Energetics and Kinetics of Step-Terrace Adsorbate Distribution: C_2H_2 on Pt{211}

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Abstract: The availability of simultaneous measurements as a detailed function of surface coverage of both the sticking probability and the differential heat for adsorption on a stepped surface provides a means of analyzing the coverage-dependent adsorbate distribution on a stepped surface. For C_2H_2 on Pt{211}, the initial heat of adsorption is measured as 270 ± 10 kJ mol^{-1} and the initial sticking probability is 0.84. On the basis of previously measured Pt−C bond strengths for adsorbates and steric considerations, it is concluded that at all coverages vinylidene is formed on the surface at 300 K. At low coverages step sites are preferred, where the adsorption heat is 280 kJ mol^{-1}, with a Pt−C bond energy of 255 kJ mol^{-1}. The terrace sites are occupied at higher coverages with an estimated adsorption heat of $\sim$210 kJ mol^{-1} and Pt−C bond energy of $\sim$220 kJ mol^{-1}. Sticking probabilities on step and terrace sites are estimated as 1 and 0.78, respectively, at low coverage.

1. Introduction

The adsorption of hydrocarbons such as C_2H_2 and C_2H_4 and the associated dissociation processes involved on single-crystal transition-metal surfaces have long been of central interest. This is particularly due to their relevance to many industrial processes that involve hydrocarbons; Pt plays an important role as a catalyst for hydrocarbon hydrogenation and dehydrogenation reactions.

However, industrial catalysts are not readily comparable to the low-index single-crystal surfaces commonly used in surface science. They are typically rough, with many steps, kinks, and defects. Extending the studies of hydrocarbon adsorption to stepped surfaces is thus an important development and greatly contributes to a more general understanding of the underlying concepts of hydrocarbon adsorption and reaction in general.

Perhaps the most important physical quantity for understanding the fundamentals of a particular surface reaction is the adsorption energy, which can be measured as the enthalpy change involved when a molecule bonds to a surface. For hydrocarbon adsorption, it is also possible to extract the metal−carbon bond energy. Single-crystal adsorption calorimetry (SCAC)[1−3] uniquely allows the direct measurement of the heat of adsorption for a broad range of adsorbates on almost any surface.

The results presented in this paper are the first measurements of calorimetric adsorption heats on a stepped surface. Pt{211}, or Pt[3(111) × (001)], exhibits three atom wide {111} terraces and one atom high steps of {100} character. Looking at the unit cell (Figure 1), the proportion of {111}-like atoms to {100}-like atoms is 2:1. The macroscopic {211} surface plane is rotated 19.47° from the {111} terrace planes. The [11$\bar{1}$] direction
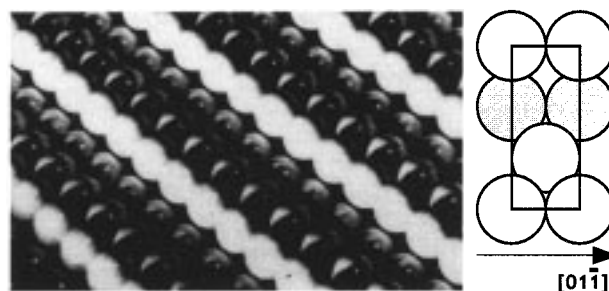

Figure 1. Schematic representation of the Pt{211} surface and the corresponding unit cell.

follows the macroscopic plane across the steps, and [$\bar{1}$10] follows the line of the steps and terraces.

There has been no previous study of the adsorption of C_2H_2 on Pt{211}. However, C_2H_2 adsorption on the long-range equivalent to the terrace sites, the Pt{111} surface, has been intensely investigated.[4−9] Somorjai and co-workers[9] recently found (partly in contradiction with previous investigations) that C_2H_2 adsorption at 125 K leads to the immediate formation of $\eta^2\mu_3$ vinylidene. Upon annealing, various other species are formed including vinylidene (the upright bridge-bonded Pt_2=C=CH$_2$ species) which is formed at $\sim$340 K. Avery[8] reports that adsorption of C_2H_2 on Pt{111} at $\leq$330 K produces $\eta^2\mu_3$ vinylidene, and at 330−400 K ethylidyne is produced. To our knowledge, no studies have been performed on the adsorption of C_2H_2 on Pt{100}, the macroscopic equivalent of the step sites. However, the adsorption of ethylene has been exhaustively

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investigated on this plane.[10–13] Hatzikos and Masel found that ethylene adsorbs molecularly at 120 K on both the hex and (1 × 1) phases, but upon heating the (1 × 1) phase, a mixture of vinylidene ($=C=CH_2$) and an acetylinic intermediate ($=CH-CH=$) was observed.[10] Fischer and Keleman[14] observed acetylene ($=CH-CH=$) at 300 K and vinyl ($-CH=CH_2$) and ethylene at 200 K.[10] C–C bond cleavage was principally not observed for the adsorption of C_2H_2 or C_2H_4 on Pt surfaces.

2. Experimental

The experiments were carried out in an ultra-high vacuum chamber with a base pressure of $\leq 7 \times 10^{-11}$ mbar, C_2H_2 was adsorbed at room temperature using a pulsed molecular beam[1] (50 ms pulse width, 2.5 s repetition period, ~8×10^{11} molecules per pulse). To achieve a measurable change in crystal temperature upon adsorption, the crystal heat capacity is kept low by employing single crystals that are approximately 200 nm thick. The temperature is monitored externally using a commercially available mercury cadmium telluride (MCT) infrared detector. Typically, the initial adsorption of a single pulse of gas leads to a temperature rise of ~0.1 K at the crystal surface with a s/n ratio of the amplified infrared signal of typically 100:1.

