

The C–H···M Interaction and Reactivity Differences of *n*-Octane on the (1×1) and (5×20) Surfaces of Pt(100)

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The interaction and reactivity of *n*-octane adsorbed on the (1×1) and (5×20) surfaces of Pt(100) have been examined by reflection–absorption infrared (RAIRS), temperature-programmed reaction (TPRS), and Auger electron (AES) spectroscopies and by low-energy electron diffraction (LEED). A strong C–H···M interaction between the adsorbate and the metal was present on both surfaces at 100 K, as evidenced by the presence of “softened modes” in the C–H stretching region of the vibrational spectra centered at ~2630 and 2750 cm⁻¹ for the (1×1) and (5×20) surfaces, respectively. The softened modes observed for *n*-octane on the (5×20) surface of Pt(100) are reminiscent of those seen when this molecule is adsorbed on Pt(111). On both of these surfaces (Pt(100)-(5×20) and Pt(111)) the molecule adopts an all-trans conformation and is adsorbed so as to align the plane of the C–C–C framework parallel to that of the surface. This organization leads to a series of bands appearing in the 2500–2840-cm⁻¹ region which result from the high-symmetry C–H···M contacts occurring between the *n*-alkane overlayer and the underlying hexagonal symmetry surfaces. The softened modes observed for an overlayer of octane on the unreconstructed (1×1) surface at low temperature, however, were broad and featureless. Relative to the case for the Pt(100)-(5×20) surface, the activity for the dehydrogenation of an overlayer of *n*-octane was much greater on Pt(100)-(1×1). These reactivity differences appear to be weakly correlated with the nature of the mode-softening seen in the low-temperature vibrational spectra.

Introduction

A central motivation of research on adsorbate–metal interactions is the hope that such studies might help elucidate the mechanistic bases of processes important in heterogeneous catalysis. Toward this end numerous spectroscopic and physical/kinetic methods have been employed to study such interactions at the fundamental level. Of particular interest in recent research are the observations that the interactions of hydrocarbon adsorbates with a variety of metal surfaces often lead to strong perturbations of the vibrational spectra.^{1–19} These per-

turbations are evidenced as strong red-shifts of the C–H vibrational modes for those segments of the adsorbate experiencing direct contacts with the surface. What remains unclear from the work conducted to date is whether these perturbations (and their spectroscopic indicators) carry any predictive qualities, viz. the reactivity patterns evidenced in the system. For example, does a strong red-shift of a particular C–H stretching mode indicate the existence of an agostic C–H···M interaction? Does such an interaction, if indeed one is present, suggest a propensity of the molecule to undergo C–H bond activation at a specific site? The present work is concerned with such questions.

Using reflection–absorption infrared spectroscopy (RAIRS), we have previously shown that there exist two general types of C–H stretching modes which are distinguished by the magnitude of their C–H···M interaction when a monolayer of *n*-alkane such as *n*-octane is adsorbed on a clean Pt(111) surface.⁹ Generally, those C–H bonds that contact the surface experience a far greater perturbation than those projecting away from the surface. This noncovalent bonding interaction (C–H···M) has a dramatic effect on the near-surface C–H oscillators in that their vibrational frequencies are substantially red-shifted. Because of the large frequency shift involved, this interaction also decouples the motions of the near-surface C–H oscillators from those of the other C–H groups in the adsorbate.

Linear hydrocarbons form ordered overlayers on Pt(111).²⁰ The chains in these overlayers form a structure in which the plane defined by the C–C framework of an all-trans chain aligns parallel with that of the surface. The simplicity of this structure makes the identification

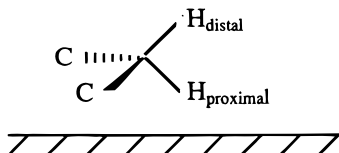
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and assignment of the various types of C–H stretching modes seen in their RAIR spectra straightforward.^{9,14,20,21} On each methylene group, for example, one C–H bond projects toward the surface and the other projects away from it (these will hereafter be referred to as the C–H_{proximal} and C–H_{distal} bonds, respectively). These arrangements are shown schematically below.

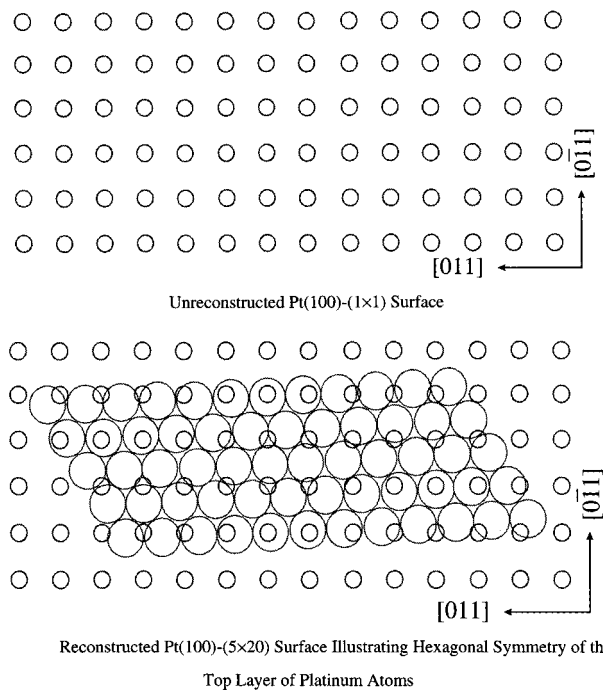


In the RAIR spectrum of an overlayer of *n*-octane on Pt(111), an intense band due to the C–H_{proximal} stretching motions of the methylene groups is seen at ~2760 cm⁻¹.⁹ This “softened mode” is an extremely sensitive marker of the site symmetry of the C–H···M interaction (although the precise structural nature of this dependence is still incompletely understood).^{9,14} For the commensurately ordered monolayer, the line width of this softened mode is unusually narrow (fwhm ≤ 50 cm⁻¹).^{2–8,12,13,16–18,22} The C–H_{distal} stretches of the methylene groups (although still slightly red-shifted) appear in a more normal region for C–H stretches (~2900 cm⁻¹). The assignments for the C–H stretching modes of the methyl groups follow in a similar fashion (i.e. there is a low-frequency feature that arises from the C–H_{proximal} stretching motions and modes that fall in the “normal” C–H stretching region due to the C–H_{distal} oscillators).^{9,14}

There are still many aspects of the adsorbate–substrate interaction leading to mode-softening which remain poorly understood. It is unclear, for example, which type of high-symmetry interaction leads to the narrow line widths of the soft modes seen for *n*-alkanes on Pt(111). Present evidence suggests that this C–H···M interaction may involve binding at atop sites.^{10,11,15} Perhaps more important, though, is the possible correlations which may exist between the mode-softening and the reactivity of the system. For example, cyclic hydrocarbon adsorbates such as cyclohexane on Pt(111) show soft modes with significant intensities and line widths in both the HREEL and RAIR spectra.^{2,4,5,8,13,17} In all cases where temperature-dependent studies were performed, it also was noted that these adsorbates demonstrate a significant propensity toward low-temperature C–H bond activation on the surface (typically around 200 K).^{2,13,23} Interestingly, measured activities for C–H bond activation were highest for cyclohexane.^{2,13,24} These findings thus suggest that a direct correlation exists between mode-softening and the propensity of the adsorbate to undergo C–H bond cleavage. Recent studies, however, suggest that such correlations may not hold generally.^{22,25,26}

