# Adsorption of Cyclohexane and Benzene on Ordered Sn/Pt(111) Surface Alloys

Chen Xu, Yi-Li Tsai, and Bruce E. Koel\*

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482 Received: June 30, 1993; In Final Form: October 18, 1993\*

Cyclohexane conversion to benzene over bimetallic Pt catalysts is an important prototypical reaction for fundamental studies of selective catalytic dehydrogenation catalysis. We have studied the adsorption and dehydrogenation of cyclohexane and benzene on Pt(111) and two ordered Sn/Pt(111) surface alloys using temperature-programmed desorption (TPD), Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS), and sticking coefficient measurements. Vapor-depositing Sn on the Pt(111) surface and annealing gives a  $(2 \times 2)$  or  $(\sqrt{3} \times \sqrt{3})$ R30° LEED pattern, producing well-defined surfaces identified as the (111) face of  $Pt_3Sn$  and a substitutional alloy of composition  $Pt_2Sn$ . Cyclohexane adsorbed onto all three surfaces at 100-155 K with an initial sticking coefficient of unity. Precursor mediated adsorption kinetics are indicated by the coverage independence of the initial sticking coefficient up to  $\frac{1}{3}-\frac{1}{4}$  of saturation coverage of the monolayer ( $\theta_{C_6H_{12}}^{sat} = 0.13 \text{ ML}$ ). The desorption temperature of the chemisorbed cyclohexane monolayer is decreased upon alloying of the Pt(111) surface with Sn, and cyclohexane desorbs in a narrow peak characteristic of each surface. The adsorption energy is reduced from 58 kJ/mol on Pt(111) by 9 kJ/mol on the  $(2 \times 2)$  Sn/Pt(111) surface alloy and by 12 kJ/mol on the  $(\sqrt{3} \times \sqrt{3})$ R30° Sn/Pt(111) surface alloy, indicating an electronic effect of Sn on cyclohexane adsorption on the Pt(111) surface. In supporting studies of benzene adsorption, Sn converts most of the strongly chemisorbed benzene to physisorbed benzene. In contrast to the reduction in chemisorption, the initial sticking coefficient shows little dependence on the Sn concentration. This phenomenon is attributed to the presence of a modifier precursor state in benzene adsorption. The decomposition of benzene is completely suppressed under UHV conditions due to the presence of Sn in the Sn/Pt(111) surface alloys. These observations bring new information into discussions of the role of Sn in selective catalytic dehydrogenation reactions over supported Pt-Sn catalysts.

## Introduction

The importance of Pt catalysts for selective hydrocarbon dehydrogenation reactions in the petroleum industry has promoted extensive studies of the adsorption and reaction of cyclohexane on the Pt(111) surface using a variety of surface science methods.<sup>1-13</sup> At low temperature ( $\sim 100$  K) cyclohexane adsorbs molecularly on Pt(111). Upon heating, some cyclohexane desorbs but most of it converts to adsorbed benzene which decomposes to hydrogen and adsorbed carbon. Under UHV conditions, no significant gas-phase benzene is produced following cyclohexane adsorption.

In commercial reforming catalysts, Pt is almost always used in combination with a second element such as Re, Ir, Au, or Sn to increase both the selectivity of this catalysis and the resistance toward poisoning by coke. Supported Pt–Sn bimetallic catalysts have been used in the petroleum refining industry, and fundamental studies of these catalysts have been carried out.<sup>14–16</sup> Despite this fact there are relatively few surface science investigations of hydrocarbon chemistry on bimetallic Pt–Sn surfaces. In this paper we report on the adsorption and reaction of an important reactant and product of cyclohexane conversion, cyclohexane and benzene, on two well-defined Sn/Pt(111) surface alloys. In order to better understand the mechanism of cyclohexane dehydrogenation, we have also studied the possible reaction intermediate cyclohexene on these Sn/Pt(111) surface alloys, but these results are published in a separate paper.<sup>17</sup>

Paffett and Windham<sup>18</sup> have showed that two different, wellordered Sn/Pt surface alloys with stoichiometry  $Pt_3Sn$  and  $Pt_2Sn$ can be prepared by evaporating Sn on a Pt(111) surface and then annealing. In contrast to surfaces of bulk Pt–Sn alloys, both of these surface alloys are very stable thermally, and no hydrocarbon adsorbate-induced surface reconstruction has been observed. The

0022-3654/94/2098-0585\$04.50/0 © 1994 Am

chemisorption of CO, H<sub>2</sub>, and O<sub>2</sub>,<sup>19</sup> C<sub>2</sub>H<sub>4</sub>,<sup>20</sup> and C<sub>2</sub>H<sub>2</sub><sup>21</sup> have been previously studied. In these studies, Sn has often been found to have a substantial electronic effect on the Pt(111) surface chemistry. In this paper, we continue along this line of investigation with more complex and catalytically interesting studies of hydrocarbon chemisorption and reaction.

## **Experimental Methods**

The experiments were performed in two ultrahigh vacuum chambers. One was equipped for Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), temperatureprogrammed desorption (TPD), and X-ray photoelectron spectroscopy (XPS) with a directed beam doser for making sticking coefficient measurements.<sup>22</sup> The second one was equipped with AES, TPD, LEED, XPS, UPS, and HREELS.<sup>23</sup> The base pressure in both chambers was  $5-6 \times 10^{-11}$  Torr. TPD measurements were made using a linear heating rate of  $\sim 4 \text{ K/s}$ and a UTI quadrupole mass spectrometer in line of sight with the sample surface. The mass spectrometer was equipped with a shield having a small entry (6-mm diameter) to the ionizer. The crystal was always placed very close ( $\sim 1 \text{ mm}$ ) to the entry hole of the shield for TPD studies. In this configuration, the contribution of the crystal back and edges to the TPD spectra was very small, as proven by the  $H_2$  TPD spectra after  $C_6H_6$  or  $C_6H_{12}$  doses on the Sn/Pt(111) surface alloys, where the H<sub>2</sub> desorption from the crystal front face was completely suppressed. In order to strongly suppress electrons coming from the QMS ionizer region, which can cause serious damage in physisorbed hydrocarbon layers,<sup>24</sup> a screen biased at -55 V was placed between the QMS ionizer and the sample.

