

The Adsorption and Decomposition of C₂H₄ on Ru(001): A Combined TPR and Work Function Change Study[†]

T. Livneh*[‡] and M. Asscher

Department of Physical Chemistry and The Farkas Center for Light Induced Processes,
The Hebrew University, Jerusalem 91904, Israel

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Work function change ($\Delta\Phi$) measurements during adsorption and surface heating in a $\Delta\Phi$ -temperature programmed reaction (TPR) mode combined with TPD are demonstrated to provide new information on the interaction and chemistry of ethylene on Ru(001). Rearrangement of second layer ethylene molecules has been observed between 82 and 120 K. This is a competing process with molecular desorption, interpreted as a result of migration of second layer molecules toward the surface. Our results are consistent with and support previous studies that suggested the formation of a surface intermediate ($\eta^2(\text{C,C})\text{CHCH}_2$) during ethylene dehydrogenation to ethylidene. Employing a derivative mode with respect to temperature $-\text{d}(\Delta\Phi)/\text{d}T$, we find an early onset for ethylidene decomposition near 265 K. $\Delta\Phi$ -TPR measurements in the range 560–720 K reveal three distinct CH decomposition peaks, reflecting different activation energies for the decomposition reaction sites. The dipole moment of an adsorbed CH has been determined to be $\mu = 0.43$ D, suggesting a rather polarized Ru-CH complex; its structure is independent of the adsorption site. Finally, carbide polymerization to form graphite has been detected above $T_s = 560$ K for the first time using work function change measurements. Good agreement was found between the contribution to $\Delta\Phi$ by the graphite layer formed on the Ru(001) surface and ab initio calculations performed previously on this system.

1. Introduction

The interaction of hydrocarbons with transition metal surfaces was the subject of extensive studies^{1,2} to understand the role of these adlayers in catalytic reactions. Despite the numerous surface sensitive techniques used to study the C₂H₄/Ru(001) system,^{3–10} the reaction pathways and assignment of surface intermediates are not yet fully understood. In addition to the “standard” techniques, these open questions can be addressed by employing work function change measurements during adsorption and surface heating ($\Delta\Phi$ -TPD and $\Delta\Phi$ -TPR modes). Structural rearrangements were observed prior to and during desorption in the case of nonreactive systems ($\Delta\Phi$ -TPD)¹¹ and decomposition of intermediates in reactive systems ($\Delta\Phi$ -TPR).^{12,13}

It is known that ethylene rehybridized to a di- σ bonded structure upon adsorption on the Ru (001) surface at 80 K.⁴ At a coverage of $\theta = \text{C}_2\text{H}_4/\text{Ru} (001) = 0.30$ (defined as 1 ML), 80% of the di- σ -bonded ethylene dissociates within the range 150–280 K. The other (20%) desorbs molecularly up to 250 K.⁴ Although it is agreed that at higher temperatures ethylene (C₂H₄) irreversibly converts to ethylidene (CCH₃), the actual conversion pathway remained controversial. According to Hills et al.⁴ ethylidene is directly produced from di- σ -bonded ethylene but not as a sole product; simultaneously the production of acetylide (CCH) takes place as a competing channel with a probability of 0.3 (compared with 0.5 for the ethylidene route). A different CCH₃ dissociation scheme was suggested by Henderson et al.⁶ These authors proposed that di- σ -bonded ethylene converts exclusively to ethylidene through an inter-

mediate, which was postulated to be $\eta^2(\text{C,C})\text{CHCH}_2$ (η -intermediate). Both schemes were based on temperature programmed reaction (TPR) and high-resolution electron energy loss spectroscopy (HREELS) studies. In the later,⁶ temperature programmed static secondary ion mass spectrometry (TPSSIMS) data defined accurately the temperature range in which the intermediates are stable on the surface during the reactions. At temperatures higher than 460 K the surface is covered by a carbon adlayer, probably carbide, and methylidene (CH) which further decomposes in a series of three distinct peaks between 450 and 720 K.

Based on early HREELS studies performed on a similar system {CH/Ni (111)}¹⁴, Barteau et al.³ have suggested that the three distinct decomposition peak temperatures of CH on Ru(001) arise from different hybridization states of the carbon atom within the CH species (sp^2 and sp), leading to different adsorption geometry.³

One of the main objectives of the studies discussed above has been the attempt to understand the role of carbidic carbon in the Fischer-Tropsch process.¹⁵ The identity of the carbon species is a key issue in understanding the reactivity pattern of the carbon adlayer on metal surfaces. Unlike carbide, the graphite phase is inert toward hydrogenation.¹⁵ Employing SIMS, Lauderback et al.⁹ reported that around 600 K the carbon transforms into a denser phase, suggested earlier to be graphite based on Auger studies.¹⁶ In a separate XPS study, this phase was reported as disordered at 750 K and therefore cannot be of graphitic nature.¹⁰ An STM study, on the other hand, suggested that only around 800 K did the disordered carbonaceous particles transform to graphite.¹⁷ The graphitic species were reported to grow initially as discrete 2D islands 10–15 Å in diameter. The hexagonal graphitic superstructure becomes continuous as the

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[‡] Present address: Department of Physical Chemistry, NRCN (Nuclear Research Center, Negev), P.O.B 9001 Beer-Sheva 84190, Israel

temperature is raised and only around 1300 K were extended graphitic monolayers observed.

Work function was proposed earlier to contain information on the state of adsorbed carbon on metallic surfaces. *Ab initio* calculations have indicated that full carbon monolayer (C/Ru(001) = 1) should lead to an increase of 0.6 V at the carbidic phase but a decrease of 1.2 V at the graphitic phase.^{18,19} These predictions were given relative to the clean ruthenium metal surface. The nature of the graphitic phase and its interaction with the Ru(001) surface at 873 K was studied also by angle resolved UV photoemission spectroscopy (ARUPS).¹⁹ The surface work function was found in these studies to decrease by 0.9 V, and the electronic structure correlated well with the *ab initio* predictions. The higher catalytic reactivity of the carbidic vs graphitic phase was attributed to the unsaturated C(2p_z) orbitals near the Fermi level, pulled down by 7 eV in the graphitic overlayer.

The purpose of the work presented here is two-fold: Correlate the work function change measurements taken during surface heating ($\Delta\Phi$ -TPD and $\Delta\Phi$ -TPR) with the "normal" (Δp -TPD) measurements. This way one can compare a method that detects directly the properties of the adsorbed species ($\Delta\Phi$), with a technique that probes the surface species indirectly by monitoring the desorption of molecular ethylene or its decomposition product (hydrogen). The second goal is to combine our results with previous data (mainly HREELS and TPSSIMS) on the same system, while attempting to correlate them with the fragmentation schemes of ethylene suggested in the above studies.³⁻¹⁰

2. Experimental Section

The experiments described here were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of $2-3 \times 10^{-10}$ Torr, obtained by a turbomolecular pump (240 L/s). Ar⁺ ions at 600 V were used to sputter-clean the Ru(001) surface (typical sample current of 8 μ A). A computer-controlled ac-resistive heating routine could control the sample heating rate or stabilize its temperature (± 0.5 K). At the same time signal is collected from either a quadrupole mass spectrometer (VG - MASSTORR) (QMS), to obtain normal TPD spectra (Δp -TPD), or from a Kelvin probe (Besocke type-S) controller, to obtain $\Delta\Phi$ -TPD spectra. The QMS was surrounded by a Pyrex shroud with a 4 mm aperture to prevent contributions to the Δp -TPD from surfaces other than the sample.