Parallel to the heat measurements, sticking probabilities were determined using the King and Wells method.[15] We use the term "apparent coverage" for the presentation; it refers to the coverage determination via integration of successive pulse-dependent sticking probabilities. Any species desorbing between pulses cannot be detected and will thus indefinitely extend the coverage scale when close to or at adsorption-desorption equilibrium. We stress, however, that the coverages are absolutely determined, and for coverages where the adsorption heat is ≥ 100 kJ mol^{-1} and the desorption rate is negligible, the coverage scale is accurate. We define the monolayer coverage as the adsorption of three C_2H_2 molecules per Pt{211} unit cell. The sticking probability and the adsorption heat measured at equilibrium state are referred to as the "steady state sticking coefficient" and the "steady state heat", respectively. A more detailed description of the experiment and principles can be found elsewhere.[1,2]

Cleaning of the Pt{211} crystal was achieved via Ar-ion sputtering at discharge currents below 8 μA and subsequent annealing to ~700 K. Crystal cleanliness and structure were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED).

3. Results

The experiment provides us with two sets of results, which are the coverage-dependent differential heat of adsorption (shown in Figure 2, top) and the coverage-dependent sticking probability (see Figure 2, bottom). The data points shown are the result of six experimental runs, and subsequent averaging of 40–50 similar data points. The error bars shown indicate the standard deviation corresponding to this averaging procedure. Looking at both curves, there are clearly three individual adsorption regimes at coverages of $0 \leq \Theta_1 \leq 0.15$ (first regime), $0.15 < \Theta_2 \leq 0.40$ (second regime), and $0.40 < \Theta_3$ (third regime). The distinction between the first and second regime at a coverage of about 0.15 is clearest when looking at the sticking probability curve. The value of the saturation coverage, however, cannot be read off easily, because of the apparent nature of the coverage measurement, which has considerable effect close to and at saturation. An exact determination of Θ_1, Θ_2, and Θ_3 will be carried out below, and it will become clear why saturation should occur at a coverage of around 0.40 ML.

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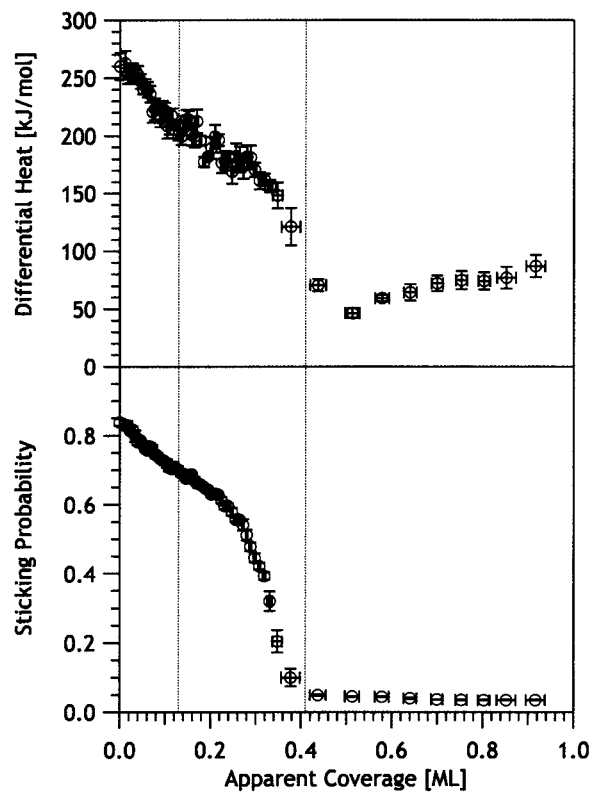(15) King, D. A.; Wells, M. G. *Surf. Sci.* **1972**, *29*, 454.

Figure 2. Measured differential heat of adsorption (top) and sticking probability (bottom) for C_2H_2 on Pt{211} as a function of adsorbate coverage at 300 K.

The third adsorption regime (dominated by reversible adsorption) sets in at a coverage of about 0.40 ML. We observe an increase in the differential adsorption heat for apparent coverages above 0.5 ML which is outside the experimental error bars. This could be due to the onset of surface carbidization. Similar behavior has been observed previously for the adsorption of hydrocarbons on various platinum surfaces.[10,12,13] The carbidization process is typically a very slow process, operating on a minute timescale, and we expect that this process is inhibited at low coverages by kinetic constraints. This distorts the heat and sticking probability measurements, both of which are sensitive only to processes that happen on a considerably shorter timescale of some 100 ms. If this is correct, the adsorption heat for the species formed in the third regime is increased by carbidization.

In the present paper, we concentrate on investigating the processes that determine the shape of the measured heat and sticking probability curves for the first and second adsorption regimes mentioned above. These regimes are separated by slope changes for both the heat and sticking probability plots at a coverage of ~0.15 ML. The initial heat of adsorption (linearly extrapolated to the zero coverage limit) is 270 $\pm$ 10 kJ mol^{-1}, and it falls linearly to 210 $\pm$ 10 kJ mol^{-1} at the end of the first regime. The initial sticking probability is 0.85, and it also falls approximately linearly to a value of 0.73 at the point where the slope change occurs. In the second regime, the differential heat of adsorption drops to its minimum value of 50 $\pm$ 5 kJ mol^{-1} ($\Theta = 0.5$ ML), this time in a nonlinear fashion. The sticking probability drops in a similar manner to its steady-state value of ~0.05.

