Coadsorption of Ethylene and Potassium on Pt(111). 1. Formation of a \( \pi \)-Bonded State of Ethylene

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High-resolution electron energy loss spectroscopy (HREELS), temperature-programmed desorption (TPD), and ultraviolet photoelectron spectroscopy (UPS) have been combined to study the effect of preadsorbed potassium on the adsorption of ethylene on the platinum(111) single-crystal surface. Addition of potassium increases the relative amount of reversible ethylene adsorption at 100 K. Upon coadsorption with potassium, we also observe a new low-temperature ethylene desorption state at 150 K, with \( E_d = 5 \pm 0.5 \) kcal mol\(^{-1}\), which is about one-half the binding energy of ethylene adsorbed on clean Pt(111). The origin of this new desorption state is the formation of a weakly interacting ethylene species, which is only slightly distorted from the gas-phase hybridization, as determined primarily by vibrational spectroscopy. An explanation is given for these effects in which the increased charge density at the platinum surface due to coadsorbed potassium inhibits the strong \( \pi \)-donation of adsorbed ethylene to platinum and greatly reduces the chemisorption bond strength.

Introduction

The bonding of ethylene on transition-metal single-crystal surfaces\(^{1-13}\) can be described by two types of interactions. A \( \pi \)-bonded state, where the ethylene largely retains its sp\(^2\) hybridization with a carbon–carbon double bond, has been identified on Cu(100),\(^2\) Pd(110),\(^4\) Ag(110),\(^7\) Ni(100),\(^8\) and Pd(111).\(^9\) The chemisorption bond of ethylene adsorbed in this state can be described by a donor/acceptor interaction. A di-\( \sigma \)-bonded state can also be formed, where the carbon atoms in ethylene significantly rehybridize toward sp\(^2\), leaving a carbon–carbon single bond. Ethylene adsorbed in this state forms two covalent bonds to the metal surface and has been observed on Pt(111),\(^1\) Ni(111),\(^2\) and Pb(111).\(^10\) There are also cases where adsorbed ethylene exists in an intermediate bonding state with partial rehybridization, such as on Rh(111),\(^10\) Pd(100),\(^11\) Ru(001),\(^12\) and Fe(111).\(^13\)

Chemical modification of single-crystal metal surfaces can alter the bonding state of ethylene. Oxygen and carbon have been added as modifiers to several of these surfaces: Pt(111),\(^1\) Ag(110),\(^7\) Ru(001),\(^14\) Fe(111),\(^13\) Pd(100),\(^11\) and Ni(111).\(^3\) Coadsorption of ethylene with either oxygen or carbon on these surfaces results in the formation of a more weakly adsorbed \( \pi \)-bonded ethylene species, except for on Ag(110)\(^7\) where oxygen enhances the adsorption of ethylene. Until now, however, no electrochemical coadsorbates, i.e., alkali metals, have been studied to determine their influence on ethylene adsorption on metal surfaces.

Potassium coadsorption should result in a considerable modification of the Pt(111) surface chemistry, due to the alteration of the surface electronic structure. This arises from a transfer of charge from potassium to the platinum due to the low ionization potential of the alkali metal. Perhaps the best experimental evidence for this effect is seen in the large decrease of the work function.\(^15\) Coadsorption with potassium on Pt(111) has been observed to alter significantly the chemisorption properties of CO,\(^16,17\) H\(_2\),\(^18,19\) and NO.\(^20\) In all three cases the presence of

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Figure 1. Two-level ultra-high-vacuum chamber used in these studies. Top view of (a) AES level and (b) HREELS level.

potassium increases the heat of adsorption. For CO and NO there is also significant bond weakening within the molecule which leads to lowered intramolecular stretching frequencies and to an increase in the dissociation probability for CO and NO on transition-metal surfaces. This bond weakening is usually thought to be due to an increase in the back-donation from the platinum $d$-orbitals into the $2\pi^*$-orbitals of these molecules, although Nørskov et al.\textsuperscript{21} promote an explanation of these changes as due to direct electrostatic effects of the adsorbed K$^+$ on the coadsorbed molecule.

At present, only a few studies have been made involving the influence of potassium on the adsorption of hydrocarbons on metal surfaces. Garfunkel et al.\textsuperscript{22} studied the benzene/K/Pt(111) system with temperature-programmed desorption (TPD) and found that the benzene chemisorption bond strength was reduced upon coadsorption with potassium. In a preliminary communication of this work,\textsuperscript{23} we also reported that the ethylene chemisorption bond strength is reduced upon coadsorption with potassium. Zhou et al.\textsuperscript{24} have recently studied the C$_2$H$_4$/K/Pt(111) system with TPD and SIMS, in work complementary to ours. In agreement with our results, they also find that potassium inhibits the adsorption of di-$\sigma$-bonded ethylene, and that potassium decreases the activity for dehydrogenation of ethylene and changes the dehydrogenation mechanism. As will be discussed in detail later, potassium coadsorption decreases the chemisorption bond energy of ethylene adsorbed on platinum, since ethylene serves as a net $\sigma$-donor to the metal and coadsorbed potassium strongly inhibits this interaction by increasing the electron density on the surface platinum atoms. This result is in contrast to the effect of potassium coadsorbed with CO and NO due to differences in the nature of the chemisorption bond, since CO and NO are both much better $\pi$-acceptor molecules than C$_2$H$_4$. The potassium inhibition of the $\sigma$-interactions for CO and NO are more than compensated for in these cases by an increase in $2\pi^*$-back-donation.