The amount of carbon left on the surface after each TPD experiment was calibrated by AES using the C<sub>2</sub>H<sub>4</sub> saturation coverage on clean Pt(111) at 300 K,  $\theta_C = 0.5.^{25}$  The AES spectra were recorded using a Perkin Elmer 10–360 hemispherical

© 1994 American Chemical Society

<sup>•</sup> Abstract published in Advance ACS Abstracts, December 1, 1993.



Figure 1. Surface structures for the  $(2 \times 2)$  and  $(\sqrt{3} \times \sqrt{3})$ R30° Sn/Pt(111) surface alloys.

analyzer and an external electron gun with an electron beam current of 20 nA so that electron beam-induced damage in this particular system is minimal.

The Pt(111) crystal was cooled to 95 K using liquid nitrogen or resistively heated to 1200 K. The temperature was measured by a chromel-alumel thermocouple spotwelded to the side of the crystal.

The Pt(111) crystal was cleaned using the procedure found in ref 26. The  $(2 \times 2)$  Sn/Pt(111) and  $(\sqrt{3} \times \sqrt{3})$ R30° Sn/Pt-(111) surfaces were prepared by evaporating Sn on the clean Pt(111) surface and subsequently annealing the sample to 1000 K for 10s. Depending upon the initial Sn coverage, the annealed surface exhibited a  $p(2 \times 2)$  or  $(\sqrt{3} \times \sqrt{3})R30^\circ$  LEED pattern. The structures for these patterns were originally assigned to the (111) face of Pt<sub>3</sub>Sn and a substitutional surface alloy of composition Pt<sub>2</sub>Sn,<sup>18</sup> and this has now been confirmed.<sup>27</sup> Models of both surfaces are shown in Figure 1. Angle-dependent low energy ion scattering spectroscopy (LEISS) measurements using 500-1000 eV Li<sup>+</sup> show that surface alloys (rather than Sn adatoms) are produced and that Sn atoms are almost coplanar with the Pt atoms at the surface; Sn only protrudes  $\sim 0.022 \pm$ 0.005 nm above the surface.<sup>27</sup> This indicates a strong interaction between Sn and Pt atoms, which is also revealed by ultraviolet photoelectron spectroscopy (UPS).<sup>19</sup> For brevity, the ( $\sqrt{3}$  ×  $\sqrt{3}$ R30° Sn/Pt(111) and (2 × 2) Sn/Pt(111) surface alloys will be referred to in this paper as the  $\sqrt{3}$  alloy and the  $(2 \times 2)$ alloy, respectively.

Cyclohexane and benzene (Fischer Scientific, 99%) were further purified by freeze-pump-thaw cycles. The purity was checked by gas chromatography (GC) and in situ mass spectrometry.

The sticking coefficient was determined using a simple kinetic uptake method which was previously described.<sup>22</sup> The coverage,  $\theta$ , was calibrated with the following equation:<sup>28</sup>

$$\theta_{\rm HC} = \frac{P_{\rm HC}}{P_{\rm C_2H_4}} \left(\frac{M_{\rm C_2H_4}}{M_{\rm HC}}\right)^{1/2} \frac{\int S_{\rm HC}dt}{\int S_{\rm C_2}H_4dt} \theta_{\rm C_2H_4}$$
(1)

using the known saturation coverage of C<sub>2</sub>H<sub>4</sub>,  $\theta_{C_2H_4} = 0.25$ , on clean Pt(111) at 100 K.<sup>25</sup>

Coverages in this paper are referenced to the Pt(111) surface atom density, i.e.,  $\theta = 1$  is defined as  $1.505 \times 10^{15}$  cm<sup>-2</sup>.



Figure 2. H<sub>2</sub> TPD spectra after different C<sub>6</sub>H<sub>6</sub> exposures on the Pt(111),  $(2 \times 2)$ , and  $(\sqrt{3} \times \sqrt{3})$ R30° Sn/Pt(111) surfaces.

## Results

Benzene. The adsorption and desorption behavior of benzene was studied with TPD.  $H_2$  evolution shown in Figure 2 monitors benzene decomposition on the surface. Several H<sub>2</sub> TPD spectra after dosing benzene on the Pt(111) surface are provided at the bottom of Figure 2. With increasing  $C_6H_6$  exposure,  $H_2$  evolution first increases and then saturates after a C<sub>6</sub>H<sub>6</sub> exposure of 0.4 L. Further increases in the  $C_6H_6$  exposure do not change the  $H_2$ TPD spectra significantly. This is quite consistent with the results of Campbell et al.<sup>29</sup> Our TPD spectra are very similar to the previous results with the one exception that all of our peaks are shifted by almost 15 K to lower desorption temperature. (This discrepancy is at least partly due to differences in the heating rates used.) H<sub>2</sub> desorption below 525 K has been assigned to the decomposition of  $C_6H_6$  to some adsorbed hydrocarbon species with C:H stoichiometry of 2:1 (C<sub>6</sub>H<sub>3</sub> or 3C<sub>2</sub>H).<sup>29</sup> Further heating to 800 K dehydrogenates this intermediate to adsorbed carbon, desorbing hydrogen between 525 and 800 K. In contrast, on the Sn/Pt(111) surface alloys, no significant H<sub>2</sub> desorption was observed at any benzene coverages used in our experiments. This is consistent with AES results that no carbon was detected on the surface after each TPD measurement on the alloys. Therefore, the thermal decomposition of benzene is completely suppressed under these conditions upon forming the two Sn/Pt(111) surface alloys.

