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Amount and Orientation of π-Bonded Ethylene Formed at 95 K on K/Pt(111) Surfaces (and O/Pt(111) Surfaces): a TDS, UPS, XPS, and NEXAFS Study

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(Received: January 21, 1992; In Final Form: April 2, 1992)

The variation in amounts of loosely-bonded (usually called π-bonded) and di-σ-bonded ethylene species adsorbed onto Pt(111) at 95 K in the presence of potassium adatoms has been independently followed, using XPS and TDS, as a function of potassium coverage. The obtained results show that, in the neighborhood of potassium atoms, di-σ ethylene formation is inhibited as well as further reactions leading to ethylidyne formation and dehydrogenation. Di-σ bonding is replaced by a weaker bonding and reversible adsorption at about 130 K. The maximum amount of π-bonded ethylene occurs at a coverage where potassium adatoms interact and give a LEED superstructure. The π-bonded ethylene species formed on the Pt(111) surface at 95 K in the presence of potassium or oxygen adatoms has been investigated, using UPS, XPS, and NEXAFS. The interpretation of data has been made using symmetry considerations and selection rules. It indicates that in the presence of oxygen atoms the carbon–carbon double bond plane is parallel to the surface while potassium adatoms induce a strong rotation of this plane along the carbon–carbon axis.

Introduction

The knowledge of the bonding and chemistry of simple unsaturated chemisorbed hydrocarbons on transition metals is essential for the understanding of their hydrogenation, a key process in industrial catalysis. The adsorption and thermal decomposition of ethylene has been the subject of many experimental (refs. 1–3 and references therein) and theoretical studies.[4–6] Ethylene bonding to the metal atoms can be described by two types of interactions, a π-bonded state where ethylene retains sp^2 hybridization (with a carbon–carbon double bond) and a di-σ-bonded state, where the carbon atoms in ethylene, significantly rehybridize toward sp^3 (leading almost to a carbon–carbon single bond). Even on clean platinum, it has been only recently shown that the structure of the platinum surface[3] and other parameters can play a major part in the formation of the adsorbed state. On Pt(111), depending on the adsorption temperature[8,9] or coadsorption with alkali metals[2,8,10,11] or oxygen,[11,12] both types of states can exist. On clean Pt(111), quite clearly, conversion of the π-bonded species obtained below 52 K to the di-σ one requires a very low activation energy.[9] The role of alkali metals can be understood as an overpromotion,[8] preventing di-σ bonding, or/and through electrostatic models[13,14] which also explain molecular orbital shifts[15] with alkali coverage. Oxygen atoms also inhibit di-σ bond formation due to the charge withdrawal from the metal atoms.[1,8] The net effect of these coadsorbed species is to prevent dehydrogenation of adsorbed ethylene into ethylidyne which occurs above 250 K[1,2,8,9,12] and to lead to weaker adsorption modes, desorbing without reaction.

The relative amounts of π-bonded species (desorbing at about 130 K) and di-σ species (desorbing at about 280 K), in the presence of potassium atoms, have been previously determined using TDS[1,8] (temperature desorption spectroscopy) and the heights of the two high–lying molecular orbitals,[15] detected with UPS (ultraviolet photoelectron spectroscopy). A discrepancy was found for the maximum amount of π-bonded ethylene formed at 95 K, which could be explained by various reasons: the conversion of π-bonded ethylene into the di-σ species upon heating the sample, the lack of surface saturation with ethylene on the clean surface or at low K coverages in some TDS results,[1] or the usual UPS inadequacy to measure coverages from the intensity of molecular (and not atomic) orbitals.

Not much is known, as well, about the orientation and distortion of the π-bonded species formed in the presence of coadsorbates.

It was, however, suggested that the carbon–carbon axis was parallel to the surface, as seen by HREELS[8] (high–resolution electron energy loss spectroscopy) in the case of coadsorption with potassium atoms. But, if the CH_2 wag mode and the C–C stretch mode were found dipole active, it only proves that the carbon–carbon double bond plane cannot be perpendicular to the surface (as pointed out by one of our referees). UPS results (with photoelectron collection away from the surface normal) seemed to indicate the absence of distortion of low temperature π-bonded ethylene[2] and π-bonded species induced by Cs and K adatoms[2,11] and some distortion in the presence of coadsorbed oxygen atoms.[11] The spacings between molecular orbitals may vary with the collection angle, due to dispersion effects, as shown by Steinrück et al.,[16] making inadequate the method described by Felter et al.[17] (based on linear variations of the spacings between the orbitals with carbon–carbon distance and HCH, HCC angles) in order to determine distortions, with the exception of detection made at the normal. However, symmetry selection rules in conjunction with UPS have been used for π-bonded ethylene adsorbed at 95 K on Pd(111)[18] and below 52 K on Pt(111).[19] In both cases, the absence of $π'_{CH_2}(1b_{2g})$ orbital[20] at the normal and its presence at other detection angles have proved a C_{2v} symmetry which in conjunction with the spacings between the molecular orbitals indicated that the molecular plane was parallel to the surface.

If various methods like ARUPS with polarized or unpolarized light (and detection at the normal) and HREELS can give answers on the orientation and distortions of adsorbed species, NEXAFS[21–25] (near-edge X-ray absorption fine structure) also is a powerful technique. Changing the incidence angle of polarized synchrotron light varies the intensity of π* and σ* resonances and brings information on the orientation of the molecule with respect to the surface. Furthermore, despite some controversy,[26,27] the σ* resonance position can be used to characterize the carbon–carbon distance. However, even for di-σ ethylene, a relatively broad resonance exists in the π* region which may be attributed either to a remaining empty orbital[22] or to a $(C_2H_4\text{-Pt})^*$ resonance.[28]

The questions addressed in this paper are the following: (i) the determination of the amount of π- and σ-bonded ethylene with potassium coverage, after postsaturation of the surface with ethylene, using TDS and XPS (X-ray photoelectron spectroscopy); and (ii) the characterization, orientation, and distortion of π-bonded ethylene species formed in the presence of K and O atoms, using UPS with photoelectron detection at the normal and NEXAFS at various angles of the incident polarized synchrotron light.