By utilizing temperature-programmed desorption (TPD), we have observed the effect of potassium on the heat of adsorption of ethylene and on the coverage and reversible character of ethylene adsorption. Changes in the nature of the chemisorption bond of ethylene were monitored with high-resolution electron energy loss spectroscopy (HREELS), ultraviolet photoelectron spectroscopy (UPS), and work function change ($\Delta\phi$) measurements. Only the bonding of the low-temperature states of these systems, before the onset of decomposition, will be discussed in this paper. Detailed studies of the effect of potassium on ethylene uptake kinetics, i.e., the sticking coefficient and saturation coverage, along with comparisons to bismuth and ethylene coadsorption results which enable the determination of ensemble effects, will be presented elsewhere.\textsuperscript{25,26} The decomposition of ethylene coadsorbed with potassium on Pt(111) will also be treated in a forthcoming paper.\textsuperscript{27}

Experimental Section

The experiments were performed in a two-level ultra-high-vacuum chamber, which is shown in Figure 1, and which has been partially described previously.\textsuperscript{28} The system base pressure was 2 \times 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 16-19 K/s. The crystal

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temperature was measured by a chromel-alumel thermocouple spotwelded to the side of the crystal. The HREELS spectrometer is constructed of single 127° cylindrical sectors in the monochromator and analyzer. For specular reflection, $\theta_{in} = \theta_{out} = 65^\circ$ from the sample surface normal. Off-specular measurements were made by rotation of the monochromator about an axis perpendicular to the scattering plane. Typical conditions for HREELS were as follows: incident energy $= 0.35\text{--}1\text{ eV}$; incident current $= 1 \times 10^{-10}\text{ A}$; resolution $= 7 \text{ meV}$ ($56 \text{ cm}^{-1}$) fwhm, and angular resolution $= 4^\circ$ fwhm. All HREELS spectra were taken at 100 K. The UPS spectra were taken with a double-pass cylindrical mirror analyzer with a pass energy of 25 eV ($\Delta E = 0.4$ eV) and at a collection angle of $42^\circ$ with respect to the surface normal. The incident angle for the UV light was $72^\circ$ with respect to the surface normal. The work function measurements were obtained by utilizing the secondary electron onset energy from a scattered electron beam with $E_s = 120 \text{ eV}$ and also from UPS. All AES, $\Delta \phi$, TPD, UPS, and HREELS data were taken by using an IBM/XT computer with a Tecomar interface.

The Pt(111) crystal was cleaned in vacuum by a combination of Ar$^+$ sputtering (1 kV, 6 $\mu$A), annealing at 1200 K under vacuum, and oxygen treatments ($2 \times 10^{-6}$ Torr, 800--1000 K). AES, LEED, and HREELS were used to ensure that the surface was clean and well-ordered. Polyimide ethylene (99.9%, SG) and ethylene-d$_4$ (99%, CIL) were used without further purification. Ethylene exposures were nominally 1,1 langmuirs (corrected for ion gauge sensitivity and for an enhancement of 50 by the multichannel array doser) to achieve saturation coverages.

The potassium was deposited on the clean Pt(111) surface with a SAES getter source which had been outgassed thoroughly. To achieve the desired potassium coverages, a multilayer was deposited on the surface and the temperature of the crystal was then increased to desorb excess potassium until the desired coverage was obtained. This dosing procedure provided both reproducibility and minimal CO and H$_2$ adsorption. No difference in the chemistry was observed for potassium adlayers prepared by direct deposition of submonolayer coverages, as was also previously reported by Pirug et al. The potassium coverage was calibrated by using AES, TPD, and LEED. In this paper, we will refer to potassium coverages relative to monolayer saturation coverage, $\theta_{K} = 1$ monolayer corresponding to $5.01 \times 10^{14}$ K atoms/cm$^2$, or 33% of the density of Pt(111) surface atoms.

**Results**

1. **Potassium Adsorption on Clean Pt(111).** Potassium thermal desorption spectra are shown in Figure 2. As the potassium coverage is initially increased, the desorption peak temperature shifts to higher temperatures. At $\theta_{K} = 0.05$ the desorption traces begin to broaden significantly and the desorption maxima start shifting to lower temperatures. Utilizing the Redhead model and a preexponential of $10^{13}$, we find this latter shift corresponds to a decrease in adsorption energy from 65 kcal/mol at $\theta_{K} = 0.05$ to 30 kcal/mol at $\theta_{K} = 1$. These results agree quite well with previous studies of the adsorption of potassium on Pt(111),$^{30,31}$ Albano$^{32}$ has recently modeled several potassium/transition-metal systems, including the K/Pt(111) system, and found the coverage dependence of the desorption energy to be due to mutual dipolar repulsion and depolarization effects within the potassium adlayer.

The desorption behavior of very low potassium coverages (0.05) has not been reported previously. Similar desorption behavior to that of potassium is seen for several alkali overlayer systems, for example, Au desorption from a Ru(001) surface.$^{33}$ The shift in the peak temperature to higher values has been determined in the Au/Ru(001) case to be due to a compensation effect where both the preexponential and $E_r$ decrease monotonically with increasing coverage due to repulsive Au--Au interactions, rather than due to attractive lateral interactions. Given the partially ionic nature of the potassium at these low coverages, one would also expect to also see repulsive K--K interactions in the K/Pt(111) case. If the desorption energy is assumed to be constant at these low coverages, we also find that to model these desorption traces the preexponential factor must decrease by approximately 2 orders of magnitude over this potassium coverage range.

A plot of AES K(252 eV)/Pt(64 eV) peak-to-peak ratios, taken at 100 K, versus coverage is shown as an inset to Figure 2. From the shape of this curve and the sharp break at 1 monolayer (as deduced by TPD), we can conclude that a layer-by-layer growth mode occurs for at least the first two layers of potassium on Pt(111). Coverages above the second monolayer were not investigated in detail.

The effect of potassium on the work function is shown in Figure 3. Adsorption of potassium leads to a sharp decrease of 4.8 eV in the work function of Pt(111) due to the partially ionic nature of the K atoms at small coverages. As the potassium coverage is further increased, the work function reaches a broad minimum at $\theta_{K} = 0.50$, and by 1 monolayer increases to nearly the value of the work function for bulk potassium, which is 2.3 eV. Both the decrease in the work function and the large dipole moment, 18.8 D, are indicative of a significant charge transfer from the potassium to the platinum surface at low potassium coverages. As more potassium atoms are adsorbed on the platinum surface the potassium adlayer gradually becomes depolarized until it takes on a metallic potassium character. Our $\Delta \phi$ measurements, and also ELS measurements, on the K/Pt(111) surface agree well with previous results.