4. Discussion

It is a well-established fact that adsorption on stepped surfaces can often be separated into two distinct adsorption processes,
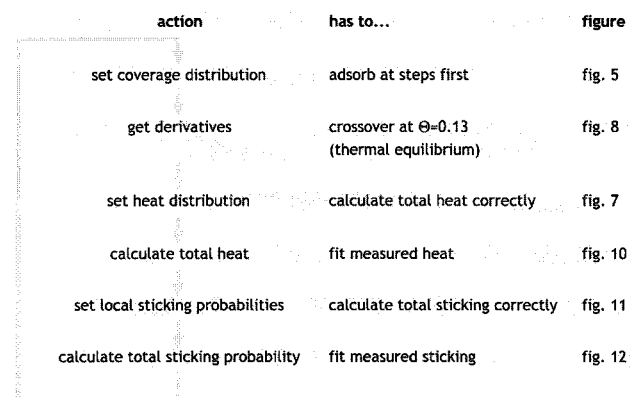
action	has to...	figure
set coverage distribution	adsorb at steps first	fig. 5
get derivatives	crossover at Θ=0.13 (thermal equilibrium)	fig. 8
set heat distribution	calculate total heat correctly	fig. 7
calculate total heat	fit measured heat	fig. 10
set local sticking probabilities	calculate total sticking correctly	fig. 11
calculate total sticking probability	fit measured sticking	fig. 12

Figure 3. Flow diagram illustrating the self-consistent procedure for the extraction of independent heat and sticking curves for step and terrace site adsorption.

indicating the sequential occupation of step and terrace sites (or sometimes in reverse order). Examples are the adsorption of Xe on Pd{810}, investigated by Wandelt, Ertl, and co-workers[16] or the adsorption of CO/Pt{211}, which was studied by Yates and co-workers[17] and Hayden et al.[18] If the stepped Pt{211} surface is viewed as being made up of two individual surface *types*, both having quite specific properties for the adsorption process, a description of the overall process as a superposition of the corresponding individual processes should be possible. We will show that this is possible for C₂H₂ adsorption on Pt{211} and also that almost all of the initial assumptions made can be confirmed via a self-consistent model.

Looking at the sticking probability (Figure 2, bottom), we observe a sharp linear drop until the "breakpoint" coverage of ~0.15 ML (about one-third of the saturation coverage) is reached. This breakpoint coverage suggests a simple correlation with the structure of the surface itself, for which terraces contribute two-thirds of the surface atoms and step sites contribute the remaining third. In the examples of adsorption on other stepped surfaces given above, the initial binding energy at the steps is significantly higher than at the terraces, favoring adsorption initially only at step sites. At some particular local step coverage, the binding energy advantage over the terrace sites will be insignificant (this particular transition regime being governed by Boltzmann statistics), leading to an even distribution between step and terrace sites of newly arriving adsorbates. For C₂H₂ on Pt{211}, exactly this seems to occur: for very low coverages, all of the incoming adsorbates bind to step sites, encouraged by the significantly higher binding energy at these sites. Only when the binding energy difference is low enough will adsorption on the terrace sites become favorable.

Despite the fact that there is no spectroscopic data available for this adsorption system, we will show that it is still possible to extract additional information by applying a self-consistent fitting and analysis procedure. Figure 3 shows a simplified schematic of how this was achieved. It is based on two arguments.

1. The initial adsorption is expected to occur mainly on step sites.

2. It is assumed that thermal equilibrium between step and terrace sites is established at a coverage of ~0.13 ML (the breakpoints of the measured sticking probability and heat

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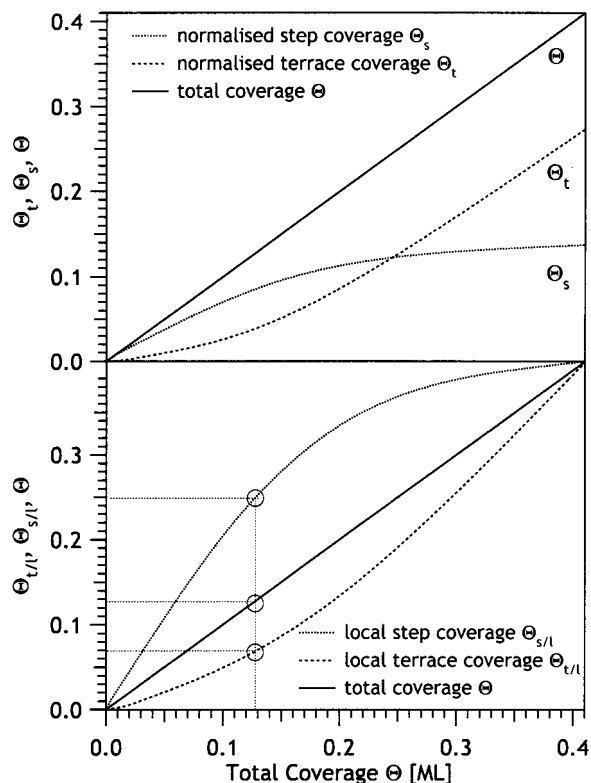(18) Hayden, B. E.; Kretzschmar, K.; Bradshaw, A. M.; Greenler, R. G. *Surf. Sci.* **1985**, *149*, 394.