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Experimental Section

The experiments have been performed, using several ultra-high-vacuum equipments.

In the first one (A), previously described,[11] line-of-sight mass spectrometry was used during TDS and simultaneous recording of mass 27 (ethylene) and 2 (hydrogen). The ionization chamber of the quadrupole mass spectrometer was surrounded by a small stainless steel cylinder with a 4-mm aperture. During TDS experiments, this aperture was accurately set at 1 mm from the front face of the platinum crystal. Rotating the sample in order to also monitor spurious desorption from the back face of the crystal and the leads reduces the signal by a factor higher than 20. Due to the small volume surrounding the ionization chamber and the pumping speed, the time constant (measured for CO desorption) was in the 0.05-s range. Analysis of UV photoelectrons (He I excitation) and measurements of work function variations were also available using a single-pass cylindrical mirror analyzer, as well as LEED and AES.

In the second one (B), a hemispherical VSW analyzer with preretarding lenses was used to detect UV (He I light) and X-rays (Al Kα line) photoelectrons, at the normal. A UV spectrum was recorded in 5 min while X-ray spectra were taken in 20 min. Despite the low signal to noise ratio, no longer times were used to prevent the surface from possible contamination. The base line was removed from the C_{1s} lines, using standard procedures,[29] and correction was made for sensitivity variations between experiments, using the base-line level at higher kinetic energies than the C_{1s} level.

Finally, the third one (C), included XPS, UPS, LEED, and NEXAFS. Two preparation chambers (for the cleaning procedure and dosing the surface with the alkali metal and ethylene) were attached to the analysis chamber. The experiments were carried out at the vacuum-UV Super ACO storage ring on the SACE-MOR beam line using a high-energy TGM monochromator (experimental resolution 0.2 eV at the carbon edge). NEXAFS spectra were collected in 15 min, using simultaneous partial secondary electron emission (measured with two channeltrons) from the sample and a clean reference gold grid. Photon energies were also calibrated using the features at 284.7 and 291 eV observed on the clean surface and the grid, due to moderate contamination of the beam line optics[30] which had been cleaned, prior to the experiments, with an oxygen plasma. In order to minimize further contamination of the line and analysis chamber, the various dosings were done in the preparation chambers, isolated from the analysis chamber through closure valves, and the sample was only transferred into the main chamber when the pressure was below 10^{-10} mbar. Let us call I_{cov}, I_{clean}, and I_g the signals measured from the covered surface, the clean surface, and the grid. The ratio $(I_{cov}/I_g)/(I_{clean}/I_g)$ removes variation in beam flux with time and leads to a signal proportional to the adsorbate features.[31] Removing the extra signal before the carbon edge, and normalization to unity at a photon energy equal to 320 eV, correspond to what we will call later the "normalized signals", when presenting the results.

In all cases, the platinum single crystal (Material Research), cut within 0.5° parallel to the (111) orientation, was mounted on cooled manipulators, the final temperature, 95 K, being available through leads connected to a cold "reservoir" filled with liquid nitrogen. After exposure to oxygen, ion sputtering, and annealing at 900 K, no impurities could be detected by AES and a sharp (1 × 1) LEED pattern was observed.

Potassium deposition rates from carefully outgassed SAES getter sources were initially calibrated through AES, work function variations (UPS), and completion of the monolayer at room temperature (the atomic ratio at saturation at 300 K is 0.44[32]).

Oxygen (Air Liquide, purity 99.95%) and ethylene (Messer Griesheim, purity 99.5%) were introduced through leak valves. When the surface is saturated with oxygen atoms at 300 K, the ratio of oxygen atoms to platinum ones is about 0.23.[12] After dosing K or O atoms, the platinum surface was exposed to ethylene at 95 K (5 langmuirs exposure). Saturation of the surface was controlled from the intensities of ethylene molecular orbitals, using
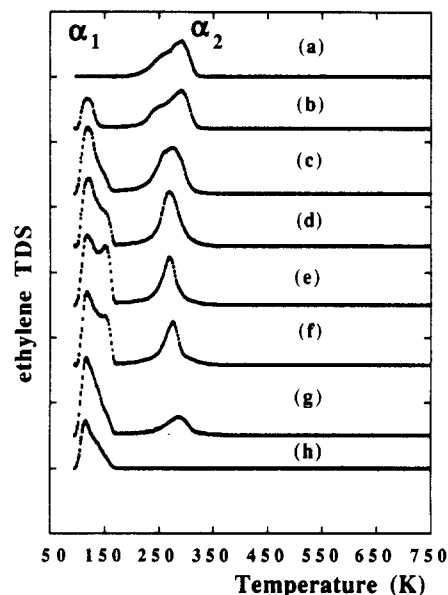

Figure 1. Desorption spectra of ethylene (27 amu) adsorbed on Pt(111) with various potassium coverages: (a) 0; (b) 0.05; (c) 0.09; (d) 0.11; (e) 0.13; (f) 0.15; (g) 0.17; (h) 0.23.
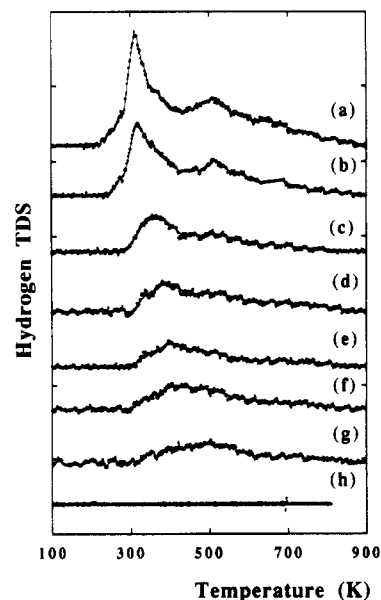

Figure 2. Desorption spectra of hydrogen (2 amu) from ethylene adsorbed on Pt(111) with various potassium coverages: (a) 0; (b) 0.05; (c) 0.09; (d) 0.11; (e) 0.13; (f) 0.15; (g) 0.17; (h) 0.23.

