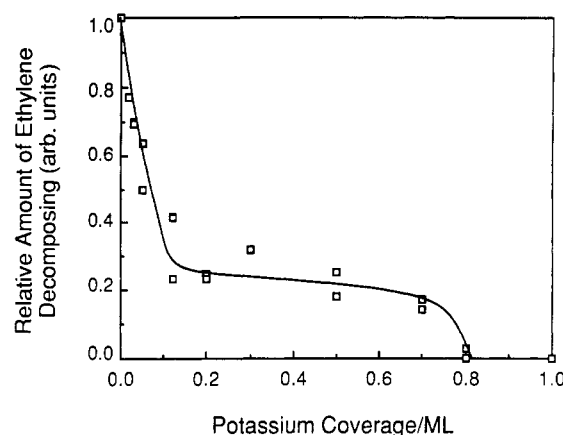


Figure 3. Relative amount of ethylene decomposition as a function of potassium coverage. H₂ TPD areas were corrected to ethylene coverage, and the amount of ethylene decomposition has been normalized to the total amount of adsorbed ethylene at each potassium coverage.

Coadsorption of even small amounts of potassium causes the β_1 state to be strongly attenuated. This state disappears completely by $\theta_K = 0.05$. Accompanying the disappearance of the β_1 state is the growth of a new state, β_2 . The amount of the β_2 state saturates at $\theta_K = 0.05$, and then it also disappears by $\theta_K = 0.50$. The peak temperature of the β_2 state is very sensitive to the potassium coverage, increasing from 350 K at $\theta_K = 0.02$ to 420 K at $\theta_K = 0.20$, corresponding to activation energies for β_2 H₂ production of 21–25 kcal mol⁻¹. At $\theta_K = 0.30$, β_2 desorption shifts even higher, into the β_3 state with $E_a = 31 \text{ kcal mol}^{-1}$. The peak temperature of the β_3 state remains essentially constant at 510 K at low θ_K , but shifts 10 K higher at $\theta_K = 0.30$ and shifts to 570 K at $\theta_K = 0.80$, corresponding to $E_a = 34 \text{ kcal mol}^{-1}$. The amount of H₂ desorption in the high-temperature β_4 state is strongly attenuated with increasing θ_K , and no desorption in the β_4 state is observed for $\theta_K > 0.12$. Above $\theta_K = 0.80$, no ethylene dehydrogenation occurs, as evidenced by the total absence of H₂ desorption.

One effect of potassium coadsorption is to cause a decrease in the amount of irreversibly adsorbed ethylene, i.e. the amount of ethylene that decomposes during TPD. This is measured by the total H₂ desorption peak areas shown in Figure 2. In Figure 3 we quantify this decrease and plot the amount of irreversibly adsorbed ethylene as a function of potassium coverage. The ordinate scale is normalized to unity for the amount of ethylene decomposition on clean Pt(111). Even low coverages of potassium cause a sharp decrease in the relative amount of ethylene decomposing (70% by $\theta_K = 0.10$). The initial slope of this curve shows that each potassium adatom affects the decomposition of 1.7 ethylene molecules, assuming the total ethylene coverage is 0.25 monolayer on Pt(111) at 100 K.^{6,25} The amount of ethylene undergoing dehydrogenation above $\theta_K = 0.20$ remains fairly independent of θ_K until $\theta_K = 0.70$, where a sharp decrease occurs in the amount of ethylene dehydrogenation. Above $\theta_K = 0.80$, no ethylene dehydrogenation occurs. This latter decrease is due to the inability of the surface to chemisorb ethylene at these potassium coverages, but below $\theta_K = 0.50$, decreased dehydrogenation is clearly not due to a decrease in the amount of adsorbed ethylene.⁶

Figure 4 shows that the relative proportions of the various H₂ desorption states change characteristically as the amount of ethylene decomposition decreases with increasing θ_K . At saturation ethylene coverage on the clean Pt(111) surface, three H₂ desorption states are present, β_1 , β_3 , and β_4 , with the relative amounts of each state described by a 1:2:1 ratio. This ratio is simply interpreted as the relative number of hydrogen atoms that are lost in each of three sequential decomposition steps: (1) loss of one hydrogen atom per molecule to form ethynylidyne (CCH₃); (2) average loss of two additional hydrogen atoms per molecule to form various C_nH fragments, and (3) loss of the final amounts of hydrogen, on average one hydrogen atom per molecule, to form C_n polymers.

(24) Berlowitz, P.; Megiris, C.; Butt, J. B.; Kung, H. H. *Langmuir* **1985**, *1*, 206.

(25) Kesmodel, L. L.; DuBois, L. H.; Somorjai, G. A. *Chem. Phys. Lett.* **1978**, *56*, 267.

(26) Creighton, J. R.; White, J. M. *Surf. Sci.* **1983**, *129*, 327.

