Microcalorimetric study of ethylene adsorption at 300 K on Pt{100}-hex and Pt{100}-(1 × 1)

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Abstract

Coverage-dependent heats of reaction and sticking probabilities have been measured for ethylene on Pt{100}-hex and Pt{100}-(1 × 1) at room temperature. The initial heats of reaction are 213 and 305 kJ/mol respectively, and the corresponding initial sticking probabilities are 0.75 and 0.71. Upon adsorption, C_2H_2, C_2H_3 and C_2H_4 species form on the surface, depending on the symmetry of the surface and the coverage. Average C–Pt bond strengths are extracted from the known structures of the species and the measured calorimetric heats. Within the accuracy of the measurement, these values are relatively insensitive to the surface structure, with a mean value of about 241 kJ/mol. There appears to be a systematic decrease in the bond dissociation energy as the number of Pt–C single bonds per adsorbate molecule increases from 2 to 4. © 1998 Elsevier Science B.V.

Keywords: Electron energy loss spectroscopy; Ethylene; Single crystal adsorption

1. Introduction

The adsorption of ethylene on Pt has been the subject of intensive research because it belongs to an important class of catalytic processes involving the initial adsorption of hydrocarbons on transition metals. As part of our on-going study [1,2] of C_2H_4 adsorption and decomposition on the low index planes of Pt, we have used the single crystal adsorption calorimeter (SCAC) [3–5] to investigate coverage-dependent heats of reaction and sticking probabilities

of C_2H_4 on Pt{100}-hex and Pt{100}-(1 × 1) surfaces at room temperature. Previous experimental studies [6–9] have shown that ethylene adsorption on Pt is reversible at low temperatures, but that it decomposes to produce various intermediates on the surface near or above room temperature. Elaborate models of the catalytic pathways have been constructed [10] in order to deduce the likely reaction mechanisms, yet the estimates of binding energies and activation barriers have lacked an experimental basis to date. Prior to the development of the SCAC, the determination of heats of reaction on a single crystal surface was restricted to reversible systems because of the limitations of the alternative indirect methods, such as temperature programmed desorption (TPD) and the measure-

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ment of adsorption isosteres [11]. [3] By measuring the heat changes calorimetrically, however, there are no such limitations in the choice of system. The technique has already been applied to measure the binding energies of various irreversibly adsorbed hydrocarbon species on Pt{111} and Pt{110} [1,2], thus contributing valuable information in generating more reliable reaction schemes.

A wide variety of techniques from surface science have been employed to investigate the reaction pathways, energetics and intermediates associated with ethylene adsorption on Pt single crystal surfaces. These include low energy electron diffraction (LEED) [9,13], high resolution electron energy loss spectroscopy (HREELS), [4] X-ray photoelectron spectroscopy (XPS) [9], temperature programmed thermal desorption spectroscopy (TPDS) [8] and X-ray photoelectron diffraction [15]. In Fig. 1, some of the intermediates that have been postulated to form from ethylene decomposition on the various surfaces of Pt are illustrated. The formation of these species depends on the orientation of the surface, and the temperature of adsorption and the extent of adsorption [6–9].

Electron energy loss spectroscopy (EELS) has been performed on the Pt{100} hex and (1×1) phases [6]. Hatzikos and Masel [6] found that ethylene adsorbed molecularly at low temperatures (120 K) on both phases. But as the sample is heated, ethylene dehydrogenates and rearranges to form an ethylidyne intermediate ($\equiv C-CH_3$) on the initially clean hex phase, while a mixture of vinylidene ($=C=CH_2$) and an acetylinic intermediate ($=CH-CH=$) was observed when they started with a clean surface in the (1×1) configuration [6]. Fischer and Kelemen [16] observed a vinyl radical ($-CH=CH_2$) and acetylene ($=CH-CH=$) on the same surface at 300 K up to half a monolayer