UPS. No attempt was made to calibrate the saturation coverage of ethylene on the clean surface, which according to the most recent result[33] seems to be 0.25.

All coverages will be given hereafter in monolayers (ML), defined as atomic ratios for K and O adatoms. They will refer to the saturation coverage for ethylene.

Results

TDS. The experiments, performed in apparatus A, were planned in order to determine the potassium coverage leading to maximum ethylene desorption at low temperatures (π-bonded species). Figures 1 and 2 show TDS spectra from ethylene adsorbed *at saturation* on the clean and potassium-covered Pt(111) surface, monitoring simultaneously mass 2 (hydrogen) and mass 27 (ethylene), respectively. These species are known to be the major desorption products, only 2% of the initial amount of ethylene being hydrogenated to form ethane.[8]

On the clean Pt(111) surface, in agreement with other authors[1,8] (who used 0.75 and 1.1 langmuir exposure, respectively), reversibly adsorbed ethylene leads to a C_2H_4 major desorption peak at 285 K (α_2, di-σ-bonded ethylene) with a shoulder at 260 K while
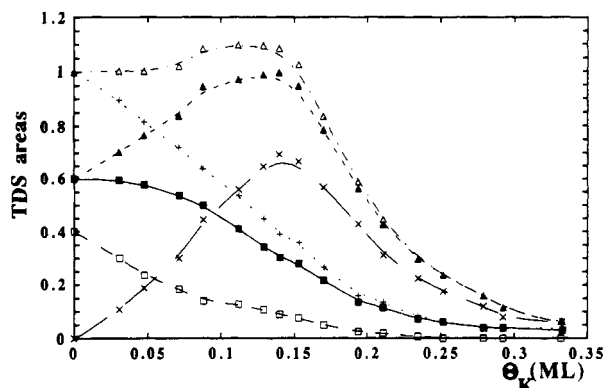
Figure 3. Desorbed amounts (integrated areas) versus potassium coverage, expressed in ethylene molecules: □, hydrogen; ■, α_2 ethylene; ×, α_1 ethylene; +, hydrogen and α_2 ethylene (di-σ-bonded ethylene); ▲, α_1- and α_2-bonded ethylene; △, total amount desorbed.
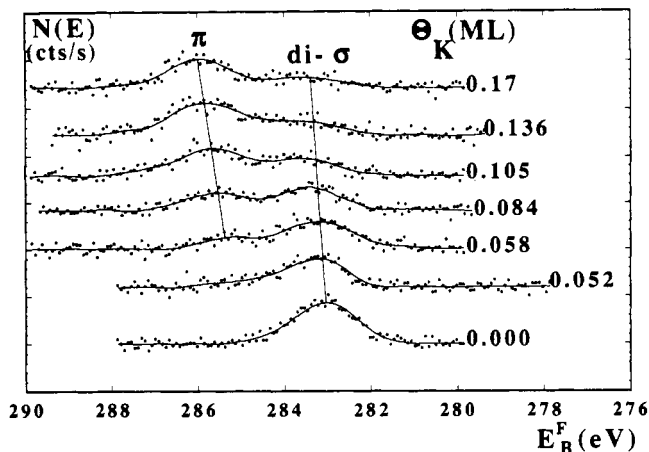

Figure 4. C_{1s} spectra of adsorbed ethylene at 95 K with ethylene coverage: (a) 0; (b) 0.052; (c) 0.058; (d) 0.084; (e) 0.105; (f) 0.136; (g) 0.17. The lines are just drawn to indicate a change in position with potassium coverage.
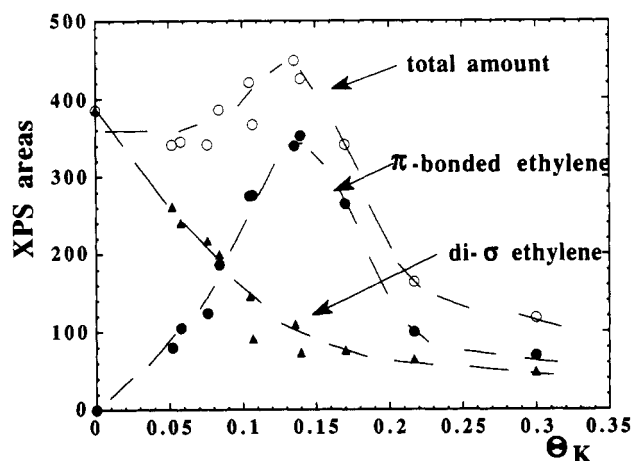

Figure 5. Adsorbed amounts vs potassium coverage (XPS results): ▲, di-σ ethylene; ●, π-bonded ethylene; ○, total amount.

hydrogen mainly desorbs at 310 and 510 K. The first hydrogen peak is due to decomposition of ethylene to form ethylidyne (CCH$_3$) while the second one is attributed to decomposition of ethylidyne to form various C_nH fragments.[1,8] Above 550 K, progressive complete dehydrogenation of the surface fragments to form polymeric carbon and graphite occurs.