We describe here a study which examines the nature of the interactions and reactions exhibited by an *n*-alkane adsorbed on a Pt single-crystalline substrate expressing different surface reconstructions. The structures and

Scheme 1. (top) Unreconstructed Pt(100)-(1×1) Surface. (bottom) Reconstructed Pt(100)-(5×20) Surface, Illustrating the Hexagonal Symmetry of the Top Layer of Platinum Atoms



reactivities of overlayers of *n*-octane on two Pt(100) surface structures ((1×1) and (5×20)) are explored and the results are compared to those found on the hexagonal surface of Pt(111).^{9,14} We show that an apparently isostructural overlayer, comprised of a close-packed assembly of all-trans chains, forms on each of these substrates. The chains lie on the surface with the plane of their carbon backbones aligned parallel to that of the surface. Because of the differing symmetries of the underlying substrate atoms, a systematic perturbation of the structure of the C–H···M contacts is effected across the series, one correlating strongly with the nature of the mode-softening seen. The effects of these variations on the temperature-dependent structure and reactivity are examined by a combination of reflection–absorption infrared (RAIRS), Auger electron (AES), and temperature-programmed reaction (TPRS) spectroscopies, as well as by low-energy diffraction (LEED).

The Pt(100) substrate provides a unique test bed for such a study in that it affords two completely different surface structures depending on the preparation conditions used (Scheme 1).^{27–30} To minimize its surface free energy, the Pt(100) surface reconstructs to give a so-called (5×20) surface.³⁰ In this structure, the surface atoms adopt a near hexagonal symmetry, one very similar to that found on the Pt(111) surface (see Scheme 1). The complex LEED pattern of this structure is indexed to a

$$\begin{bmatrix} n & -1 \\ 1 & 5 \end{bmatrix}$$

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unit cell using matrix notation ($n = 12-14$).^{30,31} Due to the mismatch of the positions of the topmost atoms with those of the underlying substrate lattice, the (5×20) surface also exhibits a significant corrugation (i.e. the top layer atoms must have different registries and therefore different heights with respect to the underlying square-net). The amplitude of the displacement of Pt atoms on the (5×20) surface has been measured by means of scanning tunneling microscopy,³²⁻³⁵ and corrugations in the $[1\ 5]$ and $[n-1]$ directions have been estimated to be as large as 0.4–0.7 Å. It is expected that the corrugation of the (5×20) surface should lower the symmetry of the C–H···M interactions for an n -octane overlayer relative to an analogous structure commensurately bound on a Pt(111) surface. This effect should be weaker, however, than that occurring on the unreconstructed (1×1) surface, since this surface symmetry prevents the formation of a comparably organized set of high-symmetry C–H···M contacts. As shown below, these structural changes are also attended by dramatic differences in both the spectroscopic markers of the C–H···M interaction (i.e. the soft modes) and the propensity of the adsorbate to undergo C–H bond activation. These differences are described below.

Experimental Section

The ultrahigh vacuum (UHV) chambers used in this work have been described previously; only a summary description is given here.³⁶ The temperature-programmed reaction (TPR) and reflection-absorption infrared (RAIR) spectroscopic studies were performed in a stainless steel chamber equipped with turbomolecular and titanium sublimation pumps, an ion-sputtering gun (PHI), a Vacuum Generators SXP 300 mass spectrometer, and a CMA Auger electron spectrometer (PHI). The base pressure was $<4 \times 10^{-10}$ Torr. A Digilab FTS 60A spectrometer with a broad-band, liquid-nitrogen-cooled, MCT detector was used to collect the RAIR spectra. Each single-beam spectrum represents 1024 scans at 4-cm^{-1} resolution, requiring a total signal collection time of ~ 7 min. The Pt(100) crystal was purchased from Aremco and was oriented to within 0.5° and polished to a fine mirror finish by standard metallographic techniques. The crystal was cleaned using argon ion-sputtering cycles (1-kV ions; $5\ \mu\text{A}$ at crystal) at 950 and 300 K (held for ~ 30 min at each temperature). Before each experiment, the crystal was sputtered for 15 min at 950 K and subsequently annealed at 1050 K. The crystal was then cleaned further by heating it at ~ 900 K in the presence of O_2 (1×10^{-6} Torr) for 3 min and then annealing it at 1050 K for 2 min. Surface cleanliness was established by Auger electron spectroscopy (detectable carbon < 0.5 atomic %).

The Pt(100)- (1×1) surface was prepared according to the procedure described by Bonzel et al.³⁷ Briefly recounted, this procedure involves dosing the clean Pt(100)- (5×20) crystal at 300 K with a saturation coverage of NO. The crystal was then heated to 470 K (1 K/s) and held at that temperature for approximately 1 min to dissociate the surface-bound NO (N_2 desorbs). This procedure was repeated, and then, finally, the oxygen was removed from the surface by exposing it to hydrogen gas at 300 K (~ 200 langmuirs). The crystal was annealed at 390 K for approximately 15 s (to desorb excess hydrogen) and then quickly cooled to the desired temperature.

Hydrogen (99.995%) was purchased from Matheson and used as received. Octane was purchased from Aldrich and was

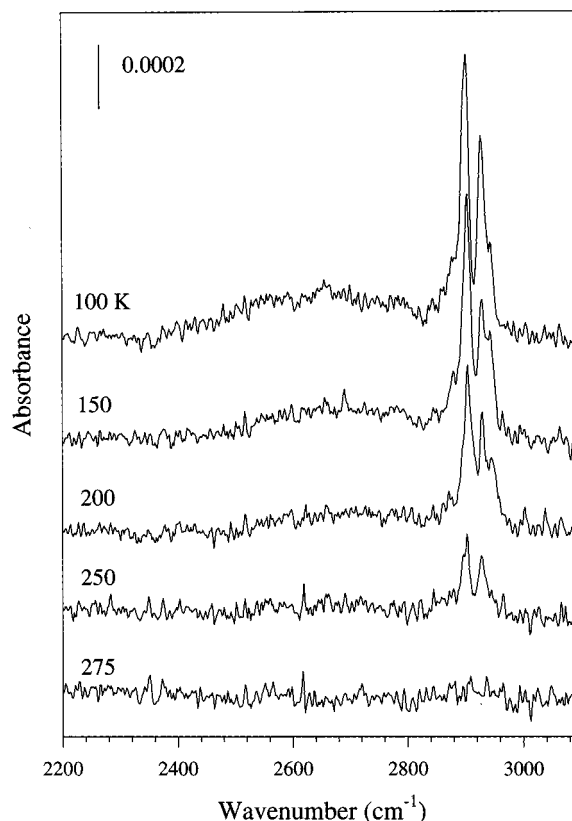


Figure 1. Reflection-absorption infrared spectra for a submonolayer coverage ($\theta_i \cong 0.75\theta_{\text{sat}}$) of n -octane adsorbed on the Pt(100)- (1×1) surface after being annealed at the following temperatures: 100, 150, 200, 250, and 275 K.

thoroughly degassed by a freeze/pump/thaw technique before being introduced into the chamber. All adsorbates and gases were introduced into the chamber through an effusive doser positioned ~ 5 cm from the crystal. Exposures, where given, have been normalized relative to saturation monolayer coverages (θ_{sat}); the latter were calibrated by means of RAIRS or LEED.