 $C_6H_6$  TPD spectra following  $C_6H_6$  exposure are summarized in figures 3 and 4. Figure 3 shows the entire temperature range for benzene desorption, while the low-temperature range is expanded in Figure 4. On the Pt(111) surface, in good agreement with previously reported results,<sup>29-32</sup> no  $C_6H_6$  desorption occurs at low  $C_6H_6$  coverage. With increasing  $C_6H_6$  exposure, a state that desorbs at 480 K is formed; this high-temperature peak grows and shifts to 450 K, and a new, broad peak forms at 320 K. Both peaks at 320 and 480 K overlap strongly. A sharp peak at 178 K also begins to develop at higher exposure. This latter peak cannot be saturated and is attributed to multilayer formation.



Figure 3. C<sub>6</sub>H<sub>6</sub> TPD spectra at different C<sub>6</sub>H<sub>6</sub> coverages on the Pt(111),  $(2 \times 2)$ , and  $(\sqrt{3} \times \sqrt{3})$ R30° Sn/Pt(111) surfaces.



Figure 4. Expanded view of Figure 3 in the 100-250 K temperature range.

The peaks between 280 and 520 K have been assigned<sup>29-32</sup> to desorption from the chemisorbed monolayer. Using Redhead analysis, and assuming first-order kinetics and a typical preexponential factor of  $10^{13}$  s<sup>-1</sup>, the desorption temperatures for the two chemisorbed states at 320 and 450 K correspond to desorption activation energies of 82 kJ/mol and 117 kJ/mol, respectively. The low-temperature state at 178 K has an activation energy for desorption of 45 kJ/mol.

On the  $(2 \times 2)$  alloy, there are still two peaks between 280 and 520 K. In comparison to the case for Pt(111), a small shift in the peaks to lower desorption temperature is visible. Before the multilayer desorption peak at 179 K dominates after large benzene exposures, a sharp peak at 200 K begins to develop. This is more clearly shown in Figure 4. This result indicates that part of the

chemisorbed benzene monolayer on Pt(111) is converted on the  $(2 \times 2)$  alloy to a very weakly bound, probably physisorbed, species. The desorption energy of this species is 50 kJ/mol according to Redhead analysis.

The  $\sqrt{3}$  alloy is characterized by very different C<sub>6</sub>H<sub>6</sub> TPD spectra in comparison to those for Pt(111) and the (2 × 2) alloy. No desorption above 350 K is observed. The two peaks between 280 and 520 K on the Pt(111) surface and the (2 × 2) alloy are reduced to one peak at 300 K on the  $\sqrt{3}$  alloy. The new peak at 200 K that appeared on the (2 × 2) alloy is shifted to 187 K on the  $\sqrt{3}$  alloy, which can be translated to a desorption energy of 47 kJ/mol using Redhead analysis. With increasing benzene coverage, the peak at 187 K disappears in the shoulder of the multilayer peak at 175 K.



Figure 5. Sticking coefficients of  $C_6H_6$  on the Pt(111), (2×2), and ( $\sqrt{3} \times \sqrt{3}$ )R30° Sn/Pt(111) surfaces at 200 K. The TPD spectrum after each sticking coefficient measurement is shown in the inset.

The influence of Sn on the molecular desorption of chemisorbed benzene shows a strong dependence on the  $C_6H_6$  coverage. At a  $C_6H_6$  exposure less than 0.4 L, a large increase in molecular desorption from the chemisorbed state is seen with increasing Sn concentration on the Pt(111) surface. This is simply because the decomposition of benzene is completely suppressed by the presence of Sn on the surface. At higher  $C_6H_6$  coverage, more benzene desorbs molecularly from the Pt(111) surface. The presence of Sn on the Pt(111) surface reduces molecular desorption from the chemisorbed state because of the formation of a new weakly bound state on the surface alloys. Desorption from this physisorbed state is strongly promoted at the expense of desorption from the chemisorbed state.

Combining the  $C_6H_6$  and  $H_2$  TPD results makes it obvious that the coverage of chemisorbed molecules on both Sn/Pt(111)surface alloys is strongly reduced compared to that on the Pt-(111) surface. Instead of being chemisorbed, most of the benzene is only weakly physisorbed in the first layer on both Sn/Pt(111)surface alloys. The binding energy of benzene on the surface is reduced from 82 or 117 kJ/mol on Pt(111) to 50 or 47 kJ/mol on Sn/Pt(111) alloy surfaces. This conclusion is also confirmed by an absolute measure of the coverage of chemisorbed benzene on the three surfaces at 200 K using sticking coefficient measurements. These results are provided in Figure 5. To verify that we can only populate the chemisorbed state at a surface temperature of 200 K, TPD spectra have been taken after each sticking coefficient measurement. These results are shown in the inset to Figure 5. It is clearly seen that no significant amount of the new weakly bonded state can be populated at 200 K. The initial sticking coefficient,  $S_0$ , of benzene on both Pt(111) and the  $(2 \times 2)$  alloy is almost unity and stays constant up to 0.05 monolayers on Pt(111) and 0.025 monolayers on the  $(2 \times 2)$ alloy. After this point, S drops gradually to zero at saturation coverages. This result indicates that precursor-mediated adsorption kinetics are important on both surfaces. The saturation coverage of benzene at 200 K is determined to be 0.18 monolayers on Pt(111) and 0.1 monolayers on the  $(2 \times 2)$  alloy. On the  $\sqrt{3}$ alloy surface at 200 K,  $S_0$  is >0.8 and the saturation coverage is reduced to only 0.02 monolayers.

**Cyclohexane.** We repeated studies of cyclohexane on the clean Pt(111) surface first. The left panel in Figure 6 shows a series of cyclohexane TPD spectra after different initial coverages of cyclohexane were adsorbed on Pt(111). Our TPD spectra are similar to the data reported in the literature.<sup>9,10</sup> However, in contrast to the previously published spectra, we only see two peaks, due to the first chemisorbed layer and physisorbed layer, at moderate cyclohexane exposures. A third peak between the monolayer and multilayer desorption peaks has often been observed,<sup>9,10</sup> and there is some controversy about the origin of



Figure 6.  $C_6H_{12}$  TPD spectra after different cyclohexane exposures on the Pt(111), (2 × 2), and ( $\sqrt{3} \times \sqrt{3}$ )R30° Sn/Pt(111) surfaces.