The Ru(001) sample (a square piece, 8 \times 8 mm, 1 mm thick) was cut from a single-crystal rod to within $\pm 1^\circ$ of the (001) crystallographic orientation, and was polished by standard metallurgical methods. Sample cleaning in UHV followed standard procedures as described elsewhere.^{3,4,12} The surface was sputter-cleaned prior to each experiment in order to remove carbon impurities. Surface cleanliness was checked by measuring the CO and O₂ thermal desorption profiles following the oxygen cleaning procedure. LEED from the clean and annealed surface showed very sharp hexagonal patterns. The sample was spot welded between two 0.5 mm diameter tantalum wires and was attached to a liquid nitrogen reservoir, via copper feed-throughs, directly welded to the bottom of the Dewar. The temperature was monitored by a W5%Re-W26%Re thermocouple spot welded to the edge of the ruthenium sample.

High purity (99.5%) C₂H₄ (Matheson) was used without further purification. Exposure was done by filling the chamber through a leak valve while the integrated ion gauge signal (exposure) is recorded directly in Langmuir units (1 L = 10⁻⁶ Torr·s).

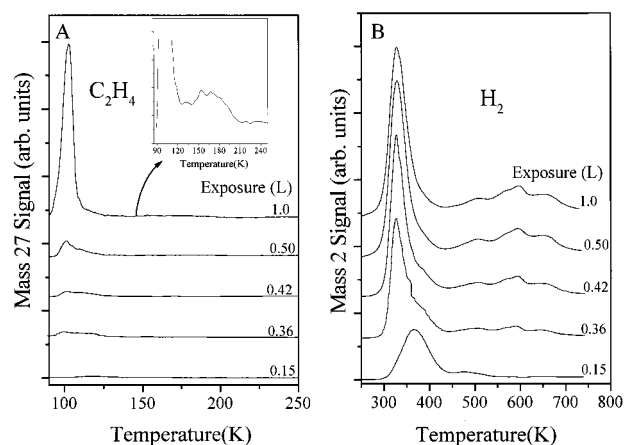


Figure 1. Δp -TPD spectra of (A) C₂H₄ and (B) H₂ from Ru(001), at the indicated exposures. In the inset of A the ethylene desorption in the 82–200 K range is expanded to clarify the details.

3. Results

3.1. Δp -TPD. Ethylene was shown to remain intact, nondissociated, upon adsorption at 80 K with initial sticking probability close to unity.⁴ Up to ethylene exposures of 1 L, corresponding to the completion of the first monolayer, ethylene sticking probability is coverage independent.^{4,5} During the sample temperature ramp from 80 K, ethylene molecules either desorb or decompose. The ultimate decomposition products obtained after heating to 1200 K are hydrogen and a graphitic layer. In Figure 1 Δp -TPD of ethylene (A) and hydrogen (B) are shown for the indicated exposures. Exposures of less than 0.5 L result almost exclusively in hydrogen desorption upon surface heating due to dehydrogenation with minor ethylene molecular desorption. Above 0.5 L the molecular desorption is faster with a wide ethylene Δp -TPD peak between 120 and 205 K (inset of Figure 1A). It is attributed to the desorption of a di- σ -bonded ethylene.⁴ Concurrently, a new peak centered at 103 K emerges before the completion of the first layer. This peak has been attributed to "multilayer" ethylene desorption, which actually corresponds to desorption from the second layer,⁴ and will be discussed as such here as well.

Most of the hydrogen desorbs within a peak centered at 325 K, displaying a small high temperature shoulder above 350 K. This peak is followed by a broad tail that consists of three distinct peaks at 505, 590, and 650 K. The major peak has been attributed to ethylidene (CCH₃) decomposition, while the shoulder above 350 K is due to hydrogen, which has been accumulated on the surface at lower temperatures.⁴ The three peaks at high temperatures, which consist of 25% of the total H₂ Δp -TPD signal, were attributed to CH fragmentation.^{3,4,6,20}

The total Δp -TPD hydrogen signal which follows 0.5 L ethylene exposure originates from dehydrogenation of the equivalent coverage of $\theta = \text{C}_2\text{H}_4/\text{Ru}(001) = 0.24$ ML. This coverage estimate is obtained by dosing the clean surface with saturation hydrogen coverage known to be $\text{H}/\text{Ru}(001) = 1$,²¹ then comparing it to the H₂ signal from ethylene decomposition, after subtracting the contribution to the signal from molecules at the UHV background. At this exposure the adsorbed ethylene almost completely dissociates upon heating to 720 K, producing hydrogen and surface carbon. Exposure beyond 0.5 L results in a gradual increase of signal due to intact molecular ethylene desorption. From our exposure-coverage correlation we conclude that the first molecular layer is filled up following 1.0 L exposure. The density of the first layer is estimated to be $\theta = \text{C}_2\text{H}_4/\text{Ru}(001) = 0.32$ ML. This number is obtained by adding

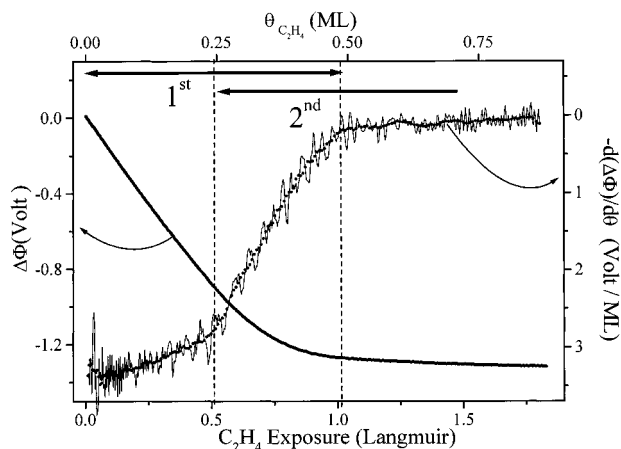


Figure 2. Work function change measurement during C₂H₄/Ru(001) adsorption at 82 K. The exposure (lower abscissa) is translated to ethylene coverage, θ , (upper abscissa) in ML units. In the right mantissa, the work function change derivative with respect to coverage ($-d(\Delta\Phi)/d\theta$) is plotted vs coverage.

the total TPD signals of the di- σ -bonded C₂H₄ molecules and the dissociated fraction via H₂ TPD. It is in good agreement with the conclusions of Hills et al.,⁴ who found that the first layer consists of C₂H₄/Ru = 0.30. This exposure–coverage relation implies that in the exposure range between 0.5–1.0 L, both first and second layers are populated simultaneously, assuming unity sticking probability as discussed above.⁴ This is indicated by the growing molecular TPD at 103 K.