Figure 4. Top: individual (step and terrace) empirically determined coverage curves as a function of overall coverage. Bottom: individual (step and terrace) empirically determined local coverage curves as a function of total coverage. The open circles and dashed lines refer to an example given in the text.

curves). From these two arguments, heat and sticking curves for the individual surfaces (step and terrace) are developed in a self-consistent manner, and the assumed initital coverage distribution is readjusted. This process was repeated until no further significant changes in the individual dependencies could be observed.

We proceed to analyze the data to obtain individual adsorption heats and sticking probabilities for step and terrace sites and the distribution of adsorbate on these sites as a function of total coverage. The fitting procedures are strongly constrained by the need to fit both the $q(\Theta)$ and the $s(\Theta)$ plots. Expressions for normalized step and terrace coverage are defined as follows:

$$\Theta_s = N_s/N_\Sigma \tag{1}$$

$$\Theta_t = N_t/N_\Sigma \tag{2}$$

so that

$$\Theta = \Theta_s + \Theta_t \tag{3}$$

Here, N_s and N_t are the densities of adsorbate species at step and terrace sites, respectively, and the total site density is $N_\Sigma = N_{\Sigma/s} + N_{\Sigma/t}$. $N_{\Sigma/s}$ and $N_{\Sigma/t}$ are the densities of step and terrace sites, respectively. The advantage of this definition is obvious. The ratio of step to terrace sites is accounted for by the coverage definition itself and will not have to be considered explicitly, e.g., in the calculation of the total coverage Θ.

With the observation stated so far, we can now make a first estimate of the distribution of the individual coverages Θ_s and Θ_t as a function of the overall coverage Θ. Figure 4 (top) reflects the adsorption kinetics to be derived below from the heat and sticking probability curves, based on the Boltzmann distribution.

At low coverage, virtually all of the adsorbate ends up on step sites, while terrace sites hardly get occupied. At some threshold coverage, the picture reverses, and once the step sites approach saturation, rapid occupation of terrace sites occurs (as seen for high total coverages). At saturation (0.41 ML), the relation of Θ_s to Θ_t simply reflects the availability of the total number of step and terrace sites. To illustrate the occupancy of step and terrace sites as a function of total coverage, figure 4 (bottom) shows the evolution of *local* (indicated with an additional index *l*) step and terrace coverage $\Theta_{s/1}$ and $\Theta_{t/1}$, which are defined as

$$\Theta_{s/1} = N_s/N_{\Sigma/s} \quad (4)$$

$$\Theta_{t/1} = N_t/N_{\Sigma/t} \quad (5)$$

and as a result of the step:terrace ratio of 1:2

$$\Theta = {}^1\!/_3\Theta_{s/1} + {}^2\!/_3\Theta_{t/1} \quad (6)$$

Obviously, this definition is equivalent to eqs 1−3.

4.1. Adsorption Heats. From the above arguments and observations, one should expect that the measured initial heat of adsorption is predominantly due to adsorption on step sites and should be close to the initial heat of adsorption on the steps. Furthermore, we expect this heat to be higher than the initial heat of adsorption for the terrace sites alone, and we expect a crossover point of step and terrace heat at a total coverage of around 0.15 ML. Figure 5 now shows the fitted set of adsorption heats $q_s(\Theta_{s/1})$ and $q_t(\Theta_{t/1})$ for the *individual* surfaces (step and terrace), as a function of their respective local coverages. Saturation on both phases occurs at 0.41 ML, and both heat curves show a shape typical for molecular adsorption. The result of the self-consistent procedure gives initial heats for step and terrace site adsorption of 280 and 210 kJ mol^{-1}, respectively.

To establish an expression for the total differential heat of adsorption we need to understand the additivity of $q_s(\Theta_{s/1})$ and $q_t(\Theta_{t/1})$ to give $q(\Theta)$. The latter is not just the sum of the individual heats but is weighted with the individual step/terrace contributions to the total heat release. As we are dealing with *differential* heats of adsorption, we need to look at the *incremental* coverage increase, i.e., the derivatives of $\Theta_s(\Theta)$ and $\Theta_t(\Theta)$. These are the weighting coefficients for the summation of the total heat, which is simply written as

$$q(\Theta) = \underbrace{q_s(\Theta_s)\frac{\partial\Theta_s}{\partial\Theta}}_{\bar{q}_s(\Theta)} + \underbrace{q_t(\Theta_t)\frac{\partial\Theta_t}{\partial\Theta}}_{\bar{q}_t(\Theta)} \quad (7)$$

The functions $\Theta_s(\Theta)$ and $\Theta_t(\Theta)$ are given in Figure 4 (top). Numerically differentiating Θ_s and Θ_t results in the curves shown in Figure 6 (bottom), and again $\partial\Theta_s/\partial\Theta$ and $\partial\Theta_t/\partial\Theta$ can be read off as a function of Θ. Now, the general shapes of the coverage plots in Figure 4 (top) become intuitively clear, because their derivatives have to intersect at the point where the individual adsorption heats for step and terrace sites are balanced, thus weighting the individual adsorption heat contributions with 50% each. Furthermore, additivity requires that

$$\partial\Theta_s/\partial\Theta + \partial\Theta_t/\partial\Theta = \partial\Theta/\partial\Theta \equiv 1 \quad (8)$$

which is a result of the relation between Θ_s, Θ_t, and Θ.