Several ordered LEED structures were observed at various potassium coverages. They are (2 $\times$ 2), ($\sqrt{3} \times \sqrt{3}$)R30°, and (3 $\times$ 3) as shown in Figure 3. At $\theta_{K} = 0.32$ we see only a diffuse background, but at $\theta_{K} = 0.50$, we see a sharp (2 $\times$ 2) pattern. For $0.70 < \theta_{K} < 1$, we see ($\sqrt{3} \times \sqrt{3}$)R30° spots with decreasing background as the coverage increases. As the potassium coverage is increased to greater than 1 monolayer, we see a superposition of a faint (3 $\times$ 3) and ($\sqrt{3} \times \sqrt{3}$)R30° pattern that with

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increasing potassium coverage gradually becomes a sharp \((3 \times 3)\) pattern. Pirug et al.\(^{29}\) have reported similar findings, with the exception of the \((2 \times 2)\) pattern. They saw no further LEED patterns below \(\theta_K = 1\), only a gradual weakening of the \((\sqrt{3} \times \sqrt{3})R30^\circ\) pattern. The LEED patterns we observe, including the \((2 \times 2)\), have also been observed by Schweizer;\(^{35}\) however, the coverage ranges of the patterns do not agree precisely.

Detailed LEED studies of \(\text{C}_2\text{H}_4 + K\) coadsorption were not made. However, upon addition of ethylene to the K/\(\text{Pt}(111)\) surface, no new LEED patterns were ever observed for the coadsorbed ethylene, and the ethylene caused no observable ordering of the disordered potassium overlayers below \(\theta_K = 0.32\).

2. Adsorption of \(\text{C}_2\text{H}_4\) on \(\text{Pt}(111)\).

Figure 4 shows TPD results for the adsorption of 1.1 langmuirs of ethylene on the clean \(\text{Pt}(111)\) surface at 100 K. This exposure gives a saturation coverage of ethylene. We observe only three desorption signals in TPD at 28, 28 and 30 amu, due to \(\text{H}_2\), \(\text{C}_2\text{H}_4\), and \(\text{C}_2\text{H}_6\), respectively.

Partially reversible ethylene adsorption leads to a \(\text{C}_2\text{H}_4\) desorption peak at 285 K with a shoulder at 260 K for the highest coverages of ethylene. This shoulder is not present at slightly less than saturation coverages and may indicate that new adsorption sites are populated near saturation coverage. The nature of the bonding of ethylene is independent of coverage, however, since HREELS spectra show no discernible changes upon annealing the surface to remove the low-temperature desorption shoulder. \(\text{C}_2\text{H}_4\) and CO are both detected at 28 amu, but the ethylene contribution can be easily determined to be correct by also monitoring the signals at 26 and 27 amu, and also by comparing results for \(\text{C}_2\text{D}_4\) at 32 amu.

In modeling the desorption energetics we used the TPD spectrum for an ethylene coverage 75% of saturation where the 260 K shoulder was not yet present. Utilizing a computer fit of the spectrum to the first-order desorption rate equation we have calculated \(E_d = 9.0 \pm 0.6\) kcal/mol with \(v = 10^{6.3\pm0.5} s^{-1}\). While these values are within experimental error of those reported by Salmeron and Somorjai,\(^{36}\) the size of the preexponential factor is too small and is difficult to explain. This low value for \(v\) was required to fit the broad width of the desorption spectrum. Site heterogeneity could also contribute to the width of the peak, and so the determination of \(v\) could be too small. If one assumes \(v = 10^{13} s^{-1}\), then \(E_d = 17\) kcal/mol.

The molecular ethylene desorption during heating in TPD is accompanied by hydrogenation and decomposition to yield ethane and hydrogen, respectively. Ethane, mass 30, desorbs in a single peak at 295 K and represents the reaction rate limited hydrogenation of ethylene. We have calculated from the TPD results that only 2% of the ethylene is hydrogenated to form ethane. Hydrogen desorbs in sharp peaks at 310 and 510 K, with a broad shoulder beginning at 550 K. The origin of these peaks can be determined by using HREELS. The first peak is due to the decomposition of ethylene to form ethylidyne, \(\text{CH}_2\). The second peak can be attributed to the further decomposition of ethylidyne to form various \(\text{C}_n\text{H}_m\) fragments. The broad feature beginning at 550 K represents complete dehydrogenation of the surface fragments to form \(\text{C}_n\) polymers on the \(\text{Pt}(111)\) surface.

Utilizing AES \(C(272 eV)/\text{Pt}(235 eV)\) peak-to-peak ratios as a function of temperature, we find that 34% of the ethylene adsorbed at 100 K is reversibly adsorbed and 46% dehydrogenates upon warming. This data is shown as an inset to Figure 4. The carbon atoms in \(\text{C}_2\text{H}_4\) adsorbed on \(\text{Pt}(111)\) have sp\(^3\) hybridization, so that upon decomposition to form ethylidyne, in which the carbon atoms are also sp\(^3\) hybridized, no large change occurs in the \(C(KV)\) line shape at the resolution used in this study (6 eV p-p modulation) and the \(C(KV)\) peak-to-peak height is proportional to carbon coverage. We note that this result agrees well with Berlowitz et al.,\(^{37}\) who found 62% molecular desorption, 36% dehydrogenation, and 2% hydrogenation using careful TPD calibration.

There is uncertainty regarding the saturation coverage of ethylene on \(\text{Pt}(111)\) at 100 K. If ethylene is dosed at 300 K a saturation coverage of ethylidyne, \(\text{CH}_2\), is formed. This ethylidyne coverage forms a \((2 \times 2)\) LEED pattern, which has been reported to correspond to either 0.25\(^{38,39}\) or 0.50\(^{40,41}\). We find from the AES \(C(272 eV)/\text{Pt}(235 eV)\) ratio that the molecular ethylene coverage due to a saturation dose of ethylene at 100 K is equal to the \(\text{C}_2\text{H}_4\) coverage formed from a saturation dose at 300 K. We favor the conclusion that the saturation ethylidyne coverage that can be formed at 300 K is \(\theta_{\text{CCH}_2} = 0.25\), and that saturation ethylene coverage for adsorption at 100 K is therefore \(\theta_{\text{CCH}_2} = 0.25\), based on modeling our low-temperature ethylene and potassium coadsorption data.\(^{36}\) In short, this is due to the difficulty of packing more than 0.25 monolayer of ethylene coadsorbed with 0.50 monolayer of potassium on the \(\text{Pt}(111)\) surface. In this paper, the exact coverage information is not as critical as in studies which attempt to determine the adsorption and decomposition ensemble size requirements,\(^{28}\) which will be reported later. All further references to ethylene coverage in this


paper will be in terms of relative ethylene coverages.