3.2. $\Delta\Phi$ Measurements Taken during Ethylene Adsorption at 82 K. In Figure 2 the work function change during the exposure of ethylene on Ru(001) held at 82 K is shown based on the ethylene exposure–coverage calibration discussed above. In the right mantissa, the derivative of the work function change with respect to coverage ($-d(\Delta\Phi)/d\theta$) is plotted vs coverage. Three different regimes are clearly distinguished: Up to exposure of 0.5 L, $\Delta\Phi$ decreases by 0.92 V and $-d(\Delta\Phi)/d\theta$ decreases from 3.4 to 2.8 V/ML. At this coverage regime most of the first ethylene layer is populated, while forming a di- σ bond with the surface.^{3–8} The decrease in $\Delta\Phi$ suggests that charge is transferred to the surface upon cleavage of the ethylene π bond. Assuming that at 82 K the surface mobility of ethylene is fast enough to form a homogeneously distributed di- σ bonded ethylene layer, the decrease in $-d(\Delta\Phi)/d\theta$ can be attributed to an enhanced depolarization effect between neighbor adsorbates as coverage increases. Between 0.5 and 1.0 L a second regime is observed with pronounced decrease in $-d(\Delta\Phi)/d\theta$ from 2.8 V/ML at 0.5 L to 0.2 V/ML at 1.0 L. This exposure range correlates with the gradually increased desorption rate of the second layer and di- σ -bonded ethylene molecules. The change in the magnitude of $-d(\Delta\Phi)/d\theta$ between 0.5 L and 1.0 L reflects the onset of second layer adsorption on the surface. Vibrational spectroscopy of the second layer, as obtained by HREELS, was found to correlate well with the IR spectra of nonperturbed gas phase ethylene molecules. These molecules were, therefore, suggested to have a sp² configuration.⁴ Above 1.0 L $\Delta\Phi$ saturates, reflecting coverages higher than the first layer saturation. Within this range and up to 1.7 L, the work function decreases by 36 mV. Above 1.7 L where $\Delta\Phi = -1.31$ V, no further change in $\Delta\Phi$ with respect to coverage is found. At this coverage regime the sticking probability drops,^{4,5} although second layer population has not yet been completed.

3.3. $\Delta\Phi$ -TPD. In Figure 3A $\Delta\Phi$ -TPD spectra are shown at different ethylene coverages. The temperature above which no hydrogen desorbs anymore is marked by an open dotted

circle, for the low exposure range. An attempt to correlate between the $\Delta\Phi$ -TPD and Δp -TPD spectra shown in Figure 1 is assisted by differentiating the $\Delta\Phi$ -TPD spectra with respect to temperature ($d(\Delta\Phi)/dT$), depicted in Figure 3B.

Upon heating the surface exposed to 0.06 L (a) only minor $\Delta\Phi$ change is observed below 250 K. In the range 250–450 K, $\Delta\Phi$ increases due to the dehydrogenation of the various dissociated fragments, leading to hydrogen desorption, while above 450 K $\Delta\Phi$ remains unchanged. The overall change in $\Delta\Phi$ at the end of the $\Delta\Phi$ -TPD run (750 K) relative to that at the beginning (82 K) is +0.1 V. This indicates that the carbon atoms, probably in the form of carbides,^{10,13} contribute positively to the surface work function. Increasing the ethylene exposure to 0.17 L (b) a different $\Delta\Phi$ -TPD profile above 400 K is observed: an increase of $\Delta\Phi$ up to 560 K followed by a monotonic decrease. Since no hydrogen desorption is associated with these changes in the work function (see the dotted circles in Figure 3A), this can be interpreted as a carbidic layer polymerization. Further increase of the exposure up to 1.85 L results in a complex $\Delta\Phi$ -TPD and $d(\Delta\Phi)/dT$ spectra, the interpretation of which is discussed below.

4. Discussion

4.1. Second Layer Rearrangement and Desorption of C₂H₄ (82 K < T < 120 K). Ethylene molecules were previously characterized by HREELS to be sp² hybridized and to have planar configuration when occupying second layer sites above the Ru(001) surface.⁴ Planar ethylene is not expected to have a permanent dipole moment. The 36 mV work function decrease upon exposing the surface beyond 1.0 L (see Figure 2) may imply that the adsorbed species are not planar. However, since the saturation surface coverage of ethylene is 0.32 ML, it is reasonable to assume that a significant fraction of these second layer molecules lay above the empty sites at somewhat longer distance from the surface. Direct contact with the surface allows the polarization of ethylene's π orbital, resulting in a decrease of the work function. This can occur without disturbing the planarity of the molecule and its parallel configuration with respect to the Ru(001) surface.

Second layer molecular desorption (near 103 K) gradually dominates over decomposition for exposures higher than 0.5 L (Figure 1). At these exposures, the rate of change of the work function decreases considerably as coverage increases (Figure 2). This indicates that the contribution of the second layer to the work function change, as one may expect, is smaller than that of the first layer due to weaker interaction with the surface.

Since no dissociation could be detected upon heating the surface to 120 K,⁴ work function change measurements up to that temperature should be sensitive to molecular rearrangement which occurs simultaneously with second layer desorption. These two processes, rearrangement and desorption, are expected to affect the work function in opposite ways. In Figure 4 $\Delta\Phi$ -TPD spectra of ethylene at the second layer desorption range (80–120 K) are depicted at the indicated exposures.

For ethylene exposures below 0.5 L, for which molecular desorption is negligible, the lack of work function change during surface heating to 120 K (Figure 4A) indicates that no molecular rearrangements take place. At higher exposures (B), yet below the first layer saturation (1.0 L), two different processes could lead to a change in the work function (assuming no structural rearrangements occur within the di- σ -bonded ethylene): molecular desorption ($\Delta\Phi$ increase) and migration of molecules from the second layer toward the surface ($\Delta\Phi$ decrease). The fact that $\Delta\Phi$ decreases by 30–40 mV upon heating to 120 K