[3] See for example Ref. [12].
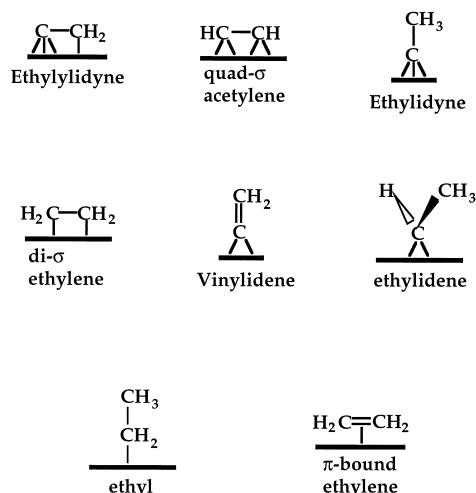[4] See for example Ref. [14].

Fig. 1. Schematic structures for the various ethylinic species known to form on Pt surfaces. The high coordination species are expected to be present at low exposures of ethylene while the di-σ bonded species is found at saturation.

coverage for the hex phase; but they observed acetylene on the (1×1) phase at 330 K, and vinyl and ethylene at 200 K. Further heating to about 500 K results in a mixture of C_nH ($n = 1,2$) species on the surface and finally, above about 550 K, the dehydrogenation is completed and only carbon remains [6,7].

For the Pt{110}-(1×2) surface, the chemistry of ethylene adsorption is uniquely complicated. In an X-ray photoelectron diffraction experiment [15] it was found that when ethylene decomposes on Pt{110}, the carbon–carbon bond in the product remains parallel to the surface. From TPD and EELS, Yagasaki et al. [8] have found that at least two different species exist at temperatures above 100 K. At 300 K their results indicate the presence of C_2H_2 and C_2H_3, possibly ethylylidyne ($\equiv C-CH_2-$) and ethylidyne ($\equiv C-CH_3$). Low exposures of ethylene produce mainly C_2H_2 species while at saturation there appears to be twice as much C_2H_3 on the surface as C_2H_2. Boronin et al. [9] reported that the missing-row (1×2) reconstruction of Pt{110} is lifted by the adsorption of ethylene at 300 K, but Yagasaki et al. [8] only found an increase in the diffuse background in their LEED experiment, with retention of the (1×2) struc-

ture. A calorimetric study performed by Stuck et al. [1] also revealed the formation of ethylylidyne on the clean Pt{110}-(1 × 2) surface at 300 K.

Pt{111} is the most widely studied surface for ethylene adsorption. Although it is accepted that the stable adsorbed species at room temperature is ethylidyne [17,18], few studies have been able to identify the adsorption and decomposition pathway. Several models have been proposed for the formation of this species: intermediates proposed include ethyl groups $(-H_2-CH_3)$ [19,20], ethylidene $(=C=CH_2)$ [21,22] and vinylidene [20,23], but direct and definitive spectroscopic evidence for these species is still lacking. The reaction of ethylene on Pt{111} has been investigated by single crystal adsorption calorimetry, and a mechanism involving ethylidene as an intermediate for the formation of ethylidyne has been proposed [2].

2. Experimental setup

The SCAC has been described in detail elsewhere [3,4]. Improvements incorporated since the design of the prototype are given by Stuck et al. [5]. Molecules from a pulsed supersonic molecular beam source are adsorbed on a single crystal which is about 2000 Å thick and freely supported in vacuum. Each pulse is only 50 ms long and the repetition rate is 0.4 Hz. The heat released by the molecules during adsorption increases the temperature of the crystal and this is monitored remotely by a MCT detector. The detector is calibrated after each experimental run by measuring the absorption of a laser beam pulse with the same spatial and temporal profile as the molecular beam. A spinning rotor gauge is used to determine the pressure in the accumulation tube with an absolute accuracy of better than 3% independent of the chemical composition of the gas. The sticking probability is measured by the King and Wells method [24], i.e., by comparing the amount of molecules scattered from an inert gold flag with that from the

sample during the molecular beam pulse. The integrated dosage-sticking product gives the coverage, which is expressed in terms of the surface layer atoms of the ideally terminated crystal, i.e., 9.2×10^{14} atoms/cm^2 for Pt{110} and 1.3×10^{15} atoms/cm^2 for Pt{100}.