TABLE I: Vibrational Frequencies (cm⁻¹) of Ethylidyne and Ethylidene Surface Species^a

mode	Co ₃ (CO) ₉ (μ ₃ -CCH ₃) ref 27	C ₂ H ₄ /Pt(111) 300-420 K	C ₂ H ₄ /Pt(111)/K 420 K	C ₂ H ₄ /Pt(111)/K 300 K	1 ^{b,c} ref 28	2 ref 29	3 ref 29
ν ^{as} _{MC}	401 (393)	425 (400)	420 (-)	415 (-)	n.o. ^d	460	505
ν ^s _{MC}	1163 (1182)	1120 (1135)	1120 (1160)		n.o.	616	629
ν(CC)				900 (880)	n.o.	945	938
γ _{CH}					968	989	971
ρ _{CH₃}	1004 (828)	900 (790)	905 (-)	1110 (-)	n.o.	1053	1056
δ _{CH}				1210 (-)	1264	1302	1313
δ ^s _{CH₃}	1356 (1002)	1345 (990)	1340 (-)		n.o.	1369	1366
δ ^{as} _{CH₃}	1420 (1031)			1435 (-)	1445	1447	1449
ν ^s _{CH₃}	2888 (-)	2915 (2085)	2905 (2110)	2855 (-)	2835	2850	2832
ν _{CH}				2955 (-)	2903	2916	2917
ν ^{as} _{CH₃}	2930 (2192)				2947	2950	2954

^a Parentheses indicate values for the deuterated species. ^b 1, [(C₅H₅)₂Ru₂(CO)₃(μ₂-CHCH₃)]; 2, [Os₂(CO)₈(μ₂-CHCH₃)]; 3, [Fe₂(CO)₆(μ₂-CHCH₃)]. ^c Some of these frequencies from ref 28 were reassigned by ref 29. ^d Not observed.

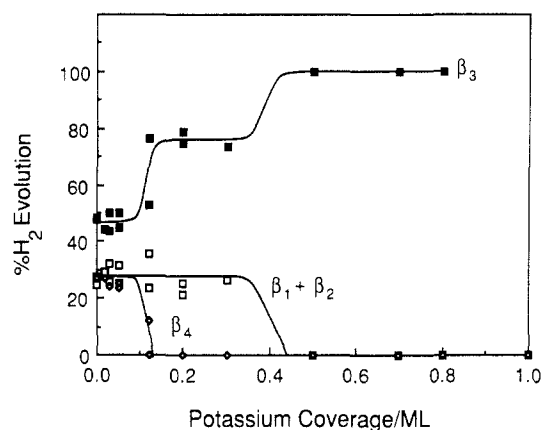


Figure 4. Relative amount of each of the H₂ desorption states as a function of potassium coverage from Figure 2. The percentage of H₂ evolving in each of the four desorption states was calculated by normalizing the area of each state to the total H₂ TPD area for each potassium coverage.

Coadsorption with potassium below $\theta_K = 0.05$ causes intensity to gradually shift from the β_1 state into the β_2 state. However, the ratio of $\beta_1 + \beta_2$, β_3 , and β_4 remains 1:2:1. At $\theta_K = 0.05$, the β_1 peak is completely eliminated, and β_2 : β_3 : $\beta_4 = 1$:2:1. The β_4 state disappears by $\theta_K = 0.20$ and β_2 : $\beta_3 = 1$:3. This 1:3 ratio remains constant up to $\theta_K = 0.30$. Above this potassium coverage, the β_2 state gradually disappears, so that at $\theta_K = 0.50$, only a single peak, β_3 is observed. This peak, then, contains all of the hydrogen due to dehydrogenation of ethylene at these large potassium coverages. It is useful to recall that the amount of ethylene undergoing dehydrogenation remains fairly constant for $\theta_K = 0.20$ – 0.70 .

As a final point concerning the TPD measurements, we note that H₂ desorption due to the decomposition of ethylene on Pt(111) during TPD is accompanied by the desorption of C₂H₆ and C₂H₄. Ethane desorbs in a single peak at 295 K. This peak represents the reaction-rate-limited hydrogenation of chemisorbed ethylene, since adsorbed ethane would desorb below 100 K. Ethylene desorbs in a peak at 285 K with a shoulder at 260 K. The TPD data indicate that only 2% of the ethylene is hydrogenated to form ethane and 54% of the ethylene is reversibly adsorbed at saturation ethylene coverage.^{6,24} We have also studied the effect of potassium on these processes. The effect of potassium coadsorption on the formation of ethane is dramatic; by $\theta_K = 0.05$, ethane is no longer a reaction product. This potassium coverage also corresponds to the loss of the β_1 desorption state. These results are in reasonable agreement with the results of Zhou et al.,⁷ who have carried out a more complete study of the effects of potassium on ethane production. The effects of potassium coadsorption on reversibly adsorbed ethylene are reported in our earlier paper.⁶

2. *High-Resolution Electron Energy Loss Spectroscopy (HREELS) Studies.* Figure 5 shows HREELS spectra of ethylidyne (CCH₃ and CCD₃) on the clean Pt(111) surface. The ethylidyne was produced by dosing the Pt(111) surface with a

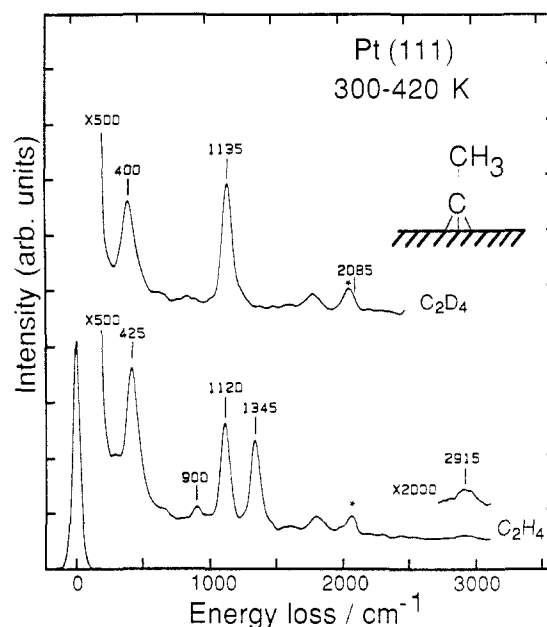


Figure 5. HREELS spectra of 1.1 langmuirs of C₂H₄ adsorbed on clean Pt(111) at 100 K and heated to 300–420 K.