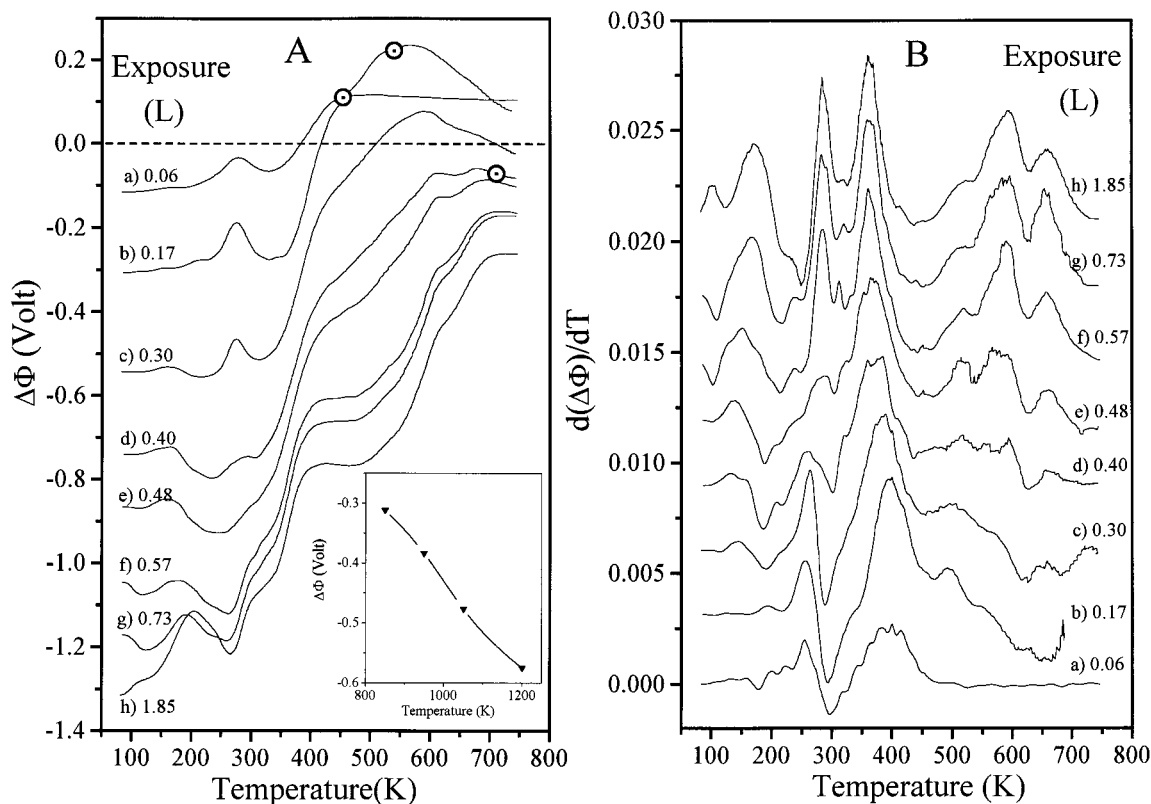


Figure 3. (A) $\Delta\Phi$ -TPD of $C_2H_4/Ru(001)$ at the indicated exposures. The open dotted circles mark the temperature above which no hydrogen desorption is detected. (B) The corresponding differential $\Delta\Phi$ -TPD spectra ($d(\Delta\Phi)/dT$). In the inset of A the $\Delta\Phi$ for 1 ML of $C_2H_4/Ru(001)$ is shown following different annealing temperatures.

while both processes take place indicates that migration of second layer molecules, leading to a direct contact with the surface and eventually adsorption on it, is dominant over desorption. Around the completion of the first layer at 1.0 L, the direction of change in $\Delta\Phi$ is reversed and an increase of 36 mV is observed at an exposure of 1.85 L (D). At these high coverages, the $d(\Delta\Phi)/dT$ profile up to 120 K overlaps the Δp -TPD peak position of the second layer molecules (inset of Figure 1A and Figure 3B,h, respectively). This indicates that the increase in the work function, shown in Figures 4C and 4D, is mostly due to desorption of second layer molecules, unlike the behavior at lower coverages.

To conclude, up to 0.5 L no change in $\Delta\Phi$ is observed while heating the surface to 120 K due to the absence of second layer molecules. At higher exposures, migration of molecules from the second layer to form direct contact with the surface ($\Delta\Phi$ decrease) competes with desorption ($\Delta\Phi$ increase). Toward first layer saturation (1.0 L), the second process dominates.

4.2. Fragmentation Scheme of Adsorbed Ethylene (120–460 K). The dissociation scheme of ethylene was extensively studied by numerous methods.^{3–8} Employing Δp -TPD, HREELS,^{3,4,6} and TPSSIMS⁶ several of the intermediates ($di-\sigma-C_2H_4$, CCH_3 , CH) were clearly identified. However, some disagreements still exist as to the nature of some of the intermediates (e.g., $\eta^2(C,C)CHCH_2$ —the η intermediate or CCH) and the temperature range of their appearance, see introduction section above. Since work function change measurements probe surface processes through the adsorbate–surface interaction (nature of bonding and its geometry), additional insight can be gained by correlating $\Delta\Phi$ with the previous studies mentioned above. Careful examination and comparison of our Δp -TPD results with those of Henderson et al.,⁶ using the same heating rates, reveal that the hydrogen

temperature programmed reaction (TPR) profiles and peak temperatures are practically identical in both studies. This enables direct comparison of the two studies and the results obtained from four different but complementary techniques ($\Delta\Phi$, Δp -TPD, TPSSIMS, and HREELS), all employed on the same system ($C_2H_4/Ru(001)$).

In Figure 5A Δp -TPD of ethylene (a) and hydrogen (b) are combined with $\Delta\Phi$ -TPD (c) and all the spectra were taken at ethylene coverage of more than 1 ML (exposure of 1.85 L in the case of Figure 5). These spectra are compared with the TPSSIMS⁶ of C_2H^- (e) and CH_3^+ (f), which probe various surface intermediates. The temperature derivative $d(\Delta\Phi)/dT$ (g) is shown as well, and the Δp -TPD of hydrogen at $T > 450$ K is magnified 10 times (d). In addition, the temperature at which maximum rate is reached for either build-up or depletion of the intermediates' population, as revealed for C_2H^- and CH_3^+ in the two TPSSIMS spectra: ($d(TPSSIMS_{C_2H^-})/dT$), ($d(TPSSIMS_{CH_3^+})/dT$), are marked on the TPSSIMS profiles by filled circles.

In an attempt to correlate the data shown in Figure 5A with the proposed decomposition mechanism discussed in the literature^{3–8} a model is presented in Figure 5B. This model explains the fragmentation process of ethylene and is consistent with both our new work function data and the information available in the literature. Thin solid lines represent the temperature range of stability for each of the various intermediates. At temperatures where the suggested presence of an intermediate is under debate in previous studies,^{4,6} a dashed line is used. Thick lines mark the temperature range at which the intermediates decompose, and filled circles represent a maximum in the Δp -TPD spectrum. Finally, arrows represent the onset of transformation from one surface intermediate to another, as concluded from the overall decomposition scheme.