On ethylene desorption, the notable effect of varying potassium coverages is the appearance of a new low-temperature peak (α_1, called also π-bonded ethylene in previous papers[9,15]) at 130 K. The population in the α_1 state increases with potassium coverage, maximizes between $\Theta_K = 0.13$ and 0.15 ML, and then decreases with larger potassium coverages. Almost no desorption signal related to ethylene is observed for coverages beyond 0.27 ML. The α_1 state population increase is accompanied by the decrease of the α_2 state (285 K) population with potassium coverage. Clearly, the effect of potassium coadsorption is to produce a new adsorbed state of ethylene (π-bonded ethylene) with a weaker adsorption energy. The conversion of di-σ-bonded ethylene into π-bonded ethylene is almost complete at $\Theta_K > 0.17$ ML. Potassium also dramatically affects dehydrogenation (and hydrogenation) of ethylene on Pt(111). The amount of ethylene that dehydrogenates (and which is related to the presence of the di-σ species) decreases continuously with increasing potassium coverage. Therefore, TDS shows that potassium inhibits the decomposition of irreversibly adsorbed ethylene on Pt(111), in agreement with previous authors.[1,8]

Using AES or nuclear techniques, several authors have measured the amount of ethylene desorbing from the clean surface, after adsorption at 100 K, compared to the amount converted into ethylidyne. Windham et al.[8] found 54% reversible adsorption, Berlowitz et al.[34] 62% and Mitchell et al.[33] 50%. Hydrogen desorbed amounts can therefore be converted into di-σ ethylene amounts, suffering chemical transformation, during the heating procedure. With such a calibration procedure, Figure 3 summarizes the quantitative results of the TDS data (after integrating the spectra), plotted as a function of potassium coverage. Also shown are the populations of α_1 (π-bonded ethylene) and α_2 (di-σ-bonded ethylene) desorption states, desorbed hydrogen amounts expressed in terms of ethylene molecules (1/2), the total amount of reversibly adsorbed ethylene ($\alpha_1 + \alpha_2$), and the total amounts of reversibly desorbed and adsorbed ethylene at 95 K, as a function of K coverage. The total amount of adsorbed ethylene at 95 K increases first slightly with potassium coverage, due to the formation of the α_1 state, and then decreases, while the amount of reversibly adsorbed ethylene passes through a more pronounced maximum, due to inhibition of dehydrogenation, in general agreement with previous authors.[1,8]

With controlled saturation of the surface with ethylene in our experiments, the maximum amount of desorbed π-bonded ethylene is found at a potassium coverage $\Theta_K = 0.14$ ML, in excellent agreement with other authors.[1,8]

XPS. The preceding results may be ambiguous, in the sense that desorbed and not adsorbed amounts are measured and some

conversion may occur during the heating procedure.

XPS (apparatus B) was applied to the ethylene/K system in order to check if π-bonded and di-σ ethylene adsorption modes could be distinguished, at 95 K, due to a C_{1s} "chemical shift". The reasons for this chemical shift which has been experimentally observed will be presented in the discussion.

Figure 4 shows the evolution of some C_{1s} spectra as a function of potassium coverage. Clearly, the appearance of the π-bonded species is characterized by a high binding energy line at about 285.6 eV, while di-σ ethylene initially exhibits a C_{1s} line at 283.1 eV. Their positions shift slightly upon varying K coverage. For a quantitative treatment, we have removed the base line and integrated the areas under the peaks, after having used a deconvolution program. Correction for sensitivity variations, using the base line level, at higher kinetic energies than the C_{1s} levels has been applied. The areas are then strictly proportional to the correct relative amount of the corresponding *adsorbed* ethylene species, *at 95 K* (the total core level ionization cross section is atom chemical environment nondependent).

Results are presented in Figure 5. They show, like the TDS ones, that the amount of di-σ ethylene continuously decreases, and meanwhile the amount of π-bonded ethylene reaches a maximum at about $\Theta_K = 0.14$ ML and then decreases. This result disagrees with our previous interpretation of UPS results[15] but is consistent with the preceding section.

UPS. The experiments were performed in apparatus B. The platinum sample, cooled down to 95 K, after the cleaning procedure, was dosed with variable amounts of potassium (known from the variations in work function[15]) or saturated with oxygen atoms at 300 K (atomic ratio = 0.23[12]) before saturation with ethylene at 95 K as checked by the leveling off of the molecular
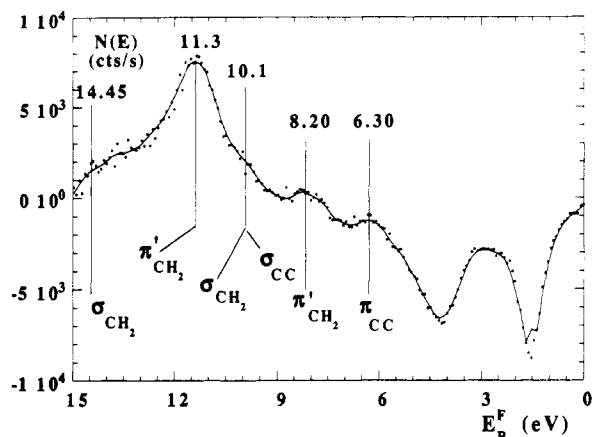
Figure 6. Difference UV spectrum of ethylene adsorbed on Pt(111) at a potassium coverage equal to 0.17. The molecular orbitals are labeled according to ref 20.
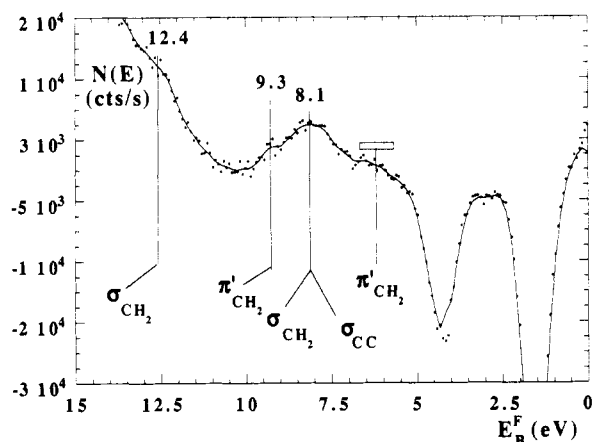

Figure 7. Difference UV spectrum of ethylene adsorbed on Pt(111) at an oxygen coverage equal to 0.23. The molecular orbitals are labeled according to ref 20. The region where π'_{CH_2} orbital is expected is drawn in the figure.

orbitals, detected at the normal, and work function variations (deducted from the low kinetic energy side of the curves).