To obtain the theoretically determined heat of adsorption $q(\Theta)$ it is necessary to generate $\bar{q}_s(\Theta)$ and $\bar{q}_t(\Theta)$, the weighted contributions to the overall adsorption heat as a function of overall coverage (from eq 7). This is straightforward but,
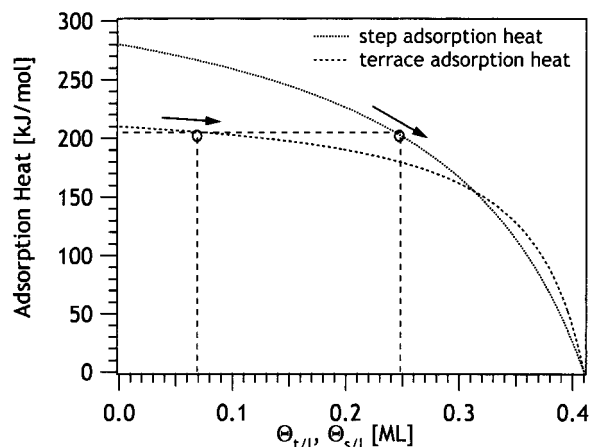

Figure 5. Individual (step and terrace) empirically determined heat curves as a function of local coverage. The open circles and dashed lines refer to an example given in the text. The arrows indicate the process of the incremental filling of local step and terrace sites.
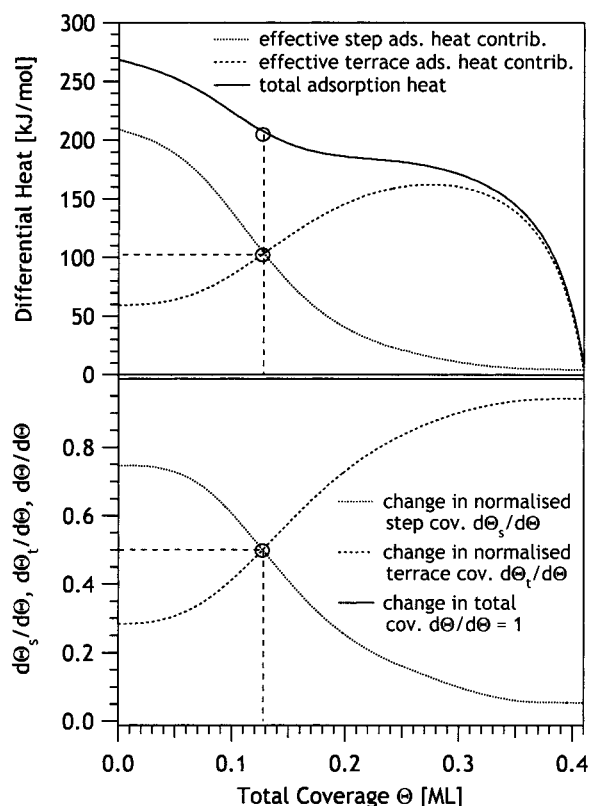

Figure 6. Top: individual and summed empirically determined heat curves as a function of overall coverage. The open circles and dashed lines refer to an example given in the text. Bottom: results of numerical differentiation of normalized coverage curves from Figure 4 as a function of overall coverage.

because of the number of quantities involved, can be confusing and misleading. We illustrate with two examples to show how these plots are generated. Let us extract $\bar{q}_s(\Theta = 0.13)$ and $\bar{q}_t(\Theta = 0.13)$, the individual heats for the breakpoint in the measured adsorption heat. We need first to extract $\Theta_{s/1}(\Theta = 0.13)$ and $\Theta_{t/1}(\Theta = 0.13)$ from Figure 4 (bottom, open circles). These local coverages can now be used to give $q_s(\Theta_{s/1})$ and $q_t(\Theta_{s/1})$ from Figure 5 (open circles). Here, the local heats are essentially the same, accounting for the fact that we are looking at the overall coverage where the Boltzmann term plays a significant role. The weighting coefficients for eq 7 can be read from Figure 6 (bottom). Obviously, at this total coverage the weighting for
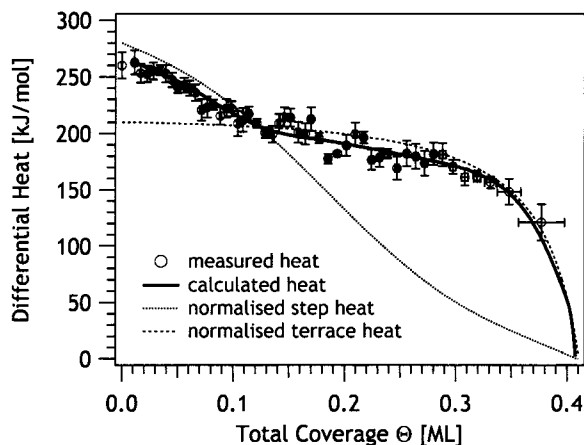
Step-Terrace Adsorbate Distribution: C₂H₂ on Pt{211}

J. Am. Chem. Soc., Vol. 121, No. 20, 1999 4849

Figure 7. Empirically determined differential heats of adsorption compared with the measured heat (open circles) as a function of overall coverage. The solid line represents the weighted sum of step and terrace heats.

adsorption onto the individual surfaces is identical (open circle). Finally, Figure 7 shows the results of putting all the terms together, plotting $q_s(\Theta)$, $q_t(\Theta)$, and the sum, $q(\Theta)$. The weighted contributions of terrace and step heats, $\bar{q}_s(\Theta)$ and $\bar{q}_t(\Theta)$, are shown in Figure 6 (top) for comparison.

The good agreement with the experimental data is not a coincidence. It is rather the result of applying a self-consistent procedure in which not only theoretical and experimental heat curves are reconciled but also the sticking probability data, as described below.