All measurements are performed at pressures lower than 10^{-10} mbar. The crystal is cleaned by repeated cycles of gentle sputtering and is annealed to about 600 K, until no contamination can be detected by Auger electron spectroscopy (AES) and until sharp LEED spots can be observed. The clean {100} surface shows a sharp LEED pattern characteristic of two domains of the hex reconstruction. Ethylene is then pulsed onto these surfaces. The clean metastable
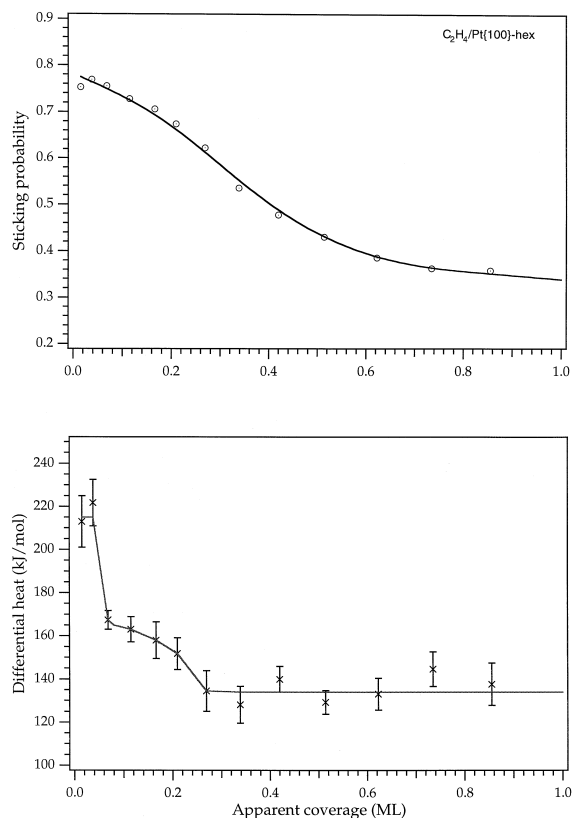

Fig. 2. (a) Sticking probability of Ethylene on Pt{100}-hex as a function of apparent coverage; for $\theta \leq 0.3$ the coverage scale is the true coverage. (b) Heat of reaction of ethylene on Pt{100}-hex as a function of apparent coverage. (All error bars given are the standard deviations between several experimental runs.) Substrate temperature: 300 K.
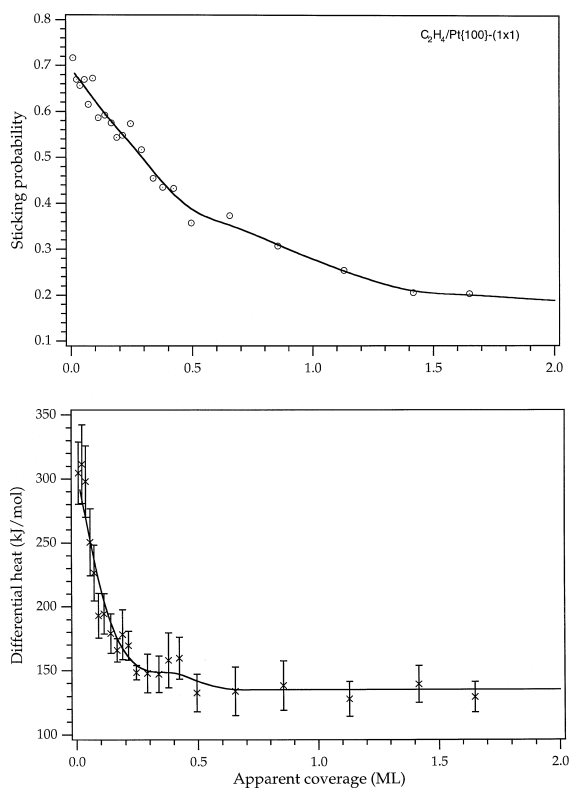
Fig. 3. (a) Sticking probability of Ethylene on Pt{100}-(1×1) as a function of apparent coverage; for $\theta \leq 0.5$ the coverage scale is the true coverage. (b) Heat of reaction of ethylene on Pt{100}-(1×1) as a function of apparent coverage. Substrate temperature: 300 K.