Heating the surface above 120 K, following exposure to 1.0

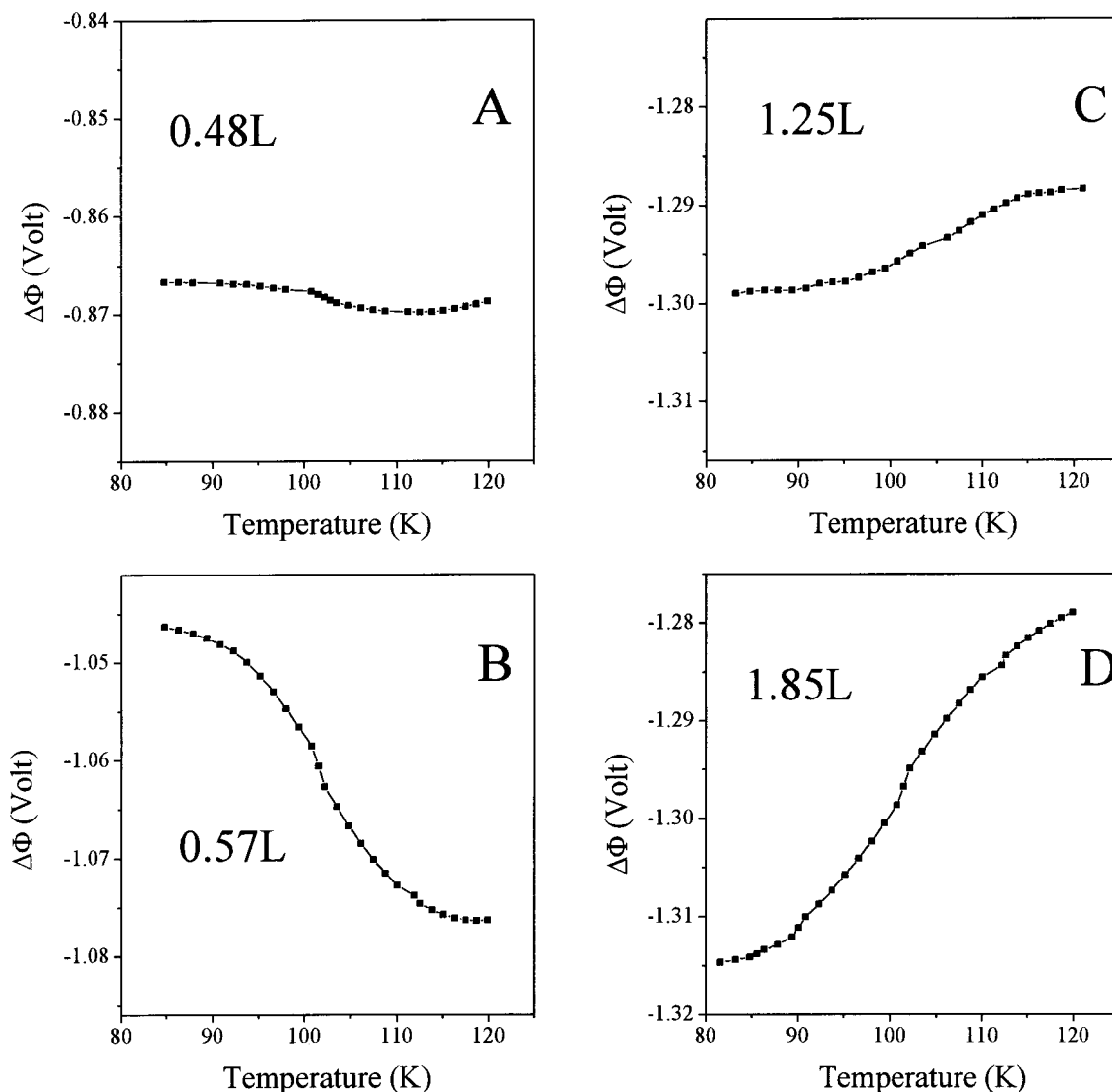


Figure 4. $\Delta\Phi$ -TPD at the indicated exposures, sample temperature was 82 K. Note that the abscissa is of 45 mV work function change for all the exposures.

L (saturation of first layer) results in the desorption of 0.08 ML di- σ -bonded ethylene, which also leads to a continuous $\Delta\Phi$ increase and extends up to 205 K.^{3,4,6} There is a very good match between ethylene $\Delta\Phi$ -TPD and $d(\Delta\Phi)/dT$ spectra in the range 120–205 K. Examination of the work function change recorded during ethylene adsorption, however, indicates that the $\Delta\Phi$ decrease due to the adsorption of 0.08 ML di- σ -bonded ethylene molecules (-0.30 V) (Figure 2) is larger than the $\Delta\Phi$ increase recorded up to 205 K during its desorption ($+0.16$ V) (Figure 3). Since this difference cannot be exclusively attributed to ethylene rearrangement, the presence of other species which induce significant charge transfer to the surface and form a layer of dipoles on the surface ($\Delta\Phi$ decrease) is postulated. This conclusion is in agreement with TPSSIMS data shown in Figure 5A,e.

A new CH_3^+ TPSSIMS peak was observed around 130 K and has been attributed to ethylidene- CCH_3 ,⁶ concurrently with ethylene desorption. The known adsorption geometry of ethylidene with its molecular axis perpendicular to the surface explains well the $\Delta\Phi$ decrease (relative to the di- σ -bonded ethylene contribution to $\Delta\Phi$) expected upon its formation. This onset temperature implies that on the crowded surface the di- σ -bonded ethylene transforms directly to CCH_3 as the only

reactivity route that competes with its desorption in this temperature range.

The production of CCH_3 continues at a constant rate up to 170 K simultaneously with the desorption of ethylene. At this temperature a maximum in both $d(\Delta\Phi)/dT$ and in the molecular ethylene rate of desorption is observed. Above 170 K an onset of C_2H^- signal in TPSSIMS is recorded. This signal grows up to 240 K with its maximum rate of formation at 200 K. It then decreases to a minimum at 300 K with maximum depletion rate at 265 K. During its rise and depletion the ethylidene TPSSIMS signal (CH_3^+) steadily grows up to 300 K. The correlation between the temperatures at which the TPSSIMS signal of ethylidene increases and that of C_2H^- terminates, suggests the formation and presence of an intermediate species on the route to ethylidene production. This intermediate was proposed to be $\eta^2(\text{C,C})\text{CHCH}_2$ (η -intermediate), based on HREELS studies.⁶ Upon completion of this intermediate's decomposition, no more CCH_3 is produced.