saturation ethylene dose at 100 K and then annealing this surface to 300 K. Identical HREELS spectra are obtained after annealing to 420 K, indicating that ethylidyne is stable over this temperature range, consistent with the TPD results. The presence of ethylidyne on Pt(111) can be identified in the CCH₃ spectra by two intense, characteristic loss peaks at 1120 cm⁻¹ due to the CC stretching mode and 1345 cm⁻¹ due to the CH₃ symmetric bending mode.¹⁰ Other characteristic CCH₃ dipole-active modes are the symmetric CH stretch at 2915 cm⁻¹ and the Pt–C stretch at 425 cm⁻¹. The weak loss peak near 900 cm⁻¹ is due to the non-dipole-active CH₃ rocking mode. The loss peak intensity for the CD₃ symmetric bending mode is much smaller, and only two peaks stand out in the CCD₃ spectra: the CC stretching mode at 1135 cm⁻¹ and the Pt–C stretch at 400 cm⁻¹. The mode assignments for adsorbed ethylidyne are based on a comparison to an ethylidyne tricobalt nonacarbonyl complex, as first outlined by Skinner et al.,²⁷ and are shown in Table I. The low CH stretching frequency is indicative of the sp³ hybridization of the methyl carbon. LEED studies have shown that ethylidyne on Pt(111) is bonded with the CC axis perpendicular to the surface with the α -carbon bonded to three Pt atoms in a 3-fold hollow site.²⁵

Figures 6 and 7 show HREELS spectra as a function of annealing temperature following saturation exposures at 100 K of C₂H₄ and C₂D₄, respectively, on the K/Pt(111) surface with $\theta_K = 0.12$. This potassium coverage eliminates the β_1 desorption state and populates the β_2 desorption state, as shown in Figure 2.

(27) Skinner, P.; Howard, M. W.; Oxtan, I. A.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Faraday Trans. 2* **1981**, 77, 1203.

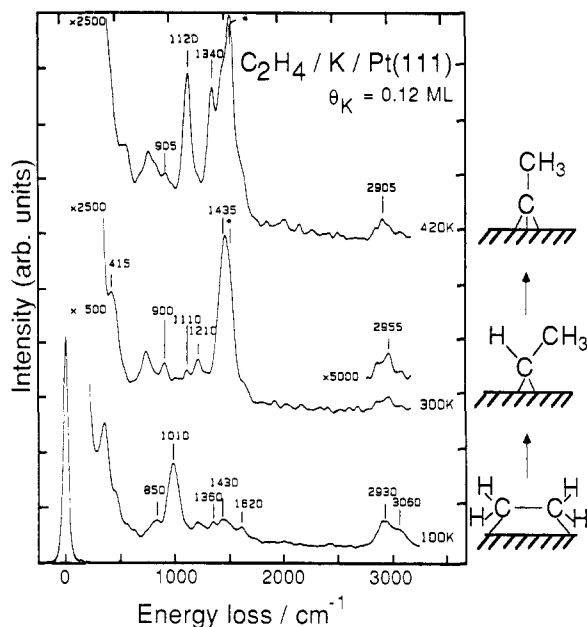


Figure 6. HREELS spectra of 1.1 langmuirs of C_2H_4 adsorbed on 0.12 monolayer of K/Pt(111) at 100 K and heated to (a) 100, (b) 300, and (c) 420 K.

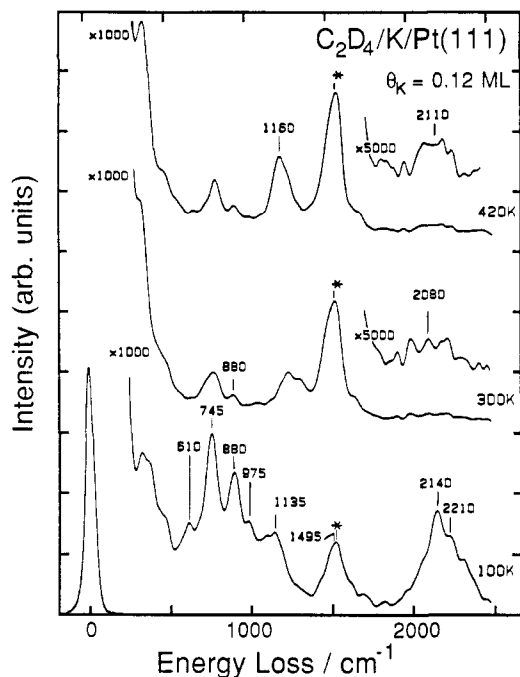


Figure 7. HREELS spectra of 1.1 langmuirs of C_2D_4 adsorbed on 0.12 monolayer of K/Pt(111) at 100 K and heated to (a) 100, (b) 300, and (c) 420 K.

Molecularly adsorbed ethylene at 100 K (bottom curves in Figures 6 and 7) is mainly di- σ -bonded at $\theta_K = 0.12$, with only a small concentration of the π -bonded ethylene species that is formed on the promoted surface, consistent with our previous results.⁶ As discussed before,⁶ very small amounts of coadsorbed CO on K/Pt(111) surfaces cause relatively large loss peaks due to the ν_{CO} mode in the HREELS spectra, and these are denoted by the asterisks in Figures 6 and 7.