Pt{100}-(1×1) surface is prepared by standard procedures [25] involving oxygen treatment, followed by a clean-off reaction with hydrogen and thermal desorption of residual hydrogen.

All results shown in Figs. 2 and 3 are the average of six independent experimental runs performed with high purity ethylene gas (> 99.95% purity from MG Gas Products) on each surface. The error bars in the figures indicate the standard deviation between these runs, and so reflect the reproducibility of the experimental results. The relative errors for both the sticking probability and the heat of reaction are smaller than about 6% [5]. However, the absolute value of the heat of reaction depends on the absolute calibration of several physical quantities (for example the pressure in the stagnation tube and

the optical reflectivity of the crystal) and we estimate the sum of these systematic errors to be smaller than 6% [5]. In each case, when the coverage of ethylene reaches a certain value upon repeated dosing, a steady-state situation is attained whereby the amount of ethylene added during each 50 ms pulse is exactly balanced by the quantity of ethylene which desorbs between pulses. Summing these finite sticking probability contributions thus yields an apparent coverage scale which extends indefinitely while the true coverage reaches some definite limit.

3. Results

3.1. Pt{100}-hex and Pt{100}-(1 × 1)

The sticking probability of ethylene on Pt{100}-hex is shown as a function of coverage in Fig. 2a. It begins at an initial value of 0.75, and decreases slowly with coverage. The adsorption is precursor-mediated. We note that the steady-state sticking probability when the hex surface is saturated at 300 K is surprisingly high (∼ 0.35) (Fig. 2a).

For comparison, we also measure the sticking probability for the metastable (1 × 1) phase (presented in Fig. 3a). An initial value of 0.71 was measured for the (1 × 1) phase, and the sticking probability falls almost monotonically as the ethylene coverage is increased to 0.8 ML. Here, unlike the {111} [2,26] and {100} hex surface, there is no evidence for a mobile extrinsic precursor. Again, as for the hex surface, the steady-state sticking probability is high.

The coverage-dependent heats of adsorption for the hex and the (1 × 1) phases are presented in Fig. 2b and Fig. 3b respectively. From a value of 213 ± 12 kJ/mol at 0.01 ML for the hex phase, the heat drops sharply to 167 ± 3 kJ/mol at 0.07 ML coverage. At coverages between 0.07 to 0.4 ML it shows a more gradual decrease and at 0.40 ML the system reaches a steady-state with a heat of 130 ± 6 kJ/mol. Although the error bars at 0.11 ML are not negligible (± 5 kJ/mol), the abrupt drop from

~ 221 kJ/mol to ~ 167 kJ/mol is not a statistical deviation but corresponds to a real effect, since all the six individual experimental runs reveal the presence of this sudden fall at or near this coverage. At saturation our LEED measurements showed a diffuse (1×1) pattern indicating that the hex reconstruction has been lifted, but with a high degree of disorder. Similar changes in the LEED pattern have been described by Fischer and Kelemen [16] who reported a weakening of the $^1/_5$ order spots upon ethylene adsorption on Pt{100}-(5×20) at 330 K and the subsequent formation of a weak $c(2 \times 2)$ structure at high exposures.