Figure 7. Expanded view of  $C_6H_{12}$  TPD spectra at low temperature.

this peak. It has been assigned to either desorption from the second layer or desorption from the back or edge of the crystal and the sample holder.<sup>9,10</sup> We can not populate this state with significant intensity, even after multilayer formation. This observation eliminates the assignment of this peak to the second layer.

In a separate experiment, we have shown that precovering the surface with carbon, oxygen, or other contamination shifts the first chemisorbed peak to this so-called  $\beta$  state. As the top curve of Figure 7, we have provided a cyclohexane TPD spectrum after a cyclohexane exposure on a carbon-precovered Pt(111) surface. The presence of surface carbon decreases the desorption at 228 K and promotes desorption in the  $\beta$  state. Therefore, we believe this state in other investigators' studies comes either from the front surface with carbon or oxygen contamination or from the crystal back and edges where the surface is undoubtedly covered with some contamination (most probably carbon). An alternative explanation for defective surfaces is that some cyclohexane undergoes low-temperature decomposition at defects, and these decomposition products act like preadsorbed carbon to induce



Figure 8. C<sub>6</sub>H<sub>12</sub> TPD spectra after monolayer cyclohexane exposures on the Pt(111),  $(2 \times 2)$ , and  $(\sqrt{3} \times \sqrt{3})$ R30° Sn/Pt(111) surfaces.

the  $\beta$  state. Further support for this view comes from a more careful investigation of the multilayer state desorption. In Figure 7, an expanded view of cyclohexane TPD below 260 K is shown. A peak at 146 K begins to develop after saturation of the first layer state. With increasing cyclohexane coverage, the peak at 146 K shifts to higher temperature, a typical behavior for zero-order desorption kinetics. At high cyclohexane exposures, we begin to see a new peak, which has not been reported previously, at 143 K. Very similar behavior has been seen for cyclohexene<sup>17</sup> and other hydrocarbons on Pt(111) and by us on Sn/Pt(111) surface alloys. Therefore, we assign the  $\alpha$  state to desorption from the multilayer condensed phase. From Figure 7 we also conclude that the cyclohexane adsorbs initially layer by layer on both Pt-(111) and Sn/Pt(111) surfaces.

The TPD spectra of cyclohexane on both Sn/Pt(111) surface alloys are very similar to those from clean Pt(111), as was shown in Figure 6. A high-temperature peak due to desorption from the monolayer is formed first, and then the multilayer peak occurs with increasing cyclohexane exposure. The desorption temperature of the adsorbed cyclohexane monolayer decreases strongly from Pt(111) to the Sn/Pt(111) surface alloys. This is more clearly shown in Figure 8 in which the TPD spectra for near monolayer coverage on Pt(111), the  $(2 \times 2)$  alloy, and the  $\sqrt{3}$ alloy are compared. The first layer desorption peak temperature shifts from 228 K on the Pt(111) surface to 194 K on the (2  $\times$ 2) alloy and then to 185 K on the  $\sqrt{3}$  alloy. Using Redhead analysis, and assuming first-order kinetics and a typical preexponential factor of 1013 s-1, we can estimate a desorption activation energy of 58 kJ/mol for the Pt(111) surface, 49 kJ/mol for the  $(2 \times 2)$  alloy, and 46 kJ/mol for the  $\sqrt{3}$  alloy. These values are good estimates of the adsorption energy of cyclohexane on the three surfaces.

The sticking coefficient and saturation coverage of cyclohexane on the Pt(111) surface and both Sn/Pt(111) surface alloys were measured and the results are provided in Figure 9. The dependence of the sticking coefficients on the cyclohexane coverage is identical on all three surfaces at temperatures below 155 K. The condensation coefficient at 100 K was measured to be unity on all three surfaces at all coverages. We have observed



Figure 9. Sticking coefficients of  $C_6H_{12}$  on the Pt(111), (2 × 2), and  $(\sqrt{3} \times \sqrt{3})R30^\circ Sn/Pt(111)$  surfaces at 155 K.

the same results for other organic molecules such as methylcyclohexane, cyclohexene, butane and isobutane, isobutylene, and toluene and heptane. At 155 K, where only a monolayer can be formed, the initial sticking coefficients were measured to be almost unity and S remains constant until a cyclohexane coverage of 0.03 monolayers is reached. With further increases in the cyclohexane coverage, S gradually decreases to zero at a saturation coverage near 0.15 monolayers, independent of the amount of Sn within experimental error. Some difference is artificially introduced by obtaining all the uptakes at 155 K, since the TPD spectra show a small monolayer desorption rate at this temperature. Precursor-mediated adsorption kinetics are important on all three surfaces.

 $H_2$  evolution from cyclohexane dehydrogenation is monitored by the  $H_2$  TPD spectra shown in Figure 10. The spectra from Pt(111) are shown at the bottom of Figure 10. Our  $H_2$  TPD spectra are in good agreement with other data reported in the literature.<sup>9</sup> The spectra are characterized by two peaks, at 350 and 520 K, and a broad feature extending from 550 to 750 K. The peak at 350 K is very similar to the  $H_2$  desorption peak after dosing  $H_2$  to the surface in both shape and desorption temperature and has been assigned to a  $H_2$  desorption-limited process (the association of two adsorbed hydrogen atoms) from the dehydrogenation of cyclohexane to benzene.<sup>9</sup> The higher temperature  $H_2$  desorption peaks are therefore reaction-limited. The broad high-temperature feature has been correlated to  $H_2$  desorption liberated by the decomposition of adsorbed benzene formed from cyclohexane.<sup>9</sup>

Alloying Pt with Sn suppresses H<sub>2</sub> evolution completely from any dehydrogenation process. On both the  $(2 \times 2)$  alloy and  $\sqrt{3}$ alloy, no H<sub>2</sub> desorption was observed at any cyclohexane coverages, as shown in Figure 10. Consistent with these TPD results, AES shows no carbon left on these surfaces after the TPD experiments.