Results

Reflection-Absorption Infrared Spectroscopy (RAIRS). Octane on the Pt(100)- (1×1) Surface. The temperature-dependent RAIR spectra of submonolayer coverages of n -octane ($\theta_i \cong 0.75\theta_{\text{sat}}$) adsorbed on the (1×1) surface of Pt(100) are shown in Figure 1 (the corresponding mode assignments are presented in Table 1). The low-temperature spectrum collected at 100 K contains two sets of modes: a sharp set of features near and above 2900 cm^{-1} falling in the “normal” region for C–H stretching motions of the methylene and methyl groups and an extremely broad feature centered at $\sim 2630\text{ cm}^{-1}$. The latter feature, commonly referred to as a “softened mode”, is due to the stretching motions of the C–H bonds experiencing direct-metal-surface contacts (C–H···M).^{9,14} The broad, featureless line shape seen here (fwhm of $\sim 300\text{ cm}^{-1}$) is similar in character to those reported for a variety of cyclic hydrocarbons adsorbed on various transition metals and stands in marked contrast with the narrow line widths of the softened modes (fwhm’s $< 50\text{ cm}^{-1}$) seen for n -octane on Pt(111).^{2-5,8,9,12-14,16-18}

The spectra are consistent with an organization of the adsorbate in which the all-trans chains lie with the plane of the carbon backbones parallel with that of the surface. This conclusion follows most simply from an analysis of the modes appearing in the normal C–H stretching region

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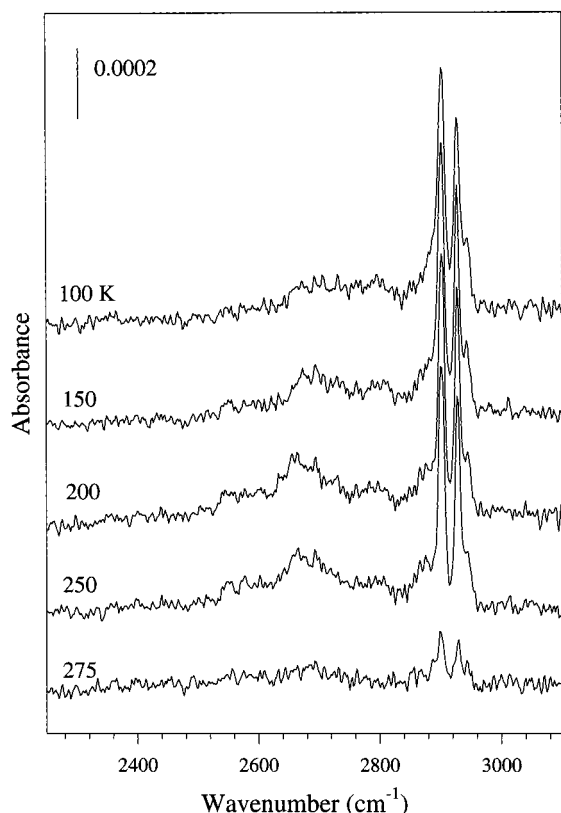


Figure 2. Reflection-absorption infrared spectra for a submonolayer coverage ($\theta_f \cong 0.75\theta_{\text{sat}}$) of *n*-octane adsorbed on the Pt(100)-(5×20) surface after being annealed to the following temperatures: 100, 150, 200, 250, and 275 K.

based on the “surface dipole selection” rule.^{38,39} The modes appearing in this region are not simple. The complex assignments for an analogous structure on Pt(111) have been described in detail in previous reports.^{9,14} On the basis of this literature precedent, we assign the bands seen at 2903, 2928, and 2943 cm^{-1} as follows: the 2903- cm^{-1} band originates from the C–H_{distal} stretches of the methylene groups while the bands at 2928 and 2943 cm^{-1} originate from the in-phase and out-of-phase stretching combinations, respectively, of the two C–H_{distal} bonds on the methyl groups. The chain length dependence of the intensity of the 2903- cm^{-1} peak (data not shown) confirms these latter assignments.

When the overlayer was annealed at 150 K, the soft mode and the bands appearing between 2900 and 3000 cm^{-1} all decreased in intensity. We show later that these changes signal the partial decomposition of the *n*-octane overlayer by means of thermally activated C–H bond scission. After the sample was heated to 250 K, it is clear that most of the adsorbed *n*-octane had either desorbed or decomposed. The data suggest that very little change occurs in the orientation of the *n*-octane molecules during this annealing process.

Octane on the Pt(100)-(5×20) Surface. The temperature-dependent RAIR spectra collected for a submonolayer coverage ($\theta_f \cong 0.75\theta_{\text{sat}}$) of *n*-octane adsorbed on the (5×20) surface of Pt(100) are shown in Figure 2 (mode assignments are given in Table 1). At 100 K, the spectrum in the C–H stretching region shows sharp C–H stretching features above 2900 cm^{-1} that are similar to those seen on the (1×1) surface. The spectrum also contains lower-

Table 1. Mode Assignments for *n*-Octane Adsorbed on the Following Surface Structures at 100 K

surface/conditions	softened mode	CH ₂ , $\nu(\text{C-H})$	CH ₃ , $\nu(\text{C-H})$
(1×1), clean	2630	2903	2928, 2943
(1×1), H ₂ predosed		2913	2947
(5×20), clean ^a	2683	2903	2928, 2945
Pt(111), clean ^a	2760	2903	2929, 2947

^a After annealing the overlayer at 200 K and recoiling to 100 K. This is the most intense feature in the softened mode envelope.

frequency components centered at $\sim 2750 \text{ cm}^{-1}$ due to softened mode(s). The data again suggest that the *n*-octane is organized in a fashion similar to that described above. As before, the bands at 2903, 2928, and 2945 cm^{-1} are assigned to the stretching motions of the C–H_{distal} bonds on the methylene and methyl groups (where the latter two bands originate from the C–H stretching motions of the methyl group).

Annealing the overlayer on the (5×20) surface at 200 K causes the soft mode to red-shift and become sharper. The major component, assignable to the proximal C–H groups of the methylenes,^{9,14} is now centered at $\sim 2683 \text{ cm}^{-1}$. Other soft modes falling in the region between 2500 and 2830 cm^{-1} (albeit weak) are also evident. The bands appearing above 2900 cm^{-1} also become narrower as a result of the annealing step. Taken together, the data suggest that annealing at temperatures near 200 K removes nonequilibrium organizational states present in the monolayer. The changes in the line widths suggest that a higher degree of bond orientational (and perhaps lateral) ordering exists in the annealed overlayer.