4.2. Sticking Probabilities. As for the differential heats, a similar procedure for the estimation of the individual step and terrace sticking probabilities s_s and s_t is applied. Again, looking at independent (local) quantities is helpful, as it is easier to develop step and terrace sticking probabilities separately.

However, it is important to note that the analysis procedure is not capable of extracting the instantaneous step and terrace sticking probabilities, but only those with respect to the final (equilibrium) adsorption states. It is therefore entirely possible that an incoming species initially adsorbs at a terrace site but then immediately diffuses to its final adsorption state at a step site, while the *instantaneous* sticking probability at the step site itself is zero. Only the partial sticking probabilities s_s and s_t corresponding to the *final* adsorption state are determined by this analysis.

Figure 8 shows the result of the self-consistent procedure for $s_s(\Theta_{s/l})$. The local terrace sticking probability is best fitted with a Kisliuk expression:[19]

$$s_t(\Theta_{t/1}) = s_t^0 \left(\frac{\Theta_{t/1}/\Theta_{t/1}^{sat}}{1 + \Theta_{t/1}/\Theta_{t/1}^{sat}} K \right)^{-1} \qquad (9)$$

where $\Theta_{t/1}^{sat} = 0.41$ is the local terrace saturation coverage, $s_t^0 = 0.76$ is the initial sticking coefficient for terrace adsorption, and $K = 0.29$ is the Kisliuk constant indicating the dominance of precursor mediation in the adsorption process. As for the heats, the individual local sticking probabilities also depend on each other to form the overall sticking probability expression, which then needs to be fitted to the actual measurement:

$$s(\Theta) = {}^1\!/_3 s_s(\Theta) + {}^2\!/_3 s_t(\Theta) \qquad (10)$$

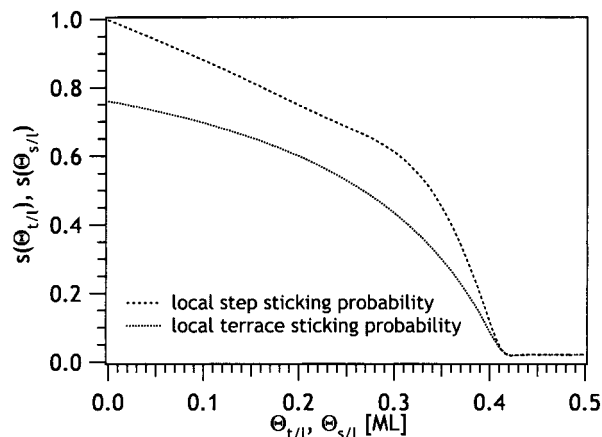(19) Kisliuk, P. *J. Phys. Chem. Solids* **1957**, *3*, 95.

Figure 8. Individual (step and terrace) empirically determined sticking probability curves as a function of local coverage.
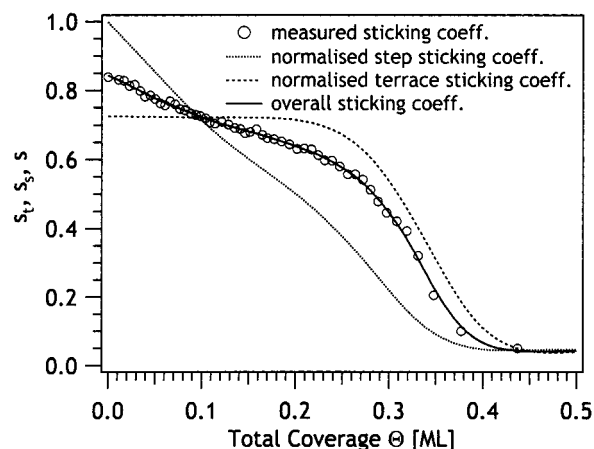
Figure 9. Empirically determined local sticking probabilities as a function of total coverage, compared with the measured sticking probability (open circles).

Here, the fractional weighting of the local sticking probabilities stems purely from one-third of the surface comprising step sites and two-thirds comprising terrace. Note that we are dealing with a molecular beam experiment, where all collisions are at normal incidence to the surface. Clearly, by a proper rotation of the crystal it is possible that the only sites visible to the molecular beam would be terrace sites. Diffusion plays an important role; as we have shown above, the adsorbate distribution between step and terrace sites is determined by Boltzmann statistics and not by kinetics.