The adsorption of cyclohexane on the two Sn/Pt(111) surface alloys has been studied also with HREELS, as shown in Figure 11. For comparison, an HREELS spectrum of cyclohexane on Pt(111) is also included. Land et al.<sup>33</sup> in a recent HREELS investigation of the adsorption of cyclohexane on Pt(111) found that cyclohexane adsorbed with the molecular plane parallel to the surface with  $C_{3\nu}$  symmetry. Our HREELS spectra of the



Figure 10. H<sub>2</sub> TPD spectra after different C<sub>6</sub>H<sub>12</sub> exposures on the Pt-(111),  $(2 \times 2)$ , and  $(\sqrt{3} \times \sqrt{3})$ R30° Sn/Pt(111) surfaces.

cyclohexane monolayer are in good agreement with their results. A detailed assignment of the observed bands can be found in their paper.<sup>33</sup> For our purposes here, we focus on the broad band at 2600 cm<sup>-1</sup> attributed to the C-H stretch of the three axial hydrogens of cyclohexane which are pointing toward the surface. The red shift and broadening of the C-H stretch vibration are a result of a strong interaction between these hydrogen atoms and the Pt surface. The presence of Sn dramatically changes the C-H bond softening. The band at 2600 cm<sup>-1</sup> disappears completely upon alloying of Pt with Sn to form either ordered surface alloy. Vibrations associated with C-H softening are still seen on the low-frequency side of the 2900 cm<sup>-1</sup> peaks for both alloys, and these shift to higher frequency with increasing Sn concentration.

Finally, a comparison between benzene and cyclohexane is very useful for understanding the chemistry and catalysis of these alloy surfaces. The influence of Sn on the initial sticking coefficient and saturation coverage of chemisorbed benzene and cyclohexane are compared in Figure 12. In Figure 12 (right side), the initial sticking coefficients of cyclohexane at 155 K and benzene at 200 K are plotted versus the Sn concentration on the Pt(111) surface. In both cases, the initial sticking coefficients are independent of the Sn concentration up to an Sn coverage of  $\theta_{Sn} = 0.25$ . Increasing the Sn concentration further may cause a slight decrease in  $S_0$  of benzene but no change for cyclohexane. In Figure 12 (left side), the saturation coverage of chemisorbed benzene at 200 K and cyclohexane at 155 K is plotted versus the Sn concentration in the surface alloy. In contrast to the behavior of  $S_0$ , the benzene saturation coverage shows a strong dependence on the Sn concentration. The cyclohexane saturation coverage slightly increases with  $\theta_{Sn}$ , but this is probably due to small experimental artifacts as discussed earlier, and thus  $\theta_{C_{4}H_{12}}$  is independent of  $\theta_{Sn}$ .

Activation of Cyclohexane by Low-Energy Electrons. The presence of Sn in the surface alloys suppresses cyclohexane dehydrogenation completely under UHV conditions. One expects that at higher pressures and temperatures cyclohexane would dehydrogenate on the Pt-Sn alloy surface. This is yet another illustration of the reactivity differences from the pressure gap



Figure 11. HREELS spectra after cyclohexane exposures on the Pt-(111),  $(2 \times 2)$ , and  $(\sqrt{3} \times \sqrt{3})$ R30° Sn/Pt(111) surfaces.



Figure 12. Comparison of the influence of Sn on cyclohexane adsorption with benzene adsorption on Pt(111) and Sn/Pt(111) surface alloys.

that exists between UHV conditions and high pressures. These same differences have been seen for many alkanes on Pt.<sup>34</sup> In order to overcome this barrier and to gain insight into the influence of Sn on cyclohexane dehydrogenation, we activate the cyclohexane with low-energy electrons. In separate experiments,<sup>24</sup> we have shown that a small flux of low-energy electrons selectively breaks one C-H bond in physisorbed cyclohexane, producing cyclohexyl. Once cyclohexyl is produced, it bonds strongly to the surface via a covalent C-Pt bond and further electron bombardment greatly reduces ( $\geq 10^3$  smaller) the cross section to break a second bond in cyclohexyl.

Figure 13 summarizes  $H_2$ ,  $C_6H_6$ , and cyclohexane ( $C_6H_{10}$ ) TPD spectra taken after cyclohexane coverages exceeding one monolayer were subjected to electron bombardment during TPD. (This small flux of low-energy electrons has a negligible influence on strongly adsorbed species such as cyclohexene and benzene.) In Figure 13, TPD spectra from Pt(111) are shown. Hydrogen is the dominant reaction product desorbed, with no cyclohexene and only small amounts of benzene desorption observed. On the  $(2 \times 2)$  surface alloy, benzene desorption becomes a main reaction channel in addition to hydrogen desorption. No cyclohexene desorption occurs. (The two small peaks at low temperature are cracking products of cyclohexane in the QMS.) H<sub>2</sub> TPD spectra from the  $(2 \times 2)$  alloy are very different than from the Pt(111) surface. Two major changes occur due to the presence of Sn on the surface: H<sub>2</sub> desorption above 450 K is strongly suppressed and two peaks are seen below 450 K. The suppression of  $H_2$ desorption above 450 K is consistent with our finding that benzene does not decompose on the  $(2 \times 2)$  alloy surface in UHV. The



Figure 13.  $C_6H_{12}$ ,  $H_2$ , and  $C_6H_6$  TPD spectra after cyclohexane exposures exceeding one monolayer on the Pt(111), (2 × 2), and ( $\sqrt{3} \times \sqrt{3}$ )R30° Sn/Pt(111) surfaces, taken during low-energy electron bombardment to produce significant concentrations of adsorbed cyclohexyl species.

two low-temperature  $H_2$  desorption peaks are assigned to hydrogen liberated from the dehydrogenation of cyclohexene or cyclohexyl to benzene.