Upon annealing the ethylene-covered surface to 300 K (just before the onset of the β_2 desorption peak), we obtain different HREELS spectra (middle curves in Figures 6 and 7). We never observed vibrational spectra similar to these by annealing ethylene adsorbed on Pt(111) without coadsorbed K to temperatures just below the onset for β_1 H_2 desorption. Most importantly, we do not observe the intense loss features seen for ethylidyne (see Figure 5), which formed prior to 300 K on the clean Pt(111) surface (and

also on Pt(111) surfaces with lower θ_K in experiments not shown here). Also, the relatively intense modes for chemisorbed ethylene have vanished. Largely on the basis of this negative evidence, i.e. the absence of CCH_3 and C_2H_4 modes and the retention of C_2H_4 stoichiometry in the adsorbed complex (no H_2 desorption occurs), we conclude that $CHCH_3$ is now formed as a stable intermediate in C_2H_4 decomposition. The observed loss peaks in Figures 6 and 7 are also consistent with the vibrational spectrum of an ethylidyne ($CHCH_3$) ligand in several organometallic complexes.^{28,29} This comparison is shown in Table I. No new loss peaks were observed in off-specular HREELS measurements made for the ethylidyne spectra of Figures 6 and 7. All of the loss peaks were found to scale with the elastic peak intensity, with only small changes in relative intensities, indicating that all of the observed vibrational modes have a strong dipole-active component. This is expected, since the ethylidyne species has C_s symmetry. The strongest evidence for this assignment is the identification of the ethylidyne CC stretching mode. The infrared data on the organometallic complexes show that the CC stretching frequency is 200 cm^{-1} lower for the $CHCH_3$ ligand than for the CCH_3 ligand. Our observation of a clear loss peak at 900 cm^{-1} (880 cm^{-1} for the deuterated species) is good evidence for an adsorbed $CHCH_3$ ligand, even in the absence of other strong mode correlations. The 760- cm^{-1} loss peak and a smaller peak contributing to the loss peak at 1210 cm^{-1} observed in the C_2H_4 and C_2D_4 warmup spectra are clearly due to a small amount of coadsorption of a contaminant, probably water, from the background due to the long times necessary to acquire the spectra. This was determined from observation of the spectra versus time and from many background experiments designed to check these observations. No contaminant peaks were ever observed at 900 or 880 cm^{-1} .

This represents the first time this species has been observed spectroscopically on a transition-metal surface, although Zhou et al.⁷ have reported evidence for this species on a K/Pt(111) surface from secondary ion mass spectroscopy (SIMS). We point out two factors that make this species very difficult to characterize spectroscopically. First, the oscillator strengths for vibrational modes of this kind of adsorbed hydrocarbon species are small in general. Second, the amount of irreversibly adsorbed ethylene has decreased by 70% at $\theta_K = 0.12$. Even on the clean Pt(111) surface, only 0.10 monolayer of ethylene decomposes in an annealing experiment, and so the concentration of hydrocarbon decomposition products for $\theta_K = 0.12$ has decreased to 0.04 monolayer!

Upon heating this surface ($\theta_K = 0.12$) to 420 K to remove the β_2 state, but just before the onset of desorption of the β_3 state, we once again observe the characteristic ethylidyne HREELS spectrum in the top curves in Figures 6 and 7. These loss assignments are also made in Table I. Coadsorbed potassium has no effect on the vibrational spectrum of ethylidyne on Pt(111).

HREELS spectra of the Pt(111) surface with $\theta_K = 0.50$ and a saturation coverage of ethylene at 100 K show that after heating, the ethylidyne characteristic loss peaks are *never* observed over the entire temperature range, 300–420 K (just prior to the onset of the β_3 H_2 desorption state). The HREELS spectra for C_2H_4 and C_2D_4 on the $\theta_K = 0.50$ surface heated to 420 K are very similar to those observed after heating the $\theta_K = 0.12$ surface to 300 K, as presented in the middle curves of Figures 6 and 7. Thus, $CHCH_3$ is the stable species on this surface over a temperature range of at least 120 K. Since the β_3 desorption state represents a dramatic reduction in the H/C stoichiometry, our conclusion is that for surfaces more heavily promoted than $\theta_K = 0.50$, ethylidyne is never formed as a stable species.

Discussion

Potassium coadsorption has two main effects on the thermal decomposition of ethylene on the Pt(111) surface. First, TPD results show that at very low θ_K there is a significant decrease in

(28) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1984**, 79.

(29) Anson, C. E.; Johnson, B. F. G.; Lewis, J.; Powell, D. B.; Sheppard, N.; Bhattacharyya, A. K.; Hembre, R. T.; Norton, J. R.; Knox, S. A. R.; Turner, M. L., submitted for publication.

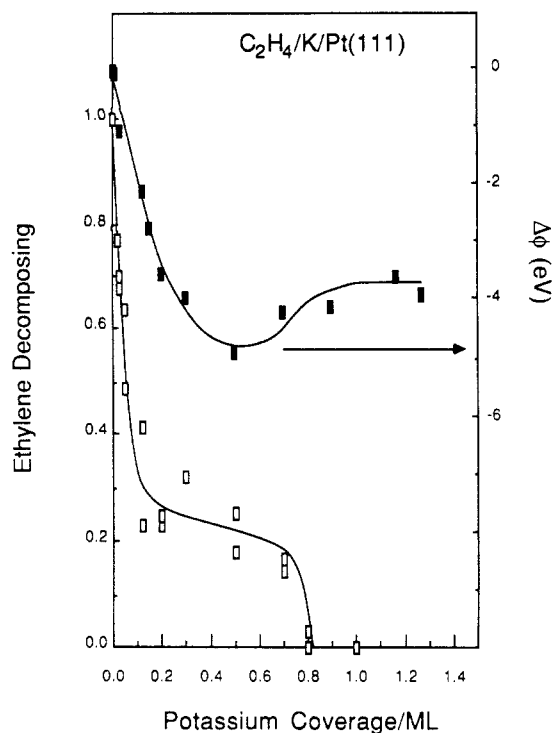


Figure 8. Amount of ethylene decomposition (□) from Figure 3 compared to the K/Pt(111) work function change⁶ (■) as a function of potassium coverage.