3. Adsorption of C2H4 on Potassium Precovered Pt(111). 3.1. Temperature-Programmed Desorption Studies. Ethylene TPD spectra after a 1.1-langmuir exposure of C2H4 to the Pt(111) surface with varying potassium precoverages at 100 K are shown in Figure 5. Uptake curves24 show that 1.1 langmuirs is sufficient to produce a saturation coverage of ethylene in all cases. The most notable effect of potassium coadsorption is the formation of a new low-temperature desorption peak, denoted α1. The population in the α1 desorption state increases with potassium coverage, saturating at θK = 0.40, and then decreases with larger potassium coverages. At very low potassium coverages, the α1 peak occurs at 130 K. At θK = 0.05, we see a shoulder begin to grow in at 150 K that continues to increase with increasing potassium coverage and saturates in intensity as the dominant peak at θK = 0.50. Increasing the potassium coverage further leads to a slight decrease in the peak temperature, back to 130 K at θK = 0.80. No C2H4 desorption is observed from the complete potassium monolayer, θK = 1.0. Utilizing a computer fit of first-order desorption kinetics to the ethylene αL desorption peak with Et = 150 K for θK = 0.50, we have calculated EA = 5.3 ± 0.3 kcal/mol and ν = 10^10 ± 5 s^-1 for the new α1 state. As discussed previously, it was necessary to use this unusually low preexponential to fit the broad width of the desorption spectra. If one assumes instead that ν = 10^13 s^-1, then EA = 9 kcal/mol. Clearly the effect of coadsorbed potassium is to produce a new adsorbed state of ethylene with a weakened chemisorption bond to Pt, decreasing from 9–17 kcal/mol on the clean Pt(111) surface to 5–9 kcal/mol on the potassium precovered Pt(111) surface.

Potassium has only a small effect on the temperature of the ethylene desorption peak at 285 K, denoted α2, which is characteristic of ethylene desorption on clean Pt(111). However, the 260 K shoulder grows in with increasing potassium coverage until it saturates at θK = 0.12. Above this coverage the shoulder decreases in intensity so that a narrow α2 desorption peak at 285 K remains for θK > 0.20, until this state is eliminated.

In Figure 6 we have summarized the quantitative results of the ethylene TPD data in a plot of ethylene coverage versus potassium coverage. In this figure we have plotted the populations of the α1 and α2 desorption states, the total ethylene reversibly adsorbed, and the total amount of ethylene adsorbed as a function of potassium coverage. The population of the α2 state is initially constant, but above θK = 0.20 it decreases fairly rapidly. The α2 state grows in almost linearly with potassium coverage, with a C2H4/K stoichiometry of 1.5 if θK,C2H4 = 0.25 on clean Pt(111). (Note that θK, = 1 is equivalent to an absolute coverage of 0.33 monolayer.) At θK = 0.40, the α2 state begins to drop off fairly rapidly with increasing potassium coverage. Thus, the amount of reversibly adsorbed ethylene increases sharply with coadsorbed potassium, due to the formation of the α1 state, until the α2 state is attenuated. However, the saturation coverage of adsorbed ethylene stays nearly constant because of the rapid decrease in the amount of dehydrogenation and hydrogenation of the di-s-bonded ethylene due to coadsorbed potassium.

In summary, we observe as much as a 60% increase in the amount of reversibly adsorbed ethylene on the surface. The total ethylene saturation coverage remains constant up to coverages of θK = 0.40 and then also begins to decrease significantly at larger potassium coverages, as the work function reaches a minimum and the potassium becomes increasingly metallic. It is somewhat surprising that the total ethylene saturation coverage remains constant over such a large potassium coverage range; however, this may be due to a reduction in the adsorption site requirement of the new adsorption state that we will later identify as σ-bonded ethylene. The behavior of the total ethylene coverage as a function of potassium coverage mimics the behavior of the sticking coefficient of ethylene on potassium-precovered Pt(111). The uptake kinetics of ethylene on the K/Pt(111) system will be discussed further in a forthcoming paper.25

Potassium also dramatically affects the dehydrogenation and hydrogenation of ethylene. For θK > 0.05 we see no further formation of ethane, in agreement with Zhou et al.24 For θK = 0.05, the amount of dehydrogenation has also decreased by 30%, and beginning at coverages as low as θK = 0.02 we also see a new intermediate in ethylene dehydrogenation. The details of these studies will be discussed in a forthcoming paper.25

3.2. High-Resolution Electron Energy Loss Spectroscopy Studies. Figures 7 and 8 show the effect of coadsorbed potassium on the vibrational spectra of adsorbed C2H4 and C2D4, respectively, for saturation ethylene exposures on Pt(111) at 100 K. Loss peaks due to coadsorbed CO are indicated by asterisks. The vibrational spectra for C2H4 and C2D4 adsorbed at 100 K on a clean Pt(111) surface are shown in the bottom curves of Figures 7 and 8, respectively. These spectra agree well with previous studies.1 The peak at 1020 cm^-1 represents the unresolved combination of two peaks, the CC stretching (υCC) mode at 1060 cm^-1 and the CH wag (ΔvCH) at 980 cm^-1. These two peaks are resolved in the C2D4 spectrum in Figure 8 where υCC = 875 cm^-1 and ΔvCDH = 675 cm^-1. The CH(CD) stretching mode at 2930 (2155) cm^-1, which is representative of hydrogen bonded to an sp^3 hybridized carbon atom, and the near-single-bond frequency of the υCC mode at 1060 (875) cm^-1 indicate that ethylene adsorbed on clean Pt(111) is extensively rehybridized from the gas-phase structure and is di-s-bonded to the surface.1