On the  $\sqrt{3}$  surface alloy, the amount of benzene desorption is smaller than on the 2 × 2 alloy. To a large extent, the adsorbed cyclohexyl species dehydrogenates to form cyclohexene which desorbs. Two cyclohexene desorption peaks are observed at 208 and 345 K. The peak at 208 K has the same desorption temperature as cyclohexene after cyclohexene adsorption<sup>17</sup> and is probably desorption-rate-limited. The peak at 345 K is clearly reaction-rate-limited.

### Discussion

Benzene Adsorption on Pt(111) and the Sn/Pt(111) Surface Alloys. The adsorption of benzene on Pt(111) has been investigated by a number of groups using many different surface science methods. The first HREELS measurements by Lehwald et al.<sup>35</sup> were interpreted with benzene adsorbed molecularly on the surface between 140 and 320 K with the molecular plane oriented parallel to the surface. Two different phases of adsorbed benzene were assigned and attributed to benzene adsorbed on atop and threefold hollow sites with a symmetry of  $C_{3v}$ . However, this assignment was challenged later by HREELS measurements of Abon et al.<sup>31</sup> NEXAFS measurements have confirmed the parallel geometry of C<sub>6</sub>H<sub>6</sub> on Pt(111).<sup>4,5</sup> The ARUPS results of Somers<sup>36</sup> et al. also showed a  $C_{3v}$  symmetry for the adsorbate with a small distortion of the  $C_6H_6$  molecule. The adsorption and desorption of benzene on Pt(111) have been studied previously by Tsai and Mutterties,<sup>30</sup> Abon et al.,<sup>31</sup> and Garfunkel et al.<sup>32</sup> and recently restudied by Campbell and co-workers<sup>29</sup> using TPD, XPS, and AES. Upon heating, multilayers of benzene desorb by 195 K and two desorption peaks from chemisorbed layers follow at 350 and 505 K.9 The origin of these two desorption peaks is not clear. There are two possible explanations. The first is that these latter two peaks are caused by repulsive interactions of benzene at higher coverage. The second, which we favor, is that these two peaks are correlated to benzene adsorbed on different sites. If atop and threefold hollow adsorption sites can be populated on Pt(111) as assigned to Lehwald et al.,<sup>35</sup> we should only be able to populate the atop benzene adsorption site on the  $\sqrt{3}$  alloy, since this surface does not contain any Pt threefold hollow sites. Indeed we only see one desorption peak on the  $\sqrt{3}$  alloy. Thus, we propose that the higher temperature desorption peak on Pt(111) is due to desorption of C<sub>6</sub>H<sub>6</sub> from threefold sites.

Both chemisorption and the decomposition of benzene are strongly inhibited on the two Sn/Pt(111) surface alloys in comparison to the Pt(111) surface. At small  $C_6H_6$  coverages, the amount of molecular desorption from chemisorbed states is increased over that from Pt(111) because decomposition of benzene is completely suppressed on the Sn/Pt(111) surface alloys. The two Sn/Pt(111) alloy surfaces have a decreased ability to chemisorb benzene on the surface, and the saturation coverage of the chemisorbed state on the Sn/Pt(111) surface alloys is smaller than on Pt(111). At high  $C_6H_6$  coverages, where the chemisorbed state on Pt(111) is already or almost saturated, Sn blocks sites and causes a decrease in the amount of molecular desorption from the chemisorbed state.  $C_6H_6$  can only physisorb on the surface. A large fraction of the first chemisorbed benzene layer on Pt(111) is coverted to physisorbed species on the Sn/ Pt(111) surface alloys.

The influence of preadsorbed Bi on the adsorption and decomposition of benzene has been studied by Campbell and co-workers.<sup>29</sup> Bi is relatively inert chemically toward many hydrocarbon molecules and has an electronegativity very similar to that of Pt. Therefore, Bi has been generally thought to have only a very small electronic effect on Pt and only act as a site blocker. Using Bi, ensemble size for reactions of a series of hydrocarbon molecules on Pt(111) has been explored. For benzene, Campbell et al.<sup>29</sup> deduced that an ensemble of  $\sim 6$  free Pt atoms was needed to adsorb benzene and a much larger ensemble of  $\geq 12$  Pt atoms was required for the dehydrogenation of benzene. The decomposition of benzene was completely suppressed for  $\theta_{Bi} = 0.25$ . We also found that decomposition of benzene was completely suppressed on the  $(2 \times 2)$  Sn/Pt(111) alloy, where  $\theta_{Sn} = 0.25$ . In Campbell's work,<sup>29</sup> the chemisorption of benzene is also reduced with further increases in the Bi coverage. Our results for the  $\sqrt{3}$  alloy show a strong suppression of C<sub>6</sub>H<sub>6</sub> chemisorption, also similar to the effects of Bi. One can conclude that Sn acts mainly as a site blocker in benzene adsorption and decomposition.

**Cyclohexane.** The adsorption of cyclohexane on Pt(111) has been extensively studied both under UHV conditions<sup>1-13</sup> and at

higher pressure.<sup>37</sup> The general picture of cyclohexane adsorption and reaction on Pt(111) under UHV conditions is that molecular adsorption occurs at low temperature with the cyclohexane molecule probably in the chair conformation and parallel to the surface at monolayer and submonolayer coverages. With increasing surface temperatures, cyclohexane begins to dehydrogenate at 180–195 K. Two intermediates in the cyclohexane dehydrogenation to benzene have been found and were assigned to cyclohexene and a C<sub>6</sub>H<sub>9</sub> species. Near 270–340 K, benzene is formed on the surface. With further heating, the adsorbed benzene decomposes to hydrogen and adsorbed carbon. No desorption of cyclohexene, benzene, or any intermediate has ever been observed with conventional TPD studies. In contrast to the UHV results, studies at higher pressure show a large gas-phase benzene production.<sup>37</sup>