At any potassium coverage, due to the better sensitivity to π-bonded ethylene compared to di-σ bonded ethylene,[12] the obtained UV spectra indicated the presence of all molecular orbitals of ethylene, and especially the π'_{CH_2} one.

Figure 6 shows a difference spectrum between the surface covered with ethylene and potassium and the surface covered with only potassium, at a potassium coverage corresponding to an atomic ratio of 0.17, at about the work function minimum.[15] In these conditions (see TDS results), a compromise is obtained between the maximum amount of π-bonded ethylene and almost no di-σ-bonded ethylene on the surface. The orbital labeling is made by comparison with our previous results,[12] taken at 43°, despite some differences in spacings and positions which may be due to dispersion effects.[16]

With coadsorbed oxygen atoms which also induce π-bonded ethylene[11,12] formation, the amount of coadsorbed π-bonded ethylene is smaller than in the case of coadsorbed potassium (or cesium) atoms, decreasing the signal-to-noise ratio. However, Figure 7 (where orbitals have been labeled according to ref 20) now indicates the possible absence of the π'_{CH_2} orbital, when detection is made at the normal.

NEXAFS. Due to the small size of the platinum sample (6 mm), angular variations of the NEXAFS signal (apparatus C) have been recorded at a maximum incident light angle with the sample normal equal to 50° or 65°.

The orientation of di-σ-bonded ethylene was first checked, by comparison with results of Stöhr et al.,[21,22] after saturation of the sample with ethylene, at 95 K. Figure 8 shows spectra taken at three incidence angles. The positions of the various resonances
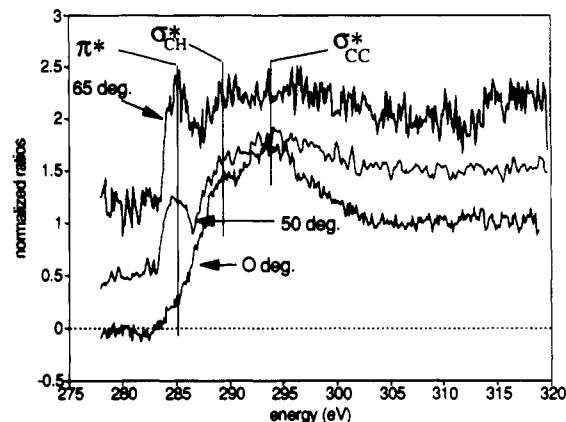

Figure 8. NEXAFS spectra of di-σ-bonded ethylene with incident angle of the synchrotron light (0° = normal incident light). The various resonances are indicated in the figure. All spectra are normalized to unity at an energy equal to 320 eV.

Figure 9. NEXAFS spectra of π-bonded ethylene (at a potassium coverage = 0.14) with incident angle of the synchrotron light (0° = normal incident light). The various resonances are indicated in the figure. All spectra are normalized to unity at an energy equal to 320 eV.
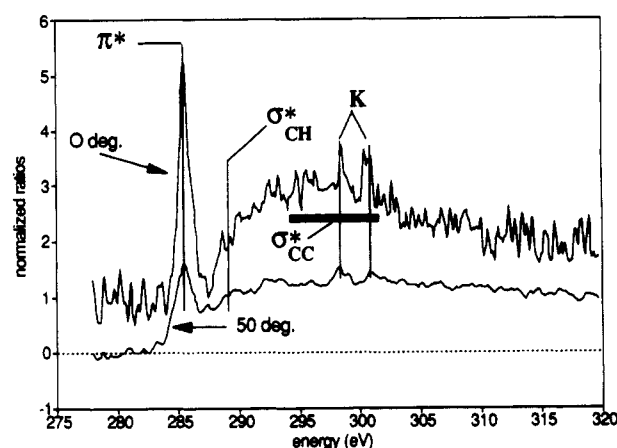
have been indicated. The π^* resonance is absent when the light is normal to the sample (and the electric vector parallel to the surface). Its intensity increases with the angle while the σ^*_{CC} resonance intensity decreases. No noticeable changes are seen in the σ^*_{CH} resonance region. These intensity variations are consistent with a carbon–carbon axis parallel to the surface.[21,22] Moreover, the σ^*_{CC} resonance location is characteristic of a carbon–carbon single bond[9,22] and confirms the di-σ-bonded nature of ethylene adsorbed on clean Pt(111) at 95 K.

In the presence of K adatoms, at a coverage Θ_K where the main adsorbed species is π-bonded ethylene, Figure 9 shows a completely different behavior of the resonances with incidence angle. Both π^* and σ^*_{CC} resonances are intense at normal incidence and weaker at 50°. Moreover, the π^* resonance is narrower than in the previous case. Despite some difficulties in removing the K_{2p} levels of potassium (while normalizing the results), it can be seen that the σ^* resonance is broad and centered at an energy compatible with a carbon–carbon double bond.[9]

Finally, Figure 10 presents the results for π-bonded ethylene, in the presence of oxygen atoms. The only significant result (due to the small amount of adsorbed ethylene and a low signal-to-noise ratio) is the absence of π^* orbital, with the incident light normal to the surface and its increase, off-normal.