At low potassium coverages the vibrational frequencies of the di-s-bonded species are only slightly perturbed. The main effect of coadsorbed potassium on the C2H4 (C2D4) spectrum is to
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Coadsorption of Ethylene and Potassium on Pt(111) and the Effect on the Vibrational Spectra

Figure 8. HREELS spectra of saturation coverages of C2D4 adsorbed at 100 K for various potassium precoverages on Pt(111). Coadsorbed CO energy loss peaks are denoted by *.

produce several new, weak losses observed at 870 (610), 1360 (980), 1620 (1495), and 3060 (2280) cm\(^{-1}\). The intensity of these new losses continues to increase concomitantly with the potassium coverage, while those losses attributed to the di-\(\sigma\)-bonded ethylene decrease. The positions of the loss peaks for both species remain constant throughout. At the highest potassium coverage (\(\theta_K = 0.80\)), we see essentially only the new vibrational loss peaks.

Vibrations; the CH bending mode at 1360 cm\(^{-1}\) is most affected by contribution from the coadsorbed CO stretching mode at 1320-1360 cm\(^{-1}\).

Two empirical parameters have been proposed which utilize the vibrational spectra of adsorbed C2H4 (C2D4) to give a measure of the degree of rehybridization of ethylene upon adsorption on a metal surface which ranges from sp2 to sp3. Parameterization of the vibrational frequencies is necessary due to the extensive coupling in ethylene between the CC stretching mode, \(\nu_{CC}\), the in-plane CH2 scissor mode, \(\delta_{CH2}\), the \(\pi\) parameter has been proposed by Stuve and Madix,\(^{14,45}\) which combines the percentage shift to lower frequency upon adsorption of both the \(\nu_{CC}\) and \(\delta_{CH2}\) modes. The DCD (Dewar, Chatt, and Duncanson) parameter has been proposed by Bent et al.,\(^{10}\) which uses the highest vibrational frequency observed between 1100 and 1550 cm\(^{-1}\) in the C2D4 spectrum. Both parameters normalize to standard values of one for C2D4 Br2 (sp3 hybridization) and zero for C2D4 gas (sp2 hybridization). The \(\pi\) parameter has the distinct advantage of being able to utilize either the C2H4 or C2D4 spectra, however, in some instances there are inconsistencies between the two values. The DCD parameter seems to give better correlation to the hybridization predicted from CH stretching frequencies. For the relevant spectra in this paper, however, there is good agreement between the two parameters.

The relative coverage information on these two species at 100 K, which is complementary to the TPD data, can be obtained if one plots the intensities of the \(\nu_{CH}\) loss peaks attributed to the two molecular ethylene bonding states versus potassium coverage. One sees that as the potassium coverage is increased the intensity of the \(\nu_{CH}\) loss peak at 2930 cm\(^{-1}\) due to di-\(\sigma\)-bonded (\(\alpha_\sigma\)-state) ethylene decreases gradually with potassium coverage up to \(\theta_K = 0.50\), at which point there is a rapid falloff. The intensity of the \(\nu_{CH}\) loss peak at 3060 cm\(^{-1}\) attributed to \(\pi\)-bonded (\(\alpha_\pi\)-state) ethylene increases with potassium coverage up to \(\theta_K = 0.19\) then remains roughly constant up to 0.50. It, too, then decreases rapidly for \(\theta_K > 0.50\).

If the crystal is warmed to 160 K, just above the peak desorption temperature of the \(\alpha_\pi\) state, we see the disappearance of the energy loss peaks due to the \(\pi\)-bonded state and then see only the peaks due to the di-\(\sigma\)-bonded state. The fact that the HREELS energy loss intensities for this warm-up experiment qualitatively reflect the TPD areas representing the two bonding states and the fact that we observe losses for both bonding states at 100 K (Figure 7 and 8) lead us to conclude that there is little interconversion between the \(\pi\) and di-\(\sigma\)-bonding states during warming in TPD.

One of the most difficult problems in making these HREELS studies is the interference from coadsorbed CO. In the absence of coadsorbed potassium, \(\nu_{CO} = 1855\) and 2105 cm\(^{-1}\), posing little interference to hydrocarbon studies, except perhaps in the \(\nu_{CD}\) region. However, in the presence of coadsorbed potassium, \(\nu_{CO}\) shifts much lower in frequency, as low as 1230 cm\(^{-1}\). Furthermore, the exact \(\nu_{CO}\) frequency is dependent both on the amount of potassium and on the amount of CO.\(^{18}\) Thus, even in comparing C2H4 and C2D4 spectra, it is often difficult to make unambiguous assignments of contaminant CO peaks. However, after evaluation of many HREELS spectra obtained under different conditions and after performing CO-spiking experiments, we have assigned the loss peaks due to \(\nu_{CO}\) as shown by the asterisks in Figures 7 and 8. The CH bending mode at 1360 cm\(^{-1}\) is most affected by contribution from the coadsorbed CO stretching mode at 1320-1360 cm\(^{-1}\).


TABLE I: Vibrational Frequencies of Gas-Phase and κ-Bonded Ethylene Surface Species

<table>
<thead>
<tr>
<th>κ</th>
<th>νmax (CH2 stretch)</th>
<th>νmax (CH wag)</th>
<th>ν′ (CC stretch)</th>
<th>ν′ (CH stretch)</th>
<th>Ref</th>
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</thead>
<tbody>
<tr>
<td>C2H4(g)</td>
<td>0</td>
<td>0</td>
<td>1444 (1078)</td>
<td>949 (720)</td>
<td>1342 (981)</td>
</tr>
<tr>
<td>K/[(11)</td>
<td>0.05</td>
<td>0(0.04)</td>
<td>nr</td>
<td>870 (610)</td>
<td>1360 (980)</td>
</tr>
<tr>
<td>O/Ag(110)</td>
<td>0.12</td>
<td>0.14</td>
<td>1452</td>
<td>952 (726)</td>
<td>1323</td>
</tr>
<tr>
<td>Cu(100)</td>
<td>0.25</td>
<td>0.21</td>
<td>903 (677)</td>
<td>1290 (950)</td>
<td>1560 (1420)</td>
</tr>
<tr>
<td>O/[(111)</td>
<td>0.38</td>
<td>0.27</td>
<td>975 (757)</td>
<td>1243 (962)</td>
<td>1515 (1353)</td>
</tr>
<tr>
<td>O/Pd(100)</td>
<td>0.47</td>
<td>(0.30)</td>
<td>940 (700)</td>
<td>nr</td>
<td>1510 (1340)</td>
</tr>
</tbody>
</table>