Our TPD spectra of molecular cyclohexane desorption, H<sub>2</sub> evolution, and benzene and cyclohexene formation on Pt(111)are in good agreement with the previously reported results. Our contribution to this body of work is first to point out that the  $\beta$ state should not be attributed to desorption from the second layer but, rather, assigned to the desorption from contaminated regions of the surface. The real second-layer desorption takes place at a much lower temperature than the  $\beta$  state. Secondly, the sticking coefficient of cyclohexane is essentially unity. The sticking coefficient on Pt(111) at 100 K was measured previously by Rodriguez et al.9 by using an indirect method with TPD and an ion gauge. They found a constant sticking coefficient of 0.25, independent of coverage. At 100 K, we also found a constant sticking coefficient at all coverages, but close to unity. This discrepancy is due to errors inherent in the method used by these other investigators, as pointed out previously.<sup>28</sup>

The presence of alloyed Sn does not have a significant influence on the sticking coefficient and saturation coverage of cyclohexane on Pt(111) at 155 K. On all three surfaces studied, a physisorbed precursor plays an important role in the adsorption kinetics and S is independent of the cyclohexane coverage up to  $1/3^{-1}/4$  of that required to form the monolayer. The cyclohexane monolayer on the two Sn/Pt(111) surface alloys has a strongly reduced desorption temperature in comparison to that on Pt(111), and the decrease in the first-layer desorption temperature takes place gradually. But, the amount of adsorbed cyclohexane does not change significantly from Pt(111) to the Sn/Pt(111) surface alloys.

Only one cyclohexane desorption peak is observed from the first adsorbed layer on the Sn/Pt(111) alloys, in contrast to bismuth<sup>9</sup> or cesium<sup>38</sup> precovered Pt(111) surfaces. On both Biand Cs-precovered Pt(111) surfaces, more than one molecular cyclohexane desorption peak is seen at a similar modifier coverage as on the  $(2 \times 2)$  or  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$  Sn/Pt(111) surface alloys. On both Sn/Pt surface alloys, our TPD and sticking coefficient results indicate that cyclohexane does not distinguish between Pt and Sn sites: the alloys adsorb and desorb cyclohexane as a whole surface. Further support for this conclusion comes from the HREELS results. As shown in Figure 11, the peak at 2600 cm<sup>-1</sup> characteristic for the C-H-Pt interaction is not simply attenuated by the presence of Sn, as we would expect for simple site blocking effects. Rather, a shift of the softened mode to higher frequencies is seen with increasing Sn concentration.

Finally, the HREELS results also demonstrate a correlation of the C-H bond softening with cyclohexane dehydrogenation reactivity. Concomitant with the strong reduction of C-H bond softening, no cyclohexane dehydrogenation was seen on the two Sn/Pt(111) surface alloys under UHV conditions.

Cyclohexane Dehydrogenation As Probed by Activation with Low-Energy Electrons. Cyclohexane is reversibly adsorbed and does not react on the Sn/Pt(111) surfaces studied under UHV conditions. The activation of cyclohexane by means of low-energy electrons to produce adsorbed cyclohexyl species gives us the opportunity to explore subsequent dehydrogenation reactions on these surfaces under well-defined UHV conditions. Cyclohexyl reacts as expected on Pt(111) to yield only hydrogen and surface carbon. Cyclohexyl also reacts strongly with both Sn/Pt(111)surface alloys, but the presence of alloyed Sn decreases the reactivity of the Pt(111) surface, promoting gas-phase benzene and cyclohexene production. On the  $(2 \times 2)$  alloy, cyclohexyl dehydrogenates to benzene which cannot decompose on the Sn/ Pt(111) surface alloy and therefore desorbs. By contrast, cyclohexyl dehydrogenates mainly to cyclohexene on the  $\sqrt{3}$  alloy. On this surface, the dehydrogenation of cyclohexene becomes a rate-limiting process. The  $(2 \times 2)$  alloy shows the best selectivity for benzene production, while cyclohexene production is best on the  $\sqrt{3}$  alloy under our conditions. The presence of Sn shifts the major products of cyclohexane reaction from carbon and hydrogen on Pt(111) to benzene on the  $(2 \times 2)$  alloy and cyclohexene on the  $\sqrt{3}$  alloy. The selectivity toward useful dehydrogenated products is greatly increased by the presence of Sn on the Pt(111) surface. In addition to this increased selectivity, the yield of surface carbon or coking activity is also strongly suppressed on the Sn/Pt(111) surface alloys. These observations are consistent with the observed improved performance of supported bimetallic Pt-Sn catalysts used for reforming and provide useful new insight into the role that Sn plays in this catalysis.

Comparisons between Benzene and Cyclohexane Chemistry on Sn/Pt(111) and Other Bimetallic Pt(111) Surfaces. Dehydrogenation and decomposition of cyclohexane on Bi-9 and Cs-38precovered Pt(111) surfaces were previously studied using TPD. Bi simply acts a site blocker, while site blocking plus an additional electronic effect are expected from Cs. Comparisons with these other bimetallic systems may yield some information that can be used to qualitatively separate the contributions from geometric and electronic effects of alloying with Sn. Both the decomposition of benzene and the dehydrogenation of cyclohexane are suppressed in the presence of Bi or Cs. On both Bi- and Cs-precovered Pt(111) surfaces, more than one molecular cyclohexane desorption peak are seen even at small cyclohexane coverages for Biprecovered Pt(111). By contrast, cyclohexane desorbs in a welldefined, characteristic peak for each of the Pt(111) and Sn/ Pt(111) alloy surfaces. The changes in the electronic structure of the surface that accompanies alloying of Pt with Sn and the presence of the modifier atoms within the surface layer rather than within the adlayer cause the Sn/Pt(111) surface to adsorb and desorb cyclohexane with no apparent sensitivity to the heterogeneous nature of the surface layer. This is a very important point that will be dealt with more in another paper.<sup>39</sup> At small Cs coverages where electronic effects dominate, the cyclohexane desorption temperature shifts higher.<sup>38</sup> Although alloying with Sn decreases the work function of Pt like Cs does, we see a shift to lower temperatures for this peak in the presence of Sn. This cannot be explained simply by charge transfer, and the Pt rehybridization that occurs in forming the alloy plays an important role.