the amount of ethylene decomposition and decomposition is eliminated as the potassium precoverage is increased. Secondly, both TPD and HREELS results indicate that potassium coadsorption increases the activation energy for C-H bond breaking. This decreased reactivity of the surface stabilizes a new ethylene decomposition intermediate that has not been observed before: ethylidene, CHCH_3 .

A primary interest in this work is to correctly determine the origin of the effects of K on ethylene surface chemistry. Two factors could have important roles in explaining the observed promoter effects: electronic (ligand) effects and geometric (ensemble size) effects. Large changes occur in the Pt electronic structure due to adsorbing potassium as seen by measurements of the work function change ($\Delta\phi$) of the Pt(111) surface.⁶ If electronic effects due to coadsorption of potassium control the ability of the surface to dehydrogenate ethylene, then some correlation may exist between the amount of ethylene decomposition and $\Delta\phi$ for Pt(111) as a function of potassium coverage. This comparison is shown in Figure 8. As potassium is added to the Pt(111) surface, the work function decreases rapidly and linearly until $\theta_K \approx 0.2$ monolayer. The work function decreases less rapidly with further K addition above $\theta_K \approx 0.2$, as the potassium adlayer gradually depolarizes, and a broad minimum occurs in the work function near $\theta_K \approx 0.5$. The work function begins to increase with further K addition as the potassium adlayer gradually becomes increasingly metallic. As the chemical nature of the potassium changes from partially ionic to metallic, one can estimate that there is an increase in the size of the K adatoms. The changes in shape of the $\Delta\phi$ curve are not correlated well with the decomposition curve. A sharp break in the decomposition curve occurs at $\theta_K = 0.1$, right in the linear region of the $\Delta\phi$ curve. A fairly uniform trend exists in the decomposition curve over the range $\theta_K = 0.1$ – 0.7 , right in the region where enormous changes are occurring in the chemical state of the K adlayer. At $\theta_K = 0.70$, the ability of the Pt(111) surface to dehydrogenate ethylene decreases rapidly until no further dehydrogenation is observed. This is also the θ_K region where ethylene adsorption is completely suppressed. This final sharp decrease in dehydrogenation can be attributed mainly to site-blocking effects, which become critically important as the K adatoms become metallic-like and increase in size.

The amount of ethylene decomposition is relatively insensitive to the amount of potassium coadsorption at higher potassium coverages. This is surprising since site-blocking should lead to a linear decrease in the amount of ethylene decomposition. One explanation is that the potassium adlayer is relatively mobile at high coverages and this allows some amount of decomposition to occur until the complete suppression of ethylene adsorption occurs. The heat of adsorption of K decreases from 65 to 30 kcal/mol⁶ over the monolayer coverage range, and therefore K is quite mobile at high coverages at 300 K. Displacement of K to an adjacent site should only be slightly activated (K diffusion energy plus overcoming an increased K-K repulsion energy due to compression) with the driving force provided by the exothermicity of the ethylene decomposition reaction (liberating H_2 and forming Pt-C covalent bonds). This effect cannot be quantified at present, but certainly it is a concern in general in site-blocking studies of strongly adsorbed hydrocarbons using metal overlayers.

The sharp decrease in dehydrogenation capability of Pt(111) due to coadsorbed potassium at small θ_K could also be the result of a geometric effect, in which the potassium simply blocks sites for dehydrogenation. We have directly studied the effect of site-blocking on C_2H_4 dehydrogenation utilizing inert Bi adatoms.³⁰ Precoverages of Bi cause a decrease in ethylene dehydrogenation on the Bi/Pt(111) surface. However, the initial rate of decrease in dehydrogenation per potassium adatom is more rapid than occurs per Bi adatom on the bismuth precovered surface. Another paper compares the two systems, Bi/Pt(111) and K/Pt(111), in detail.³¹ Clearly a large contribution to the decrease in dehydrogenation caused by coadsorbed potassium is due to site-blocking by the potassium adatoms. Some additional decrease due to an electronic effect of the potassium on the capability of the Pt(111) surface to dehydrogenate ethylene is also present.

Another interest in this work is to determine the mechanism of ethylene dehydrogenation on the promoted Pt(111) surface, and also to use this information to help understand the mechanism on the unpromoted Pt(111) surface. The second main effect potassium has on the dehydrogenation of ethylene on Pt(111) is to change the stable intermediates in the decomposition pathway, as evidenced by the new β_2 H_2 desorption peak in TPD and the presence of a new species in the HREELS spectra. Both of these effects are clearly due to changes in the electronic structure of Pt due to adsorbing potassium adatoms, since neither of these effects was observed in $\text{C}_2\text{H}_4 + \text{Bi}$ coadsorption studies on Pt(111).³⁰ Importantly, we propose that ethylene decomposes by essentially the same mechanism on the promoted and unpromoted surface, with only an increase in the activation energy for the formation of ethylidyne observed for the promoted surface. Support for this interpretation is found in the TPD data and in the HREELS data. Only one hydrogen atom equivalent desorbs in the β_1 or β_2 region throughout the potassium coverage range below $\theta_K = 0.30$. The formation of ethylidyne no longer occurs at 300 K, as is evidenced by the absence of the characteristic 1120 (1135) cm^{-1} and the 1345 (990) cm^{-1} modes for ethylidyne. However, following the desorption of the β_2 state after annealing to 420 K, we again see the characteristic ethylidyne spectra. A change in decomposition mechanism could occur, however, at very high K coverages, since for $\theta_K \geq 0.30$, where the β_2 state has been eliminated, we see no evidence for ethylidyne formation at any temperature.