It has been shown in earlier studies that *n*-octane forms a commensurately ordered overlayer on the hexagonal Pt(111) surface.^{9,20} The (5×20) reconstruction of Pt(100) is remarkably similar to the Pt(111) surface in that the atoms of the top layer of the former adopt a near-hexagonal symmetry.^{29,30} The data suggest that *n*-octane adopts an organized habit on Pt(100)-(5×20) which is very similar to that seen on Pt(111). Annealing the assembly at even higher temperatures (e.g. 275 K) leads to large changes in the RAIR spectra, which suggest that the *n*-octane in the monolayer either reacts or desorbs into the gas phase.

To facilitate later comparisons, Figure 3 shows an overlay of RAIR spectra of *n*-octane monolayers adsorbed on Pt(111), Pt(100)-(5×20), and Pt(100)-(1×1) surfaces; the spectra were taken after annealing the overlayers at 200 K. Several similarities among the spectra are evident. Foremost among these is that the bands appearing in the region above 2900 cm^{-1} are very similar. This finding strongly supports the contention that the organizational states of the chains are similar on the three surfaces. Some differences are evidenced, however, especially in the line shapes of the softened modes appearing at frequencies below 2800 cm^{-1} . The trend evidenced here (and the data presented below) suggest that the intensities, red-shifts, and line widths of the soft modes seen in these spectra are directly correlated with the degree to which the overlayer adopts a precise set of high-symmetry C–H \cdots M contacts and the extent to which adsorbate decomposition reactions have generated other surface-bound species via C–H bond scission processes. The narrowest soft mode line widths are seen on Pt(111), where the commensurate overlayer adopts only a single structural type of metal contact. We defer further comment on these points to later.

Temperature-Programmed Reaction Spectroscopy (TPRS). In order to better understand the changes observed in the RAIR spectra, we have performed a series of temperature-programmed desorption/reaction studies

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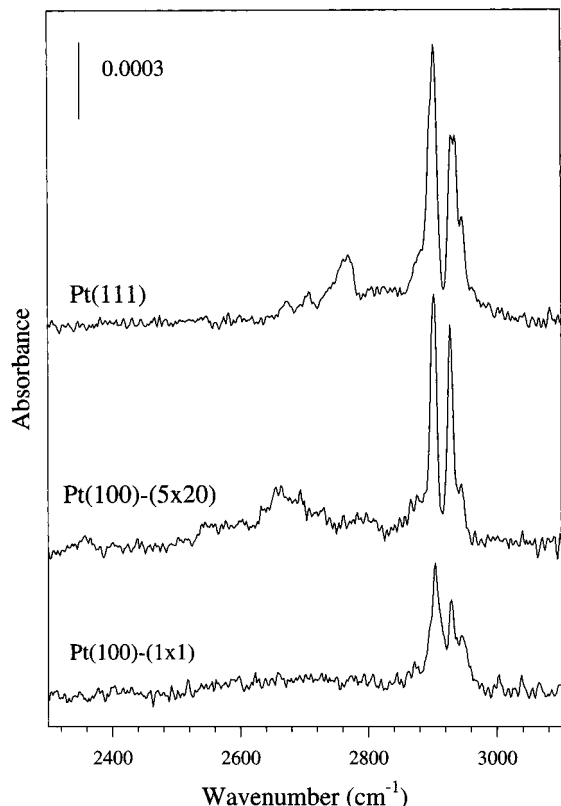


Figure 3. Reflection-absorption infrared spectra for sub-monolayer coverages of *n*-octane on the Pt(100)-(1×1), Pt(100)-(5×20), and Pt(111) surfaces. The RAIR spectra were collected at 100 K after annealing the overlayer at 200 K.

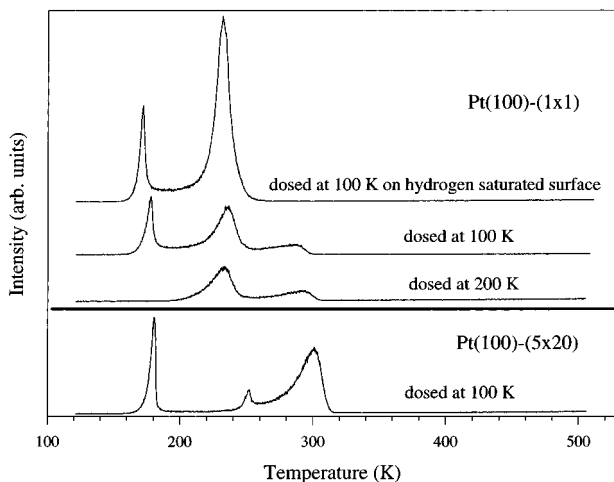


Figure 4. Temperature-programmed reaction profiles for a large coverage of *n*-octane ($\theta_i \lesssim 2.0\theta_{\text{sat}}$) adsorbed on either the (1×1) or (5×20) surface of Pt(100), monitoring the desorption of molecular octane (parent ion, $m/e = 114$).

for octane bound on the different Pt(100) surfaces. For ease of comparison and quantitative analysis, identical acquisition parameters were used to monitor the species desorbing from the two Pt(100) surfaces. Figure 4 follows desorption of the molecular ion of *n*-octane ($m/e = 114$), and Figure 5 follows the desorption of dihydrogen ($m/e = 2$). Survey spectra measured at other m/e values showed that no other products desorbed into the gas phase. In all the experiments, an octane exposure exceeding one monolayer ($\theta_i \lesssim 2.0\theta_{\text{sat}}$) was used in order to observe the multilayer desorption features. The data presented below demonstrate that some of the changes seen, especially for

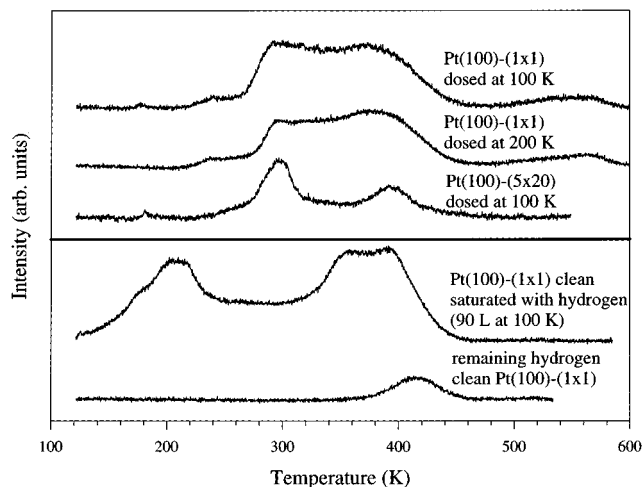


Figure 5. Temperature-programmed reaction profiles for a large coverage of *n*-octane ($\theta_i \lesssim 2.0\theta_{\text{sat}}$) adsorbed on either the (1×1) or (5×20) surface of Pt(100), monitoring the desorption of dihydrogen ($m/e = 2$).

overlayers adsorbed on the (1×1) surface, are correlated with the activation of the *n*-alkane by the substrate.