*Parentheses indicate values for the deuteriated species.         bDewar, Chatt, and Duncan.10

3.3. Ultraviolet Photoelectron Spectroscopy and Work Function Change Studies. Figure 9 shows the photoelectron spectra obtained with He I radiation before and after a saturation exposure of ethylene to the K/[(111) surface with 0.25. We also show the gas-phase ethylene UPS spectra. 47 We assign the energies of the molecular framework orbitals of adsorbed ethylene to the 9.9-eV shoulder, 8.7- and 6.6-eV peaks, and the energy of the πCC orbital to the 4.9-eV peak. Alignment of the gas-phase spectrum with the adsorbate spectrum to approximately account for final-state effects due to relaxation changes upon adsorption shows that only the highest lying π-level undergoes a differential shift of 0.2 eV to higher binding energy upon adsorption. This π-level shift is small compared with the shift of 0.4 eV seen on the Ni(100) surface, 48 where ethylene is also κ-bonded, but where the chemisorption bond strength is somewhat larger. For di-κ-bonded ethylene on Ni(111), a shift of 0.9 eV is observed. 49 Thus, UPS clearly confirms our assignment from TPD and HREELS of a weakly bound, κ-bonded ethylene species.

Work function measurements were also obtained using the secondary electron onset energy from UPS. On the clean Pt(111) surface (φ0 = 5.7 eV), ethylene adsorption causes a 1.05-eV decrease in the work function at saturation coverage, consistent with a large charge transfer from ethylene to the Pt(111) surface expected in forming the di-κ-bonded species. Upon adsorption of potassium (θK = 0.50) on Pt(111), a large work function decrease is seen with Δφ < -4.8 eV. When ethylene is adsorbed on this K/Pt(111) surface there is no change in the work function, Δφ < 0.1 eV. Since the ethylene coverage on clean Pt(111) and on K/Pt(111) with θK = 0.50 is about the same, we interpret this result as due to very little charge transfer between the ethylene and the surface. This is also consistent with ethylene forming a very weakly interacting κ-complex with the Pt(111) surface. These

Δφ results are in agreement with Zhou et al., 24 who report more extensive Δφ studies.

Discussion

We have observed using TPD that coadsorption of potassium with ethylene on Pt(111) causes the formation of a new, weakly bound adsorption state of ethylene. Utilizing HREELS, UPS, and Δφ measurements, we conclude that this new state is due to a very weakly interacting, κ-bonded ethylene species.

In order to explain the observed effects of potassium coadsorption it is useful to review the bonding of ethylene in transition-metal complexes, since little is known about these interactions on metal surfaces. It is recognized, however, that the bonding of ethylene to a metal surface can essentially take two forms, a κ- or di-κ-complex. The κ-complex can be described in terms of the Dewar, Chatt, and Duncan (DCD) model. 50, 51 This model describes a synergistic relationship in which there is both a σ-donor interaction that involves a donation of charge from the filled ethylene π-orbital to a metal d-orbital and a π-acceptor interaction that involves a back-donation of charge from the filled metal d-orbital into the empty ethylene πκ-orbital. Thus, adsorbed κ-bonded ethylene is formally a two-electron σ-donor, but the κ-molecular orbital, allows it to also be a πκ-acceptor. The relative importance of these two bonding interactions depends on the metal electronic structure. If the transition metal in an organotransition-metal compound has a significant positive charge, the σ-donor interaction is favored, while more electron density on the transition metal favors a stronger πκ-donor interaction leading to greater back-bonding. Back-bonding, which involves electron density that is delocalized from the metal d-orbital into the ethylene πκ-orbital, decreases the carbon-carbon bond order and increases the hybridization of the carbon atoms toward sp2. However, in the σ-complex, backbonding plays a relatively minor role and ethylene essentially retains its sp2 hybridization. For example, coordinated ethylene in Zeise’s salt52, 53 has empirical vibrational parameters denoted DCD10 and κ11 of 0.43 and 0.38, respectively.

If back-bonding is carried far enough, the σ-bond in ethylene is broken and the p-orbitals on each carbon atom form σ-bonds to the metal atoms on the surface. When the carbon-carbon σ-bond is broken the change to sp2 hybridization at the carbon atoms is complete and the adspecies can be described as a covalently bonded metalalloy. Previous surface chemistry studies have often referred to this bonding configuration as a di-κ-bonded species. Ethylene adsorbed on Pt(111) is a good example of this type of species, with DCD and κ parameters of 0.96 and 0.92, respectively.

For di-κ-bonded ethylene adsorbed on Pt(111), there can be no additional increase in back-bonding caused by coadsorbed potassium, since there are no longer π or πκ molecular orbitals. In this case, adding potassium to the platinum surface might be thought of as "overpromotion", since potassium actually decreases the chemisorption bond strength of ethylene by inhibiting the formation of strong covalent bonds between the carbon p-orbitals.

References:

Coadsorption of Ethylene and Potassium on Pt(111) and metal d-orbitals. This inhibition causes the formation of a π-bonded ethylene species. Furthermore, the chemisorption bond energy of this π-bonded ethylene species on the K/Pt(111) surface is observed to be very small, 5–9 kcal mol⁻¹. This observation can be understood by considering that ethylene is a relatively poor π-acceptor. The increased electron density on the Pt atoms, due to coadsorbed potassium, inhibits the strong σ-donor interaction of the ethylene π-bond with the metal surface, which is not sufficiently compensated for by a possible increase in the π-acceptor interaction.