Discussion

TDS and XPS Results. The integrated TDS curves shown in Figure 3 compare well with the results of Zhou et al. (see Figure 2 in ref 1). We have found like these authors a smooth decrease of the amount of decomposed ethylene with potassium coverage
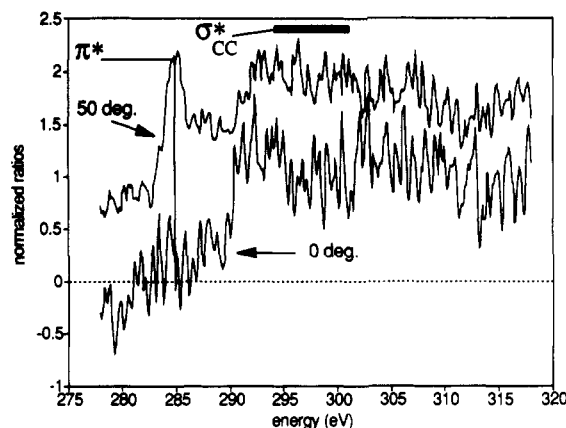
Figure 10. NEXAFS spectra of π-bonded ethylene (at an oxygen coverage = 0.23) with incident angle of the synchrotron light (0° = normal incident light). The region where various resonances are expected are indicated in the figure. All spectra are normalized to unity at an energy equal to 320 eV.

(and a similar behavior was exhibited by $C_2H_4/Cs/Pt(111)$[2] system) while Windham et al.[35] found a fast decrease at low coverages (till an atomic ratio equal to 0.03), followed by a "plateau". We have no explanation for this discrepancy.

The potassium coverage at which the π-bonded species (α_1) (and the total amount of adsorbed ethylene molecules) passes through a maximum is comparable in Figure 3 (desorption results) and Figure 5 (XPS results), namely at $\Theta_K \approx 0.14$. This coverage agrees well with the other results of literature.[1,8] It cannot be reconciled with our previous value,[15] obtained using UPS and the heights of the two high-lying molecular orbitals, and it indicates that valence level photoemission cannot be used as a quantitative method to derive coverages. The general agreement now found shows that ethylene exposures used by other authors, even if they were too low to saturate the clean surface with ethylene,[1] were high enough in the presence of potassium atoms to do so. On clean Pt(111), at the potassium coverage leading to the maximum amount of π-bonded ethylene, the first potassium LEED pattern[32] $((\sqrt{7} \times \sqrt{7})R19°)$ appears and a net interaction of the potassium adatoms exists. Consistently, above this coverage the number of adsorbed ethylene molecules decreases.

The total amount of ethylene at maximum is about 110% in Figure 3 (in agreement with ref 8) and Figure 5, when normalized to the coverage of di-σ-bonded ethylene on the clean surface (0.25). At the corresponding potassium coverage (0.14), we have on the surface two ethylene molecules per potassium atom.

We have observed (and used) a strong C_{1s} core level shift between π-bonded ethylene formed in the presence of potassium atoms and di-σ-bonded ethylene on the clean surface. Such a shift also exists between the low-temperature π-bonded species[9] and di-σ ethylene[36] (see also Figure 4 in this paper). The binding energies are then 284.4 and 283.1 eV, respectively. These values are reported in Figure 11 which also shows variations in positions of both ethylene species, with potassium coverage.

The general mechanism proposed for the generation of satellite structures for adsorbate core levels has been proposed by Schönhammer and Gunnarson.[37,38] In essence, the formation of a core hole in an adsorbate with an empty molecular orbital just above the Fermi level pulls this orbital well below E_F. When this orbital remains empty, the final state is unscreened. However, occupation by metal valence electron (a shake-down process) can decrease its binding energy and a "screened final state" is obtained. The existence of strong satellite structures has been experimentally observed and interpreted later within this model for instance by Umbach.[39] The model calculations[37,38] indicate that, for a weak coupling between the substrate and empty molecular orbital from the adsorbate, the unscreened final state should dominate while, for a strong coupling, it is the screened final state which dominates. This model is consistent with the experimental C_{1s} shift observed on the clean surface (1.3 eV) between the two species formed below and above 52 K.
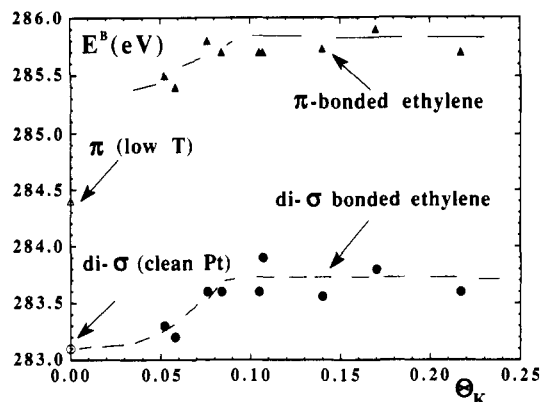

Figure 11. Positions of C_{1s} for di-σ- and π-bonded ethylene vs potassium coverage. The lines are drawn to guide the eye. At zero potassium coverage are indicated the C_{1s} positions of ethylene adsorbed on clean Pt(111) below 52 K and at 95 K.

However, not only does a stronger shift occur in the presence of potassium atoms, but it also depends on potassium coverage (see Figure 11). This is reminiscent of the behavior of the molecular levels of π-bonded ethylene upon increasing K coverage.[15] These levels were seen to shift toward higher binding energies up to $\Theta_K \approx 0.14$. The shifts were ≈1 eV for Θ_K increasing from 0.06 to 0.14 and 2 to 2.4 eV between zero coverage (<52 K adsorption on bare Pt(111)) and $\Theta_K \approx 0.14$. Under the same conditions, the C_{1s} core-level shift amounts to 0.4 and 1.3 eV, respectively (Figure 11). The core-level and molecular-level shifts attached to the C_2H_4 π-bonded species thus show the same trend upon increasing potassium coverage. In the vicinity of K atoms, the local work function is lowered. As in PAX[40] (photoemission of adsorbed xenon), a shift toward higher binding energies may occur for weakly bonded species, even for core levels.[41] The local work function is potassium coverage dependent and a continuous shift is observed. This is consistent with the description of the adsorption of π-bonded ethylene by an electrostatic model.[15] However, shift amplitudes are clearly lower for the core level than for molecular levels. It indicates that shifts cannot only be explained by changes in surface potential but must take into account screening effects.