Molecular Desorption of *n*-Octane from the (5×20) and (1×1) Pt(100) Surfaces. The bottom TPR trace ($m/e = 114$) of Figure 4 shows that octane desorbs molecularly from the Pt(100)-(5×20) surface in primarily two temperature regimes. The lowest-temperature feature centered at 180 K does not saturate with exposure and thus arises from multilayer desorption. The feature at 300 K is for *n*-octane desorbing from a more tightly bound monolayer. We also observe an additional weak feature at ~250 K whose assignment is unclear from the data currently available. With the exception of this latter desorption feature, the $m/e = 114$ TPR spectra on the (100)-(5×20) surface and that on Pt(111) are remarkably similar; for the latter, desorption features are seen at 179 and 268 K (for the multilayer and monolayer states, respectively).

The three traces shown in the top panel of Figure 4 were obtained for overlayers of *n*-octane dosed on the (100)-(1×1) surface under three different conditions. As before, the low-temperature feature at 178 K is assigned to the desorption of the alkane from a multilayer. The two higher-temperature desorption features at 235 and 284 K are assigned to desorption of the alkane from two different bound states of the monolayer. In agreement with the RAIRS studies, most of the *n*-octane desorbs below 250 K, and very little remains on the surface above this temperature. The middle trace, taken for an identical exposure made at 200 K, demonstrates that the partitioning between the two bound states does not depend on the dosing temperature. The origin of the bound state that gives rise to the 235 K desorption feature on the (100)-(1×1) surface is easily understood by examining the top trace of Figure 4. This latter spectrum was obtained for a multilayer coverage of *n*-octane on a Pt(100) surface that had been previously saturated with hydrogen (a 90 L exposure of H₂ at 100 K was used). It is expected that the dissociatively adsorbed H₂ will either hinder or prevent the direct contact of the octane C–H bonds with the surface atoms of the metal (assuming that *n*-octane does not displace the hydrogen) and thus lower the binding energy of the *n*-alkane adsorbate. For a first-order desorption process, the ~50 K shift in the desorption maxima suggests that the adsorbed H reduces the binding enthalpy of the chain by ~3 kcal/mol (assuming a preexponential factor of 10¹³ s⁻¹).

A quantitative analysis of the data shown in the upper three traces of Figure 4 is enlightening. It is possible to estimate the total yield of the *n*-octane desorbing from the two monolayer states (on the non-hydrogen-treated (1×1) surface) by integrating the areas of these peaks and comparing them to that seen for the 235 K peak on the H-atom passivated surface. This analysis suggests that a substantial fraction of the monolayer on the nonpassivated surface (perhaps as much as 50%, as judged from the relative areas of the TPR traces) does not desorb molecularly. The data, therefore, suggest that the Pt(100)-(1×1) surface is very active toward the cleavage of the C–H bonds of *n*-octane, much more so than is either Pt(100)-(5×20) or Pt(111) (see below). It is important to note that the reactivity differences suggested here are only approximate and are mitigated by factors which cannot be eliminated from the experimental protocol. The most significant of these is the fact that the procedure used to prepare the (100)-(1×1) surface yields a substrate which still bears a small coverage of dissociatively adsorbed H₂. Under the best conditions (as judged from TPRS), we have been able to reach coverages of H with $\theta_H \cong 0.08\theta_{\text{sat}}$ (see below). Since adsorbed H passivates the (100)-(1×1) surface toward C–H bond cleavage, the reactivity differences described below likely underestimate the true activity of this surface in this prototypical reaction.

Desorption of Hydrogen from the (5×20) and (1×1) Pt(100) Surfaces. The bottom two traces of Figure 5 show the recombinative desorption of hydrogen from the Pt(100)-(1×1) surface both as prepared and after a 90 L exposure to H₂. The small amount of hydrogen which remains on the surface after preparation (desorption temperature at 415 K) is very similar to that reported in other studies.⁴⁰ It is believed that this small amount of hydrogen helps to stabilize the (1×1) phase at temperatures up to ~420 K (surfaces with little or no adsorbed hydrogen reconstruct to the (5×20) structure at very low temperatures).⁴¹ The H₂ desorption intensity seen when the (1×1) surface is saturated with hydrogen (90 L) is much greater (Figure 5, upper trace of the bottom panel), thus confirming that the amount of hydrogen retained on the as-prepared surface (bottom trace) is low.

The data shown in the upper panel of Figure 5 reveal that significant desorption intensity also is seen in the *m/e* = 2 channel when *n*-octane is used as an adsorbate. On the (100)-(5×20) surface two main desorption features are seen. The lower-temperature desorption feature ($T_{\text{max}} \cong 296$ K) overlaps the desorption feature seen in the *m/e* = 114 channel. Some portion of this peak is thus attributable to an electron-impact ionization cracking fragment of *n*-octane. The higher temperature desorption peak contains contributions from both hydrogen adsorbed from the background and a small degree of dissociative adsorption of the *n*-octane (see below).

The top two TPR spectra shown in the upper panel of Figure 5 were obtained when octane was dosed on a Pt(100)-(1×1) surface at either 100 or 200 K. Even a casual inspection of the data reveals that *n*-octane is activated and dehydrogenated to a significant degree on the (100)-(1×1) surface. This inference is strongly supported by the results of Auger electron spectroscopy studies which are described below.

Auger Electron Spectroscopy. Auger electron spectroscopy (AES) strongly supports the conclusion that an

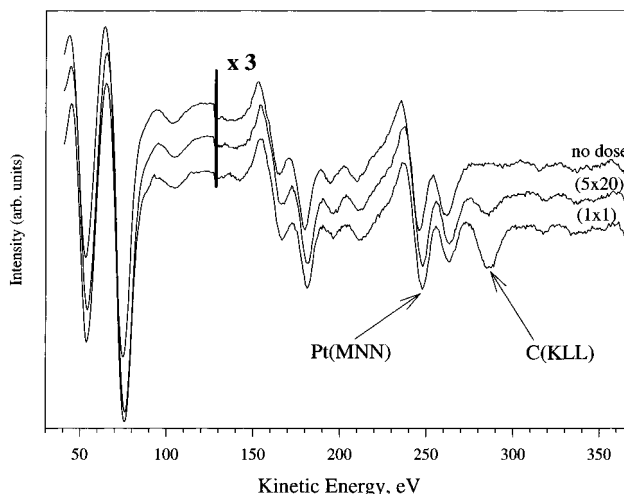


Figure 6. Auger electron spectra obtained after annealing a high coverage of *n*-octane ($\theta_i \cong 2.0\theta_{\text{sat}}$) at ~800 K on the (1×1) and (5×20) surfaces of Pt(100). The top spectrum is illustrated for a reference (annealing a clean surface with no dose to 800 K).