The effect of potassium coadsorption on ethylene bonding is in contrast to the increased chemisorption bond strength observed for CO upon coadsorption with potassium on Pt(111).16,17 The origin of these different chemical effects can be understood by considering the differences in the chemisorption bonding interactions for ethylene and carbon monoxide on transition metals. The 5r-orbital of CO, which is essentially a lone pair on carbon, donates charge into metal σ-orbitals forming a σ-bond, while the filled metal 5r-orbitals back-donate charge into the empty 2π*-orbital of CO. CO is one of the best π-acceptor ligands and back-bonding is known to play an important role in CO-metal coordination. Since potassium donates charge to the metal surface atoms, one can understand that when potassium is adsorbed on Pt the metal back-donation into the CO 2π*-orbital should be enhanced resulting in an increase in the strength of the metal–CO chemisorption bond and a decrease in the C=O bond order, which is what is observed experimentally.16,17 This back-bonding increase more than compensates for any decrease in 5r donation that may be induced due to coadsorbed potassium.

Further evidence supporting this explanation is found in the work function data for CO and ethylene on the Pt(111) surface. For CO on Pt(111), the work function increases by approximately 1.2 eV,16 indicating significant charge donation from the surface to the adsorbate, as would be predicted for a net π-acceptor ligand. For ethylene adsorption on Pt(111), there is a 1.05 eV decrease in the work function indicative of significant charge donation from the surface to the adsorbate, as expected if ethylene serves as a net σ-donor. Note that when ethylene is coadsorbed with potassium on Pt(111), there is no significant change in the work function from the K + Pt(111) value, indicating little or no charge transfer from C₂H₄ to Pt or from Pt to C₂H₄ has occurred.

Using the above reasoning we would predict that coadsorbing potassium with other donor molecules on transition-metal surfaces should decrease the binding energy as seen for ethylene. These effects have been observed. The effects of alkali metal coadsorption on the adsorption properties of a σ-donor, NH₃,18 and a π-donor, benzene,21,22 have been studied. In both cases there is a decrease in the activation energy for desorption indicating a weaker chemisorption bond.

Interestingly, the coadsorption of electronegative adatoms, i.e., C and O, with ethylene on a number of single-crystal metal surfaces also results in a decreased ethylene chemisorption bond strength. The effect of coadsorbing oxygen and ethylene has been studied on Pt(111).1 Fe(111),13 Ru(001),14 and Pd(100).11 The hybridization of adsorbed ethylene bonding on these clean metal surfaces ranges from almost entirely sp³ for Pt(111) (πσ = 0.92) to intermediate on Pd(100) (πσ = 0.77), but in all cases is well described as a di-σ-bonding interaction. Upon coadsorption with oxygen, the hybridization of ethylene on all these surfaces decreases to more sp²-like with πσ < 0.42, resulting in the formation of a π-bonded species. Carbon has also been shown to modify the bonding of ethylene at metal surfaces in a similar fashion. Ethylene adsorbs as a di-σ-bonded species with nearly sp² character on Ni(110)3 and Fe(111)13 surfaces (πσ > 0.73). Upon coadsorption with carbon, the hybridization is again reduced toward sp² (πσ < 0.35). All of these results can be understood by considering that coadsorbed electronegative adatoms such as carbon and oxygen withdraw charge from the surface metal atoms. This should result in a strong Lewis acid–Lewis base interaction between the surface and donor coadsorbates, i.e., π-bonded ethylene. The strongly adsorbed di-σ-bonded species is inhibited from forming due to the decreased electron density at the metal atoms compared to the clean surfaces; however, the σ-donor interaction of the π-bonded species should be enhanced for these systems, giving a strongly bound π-complex, as in Zeise's salt. Evidence for this effect can be seen by looking at the DCD and πσ parameters for several of the C₆H₆/O/metal systems in Table I. Nonetheless, these π-bonded species are still more weakly adsorbed than the di-σ-bonded species on the clean surfaces. Potassium coadsorption forms an even weaker adsorbed π-bonded species, since it interferes strongly with the σ-donor (Lewis base) interaction, opposite to the effect of coadsorbed oxygen.

If these arguments are correct, then one would expect to see an increased adsorption energy for existing π-bonded ethylene species upon oxygen coadsorption. Some evidence for this exists in studies on Ag(110)3 in which coadsorbed oxygen was used to stabilize ethylene bonding.19,20,21,22,23,24,25 Minimal adsorption was observed on the clean Ag(110) surface. Further studies are planned in our laboratory that will explore the effect of oxygen coadsorption on π-bonded ethylene on Ni(100) and Pd(111) surfaces.

We do note that while coadsorption of CO and ethylene can provide an intuitive interpretation of the electronic effects induced by potassium on ethylene adsorption, another model proposed by Nerskov et al.21 utilizes a direct interaction occurring through an electrostatic potential induced by the potassium. Both models, however, qualitatively predict the same results, and our studies do not directly distinguish between the two models.

TPD and HREELS studies have been conducted on the C₂H₄/Bi/Pt(111) system which confirm that the effects due to coadsorbing potassium with ethylene on Pt(111) that are noted above are indeed electronic in nature.19,21,22,24,25 Bismuth has been shown previously19,22,24,25 to be a potentially useful probe of site-blocking on the Pt(111) surface. Neither the TPD nor HREELS studies on valene were able to provide evidence of any weakly adsorbed state.25 Plots of total ethylene coverage versus bismuth coverage yield a straight line, indicating a purely site-blocking mechanism, in contrast to the results in Figure 6. Thus, we have concluded that the formation of a high-coverage, weakly interacting, π-bonded state of ethylene due to potassium coadsorption is electronic in origin for θ₂ ≤ 0.4. However, for θ₂ > 0.4 site-blocking becomes a dominant effect. These K and Bi comparison studies will be discussed in more detail in a forthcoming paper.25

An interesting question remains concerning the range of the observed electronic effects and the influence of potassium on ethylene chemisorption at sites more distant than next-nearest neighbor. In our study potassium has only a short-range interaction with coadsorbed ethylene. At low coverages of both ethylene and potassium, no π-bonded ethylene is observed. As we increase the ethylene coverage, however, the π-bonded ethylene state begins to be populated and is directly proportional to the potassium coverage. The formation of π-bonded ethylene species is due to a short-range or local interaction, since the population of this state depends upon both potassium and ethylene coverage and even at relatively high potassium coverages some unaltered di-σ-bonded ethylene remains.