The individual sticking probabilities as a function of total coverage compared with the measured sticking probability are shown in Figure 9. Assuming the Kisliuk fit to the local terrace sticking probability is a good one, the local step sticking probability can be easily derived from eq 10, using the measured overall sticking probability. Interestingly, plotted as a function of total coverage, the terrace sticking probability remains constant for coverages up to ~0.2 ML, whereas the step sticking probability drops in a practically linear fashion. Once the steps are almost completely filled at ~0.2 ML (refer to Figure 4, top), the decline of the step sticking probability steepens and soon the terrace sites also start to saturate. The linear drop in the step sticking probability at low step coverages is even more evident when looking at the local step sticking probability as shown in Figure 8, and this behavior has a simple explanation. On the Pt{211} surface, the steps are only one atom high but infinitely long, which means they essentially represent a one-
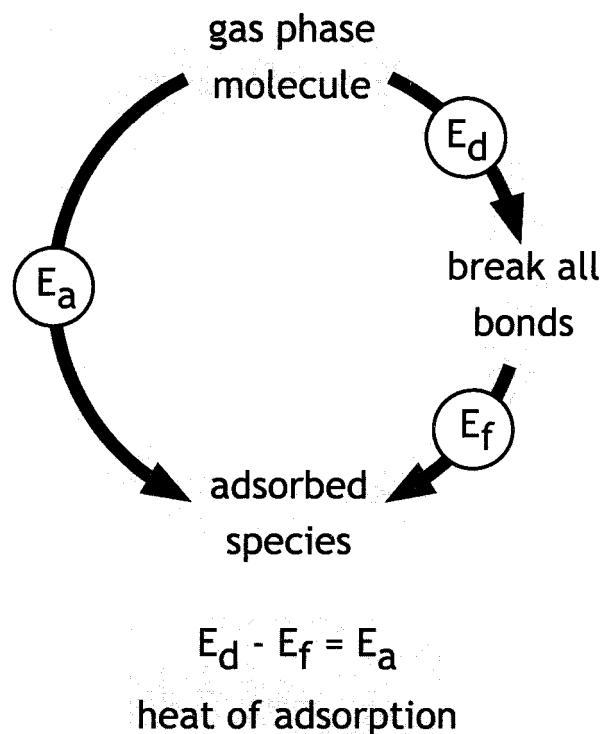
Figure 10. Schematic diagram for the determination of Pt—C bond energies (when spectroscopic data is available) and for the estimation of adsorption heats (when Pt—C bond energy is known).

dimensional surface. The sticking probability for nondissociative adsorption on such a "surface" is simply proportional to $(1 - \Theta)$.

4.3. Adsorbate Species and Bond Energies. To our knowledge, there is no spectroscopic data available for the adsorption of C_2H_2 on Pt{211}. This makes it initially difficult to associate specific adsorption heats or sticking probabilities with the presence of a particular surface species. However, a significant database for the adsorption of C_2H_4 on low-index Pt surfaces has been accumulated in the past, accompanied by the availability of adsorption heat data.[3] No matter what the surface coordination, the average Pt—C bond energy is constant for all surfaces: 242 kJ mol^{-1} for Pt{110}, 244 kJ mol^{-1} for Pt{111}, and 240 kJ mol^{-1} for Pt{100}.[3] Assuming that the Pt—C bond energy is also very similar for the Pt{211} surface, we can make some estimates of the actual species present, without having spectroscopic data to hand. To do so, we reverse the process by which Pt—C bond energies were previously calculated, using the so-called "average bond energy method" (abe method).[3]

The underlying principle is very simple and is illustrated schematically in Figure 10. When a molecular species is adsorbed at the surface, it has to rearrange to produce free bonds available for bonding to the substrate. Thus the adsorption process involves a sequence of bond-breaking and bond-making. Simply speaking, if one takes the free gas molecule, breaks all the individual bonds and reassembles the new species at the surface, then the difference between the energy needed to break all the bonds and the energy released when making all of the new bonds is the heat of adsorption. The individual bond strengths[20] and a Pt—H bond energy of 250 kJ mol^{-1} derived from a combination of the heat of adsorption of H_2 on Pt[21] and the dissociation energy of H_2 were used.

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Table 1. Expected Initial Heats of Adsorption for Various Species That Could Form upon Adsorption of C_2H_2 on Pt{211} at 300 K[a]

no.	species	bonds formed	formation energy	calc. heat
1	quad-σ HC—CH	C—C 2 (H—C) 4 (Pt—C)	376 2 (439) 4 (242) 2222	−436
2	ethylylidyne C—CH$_2$	C—C 2 (H—C) 4 (Pt—C)	376 2 (439) 4 (242) 2222	−436
3	vinylidene CH$_2$ C	C=C 2 (H—C) 2 (Pt—C)	733 2 (412) 2 (242) 2041	−255
4	2 (CH) H H C C	2 (H—C) 6 (Pt—C)	2 (412) 6 (242) 2276	−490
5	σ-bonded CCH, H C=CH H	Pt—H C=C H—C	250 733 2 (465) 2174	−388
6	di-σ HC=CH	2 (H—C) C=C 2 (Pt—C)	2 (465) 733 2 (242) 2147	−361
7	CH$_2$, C H H C C	2 (H—C) 6 (Pt—C)	2 (439) 6 (242) 2330	−544

[a] Values shown are in units of kJ/mol. The numbers calculated are based on a C_2H_2 total dissociation energy (gas phase) of 1786 kJ mol^{-1}.

We assume a set of reasonable species that could be formed upon adsorption on the basis of the following criteria:

1. Approximate agreement with initial heats of adsorption on step and terrace sites. Effects such as species already present at the step sites influencing the adsorption properties of species adsorbing at terrace sites are non-negligible.

2. Steric requirements exclude the formation of certain species.

3. Saturation coverages for step and terrace sites. Note that coverages are always expressed in terms of incoming gas molecules.

4. The presence (or absence) of certain species on other platinum surfaces can support arguments for the formation of certain species.