On the metastable (1×1) phase, an initial heat of reaction of 305 ± 24 kJ/mol is measured (Fig. 3b) and at ~ 0.25 ML coverage the heat drops to 150 kJ/mol. It is interesting to note that it then remains quite constant up to a coverage of 0.42 ML. The heat on the (1×1) phase remains higher than that on the hex phase up to a coverage of ~ 0.50 ML. But at coverages exceeding half a monolayer, the steady-state heats (~ 130 kJ/mol) on both hex and (1×1) phases coincide. This effect would be expected if the hex surface reconstruction is completely lifted. However, we note that the sticking probability curves are not identical above 0.5 ML, suggesting an incomplete lifting of the hex reconstruction. The surface which is initially hex shows a higher sticking probability than that which is initially (1×1), consistent with the existence of defects in the ethylene-reconstructed hex surface.

4. Discussion

The initial hex reconstruction is lifted by ethylene adsorption at 300 K although, as noted above, the surface contains a significant fraction of defects, such as steps. For ethylene adsorption on Pt{100}-hex at 120 K, previous studies by Fisher and Kelemen [16] and Hatzikos and Masel [6] report di-σ ethylene on the surface which desorbs partially as ethylene between 250

K and 350 K. The rest dehydrogenates to ethylidyne between 270 K and 370 K. At around 300 K one expects a mixture of acetylene, ethylidyne and ethylene on the surfaces of both the hex phase of Pt{100}, and acetylene and ethylene on the (1×1) phase. Ultraviolet photoelectron spectroscopy (UPS) has also indicated the presence of an acetyl species at 330 K on Pt{100}-hex [16] and a small amount of acetylene at 350 K on the surface.

From our measurements for ethylene adsorption on both Pt{110}-(1×2) and Pt{111} [1,2,26] surfaces, the heat of reaction of ethylene to form ethylidyne was found to be 190 kJ/mol:

$$3Pt + H_2C=CH_2 \rightarrow Pt_3C-CH_3 + H_{(a)}$$
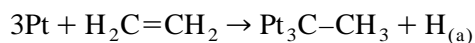
$$\Delta H_R = -190 \, kJ/mol$$

This value is significantly lower than that found on Pt{100}-hex extrapolated to zero coverage, 225 ± 12 kJ/mol. Based on this and the earlier spectroscopic studies [6,16], we therefore conclude that at low coverage acetylene is formed on the {100}-hex surface. LEED studies show that adsorption of acetylene on Pt{100}-hex at 120 K lifts the reconstruction to form a disordered (1×1) structure [6]. By analogy with the (1×1) surface [6] where quad-σ acetylene is found after ethylene adsorption, we propose that the same compound is produced on the initial hex phase, accompanied by a lifting of the reconstruction to give a defective (1×1) surface, as also indicated by LEED. The integral heat ΔH_{in} can be calculated from the differential heat ΔH_{diff} by summing the coverage-differential heat product and then normalizing this result against the coverage θ.

$$\Delta H_{in} = \left(\int \Delta H_{diff} d\theta \right) / \left(\int d\theta \right)$$

As we have seen, at $\theta_{C_2H_4} = 0.5$ ML the steady state differential heats coincide; if the adlayer formed from the initial hex and the initial (1×1) surfaces were identical at this coverage, the difference between the two integral heats of reaction would be the difference in surface energies between the clean (1×1) and hex. Because the heats are expressed per mole

of ethylene molecules and because, for a total coverage of $\theta_{C_2H_4} = 0.5$ ML, there are two surface platinum atoms (Pt_s) for each reacted C_2H_4 molecule, the integral adsorption heats of C_2H_4 on the hex and (1×1) phases are halved to calculate the heat per mole of Pt_s atoms. In this way we estimate the energy necessary for the hex to (1×1) phase transition to be about 13 ± 3 kJ/(mol Pt_s) [27]. Calorimetry studies on the adsorption of CO on Pt{100} hex and (1×1) phases have been performed and reported elsewhere [28]. At 0.5 ML coverage of CO on the initially clean Pt{100}-hex surface the hex reconstruction is completely lifted, and the CO molecules form a c(2×2) adlayer, identical to that formed at 0.5 ML coverage on the initially (1×1) phase. Using the CO adsorption heats, the energy difference between the hex and (1×1) phases of Pt{100} at room temperature was measured to be 10 ± 2 kJ/mol [27,28]. We note also that the initially hex surface produces a defective (1×1) surface with ethylene adsorption, which would imply that the current figure of 13 kJ/(mol Pt_s) might be an overestimate.