As a final note, we suggest that our discovery of a weakly interacting, π-bonded adsorbed state of ethylene caused by potassium coadsorption may provide new insights into the role of potassium as a promoter in the Fischer–Tropsch synthesis. Upon promotion, the rate and selectivity of catalysts toward the heavier, more desirable hydrocarbons, particularly olefins, is enhanced.57 Considering the results of our study, the promotion capability of potassium to increase the percentage of olefins may lie at least

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in part in its ability to destabilize the chemisorption bonding of olefins formed during catalytic reaction, removing them from further hydogenation or other subsequent reaction.

Summary

In summary, we have observed the following effects of coadsorbed potassium on the chemical nature of ethylene adsorption on the Pt(111) surface:

1. Coadsorption of ethylene with potassium on Pt(111) results in the formation of a new, reversibly adsorbed species with a small binding energy of 5–9 kcal/mol, or about one-half the bonding energy of ethylene on Pt(111). The identification of this surface species comes primarily from vibrational spectroscopy using HREELS. Comparisons to other ethylene–metal complexes indicate that a very weakly interacting, π-bonded ethylene species is formed. This assignment is consistent with UPS spectra which show only a 0.2–eV bonding-induced shift of the highest lying π-level of ethylene from the gas-phase UPS spectra, and work function measurements of the K/Pt(111) surface which show no change in the work function upon subsequent adsorption of ethylene.

2. Initially, the population of this new π-bonded state of ethylene increases concomitantly with increasing potassium coverage. The saturation coverage of ethylene remains constant, even though it is coadsorbed with substantial amounts of potassium. This may be due to a reduction in the adsorption site requirement of the π-bonded ethylene. At \( \theta_K < 0.40 \), the influence of potassium is clearly an electronic (ligand) effect. As the potassium surface becomes increasingly metallic (\( \theta_K > 0.40 \)), however, the total ethylene coverage decreases sharply as site-blocking by potassium becomes a dominant factor.

3. We observe two chemically distinct types of ethylene to coexist on the surface, even at fairly high potassium coverages (\( \theta_K = 0.70 \)). Thus, we conclude that the electronic effects induced by potassium coadsorption on the bonding of ethylene are short range in nature.

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Effect of the Nonaqueous Phase on Interfacial Properties of Surfactants. 1. Thermodynamics and Interfacial Properties of a Zwitterionic Surfactant in Hydrocarbon/Water Systems

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Interfacial and thermodynamic properties of the zwitterionic surfactant, C\(_{12}\)H\(_{25}\)N\(^+\)(CH\(_2\)C\(_6\)H\(_5\))(CH\(_3\))CH\(_2\)COO\(^-\) (C\(_{12}\)BMG), were investigated at 25, 35, and 45 °C in various hydrocarbon/water systems. The hydrocarbons used were hexadecane, dodecane, heptane, isoctane, heptamethylnonane, cyclohexane, and toluene. From the interfacial tension vs log concentration in the water-phase curves, the standard parameters of micellization and adsorption, the critical micelle concentrations (cmc's), the minimum area per molecule at the hydrocarbon/water interface, and the efficiency and effectiveness of interfacial tension reduction were determined. The effect of the hydrocarbon phase on the micellization parameters is explained in terms of its effect on the structure of the micelle, on the adsorption parameters, in terms of its intercalation between the surfactant tails.

Introduction

The effect of the nonaqueous phase on the adsorption and micellization of an anionic surfactant, sodium dodecyl sulfate, in hydrocarbon/water systems was previously investigated by Rehfeld.\(^1\) We report here the results of our investigation on the effect of the nonaqueous phase on the thermodynamic and interfacial properties of a zwitterionic surfactant, C\(_{12}\)H\(_{25}\)N\(^+\)(CH\(_2\)C\(_6\)H\(_5\))(CH\(_3\))CH\(_2\)COO\(^-\) (C\(_{12}\)BMG), in hydrocarbon/water systems.

Experimental Section

Materials. N-Dodecyl-N-benzyl-N-methylglycine, C\(_{12}\)H\(_{25}\)N\(^+\)(CH\(_2\)C\(_6\)H\(_5\))(CH\(_3\))CH\(_2\)COO\(^-\) (C\(_{12}\)BMG), >98% purity, was synthesized in this laboratory.\(^2\)

Before being used for interfacial tension measurements, aqueous solutions of the surfactant (in water that had first been deionized and then distilled twice, the last time through a 1-m-high Vigreux column with quartz condenser and receiver) were further purified by repeated passage\(^3\) through minicolumns (SEP-PAK C\(_{18}\) Cartridge, Waters Assoc., Milford, MA) of octadecylsilanized silica gel to remove any traces of impurities more interfacially active than the C\(_{12}\)BMG.

The hydrocarbons used were hexadecane and heptamethylnonane, >98% (Humphrey); dodecane and isoctane, >99% (Aldrich); heptane, spectro grade (Eastman); cyclohexane and toluene, certified A.C.S. spectranaalyzed (Fisher Scientific).

The UV absorbance of each of the saturated hydrocarbons was measured at 255 nm against a blank of 95% ethanol when received. If the absorbance was less than 0.015, the saturated hydrocarbon was used as received. If the absorbance was greater than 0.015, the saturated hydrocarbon was passed through a 31 × 3.4 cm column (Fisher and Porter Co.) of silica gel 922 (Will Corp.) and that had been heated at 120 °C for 3 h before use, until the absorbance was less than 0.015. The toluene was used as received.

Interfacial Tension Measurements. All interfacial tension measurements were made by the spinning drop technique using a Model 500, spinning drop interfacial tensiometer (University of Texas). The solutions to be measured were allowed to stand