overlayer of *n*-octane has a higher propensity to undergo dissociative adsorption on the (100)-(1×1) surface than it does on either the (100)-(5×20) or (111) surface.⁹ Figure 6 shows the Auger electron spectra obtained after flash-annealing an overlayer of *n*-octane ($\theta_i \cong 2.0\theta_{\text{sat}}$) adsorbed on the (100)-(1×1) and -(5×20) surfaces at ~800 K. The spectra clearly show that a larger amount of carbon is deposited on the (1×1) surface. The control spectrum shown demonstrates that essentially no carbon is deposited via the electron beam or from interactions with the background gases. By measuring the intensities of the Pt(MNN) and C(KLL) Auger transitions, we can estimate the relative amounts of carbon present on the two surfaces (expressed as a Pt:C atomic ratio).^{24,42} The atomic ratios (Pt:C) calculated from the AES data are ~0.49 and 0.19 for the (1×1) and (5×20) surfaces, respectively. Using the structural data of Firment and Somorjai,²⁰ it is possible to estimate the amount of the densely packed monolayer that would need to be exhaustively dehydrogenated to give the carbon coverages seen by AES. Firment and Somorjai showed that, on Pt(111), *n*-octane densely packs in a commensurately ordered overlayer in which each chain occupies an area of ~60 Å². Since the organizational habits of the adsorbate on the two (100) surfaces appear to be very similar, we conclude that ~50% of the *n*-octane chains must exhaustively dehydrogenate on the (1×1) surface to give the carbon coverage seen by AES (and about 20% on the (5×20) surface). This latter conclusion is in complete agreement with a similar analysis made on the basis of the TPRS results.

Coverage and Temperature-Dependence of the Thermolytic Activation of *n*-Octane on Pt(100)-(1×1). To better understand the underlying reactivity of *n*-octane on the (1×1) surface of Pt(100), we have examined by RAIR spectroscopy the structure of the overlayer remaining after annealing a lower ($\theta_i \cong 0.75\theta_{\text{sat}}$) and higher ($\theta_i \cong 2.0\theta_{\text{sat}}$) coverage of *n*-octane to ~200 K (Figure 7). A small frequency region (2800–3050 cm⁻¹) is shown in an expanded format in order that the changes which occur in the positions and shapes of the C–H stretching bands can be more easily illustrated. The bottom two spectra were obtained for a submonolayer of *n*-octane (dosed on

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(41) Kuhnke, K.; Kern, K.; Comsa, G. *Surf. Sci.* **1995**, *343*, 44–52.

(42) Campbell, J. M.; Seimanides, S.; Campbell, C. T. *J. Phys. Chem.* **1989**, *93*, 815–826.

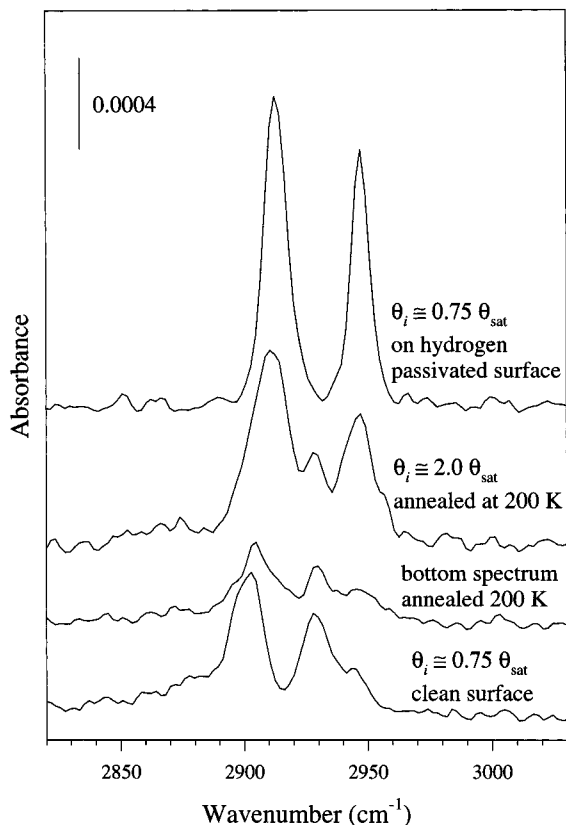


Figure 7. Reflection-absorption infrared spectra for *n*-octane adsorbed on differently prepared Pt(100)-(1×1) surfaces (all dosing was accomplished at 100 K). Annealing the bottom spectrum to 200 K and subsequently cooling to 100 K produce the second to the bottom spectrum.

the (100)-(1×1) surface at 100 K and then annealed at 200 K). These spectra suggest that, at this coverage, some fraction of the *n*-octane overlayer either desorbs or reacts by 200 K. The TPRS data shown below reveal that the latter is in fact the more important process. The character of the bands present in the 200 K spectrum suggests that a small amount of the *n*-octane overlayer is retained on the surface, as judged from the modes seen at 2905, 2930, and 2946 cm^{-1} (which are characteristic of *n*-alkane adsorbates experiencing direct C-H···M contacts). We do not see bands in the 200 K spectrum which can be assigned to an activated form of the adsorbate (as would arise from C-H bond activation). This suggests either that the fragmentation is very extensive or that it involves a binding geometry for the adsorbed species in which the intensities of the C-H modes in RAIRS are weak. At higher coverages, it is clear from the RAIRS data that some of the chains present in the monolayer after annealing reside on top of fragments derived from the decomposition of part of the adsorbate layer (recall that the multilayer desorbs below this limit at 178 K). On the basis of the correspondence with the spectrum taken for chains adsorbed on a hydrogen-passivated surface (upper trace of Figure 7), we believe that some fraction of the chains in the latter high-coverage, annealed sample reside on hydrogen-covered regions of the sample (with the latter adsorbate derived from partial decomposition of the *n*-octane).

To confirm that a part of the monolayer largely decomposes on (rather than desorbs from) the (100)-(1×1) surface, we acquired TPRS data for the $m/e = 114$ and 2 channels for these two coverages. The top two traces of Figure 8 monitor the molecular ion ($m/e = 114$) for