The heat of adsorption for the initial hex phase surface drops sharply with increasing coverage. With $0.05 \le \theta < 0.2$, the heat of reaction of 165 kJ/mol together with the hex $\rightarrow (1 \times 1)$ transformation energy coincides with the value expected for the formation of ethylidyne from our previous studies on Pt{111} as well as on Pt{110} of about 190 kJ/mol. By analogy with the Pt{110}-(1×2) and Pt{111} [1,2,27] surfaces, di-σ ethylene formation is expected to begin somewhere in the region of 150 ± 9 kJ/mol. At coverages above 0.3 ML the heat of adsorption remains constant at 130 ± 4 kJ/mol which is close to the steady-state value found on Pt{110} [1]. It is possible that at high coverages ethylene adsorbs reversibly as π-bound ethylene on Pt{100}; however, the nature of the species formed at steady-state is discussed further below.

The heat of adsorption of ethylene on the (1×1) phase exhibits a sharp fall as the coverage rises from zero to 0.25 ML, and a plateau is subsequently observed up to 0.42 ML coverage of ethylene. Similar to the hex surface, we propose that di-σ ethylene is formed in the plateau regime where the heat measured is approximately 148 kJ/mol. Due to the absence of three-fold sites, ethylidyne is not observed on this surface [6]. At coverages exceeding 0.5 ML, the heats of adsorption of both phases coincide exactly, although the sticking probability is lower than for the hex phase. When the experiment was allowed to run for higher coverages (up to 3 ML), the sticking probability falls continually, indicating a slow decomposition or adsorption process on the surface. True steady-state is not achieved. The heats of adsorption at $\theta > 0.5$ ML indicates that the hex reconstruction is completely lifted and further adsorption of ethylene therefore occurs on the (1×1) phase after this coverage is attained [28]. The 'steady-state' heat of adsorption is remarkably high at ~ 135 kJ/mol compared to the steady-state heat of only 40 kJ/mol assigned to the π-bonded acetylene on Ni{100} and Pd{100} at room temperature [29]. First, we make the assumption that the steady-state heat is assigned to the formation of π-bonded ethylene. We can then estimate the frequency factor by assuming first order kinetics using the equation given below

$$\nu = \theta N_s \exp\left(\frac{-E_d}{RT}\right)$$

where ν is the frequency factor, E_d is the Arrhenius energy barrier, θ is the fractional coverage, N_s is the number surface atoms (1.3×10^{15} atoms cm^{-2}) T is the temperature and R is the gas constant. The rate can be calculated as the product of the molecular beam flux (1×10^{12} molecules cm^{-2} per 50 ms pulse) and the sticking probability at steady-state (0.25), and the saturation coverage is taken to be 0.5 ML. From these values, ν is estimated to be 2.3×10^{20} s^{-1} for the (1×1) phase (and 2.9×10^{20} s^{-1} for the hex phase), which is unreasonably high compared to the accepted values of the order of 10^{14} s^{-1}. It is therefore likely that this

Table 1
Average bond strengths for Pt–C bonds on various low index planes of Pt

Number of Pt–C bonds	Adsorbed species	Pt{111}	Pt{110}	Pt{100}-(1 × 1)	Average
4	C_2H_2	*	226	242	234
3	C_2H_3	238	237	*	234
2	$CHCH_3$	250	*	*	
2	C_2H_4	*	257	253	255

The Pt{111} and Pt{110}-(1 × 2) data [1,2,27] is included for a comparative study. An * indicates the absence of a C_xH_y species on the particular surface.

apparent steady-state regime correspond to the slow formation of carbon, as observed in previous studies [6,9]. Indeed when more ethylene was pulsed onto the Pt{100} hex and (1 × 1) surfaces, the sticking probability falls very slightly but continuously (above $\theta = 2.0$ ML), indicating slow decomposition or possibly the formation of a carbide-like phase [9]. It is unlikely to be simply attributable to adsorption–desorption steady-state, since the 'steady-state' heat evolved is about 135 kJ/mol. This is too high for significant desorption at 300 K, which is why we favour the slow formation of a carbide layer.