Accompanying the increase in the activation energy for the formation of ethylidyne on the K/Pt(111) surface, we see evidence for a new surface species between 285 and 350 K in the HREELS spectra of Figures 6 and 7. Possible candidates for this intermediate can be found by looking at other intermediates that have been proposed in the formation of ethylidyne from ethylene on the Pt(111) surface. Several intermediates have been proposed; vinyl (CHCH_2) and vinylidene (CCH_2),^{7,32} and ethyl (CH_2CH_3)

(30) Windham, R. G.; Koel, B. E.; Paffett, M. T. *Langmuir* **1988**, *4*, 1113.

(31) Jones, M.; Windham, R. G.; Koel, B. E., to be submitted for publication in *J. Phys. Chem.*

(32) Kang, D. B.; Anderson, A. B. *Surf. Sci.* **1985**, *155*, 639.

and ethylidene (CHCH_3).^{33,34} Ethylidene has also been proposed as an intermediate in the hydrogen isotope exchange reaction with ethylidyne.^{35,36} First, we can definitely rule out the formation of π -bonded vinyl ($\text{CH}=\text{CH}_2$) and vinylidene ($\text{C}=\text{CH}_2$) intermediates from the ν_{CH} mode frequency of $\approx 2930\text{ cm}^{-1}$. It is much more difficult to rule out *rehybridized* vinyl ($\text{CH}-\text{CH}_2$) and vinylidene ($\text{C}-\text{CH}_2$) species (bonded to the surface with multiple Pt-C covalent bonds, in a manner similar to that of di- σ -bonded ethylene, CH_2-CH_2). The bending modes for all of these intermediate species (vinyl, vinylidene, ethylidene) are very similar. However, on the basis of the C:H stoichiometry deduced from TPD and the close comparison to the ethylidene organometallic complexes shown in Table I, we favor the identification of ethylidene as an intermediate in the decomposition of ethylene to ethylidyne on the K/Pt(111) surface.

There is additional support for this assignment. Zhou et al.⁷ have secondary ion mass spectroscopy (SIMS) evidence that also supports the ethylidene intermediate on the K/Pt(111) surface. At 300 K and at $\theta_{\text{K}} > 0.02$ in temperature programmed SIMS, both CCH^- and CH_3^+ ions are ejected from the surface. Ethylidyne does not form the CCH^- ion fragment. Therefore, another methyl-containing species (i.e. CHCH_3) must be present on the surface.

On the K/Pt(111) surface with $\theta_{\text{K}} = 0.50$, we see the ethylidene vibrational spectra persist until at least 420 K, where the onset of the single β_3 desorption peak occurs. Thus, at these potassium coverages, ethylidene is stable until 420 K and then undergoes complete dehydrogenation over a narrow temperature range to form a graphitic overlayer. This differs slightly from the results reported by Zhou et al.,⁷ who propose that for $\theta_{\text{K}} \geq 0.14$, the only intermediate formed is CCH. While it is difficult to identify this intermediate in our HREELS spectra, our H_2 TPD results are inconsistent with CCH formation below 420 K. If CCH were an intermediate, some H_2 desorption should occur prior to the β_3 H_2 desorption state at 510 K. At these potassium coverages, for the $\text{H}_2/\text{K}/\text{Pt}(111)$ system, the H_2 desorption peak temperature in our studies occurs at lower temperatures.⁴ Thus, at high potassium coverages, H_2 desorption is reaction-rate-limited by the decomposition of ethylene. We conclude that the decomposition reaction intermediate, ethylidene, is present on the surface throughout the entire potassium coverage range and that the range of temperature within which it is stable on the surface increases with increasing potassium coverage.

A critical question is whether ethylidene is a new reaction intermediate that is formed only on the potassium-promoted surface, or whether it is the same reaction intermediate in the decomposition of ethylene on the unpromoted Pt(111) surface, merely stabilized by the presence of potassium. First of all, we agree with the mechanism for ethylene decomposition on K-promoted Pt(111) developed independently and concurrently by Zhou et al.,⁷ in which ethylene isomerizes to ethylidene, which then dehydrogenates to form ethylidyne. However, Zhou et al.⁷ did not suggest this mechanism on the unpromoted Pt(111) surface. Two different mechanisms have been proposed for the dehydrogenation of ethylene to ethylidyne on Pt(111). A fundamental difference in the two mechanisms lies in nature of the step that initiates the decomposition. In one mechanism, ethylene is initially dehydrogenated, while in the second mechanism the reverse process, hydrogenation of ethylene, is proposed as the initial step. These two mechanisms also differ in the intermediates formed during the reaction.