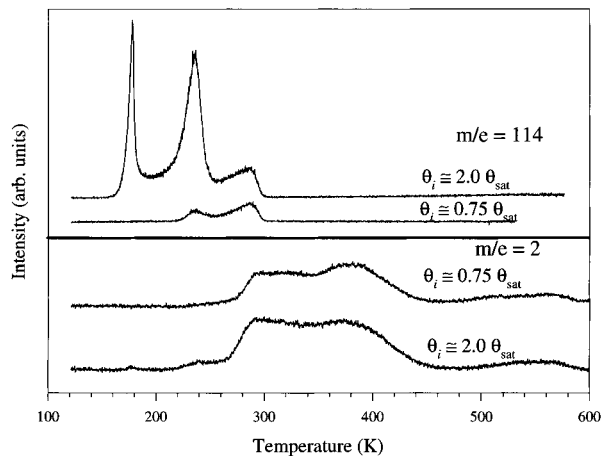


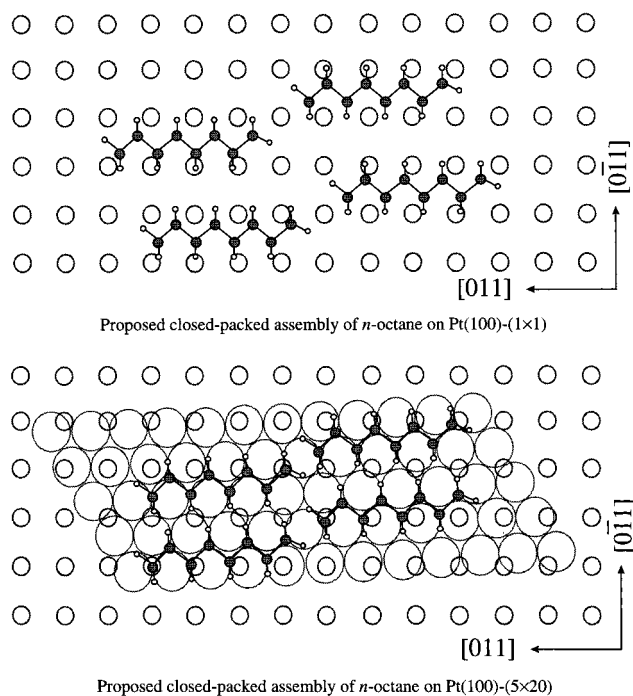
Figure 8. Temperature-programmed reaction spectra for *n*-octane at either high ($\theta_i \leq 2.0\theta_{\text{sat}}$) or low ($\theta_i \cong 0.75\theta_{\text{sat}}$) coverages adsorbed on the Pt(100)-(1×1) surface, monitoring either dihydrogen desorption (bottom panel, $m/e = 2$) or molecular desorption (top panel, $m/e = 114$).

n-octane. At the lower coverage, no desorption of the molecular species is seen below 200 K. Two small molecular desorption features are observed at 235 and 288 K in this experiment; however, the low intensities of these features relative to those of the high-coverage trace again confirm a significant fraction of *n*-octane fragments on the (100)-(1×1) surface (rather than desorbs).

The conclusions reached above are supported by data recorded in the $m/e = 2$ channel. As shown in the lower panel of Figure 8, hydrogen is produced as a result of the low-temperature fragmentation of the adsorbate. The hydrogen produced in these fragmentation processes combines and desorbs in a broad envelope between 275 and 450 K, leaving behind a significant quantity of surface-bound carbon. Only a slightly larger amount of dihydrogen desorbs from the surface when a high coverage monolayer of *n*-octane is present on the (1×1) surface. Taken together, the data presented in Figures 7 and 8 support an interpretation which suggests that the Pt(100)-(1×1) surface readily activates the C-H bonds of *n*-alkanes. It appears from the data currently available, especially the RAIRS spectra shown in Figure 7, that these reactions proceed at (or below) temperatures as low as 200 K.

Low-Energy Electron Diffraction. We have utilized low-energy electron diffraction (LEED) in order to understand in more detail the organizational aspects of the octane overlayers present on the various surface structures of Pt(100). These data confirm the formation of the stable (5×20) surface structure and the conversion of this reconstruction to the Pt(100)-(1×1) form by the treatment described in the Experimental Section. The LEED results obtained for overlayers of *n*-octane at saturation coverages largely confirm the structural conclusions reached by RAIRS (as discussed previously). LEED clearly shows that the *n*-alkane does not lift the (5×20) reconstruction at 100 K, nor does it lead to the reconstruction of the (1×1) surface at this same temperature. The LEED data also suggest that the *n*-alkane orders on the (5×20) surface. As discussed previously, this is expected, since the (5×20) surface structure is very similar to that of Pt(111), where a commensurately ordered overlayer is known to be formed.^{9,20} The character of the diffraction data seen here, however, was extremely poor, due in part both to the limitations of the chamber design and to the apparent extreme sensitivity of the overlayer to the electron beam. Low-current LEED studies will be necessary to clarify this structural aspect. The LEED data obtained for a

Scheme 2. (top) Proposed Closed-Packed Assembly of *n*-Octane on Pt(100)-(1×1). (bottom) Proposed Closed-Packed Assembly of *n*-Octane on Pt(100)-(5×20)



monolayer of octane on the (1×1)-(100) surface showed no evidence of long-ranged ordering.

Discussion

Structure of the *n*-Alkane Overlayer and the Nature of C–H···M Interaction on the Pt(100)-(1×1) and (5×20) Surfaces. Two interrelated issues must be considered in order to develop an understanding of the nature of the C–H···M interaction and the structural correlations which exist in the spectroscopic data characterizing it. Foremost among these is the nature of the organizational habits adopted by the *n*-alkane chains on the various Pt(100) surface structures. The second is the manner in which these chain structures interact with specific surface atom sites of the supporting substrate. Developing an understanding of both of these issues is made easier by the fact that the qualitative aspects of the chain structure adopted at low temperature (100 K) appear to be conserved features on both the (1×1) and (5×20) substrates. This assembly appears to pack densely in a manner directed by attractive intermolecular interactions on each substrate. The interaction with the substrate is too weak to effect a significant reconstruction of either the (1×1) or (5×20) surface structures. Thus, the adsorption of *n*-octane occurs on substrates whose surface atoms are arranged in a fashion nearly identical to that found on the clean substrates.

The structures shown in Scheme 2 are a geometric model of what we believe are likely high-symmetry arrangements adopted by a dense assembly of *n*-octane chains on the various Pt(100) surface structures. These structures differ only in the way in which the C–H bonds of the chain lattice project toward the surface atoms of the Pt(100)-(1×1) and -(5×20) substrates. The structures shown here were constructed so as to maximize the symmetry of the C–H···M contacts produced. The chain lattice shown in the scheme is taken from the earlier studies of Firment and Somorjai, who established by LEED the adoption of this organizational habit on the Pt(111) surface.²⁰ The

lattice spacings seen here are in fact very similar to those found in the bulk triclinic structure of the hydrocarbon and thus are entirely consistent with the organizational energetics of *n*-alkanes in such phases.⁴³

At first glance, the assumption that the low-temperature chain–lattice structure is similar on the (111) and (5×20)- and (1×1)-(100) surfaces must seem extreme. In point of fact, other data strongly support this assumption, at least along qualitative lines. The best insights as to the similarities of the orientational ordering come from RAIRS. On each surface, the chains adopt all-trans conformations and lie with their C–C–C planes parallel with the plane of the surface. It is this organization that gives rise to the characteristic “three”-peak pattern seen by RAIRS in the normal C–H stretching mode region between ~2890 and 2980 cm⁻¹. This state is a deeply bound one, since little evidence of conformational isomerism is noted up to the temperature where decomposition ensues or the chains desorb.^{9,20} The most important point to make from the RAIRS data, though, is that the coverages are also very similar on the three surfaces (as judged from the integrated band intensities measured in this specific frequency region at 100 K for a saturation coverage). This latter finding is somewhat surprising and not completely understood. Consider, for example, the ~4.8-Å interchain spacing shown in the scheme. This distance, while similar to that found in bulk phases, is not one of closest approach. In the bulk, such distances would not be stable in the absence of interactions occurring with chains in other planes of the three-dimensional structure. It seems likely that the Pt potential surface must serve an equivalent function, albeit one mechanistically very different from the steric interactions important in the bulk crystal structures of hydrocarbons.