We summarise the heats of reaction which give rise to the two species on Pt{100}-(1 × 1) as follows:

1. $4Pt + H_2C=CH_2 \rightarrow Pt_2CH-CHPt_2 + 2 H_{(a)}$
   $\Delta H_1 = -305$ kJ/mol
2. $2Pt + H_2C=CH_2 \rightarrow Pt-CH_2-CH_2-Pt$
   $\Delta H_2 = -148$ kJ/mol

Here $H_{(a)}$ designates hydrogen atoms adsorbed on the surface and Pt denotes a surface Pt atom. Based on these reactions, the appropriate C–Pt bond dissociation energy for each species can be evaluated, as illustrated in the following example for the formation of quad-σ acetylene, in which each C atom forms two bonds with the surface:

ΔH_1 is obtained from the present work; the calorimeter measures the heat released during the time period of a gas pulse, i.e., 50 ms, and the half-life at 300 K for H adatoms is significantly longer than this [30–32]. The measured initial heat therefore refers to Eq. (1) corresponding to the retention of H atoms on the surface. The Pt–H bond dissociation energy is obtained from the heat of adsorption of H_2 on Pt{100} (82.4 kJ/mol), determined from the desorption data of Jackman et al. [11] and the dissociation energy for H_2 (436 kJ/mol) [33]. The C–H bond dissociation energy (412 kJ/mol) is the average bond dissociation energy while the C–C (376 kJ/mol) and the C=C (733 kJ/mol) bond energies, which are somewhat larger for C_2 species than longer hydrocarbons, are taken from ethane and ethylene respectively [33]. From the sum of these enthalpy changes, we obtain

$$\Delta H_1 = -376 + 733 + 2(412) - 2(259)$$
$$- 4D_{(Pt-C)} = -305$$
$$D_{(Pt-C)} = 242 \text{ kJ/mol}$$

where $D_{(Pt-C)}$ is the average platinum–carbon bond strength. For quad-σ acetylene on Pt{100}-(1 × 1), the C–Pt bond dissociation energy is estimated to be 242 kJ/mol. This procedure is approximate, as it is based on the use of average bond dissociation energies and the assumption that Pt–Pt and C–H bond energies are unaltered by adsorption. In the same way, the C–Pt bonds for the other species on the (1 × 1) phase are evaluated and are summarized in Table 1. The values obtained for Pt{111} are included for comparison.

5. Conclusion

The coverage-dependent heats of adsorption of ethylene on Pt{100}-hex and Pt{100}-(1 × 1) surfaces have been investigated by SCAC at room temperature, and correlated with the

chemical reactions which occur on the surface. Initially, a highly coordinate species is generally observed, but at high exposures di-σ ethylene is probably formed before a steady-state situation is attained where ethylene adsorbs and desorbs reversibly. From these data we were able to determine the average C–Pt bond dissociation energy for di-σ ethylene, =HC–CH= and CH_3–C$\equiv$ on the Pt{100} single crystal planes. These bond dissociation energies decrease systematically from 247 (for H_2C–CH_2) to 226 (for C_2H_2 species) kJ/mol as the number of bonds per molecule increases from 2 to 4. A weakening of the average bond strength with increasing bond number is not surprising, particularly since bonding to a metallic surface mediates charge distributions very efficiently. Based on work of this nature, the formation of a database for average bond dissociation energies of carbon on transition metal surfaces should enable predictions to be made about the behaviour of chemical reactions on single crystal surfaces.

Acknowledgements

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