The XPS results are therefore consistent with both final state (σ-bonded to π-bonded ethylene conversion) and initial effects (potassium coverage, noting particularly in this case that shifts have a more complex origin).

UPS Results. Let us recall some selection rules[42] which have been previously used[19] in order to show that π-bonded ethylene, adsorbed below 52 K, was flat and parallel to the surface, during completion of the first layer.

The gas-phase ethylene molecule belongs to point group D_{2h}. Adsorbing it on a platinum dense face as a π-bonded complex may result in a symmetry reduction to C_{2v} group (carbon–carbon double-bond plane parallel to the surface) or lower. In the C_{2v} group (where the molecule is not automatically plane), the π'_{CH_2} molecular orbital belongs to a_2 representation.

During a photoemission experiment, information on the initial state can be obtained by placing symmetry constraints on the final state. In the C_{2v} group, for normal emission, i.e., along the z axis chosen as surface normal, the final-state wave function must belong to the totally symmetric representation a_1 of the group and transitions are allowed only when the symmetries of the electric field vector and of the initial state are the same. For unpolarized light, the projections of the electric field vector along x (C–C bond), y, and z axes (perpendicular to the molecular plane) belong to b_1, b_2, and a_1 representations, respectively. The initial states of a_2 symmetry gives b_2, b_1, and a_2 final states which are not allowed along the z axis. In the C_{2v} C_2H_4 molecule, there is one (and only one) orbital of a_2 symmetry, i.e., π'_{CH_2}. It therefore gives no emission at the surface normal. Off-normal, however, the symmetry constraints on the final state are less severe and the a_2 final state originating from the z-component of the electric field is now allowed. With unpolarized light, further symmetry

lowering allows emission from all orbitals in all directions, including the normal direction. For instance, the C_2 situation (with a totally symmetric a orbital replacing a_2) would correspond to a twist about the C–C bond while the two possible C_s configurations would correspond to a plane of the ethylene molecule no longer parallel to the surface.

From these selection rules, it is obvious that the only configuration of ethylene which has no normal emission of the π'_{CH_2} orbital (using unpolarized He I light) is that where the carbon–carbon double-bond plane is parallel to the surface and the molecule belongs to the C_{2v} group. It explains why we have chosen this experimental setup to try to obtain some informations on the π-bonded species formed in the presence of potassium atoms or oxygen atoms.

Going back to the experimental results, it is obvious that the presence of the π'_{CH_2} orbital in Figure 6 indicates that π-bonded ethylene formation induced in the neighborhood of potassium atoms does not lead to a molecule belonging to the C_{2v} group. However, a comparison can be made with the orbital spacings observed in the gas phase.[43,44] Differences are negligible, indicating no distortion, compared to the plane gas-phase molecule. Therefore, π-bonded ethylene is *plane*. Compared to previous results[15] taken with a CMA at the same potassium coverage and about 43° detection angle, all orbitals are shifted toward lower binding energies. This result is consistent with possible dispersion effects.[16]

The spectrum of π-bonded ethylene in the presence of oxygen adatoms is clearly different. In the region where the π'_{CH_2} orbital is expected, no significant signal is observed, while it was clearly seen off-normal.[11] Again, all orbitals detected at the normal are shifted to lower binding energies, when compared to the 43° detection angle. However, the spacing between the two low-lying orbitals (σ_{CH_2} and π'_{CH_2}) is smaller than in the gas phase. Attempts to derive carbon–carbon distance and the HCC and HCH angles, using the method of Felter and Weinberg[17] (based on linear variations of spacings with various distortions), lead to inconsistent results (a sum of angles higher than 360°, and a carbon–carbon distance shorter than in the gas-phase molecule). There is therefore no clear answer from this method concerning possible distortions of this species from the UPS results alone. They, however, favor a C_{2v} configuration with the carbon–carbon double bond plane parallel to the surface but do not fully support a plane configuration (possible distortions).

NEXAFS Results. There is a striking difference between the angular variations of the π^* and σ^* resonances in Figures 8 and 9. Especially, at normal incidence of the synchrotron light, π^* resonance is absent for di-σ ethylene and intense for π-bonded ethylene coadsorbed with potassium atoms. The shape of the σ^* resonance is broader in Figure 9 than in Figure 8 and its position is shifted toward higher energies. But, just as for the σ^* resonance in Figure 8, its intensity decreases strongly with increasing angles of incidence. It therefore strongly suggest that the C–C axis is parallel to the surface. Moreover, the σ^* and the π^* resonances must have a surface in-plane component.

The width of the π^* resonance may be considered as indicative of the bonding strength to the surface. Indeed, the existence of a π^* resonance for the di-σ species is explained either by a remaining double bond character[22] or by the existence of a $(C_2H_4\text{–Pt})^*$ resonance.[28] It is equal to 3.4 eV in Figure 8 and to 1.8 eV in Figure 9, far above the instrumental resolution at the carbon edge (0.2 eV). The latter value compares well with the width obtained below 52 K for ethylene monolayer and multilayers.[9] We must therefore conclude, in agreement with UPS results, that the π-bonded ethylene adsorbed molecule formed in the presence of potassium atoms is not distorted, compared to the gas-phase molecule, and is *plane*.

As a consequence, NEXAFS results are interpreted as a rotation of the plane ethylene molecule with the carbon–carbon axis parallel to the surface (C_s configuration). The platinum crystal size did not allow experiments at more grazing incidence from which the angle of rotation could have been determined. But the fact that, clearly, the molecular plane is strongly rotated at all potassium

coverages and that the π^* resonance width is comparable to the low-temperature results[9] means that no strong interaction between the π orbital and the metal d band or the potassium orbitals exists as also shown by the desorption temperature (130 K).