The RAIRS data also show ways in which the organizations of *n*-octane differ on the (100)-(1×1) and -(5×20) surfaces. It is our belief that the nature of the C–H···M interaction is most sensitively reported by the mode-softening seen in the C–H stretching region of the RAIR spectra. It is clear, for example, that the intensities, line shapes, and multiplicities of soft modes present between ~2200 and 2800 cm⁻¹ are very different on the (1×1) and (5×20) surfaces. These differences in turn reflect on the different kinds of surface sites probed by the proximal C–H bonds. In a previous study, we showed that narrow soft modes are seen when the C–H bonds of the adsorbate interact primarily with the same high-symmetry surface sites.^{9,44} The line width of the soft mode increases markedly when a more diverse set of structural environments are involved in the C–H···M contacts.

In the present case, we believe that the registry of the adsorbate C–H bonds with the surface atoms is higher on the Pt(100)-(5×20) surface, whose hexagonal pattern resembles that of the Pt(111) surface. The low-temperature RAIRS data (≤200 K) for *n*-octane adsorbed on Pt(100)-(5×20) suggest that the ordering is substantially improved by annealing, especially at coverages of less than one monolayer. This implicitly suggests that island growth occurs on Pt(100)-(5×20) as it does on Pt(111). Even with annealing and careful control of the *n*-octane coverage (data not shown), it is also clear that the soft modes seen on the (100)-(5×20) surface never become as narrow as those found for well-ordered overlayers on Pt(111). We believe that this latter difference may be due

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(44) While it is known that the octane adsorbates form a commensurately ordered overlayer on Pt(111), it is not known which high-symmetry surface sites are involved in the mode-softening mechanism.

to the corrugation of the Pt(100)-(5×20) surface, a feature which must serve to lower the regularity of the interaction with the adlayer.

The softened mode envelope seen by RAIRS for a monolayer of *n*-octane adsorbed on Pt(100)-(1×1) is significantly broader (and more strongly red-shifted) than is that seen for a monolayer on Pt(100)-(5×20). Annealing (albeit limited by the reactivity seen on this surface structure) does not change the appearance of the softened mode seen for the former. Again, the data suggest that the line widths seen reflect the structural heterogeneity of the C–H···M interactions. Some uncertainty exists, viz. this latter point, though, given that the adsorbate appears to undergo C–H bond activation on this latter substrate even at temperatures below 200 K.

Reactivity of the Pt(100)-(1×1) and -(5×20) Surfaces toward *n*-Octane. As judged from both RAIRS and TPRS data, the Pt(100)-(1×1) surface is clearly more effective at activating the C–H bonds of *n*-octane than is the more stable (5×20) surface. Since no other volatile carbon-containing product is formed when the *n*-octane-dosed surface is heated, we believe that the principal pathway followed is an exhaustive thermolytic dehydrogenation of the hydrocarbon. This assumption is strongly supported by the AES data. Integration of TPR traces for dihydrogen desorption (*m/e* = 2) allows one to estimate the relative reactivities of the two surfaces. This analysis suggests that the (1×1) surface is more than twice as active toward C–H bond activation than are (5×20) surface structures. Auger electron spectroscopy confirms this finding. As judged by RAIRS, the fragmentation of the octane overlayer on the (1×1) surface has an unusually low activation energy and, given the high rates seen for this process below 200 K, may well have an activation energy below 12 kcal/mol.⁴⁵ The reaction on the (1×1) surface appears to be self-poisoning, since RAIRS indicates that the adsorbed octane is dehydrogenated until the surface becomes covered with a hydrogen/carbonaceous layer. This finding also has literature precedent, as previous studies of cyclohexane and ethylene adsorbed on Pt(100) also showed a larger propensity toward C–H bond activation on the (1×1) surface than on the (5×20) surface.^{22,26}

We close by considering the more qualitative correlations which seem to exist between mode-softening and the activity seen for C–H bond activation. The present study suggests that the facility of C–H bond activation for *n*-octane falls in the order Pt(100)-(1×1) > Pt(100)-(5×20) > Pt(111). The RAIR spectra shown in Figure 3 reveal that the most reactive surface also causes the greatest red-shift (and thus presumably the strongest interaction) and the largest line widths for the soft mode (for Pt(100)-(1×1), the component line widths of the soft modes are too broad to distinguish the contributions made by the methyl and methylene C–H bonds). The deeper meaning of this qualitative correlation, however, is not clear from the information currently available. The correlation we see is similar to one made by Raval et al., who examined the nature of the soft modes observed for

cyclohexane on various transition metal surfaces and who concluded that the magnitude of the mode-softening was directly correlated with the propensity for C–H bond activation.¹⁷ The importance of such correlations has not been universally embraced, however. For example, Lamont et al. were not able to establish a link between red-shifts of the C–H stretching bands and the facility of the bond cleavage process or its selectivity for cyclohexane on the surface structures of Pt(100).²² This controversy provides a focus for understanding this study in a broader context.

It is now clear that soft modes are a very sensitive probe of the C–H···M interaction, albeit one for which a detailed structural understanding is still lacking. One motivation which has inspired the study of this phenomenon has been the hope that such perturbations might have predictive value, viz. patterns of reactivity as well. It is sensible, after all, to expect that larger red-shifts might correlate with lower bond-activation barriers. We see in the present case, though, that the correlations with respect to both the energetics and selectivity are somewhat more complex than one would have hoped for. For example, we do not know which C–H bond in *n*-octane (methyl or methylene) is activated first on Pt(100)-(1×1) or on any other Pt surface for that matter. On Pt(111) it is possible to identify specific red-shifted components for the methyl and methylene groups for the commensurately ordered phase present at low temperatures. As the temperature is raised to promote reaction and the system passes through order–order and order–disorder phase boundaries, the red-shifted bands broaden and become difficult to detect. It may well be, given the sensitivity of the soft mode to the site-binding geometry, that only very specialized systems, ones with exceptionally hindered conformational dynamics, will allow the selectivity patterns to be examined. In conformationally rich systems, such as those examined here, the correlations made with reactivity will likely remain much more limited. Since the adsorbates can explore many conformations and sites during the time scale of a typical catalytic reaction, it may never be possible to make a correlation between the red-shift of a specific mode and the bonds which are activated. In the absence of an understanding of the underlying dynamics and how they affect adoption of adsorbate binding geometries more closely relevant to that of the rate-determining transition-state complex, the correlation will always be qualitative at best. Even so, the study of mode-softening remains an interesting topic especially if structural aspects of its mechanism can be resolved by diffraction techniques. Such studies would reveal such information as the sites (atop, bridge, etc.) which produce the largest red-shifts and possibly help develop a deeper structural understanding of the fundamental mechanisms involved in C–H bond activation on Pt. These understandings remain important but, still, unrealized research goals.

Acknowledgment. The support of the Department of Energy (Grant DEFG02-91-ER45439) through the Seitz Materials Research Laboratory of the University of Illinois at Urbana-Champaign is gratefully acknowledged.

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(45) This assumes that the kinetics follow a first-order rate law and that the pre-exponential factor is $\sim 10^{13} \text{ s}^{-1}$.