At 205 K $d(\Delta\Phi)/dT = 0$ and the $\Delta\Phi$ signal switches its direction of change. This change from a positive to a negative slope in $\Delta\Phi$ vs temperature is a consequence of the completion of the di- σ -bonded ethylene desorption. Hence, the decrease in $\Delta\Phi$ above 205 K is associated with the production of ethylidene

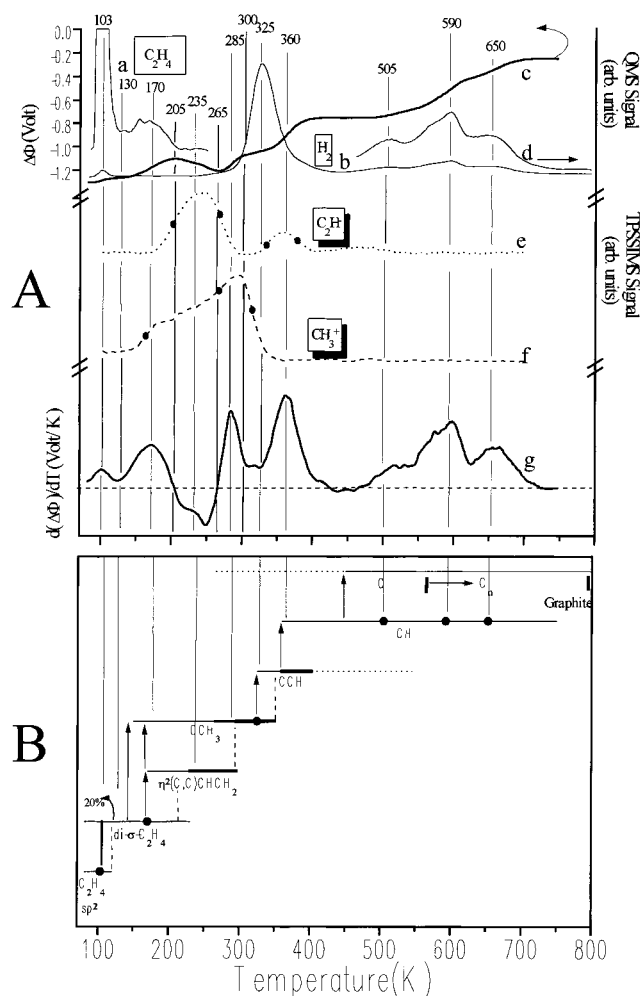


Figure 5. (A) Combined representation of the spectra upon heating a saturated $C_2H_4/Ru(001)$: (a) Δp -TPD spectrum of ethylene (mass 28), (b) Δp -TPD spectrum of hydrogen (mass 2), (c) mass 2 magnified ($\times 10$) at temperatures above 450 K, (d) $\Delta\Phi$ -TPD spectra of C_2H_4 , TPSSIMS of C_2H^- (e) and CCH_3^+ (f) from ref 6 after subtracting "background" and $d(\Delta\Phi)/dT$ (g). (B) Model for explaining the fragmentation scheme shown in 5A above based on refs 3–8.

via the η -intermediate discussed above. At 170 K where a maximum is observed in the desorption rate of ethylene, the resulting decrease in adsorbates surface density facilitates the formation of the η -intermediate. The lower density is necessary since upon its formation a vacant site for an adsorbed hydrogen atom should be available. The production rate of the η -intermediate increases concurrently with the ethylene desorption and it maximizes at 205 K, the temperature at which ethylene desorption is completed. Above 205 K the rate of production decreases, possibly due to the efficient transformation of the η -intermediate to ethylidene.

An interesting observation is that during the course of CCH_3 production, which terminates at 300 K, the work function starts to increase at 265 K ($d(\Delta\Phi)/dT = 0$) and a $d(\Delta\Phi)/dT$ peak emerges, centered at 285 K and terminating at 300 K. According to TPSSIMS the η -intermediate conversion rate to ethylidene is maximum at 265 K and has not been completed yet. Assuming that these are the only relevant processes ($di-\sigma$ -bonded $\rightarrow \eta^2-(C,C)CHCH_2 \rightarrow CCH_3$) we would expect that the work function will continue to decrease at higher temperatures up to the maximum TPSSIMS signal of CH_3^+ at 300 K. This is due to the negative contribution of ethylidene to the work function change, which is significantly larger relative to all other surface species that are present at this temperature range.

A possible explanation for this early and pronounced change in sign of the $d(\Delta\Phi)/dT$ spectrum is that it marks the actual onset of ethylidene decomposition near 265 K, which occurs during its formation. This process may be initiated by the accumulation of CCH_3 , as a result of the fast decomposition of the η -intermediate. This hypothesis is supported by the onset of the hydrogen thermal desorption signal (see Figure 5A,b) which is recorded around that temperature.

Once decomposition of the η -intermediate has been completed at 300 K, the CH_3^+ signal in TPSSIMS starts to decrease. Most of the hydrogen desorption resulting from CCH_3 dissociation^{3–8} takes place up to 360 K. Examining the temperature dependence of both hydrogen desorption and the ethylidene decomposition indicates that the maximum rate of ethylidene depletion appears at lower temperature (by 13 K) than the maximum rate of hydrogen desorption. If the hydrogen desorption signal was exclusively determined by the CCH_3 dehydrogenation kinetics, we would have expected the rates of CCH_3 dissociation and of H_2 desorption to overlap in their temperature range, which is not the case. In addition, we note that the surface work function is almost constant in the range 305–325 K where the hydrogen desorption peak builds up toward its maximum temperature (325 K) and that CCH production onset is observed only at 315 K.

The dissociation pathways of CCH_3 on $Ru(001)$ are not yet fully resolved in the literature: According to Henderson et al.⁶ ethylidene converts to $CCH + 2H$ while according to Hills et al.⁴ it decomposes to $C + CH + 2H$. Since the second TPSSIMS peak of C_2H^- (Figure 5A,e), attributed to CCH , appears near 315 K, which is 50 K higher than the CCH_3 decomposition onset temperature, a second CCH_3 decomposition pathway appears to exist at $T < 315$ K. The fact that the work function is almost constant in the temperature range where the ethylidene depletion rate reached its maximum suggests that the surface dipole of the transient species formed as a result of CCH_3 decomposition is similar to the dipole moment of its parent fragment. It may, therefore be CCH_2 , although there is no other direct evidence for this assignment. A decomposition pathway in which C–H bonds are sequentially cleaved is also consistent with the higher hydrogen desorption peak temperature relative to the temperature at which the CCH_3 decomposition rate is maximum.

Finally, in the range 325–360 K, the increase in the work function is due to the higher dipole moment of CCH_3 relative to CCH , which is produced in these temperatures according to TPSSIMS. The maximum in the $d(\Delta\Phi)/dT$ spectrum observed at 360 K reflects the increased density of CCH on the surface. The lower $d(\Delta\Phi)/dT$ values above 360 K are due to further decomposition to $C + CH$ as reflected by the diminishing C_2H^- TPSSIMS signal. The only H_2 desorption in these temperatures is due to surface hydrogen recombination,⁴ which is not expected to affect the work function change measurements in a significant way.²³

4.3. CH Decomposition (460–720 K). The desorption of hydrogen from $Ru(001)$, which has been saturated (1 ML) by ethylene, at temperatures above 460 K is attributed to CH dehydrogenation^{3,4,6} at three distinct peaks centered at 505, 590, and 650 K. Minor contribution from CCH cannot, however, be excluded.²⁰ Based on HREELS data, the CH bond was claimed to orient parallel to the $Ru(001)$ surface.³ The minor changes in the HREELS spectrum between 470 K and 570 K were interpreted¹¹ as a result of a conversion between two types of CH surface binding: sp^2 and sp . In the sp^2 configuration, the carbon atom was suggested to bridge two Ru atoms. The CH bond is inclined toward the third Ru atom to allow the carbon to interact with it, via the third unpaired electron in its 2p orbital.