Figure 10 indicates from the π^* resonance width (2.2 eV) that π-bonded ethylene coadsorbed with oxygen atoms is more strongly bonded to the surface than the species induced by potassium atoms. This result agrees with TDS results[11,12] (desorption at 130 and 190 K, respectively). The π^* resonance is absent at the normal and its intensity increases with the incidence angle. Due to the low signal-to-noise ratio, nothing specific can be seen in the σ^* resonance region. However, it is clear from Figure 10 that the carbon–carbon axis is parallel to the surface. With the UPS results (absence of the π'_{CH_2} orbital at the normal), the experimental results are consistent with an ethylene molecule in the C_{2v} configuration.

The relative bonding strength of π-bonded ethylene to Pt(111) in the presence of oxygen or potassium atoms is now understandable from geometrical considerations. With the C–C double bond plane parallel to the surfce, the overlap of the π orbital with the d band of the metal is strong. Contrary to this situation, it is smaller when the molecular plane is rotated, due to the electrostatic potential existing in the vicinity of potassium atoms.

Conclusions

TDS and XPS have allowed us to compare the amount of ethylene molecules in various forms, adsorbed on Pt(111) and desorbed from the same surface, in the presence of potassium atoms and versus coverage. There is a general agreement between these two types of experiments and particularly on the coverage at which the maximum amount of π-bonded ethylene molecules occurs. This coverage is such that potassium atoms interact on the clean surface, leading to the first LEED pattern. We have explained the C_{1s} shift between di-σ-bonded species and π-bonded species through a model involving final- and initial-state effects.

Comparison of UPS results and NEXAFS results has led us to propose for π-bonded ethylene formed in the presence of potassium atoms a plane structure, rotated along the carbon–carbon axis with respect to the surface, minimizing the interaction with the surface. In the presence of oxygen atoms, a more strongly π-bonded ethylene molecule is obtained which has a C_{2v} symmetry.

In all cases, results are consistent with the carbon–carbon axis parallel to the surface.

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Nonionic Bilayers in Dilute Solutions: Effect of Additives

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(Received: February 18, 1992)

We have investigated the effect of alcohols and other additives on the binary phase diagram water–$C_{12}E_5$. In particular, we have located the dilute lamellar L_α phase and the L_3 phase as function of additive concentration on the temperature scale. In the L_α phase undulations stabilize bilayer membranes at distances on the order of hundred nanometers. We have determined their repeat distance quantitatively by light scattering. By addition of medium-chain alcohols, the projected area of the undulating membranes was found to increase drastically. We quantitatively determined the fraction of alcohol molecules dissolved in the membranes by ^2H NMR using deuterated alcohols. The longer the hydrocarbon chain of the alcohols, the stronger the partitioning of the alcohols into the membranes. From our experiments we conclude that the bilayers act as a two-dimensional phase into which the medium-chain alcohols preferentially dissolve, apparently because of the favorable polarity gradient of the films. This latter conclusion arises from the surfactant-like order parameter profile observed by ^2H NMR for the alcohols. The effect of adding salt, increasing the hydrocarbon chain length of either surfactant or alcohol, as well as reducing the number of ethylene oxide units of the surfactant is, in each case, to render the bilayers more hydrophobic. We discuss the effects in terms of the geometric properties of the molecules and bending properties of the membranes.

I. Introduction

The physics of amphiphilic layers leads to a rich variety of amphiphilic structures in dilute solutions.[1] Perhaps the most striking observation is the ubiquitous appearance of a dilute lamellar L_α phase that can be diluted down to amphiphile concentrations on the order of 1 wt %. Thus, the spacing of the stacked bilayers amounts to hundreds of nanometers, and a long-range repulsive interaction has to be operative. In general one finds in coexistence with the anisotropic L_α phase the isotropic L_3 phase in which the bilayers form a randomly connected network. These phases are found with anionic,[2] cationic,[3] zwitterionic,[4] and nonionic surfactants.[5] Prerequisite for the formation of a dilute lamellar phase in ionic systems are a high salt concentration and the addition of a medium-chain alcohol.[2,3] The salt is added to screen the long-range electrostatic interactions, while the role of the alcohol is to reduce rigidity of the film leading to undulations. Thus, the lamellar phase is sterically stabilized while the electrical charges are screened. The stabilizing mechanism by the undulation force has been suggested by Helfrich.[6] Theoretically, one expects that, depending on the undulation spectrum and amplitudes, the total effective area should be reduced compared to a flat bilayer due to crumpling.[6,7] The strength of the interaction and degree of crumpling should thus depend on

the rigidity of the bilayers. Unfortunately, alcohol and salt are needed as ingredients in forming the lamellar phase, and their effects cannot be studied independently without destroying the structure. It would be desirable to start with a system containing only water and uncharged bilayers that does not require alcohol and salt as formulation ingredients. A binary system water–nonionic surfactant would serve this purpose. In a recent paper[5] we were able to show that indeed the binary system water–$C_{12}E_5$ shows a stable dilute lamellar phase down to 1 wt % of surfactant. Experimentally, we observed that the undulations of the bilayers apparently consumed a substantial amount of up to 30% of total bilayer area, confirming the theoretical presumptions. In performing these experiments, we utilized the characteristic brilliant color spectrum that these systems display upon illumination with white light.

In this paper we describe experiments to further study the undulation concept and report some interesting new observations. The basic idea was to add medium-chain alcohols expecting to increase the flexibility of the membranes. As mentioned above this should increase the undulations and, accordingly, further reduce the total projected area. Such a reduction would be observable as a shift of the wavelength of the scattered light toward larger wavelength. But we were surprised to learn by experiment that the opposite was the case. A strong blue-shift is observed.

In a recent paper on the effect of medium-chain alcohols on the phase behavior of microemulsions, Kahlweit et al.[8] concluded

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