The dehydrogenation/hydrogenation mechanism, illustrated in Figure 9I, has been discussed by Kang and Anderson.³² The adsorbed ethylene loses one hydrogen in the initial step of the process to form a vinyl ($\text{CHCH}_2(\text{a})$) surface species. This species then undergoes further dehydrogenation to form adsorbed vi-

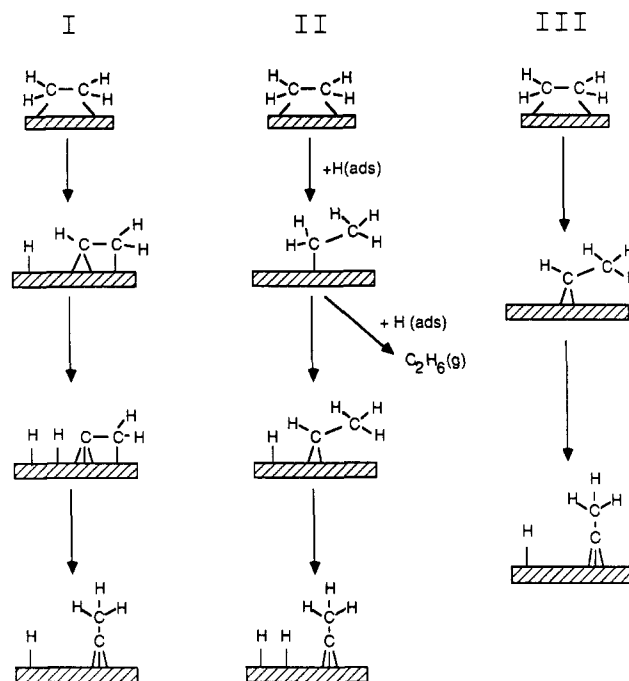


Figure 9. Schematic representation of three proposed ethylene decomposition mechanisms: (I) dehydrogenation/hydrogenation mechanism,³² (II) hydrogenation/dehydrogenation mechanism,³³ and (III) isomerization mechanism.

nylidene ($\text{CCH}_2(\text{a})$). The $\text{CCH}_2(\text{a})$ species then rehydrogenates to form ethylidyne ($\text{CCH}_3(\text{a})$). The problem with this mechanism is that it seems unlikely that strongly adsorbed species such as vinyl or vinylidene (which would be expected to extensively rehybridize as ethylene and acetylene do and therefore form either three or four strong, covalent Pt-C σ bonds) would hydrogenate to form ethylidyne. Also, there are no unambiguous experimental observations of vinyl or vinylidene intermediates to date, although Zhou et al.⁷ report that these intermediates are not inconsistent with their SIMS data on clean Pt(111).

Somorjai et al.³³ proposed an alternative ethylene decomposition mechanism, illustrated in Figure 9II. The initial step in this mechanism involves hydrogenating adsorbed ethylene to form adsorbed ethyl ($\text{CH}_2\text{CH}_3(\text{a})$). The adsorbed hydrogen necessary to initiate this reaction is thought to come from the adsorption of hydrogen from the background gases or from ethylene which is decomposed at defect sites at lower temperatures. The $\text{CH}_2\text{CH}_3(\text{a})$ can then be hydrogenated to form ethane, which immediately desorbs, or can be dehydrogenated to form ethylidene ($\text{CHCH}_3(\text{a})$). Ethylidene then dehydrogenates to form ethylidyne ($\text{CCH}_3(\text{a})$). The main problem with this mechanism is that adsorbed ethyl is proposed to be more stable than adsorbed ethylene. Recent work by Lloyd et al.³⁷ on ethyl iodide adsorption on Pt(111) shows that adsorbed ethyl dehydrogenates to form coadsorbed ethylene plus hydrogen, in direct contrast to this proposal.

Our observation of ethylidene formation on the K-promoted surface forces us to consider another mechanism on the unpromoted Pt(111) surface as well, involving the simple isomerization of adsorbed ethylene to ethylidene as the rate-limiting step in ethylene decomposition, as shown in Figure 9III. On the basis of SIMS evidence, Zhou et al.⁷ agreed that this mechanism is the dominant pathway on K-promoted Pt(111), but did not suggest this scheme for the clean Pt(111) surface. Ethylidene has been suggested previously as an important intermediate in H, D exchange in ethylidyne and is also present in the proposed mechanism in Figure 9II.

Our observation of ethylidyne prior to formation of ethylidyne indicates that potassium stabilizes ethylidene relative to the clean

(33) Somorjai, G. A.; Van Hove, M. A.; Bent, B. E. *J. Phys. Chem.* **1988**, *92*, 973.

(34) Bent, B. E. Ph.D. Thesis, University of California, Berkeley, 1986.

(35) Koel, B. E.; Bent, B. E.; Somorjai, G. A. *Surf. Sci.* **1984**, *146*, 211.

(36) Creighton, J. R.; Ogle, K. M.; White, J. M. *Surf. Sci.* **1984**, *138*, L137.

(37) Lloyd, K. G.; Roop, B.; Campion, A.; White, J. M. *Surf. Sci.* **1989**, *214*, 227.

Pt(111) surface. This stabilization can occur either by potassium increasing the activation barrier to the formation of ethylidyne or by potassium stabilizing the ethylidene surface species. Both explanations could be important. We have argued⁶ that the increased electron density at the surface due to charge donation by the potassium adatoms disrupts the strong di- σ bonding of ethylene to the surface, resulting in the formation of a weakly interacting, π -bonded ethylene species. Thus ethylidyne, which forms three covalent Pt-C σ bonds, could be even more destabilized than ethylene on Pt(111). It is reasonable then for potassium coadsorption to destabilize ethylidyne to a greater extent than ethylidene (which forms two covalent Pt-C σ bonds), thereby relatively stabilizing the ethylidene intermediate and increasing the activation barrier for ethylidyne formation. In a recent paper,³⁸ we have also argued that the gas-phase electron affinities of surface hydrocarbons can indicate which adsorbates will be stabilized by the presence of potassium, and these results indicate that ethylidene will be stabilized to a greater extent than ethylidyne due to its larger electron affinity. In that paper, we also report equilibrium thermodynamic estimates of the energetics of ethylene decomposition on Pt(111), by calculating the heats of formation of several adsorbed hydrocarbons and using the measured activation energies for decomposition. These calculations support our proposed mechanism involving ethylidene on the unpromoted Pt(111) surface.