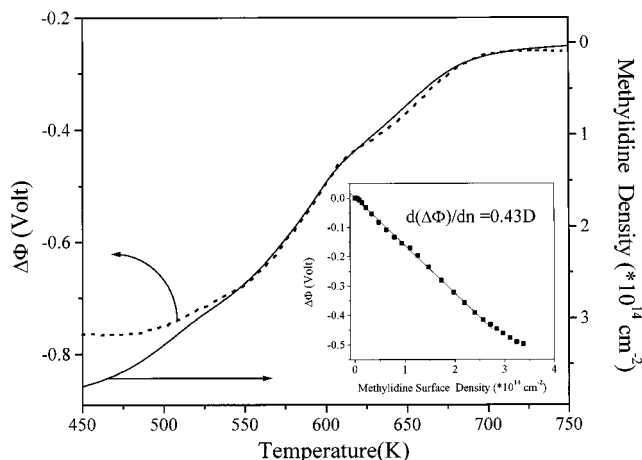


Figure 6. Temperature dependent $\Delta\Phi$ (left) and n , methyldiene density (right) following saturated ethylene layer exposure. In the inset: the calculated $\mu(n)$ according to Helmholtz equation.

In the sp configuration, however, the CH fragment is claimed to be bonded to a single Ru atom and is inclined over a 3-fold hollow site to interact with two additional metal atoms.

The clear similarity between the $d(\Delta\Phi)/dT$ (Figure 5A,g) and the Δp -TPD signals for the saturated layer at $T > 450$ K (Figure 5A,d) may be used to obtain information on the surface fragments. We assume that the only hydrogenated species left on the surface above 450 K is methyldiene, CH.^{3,4,6} The integrated areas under the Δp -TPD peaks of hydrogen add up to 25% of the overall hydrogen desorption. Considering that the total ethylene decomposition amounts to 0.24 ML, as discussed above, the number of CH species accumulated on the surface at 450 K can be estimated. Assigning each of the H₂ Δp -TPD and the $\Delta\Phi$ -TPD peaks (505, 590, and 650 K) to a specific subgroup of adsorbates, an attempt can be made to estimate the CH dipole moment based on the Helmholtz expression: $\Delta\Phi(n) = -n\mu(n)/\epsilon_0$.

To use this expression a linear dependence between the dipole moment and the adsorbate (CH) density should be established. In Figure 6 both $\Delta\Phi(n)$ and the CH surface density extracted from the H₂ Δp -TPD of the saturated layer are shown. $\Delta\Phi$ follows very well the methyldiene coverage at $T > 530$ K. Up to that temperature ($450 \text{ K} < T < 530 \text{ K}$), the increase in the work function is compensated by a process which is not accompanied by hydrogen release, possibly C–C bond cleavage due to minor CCH dissociation (see C₂H⁻ TPSSIMS signal in Figure 5A,e).

The dipole moment of the adsorbed CH is obtained from the slope of $\Delta\Phi(n)$ vs n shown in the inset of Figure 6. The linear relation between $\Delta\Phi(n)$ and n across all three CH species indicates that the dipole moment is coverage and adsorption site independent. The value obtained from the slope is $\mu = 0.43$ D.

We now correlate our results with previous interpretation of the CH/Ru(001) system,³ which was based on HREELS, and concluded that (1) the difference between the three H₂ desorption peaks is attributed to changes in the extent of hybridization from sp² to sp, which occur during the desorption process and (2) all forms of CH fragments are inclined toward the surface.

According to the above interpretation we would expect that polarization of the CH bond should not lead to changes in $\Delta\Phi$, due to the fact that it lies parallel to the surface. However, in case that a change in $\Delta\Phi$ is detected, we would expect a strong variation of $\Delta\Phi$ with temperature due to the various populations reflected in various TPD peaks. These discrepancies can be

rationalized by assigning the $\mu = 0.43$ D to the dipole moment of a CH–Ru complex. This dipole moment contains contributions from polarization of the carbon–metal bonds as well as the dipolar CH bond.

4.4. Carbon Polymerization and Graphite Formation (560–1200 K). Carbide is the product of methylene surface decomposition. Upon elevating the temperature above 560 K carbide species polymerize to form graphite.¹³ For a full carbon monolayer (C/Ru(001) = 1) the work function was predicted to increase by 0.6 V and decrease by 1.2 V for carbidic and graphitic phases, respectively, based on ab initio calculations.^{18,19} This indicates that the state of the adsorbed carbon on the surface can be probed by $\Delta\Phi$ measurements.

The work function change attributed to carbide polymerization can be estimated when measured at temperatures above the completion of CH dissociation. As shown in Figure 3A, this CH bond cleavage ($\Delta\Phi$ increase) is expected to contribute in an opposite way to $\Delta\Phi$ -TPD than the carbide polymerization ($\Delta\Phi$ decrease). Up to exposures of ≈ 0.2 L the temperature ranges in which these two processes take place do not overlap. At higher exposures they completely overlap; therefore, the carbon polymerization steps, $n\text{C} \rightarrow \text{C}_n$ (amorphous) \rightarrow discrete Graphitic islands \rightarrow Graphitic layer, cannot be distinguished or followed separately by $\Delta\Phi$ measurements.

In Figure 3A $\Delta\Phi$ -TPD spectra are shown for exposures of 0.06 L (a) and 0.17 L (b), respectively. The temperature at which hydrogen desorption terminates is marked by the dotted open circle to emphasize the work function change due to carbide polymerization. For 0.06 L, $\Delta\Phi$ is constant for the temperatures above the point of the dotted circle (400 K), at least up to 720 K, see Figure 3A. In contrast, at 0.17 L the work function continuously decreases at temperatures beyond the hydrogen termination point between 560 and 720 K. The transition between the two different behaviors, namely the exposure at which polymerization starts to be resolved by $\Delta\Phi$ measurements at 560 K, is 0.12 L.

Assigning 0.5 L with a coverage of 0.24 ML ethylene, while assuming coverage independent sticking probability, we estimate the resulting decomposed material (surface carbide) arising from an exposure of 0.17 L to be 0.16 ML at 560 K. If carbon dissolves into the Ru bulk it should result in a decrease of the carbide coverage on the surface. In addition, carbon dissolution is expected to induce an opposite surface dipole. However, no change in the work function is observed in the range of 400–720 K for coverages below 0.12 L. We conclude, therefore, that dissolution into the bulk is unlikely to happen at this coverage. At higher coverages, where polymerization takes place above 560 K, the carbon atoms are further stabilized on the surface, therefore dissolution is again unlikely to occur. Carbon dissolution at temperatures above 800 K needs to be examined. We regard the formation of the graphitic layer at these temperatures a thermodynamically favorable process, thus slowing down or preventing dissolution into the bulk.