Table 1 shows a calculation of expected adsorption heats for a set of species that may form under the present conditions upon adsorption of C_2H_2 on Pt{211}. Breaking all bonds of the gas-phase C_2H_2 molecule requires 1786 kJ mol^{-1}. The expected heats need to be compared with the initial heats of adsorption determined for step and terrace adsorption, which are 280 and 210 kJ mol^{-1}, respectively. We look for possible species formed on the step sites first. From the corresponding adsorption heats, it seems unlikely that any of the species numbered 1, 2, 4, or 7 are formed, as their expected adsorption heats are almost a factor of two larger than the measured heat. Of the three remaining species, vinylidene is clearly favored, not only for the almost perfect match in adsorption heat—the step sites could actually
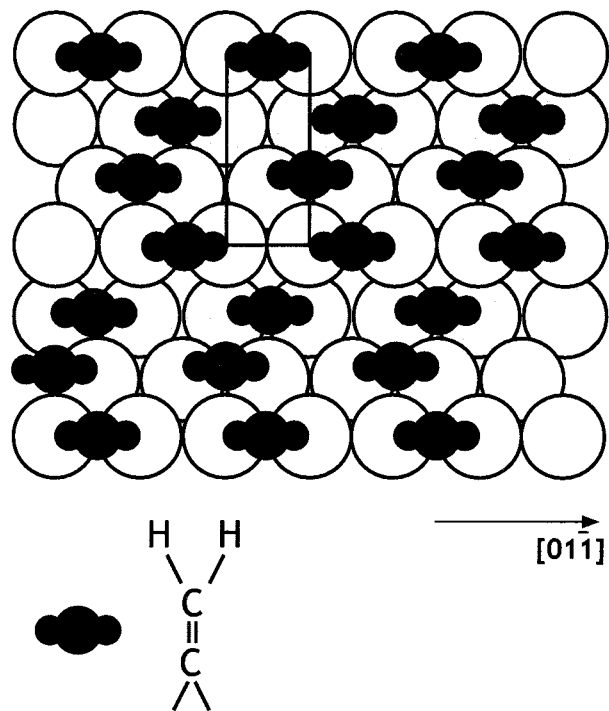
Figure 11. Proposed structure for vinylidene on Pt{211}, see text. The rectangle indicates the size of the Pt{211} (1 × 1) unit cell. Open circles represent step edge atoms, medium shaded circles are terrace through atoms, and dark filled circles are terrace plane atoms.

enhance the bonding (thus the observed higher adsorption heat)—but also because of all the proposed species this one seems to be the ideal candidate to bond to the steps, having an almost perfect match to the local saturation coverage of ~0.41; Figure 11 gives a possible structure. For the terrace sites, the situation seems even more clear. Again, the only sensible species is vinylidene. Again, the local saturation coverage matches nicely, as does the adsorption heat. This time, protruding step-vinylidene will introduce an adsorbate–adsorbate repulsion term, thus lowering the measured heat of adsorption. There is, however, still a discrepancy between the saturation coverage expected from the proposed model ($\Theta = 0.5$) and the actual measured values (~0.41). This, we argue, is mainly an effect of adsorbate–adsorbate interactions and steric hindrances which are at least in part due to the nature of the stepped surface.

With all this information at hand, we can now reverse the entire process and recalculate the actual Pt–C bond strength, assuming the named species are formed, using the empirically determined heats of adsorption for step and terrace adsorption. For the preferred case, formation of vinylidene on step and terrace sites, and the initial heats of adsorption of $q_0^s = 280$ kJ mol⁻¹ (step) and $q_0^t = 210$ kJ mol⁻¹ (terrace), the calculation yields a Pt–C bond energy of 255 kJ mol⁻¹ for step site adsorption and 220 kJ mol⁻¹ for terrace adsorption. Unlike the

findings for the determination of metal–carbon bond energies for the adsorption of hydrocarbons on Pt{100}, Pt{110}, and Pt{111}, the Pt–C bond energy is not a constant but seems to vary with the coordination of the individual surface atom. From an energetic point of view, this is not surprising, as the step atoms on Pt{211} are highly unsaturated leading to a Pt–C bond energy of 10 kJ mol⁻¹ above average, whereas for the subsequent adsorption on the terraces the bond energy is some 20 kJ mol⁻¹ below the value for the macroscopic equivalent Pt{111}. The latter observation, however, could be due to the influence of species already present at the step sites; lateral interactions between these species and the adsorbate forming on the terraces could lead to a reduced Pt–C bond strength for the latter.

From Table 1 we note that vinylidene is not the most stable species that could be formed from C₂H₂ on a Pt surface. Of the species shown, $C_2 + CH_{2a}$ has the highest heat release, but of course the entropy gain in producing gaseous H₂ would mean that the most stable is adsorbed carbon. We conclude that vinylidene is a readily accessible metastable state, with kinetic constraints preventing its transformation to other more stable species, at least at temperatures up to 350 K.[9]

5. Summary and Conclusions

We have presented the first heat of adsorption data for the adsorption of C₂H₂ on a stepped surface. Although there is to date no spectroscopic data for the adsorption of C₂H₂ on Pt{211}, we are able to deduce the nature of the species formed upon adsorption as a function of coverage from estimates of adsorption heats for all plausible species. With the aid of steric and thermodynamic arguments, predictions about the coverage-dependent evolution of step and terrace coverage have been made, and individual (step and terrace) heat of adsorption and sticking probability curves have been assigned. Our model predicts that adsorption occurs on the steps first and then increasingly proceeds on the terraces. Comparing the local step and terrace heats of adsorption derived by this procedure with the calculated heats, we suggest that vinylidene is the only species to be formed over the whole coverage range (this finding agrees with the adsorption of C₂H₂ on Pt{111}, where vinylidene is formed immediately upon adsorption even at 125 K[9]. Applying the reverse procedure provides the actual Pt–C bond strength for step and terrace site adsorption which was determined to be 255 and 220 kJ mol⁻¹, respectively, assuming vinylidene is the species formed on Pt{211}.