Summary

Potassium initially ($\theta_K \cong 0.05$) causes an increase of 2-3 kcal mol⁻¹ in the activation energy for C-H bond breaking, allowing

us to trap ethylidene (CHCH₃) as a stable intermediate in ethylene decomposition. Ethylidene dehydrogenates to form ethylidyne, which decomposes (as on the unpromoted Pt(111) surface) to form C_nH species above 420 K and C_n species above 550 K. Higher potassium coverages increase the activation energy for C-H bond cleavage further to 31 kcal mol⁻¹ (13 kcal mol⁻¹ higher than on Pt(111) without K), stabilizing ethylidene over the range 300-420 K. Complete dehydrogenation of the surface species occurs over a small temperature range, yielding a single hydrogen desorption peak at 570 K. Thus, under these conditions, sequential C-H bond breaking reactions must have nearly the same activation energies. Ethylene decomposition on the K-promoted Pt(111) surface proceeds through an ethylidene intermediate. We propose that this intermediate is also important in ethylene decomposition on the unpromoted Pt(111) surface. In regard to the origin of the effect of K on ethylene surface chemistry, we conclude that geometric (ensemble size) effects due to K blocking sites required for ethylene decomposition are largely responsible for the decrease in the amount of dehydrogenation occurring (irreversible adsorption), but that the change in activation energy for CH bond cleavage is clearly an electron effect due to the chemical modification of the Pt electron structure.

Acknowledgment. Acknowledgment is made to the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, for support of this work. We thank Professor J. M. White and Professor F. Zaera for useful discussions and for making data available to us prior to publication. We also gratefully acknowledge Professor E. A. Carter for helpful comments on the paper.

Registry No. K, 7440-09-7; C₂H₂, 74-85-1; Pt, 7440-06-4; C₂H₆, 74-84-0; CHCH₃, 4218-50-2.

(38) Carter, E. A.; Koel, B. E. *Surf. Sci.*, in press.

Copper Overlayers on Rhenium(0001)

J.-W. He and D. W. Goodman*

Department of Chemistry, Texas A&M University, College Station, Texas 77843 (Received: April 11, 1989; In Final Form: July 26, 1989)

The interaction of Cu overlayers with a Re(0001) surface has been studied by low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS), and electron energy loss spectroscopy (ELS). The thermal desorption spectra of Cu from Re(0001) indicate two desorption peaks, designated as β_1 and β_2 states. The β_1 state begins to appear upon saturation of the β_2 state. Both states follow approximate zero-order kinetics. The activation energy for the β_1 and β_2 states is estimated from TD spectra to be ~ 74 and ~ 93 kcal/mol, respectively. AES measurements show that with Cu coverages less than 2 monolayers (ML), the Cu to Re AES ratios remain constant upon annealing to 1000 K. At higher coverages of Cu, the Cu/Re AES ratios decrease when annealed between 110 and 900 K, consistent with the formation of 3-D Cu clusters. Some Cu nucleation appears to take place during the deposition at 110 K. Several surface phases are observed by LEED following Cu deposition at 110 K and subsequent annealing. At a submonolayer coverage of Cu, a faint 2×2 structure is observed upon annealing to ~ 470 K whereas further annealing to ~ 1070 K produces satellite patterns. Cu deposition to 2 ML at 110 K induces a 10×1 phase, which upon annealing to ~ 500 K forms a new fractional pattern with hexagonal symmetry. This pattern appears to correspond to Cu clusters with (111) facets, superimposed on the pattern from the substrate. A Cu coverage of ~ 3 ML, annealed to 600 K, yields a rectangular pattern, due to an incommensurate structure of Cu with respect to the Re substrate. Further annealing nucleates the Cu atoms into clusters with (111) facets. ELS results support the above conclusions that the first layer of Cu is stable while multilayers of Cu coalesce into 3-D clusters when annealed to temperatures above 600 K.

1. Introduction

Recently considerable attention in the surface science community has been directed toward the study of bimetallic surfaces. In a typical study, one metal is deposited onto a single-crystal substrate of a second metal. Structural and electronic properties of the interface as well as the interaction of gases with the bimetallic surface can then be studied by surface analytical techniques, such as Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and thermal desorption spectroscopy

(TDS). Such studies are fundamentally important to the understanding of bimetallic catalysts and thin-film materials.

Previous work in our laboratories has addressed metal overlayers on substrates of W(100), W(110),^{1,2} and Ru(0001).³⁻⁵ The

(1) Berlowitz, P. J.; Goodman, D. W. *Surf. Sci.* **1987**, *187*, 463.

(2) Berlowitz, P. J.; Goodman, D. W. *Langmuir* **1988**, *4*, 1091.

(3) Houston, J. E.; Peden, C. H. F.; Blair, D. S.; Goodman, D. W. *Surf. Sci.* **1986**, *167*, 427.

(4) Campbell, C. T.; Goodman, D. W. *J. Phys. Chem.* **1988**, *92*, 2569.