Based on the +0.2 V contribution to $\Delta\Phi$, attributed to the adsorbed carbide at that temperature, full carbide layer (C/Ru(001) = 1 ML) is expected to lead to 1.2 V work function increase. The relatively poor agreement between the experimentally determined $\Delta\Phi$ (1.2 V) and the ab initio calculated value (0.6 V)^{18,19} can be explained by the fact that carbide species are not necessarily monoatomic. They may appear in different forms, e.g., dimers, trimers, or larger carbon islands.^{3,4} Therefore, one should not expect to find a good agreement with the numbers calculated for an ideal extended monocarbide layer.

Table 1 summarizes values of $\Delta\Phi$ and the relevant temper-

TABLE 1: Experimental vs Ab Initio Calculated^{18,19} $\Delta\Phi$ due to Each of the Adsorbed Carbon Phases

| carbon phase | temp range (K) ¹⁴ | C/Ru(001) = 1 | |
|--|------------------------------|------------------------|--------------------------------------|
| | | exptl $\Delta\Phi$ (V) | calcd ¹⁶ $\Delta\Phi$ (V) |
| C _(a) – carbide | <800 | +1.2 | +0.6 |
| disordered carbonaceous C _n | 560–800 | –0.6 | |
| graphite | 800–1300 | –1.2 | –1.2 |

ature range obtained from the experimental measurements and the ab initio calculations.

Heating the surface above 560 K initiates carbide mobility and sintering only at ethylene exposures above 0.12 L. The polymerized phase ($\Delta\Phi$ decreases upon its formation) is inert to hydrogenation.^{3,9} Again, taking the extent of decomposed ethylene to be 0.24 ML, the minimum carbide coverage needed to initiate polymerization is 0.11 ML. This is in reasonable agreement with previously reported polymerization onset of 0.08 ML around 600 K.⁹ The fact that carbon atoms in the form of carbides require a minimum density in order to polymerize is interpreted as a result of adsorption at step edges or defect sites that are favored energetically. These sites are occupied before the polymerization process begins.

The chemical nature of the adsorbed carbon species is a key factor in the reactivity of the carbon adlayer on metal surfaces. Auger studies have identified a graphitic dense phase around 600 K. In a later XPS study this phase was found to be disordered at 750 K,¹⁰ which excluded the possibility that at this temperature the carbonaceous adlayer is of graphitic nature. In a more recent STM study¹⁷ it was shown that only around 800 K do the disordered carbonaceous particles transform to graphite. The graphitic species initially form discrete 2D islands 10–15 Å in diameter. The hexagonal graphitic superstructure becomes continuous as the temperature is raised, and only around 1300 K are extended graphitic layers observed.

It is interesting to note that a similar scheme was reported in the case of carbon deposited on Pt (111), based on STM data,²⁴ as a result of ethylene decomposition: The carbonaceous adlayer at 500 K consisted of small agglomerates (~20 atoms) having bimodal distribution (single and two layers height). Annealing to 700 K increased the average size of the carbonaceous particles (~34 atoms) and they also became more uniform and limited to one layer thickness. Only around 800 K did the carbonaceous particles (on Pt(111)) coalesce to form graphite, growing from step edges at 1000 K.

In the inset of Figure 3A, $\Delta\Phi$ is shown during the polymerization process of carbide on the Ru (001) surface following the decomposition of saturated C₂H₄ layer. The work function change at 800 K (relative to the clean surface) is –0.3 V, and it further decreases by additional 0.27 V upon heating from 800 K (where disordered carbonaceous particles were found¹⁴) to 1200 K. Therefore, at 1200 K a total decrease of 0.6 V relative to the clean surface is attributed to 0.48 ML of continuous graphitic layer (twice the amount of ethylene, which decomposes from initial coverage of 1 ML). This nicely correlates with the ab initio calculated 1.2 V decrease for a full graphitic monolayer on Ru (001).^{18,19}

ARUPS experiments have characterized the carbonized layer at 873 K to be of pure graphitic nature, measuring a $\Delta\Phi$ decrease of 0.9 V.¹⁶ The small discrepancy found between ours and the results of the ARUPS measurements may be explained on the basis of different layer preparation methods. In particular, higher annealing temperatures would probably cause a larger $\Delta\Phi$ decrease, based on our temperature-dependent data shown in Figure 3A.

5. Conclusions

Work function change measurements during adsorption and surface heating in a $\Delta\Phi$ –TPR mode combined with TPD of hydrogen products correlated with previous TPSSIMS study are shown to provide new insight into the chemistry of ethylene on Ru (001) in the range 82–1200 K.

Ethylene molecules dehydrogenate completely to hydrogen and carbon at coverages up to C₂H₄/Ru(001) = 0.24 ML, with a small fraction of molecular ethylene desorption. $\Delta\Phi$ –TPD measurements have shown that second layer molecules adsorb in an unstable structure at 82 K. As a result, rearrangement and migration of ethylene from the second layer to the surface (Φ decrease) takes place simultaneously with molecular desorption (Φ increase).

The presence of an intermediate on the route to ethylidene formation (di- σ -bonded C₂H₄ → η^2 (C,C)CHCH₂ → CCH₃), which was previously suggested (based on HREELS and TPSSIMS studies), is consistent with our work function change measurements. Initial signs of decomposition of ethylidene are found around 265 K, at the same temperature range in which ethylidene is also formed. This conclusion is supported by the fact that the hydrogen desorption as a consequence of ethylene TPR is observed around that temperature as well.

A similarity is found between the $d(\Delta\Phi)/dT$ and the TPR signals at the CH decomposition temperature range. This similarity implies that the orientation and the polarization of the CH–metal bonds do not change considerably during the course of the TPR. An approximate dipole moment of $\mu = 0.43$ D for CH/Ru(001) was calculated.

These results disagree with the former interpretation based on HREELS, suggesting practically no dipole moment of the adsorbed CH. This discrepancy can be rationalized considering that the measured dipole moment includes contributions from the CH bond as well as from polarization of the unpaired carbon electrons which results from their interaction with the Ru surface.

Our work function change measurements support previous experimental evidence for the carbon polymerization mechanism, its coverage dependence, and the temperature range in which it occurs. A minimum coverage of C/Ru(001) = 0.12 ML was found necessary to trigger the polymerization of carbide above 560 K. Graphite formation at higher temperatures leads to a gradual decrease of the work function by 1.2 V per monolayer (initial coverage C/Ru(001) = 1 ML). This value is in very good agreement with ab initio calculations reported in the literature. Carbide was found to increase the work function by 1.2 V per monolayer, compared with only 0.6 V found by the calculations. The lack of quantitative agreement between the two can be partially explained by the formation of dimers, trimers, and longer carbon chains, in contrast with the ideal extended monocarbide layer considered in the calculations.

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