The presence of Sn in the Pt(111) surface blocks the chemisorption of benzene, but not that of cyclohexane. Only a gradual decrease in the adsorption energy of cyclohexane with increasing Sn concentration occurs. Consistently, the initial sticking coefficient of cyclohexane is also independent of the Sn concentration. In the case of benzene, only the saturation coverage of chemisorbed benzene decreases with increasing Sn concentration. The initial sticking coefficient, however, stays constant up to a Sn coverage of at least 0.25 and possibly higher. This is not consistent with a simple site-blocking model. According to the Langmuir isotherm,  $S_0$  should scale with the concentration of the site blocker on the surface. For example, the dependence of the initial sticking coefficient on the site-blocker concentration has been used often to determine the size of the site blocker. In the case of benzene on Sn/Pt(111), this simple description is obviously not correct. Recently, we have pointed out that the influence of a surface modifier or site blocker on adsorption kinetics often cannot be simply described by the Langmuir isotherm as is usually done. Rather, precursor-mediated kinetics must be

### Adsorption of Cyclohexane and Benzene

considered. A third kind of precursor, a modifier precursor, in addition to extrinsic and intrinsic precursors, must be taken into account.<sup>39</sup> The basis for this modifier precursor is as follows: if a physisorption well can hold a molecule on top of the clean surface (intrinsic precursor) and on top of the adsorbed molecule (extrinsic precursor), it is reasonable to assume that the molecule can also be physisorbed on top of the inert modifier and this species trapped in this well behaves as a modifier precursor. As in the case of the intrinsic and extrinsic precursors, the modifier precursor will also have a strong influence on the adsorption kinetics. For example, benzene which impinges on Sn will not be reflected back to the gas phase but will be trapped in the modifier physisorption well and diffuse, increasing the probability that a Pt site is eventually reached and benzene becomes chemisorbed. Therefore, a linear decrease of  $S_0$  with  $\theta_{Sn}$  is not observed on the alloy surfaces. These kinetics on Sn/Pt(111)surfaces are also consistent with the kinetics on Pt(111) and the important role of the extrinsic precursor on Pt(111) as indicated by the independence of the benzene sticking coefficient on the benzene coverage at small benzene coverages.

Historically, two different approaches have been developed to explain how Sn modifies the adsorption behavior of the Pt(111)surface. Rigid-band theory was used first to describe and predict the catalytic behavior of binary alloys. In this model, it was assumed that the valence electrons of both constituents in an alloy form common bands consisting of one d-band and one s,pband overlapping the former. However, many ARUPS and adsorption results over the years have contradicted this theory. The failure of rigid-band theory led to the "individual surface atom" concept normally considered now, where the atoms retain their individuality when forming alloys. The electronic structure of the two Sn/Pt(111) surface alloys was briefly characterized previously with UPS.<sup>19</sup> The UPS spectra of the alloys were not a simple addition of Pt and Sn spectra. Some new features were present, which can be attributed to either a strongly modified band of a single component or some kind of common band of Sn and Pt. Consistent with this finding, we see a single well-defined desorption temperature of cyclohexane on both Sn/Pt(111) surface alloys. We have seen the same results for all of the other alkanes that we have investigated from butane and isobutane to methylcyclohexane and heptane. No significant change of the monolayer saturation coverage for any alkane was ever observed in going from Pt(111) to these two Sn/Pt(111) alloys. This indicates a common weak interaction between the surface and the alkane and a common sensitivity to the changes in the electronic structure induced by Sn. On the other hand, the presence of Sn efficiently blocks one state of chemisorbed benzene, and a new, weakly adsorbed state (probably physisorbed state) is formed. The amount of chemisorbed benzene scales well with the Pt atom concentration on the surface. This shows that the adsorption of benzene is site-specific, and benzene distinguishes well between Sn and Pt surface atoms. As far as benzene adsorption is concerned, the identities of Sn and Pt are retained upon alloying. Therefore, depending on the alloy, the molecule, and the chemical nature of the interaction between the surface and the molecule, either the rigid-band theory or "individual surface atom" concepts can be used to help understand the experimental results.

#### Conclusions

The (2 × 2) Sn/Pt(111) and ( $\sqrt{3} \times \sqrt{3}$ )R30° Sn/Pt(111) surface alloys adsorbed and desorbed cyclohexane with a single, well-defined binding energy, indicating uniform interactions with the surface atoms due to alloying between the Sn and Pt atoms on the surface. The adsorption energy decreases gradually with increasing Sn concentration in the surface layer. By contrast, the influence of Sn on benzene adsorption and desorption on Pt(111) is best described by site-blocking effects. Benzene is only weakly bonded to the alloy surfaces with a binding energy of 50 kJ/mol on the  $(2 \times 2)$  alloy and 47 kJ/mol on the  $\sqrt{3}$  alloy. The adsorption kinetics of benzene on the Sn/Pt(111) surface alloys can be understood by introducing a third kind of precursor, a modifier precursor, in addition to the intrinsic and extrinsic precursors. The reactions of cyclohexyl on the three surfaces, following activation of cyclohexane multilayers by low-energy electrons, show that the presence of Sn shifts the product distribution of cyclohexane reactions from carbon and hydrogen on Pt(111) to benzene on the  $(2 \times 2)$  alloy and to cyclohexene on the  $\sqrt{3}$  alloy. The amount of surface carbon formed by heating of cyclohexyl is also suppressed by the addition of Sn. This behavior (enhanced aromatic formation and reduced carbon buildup) is consistent with desirable features of Pt-Sn bimetallic reforming catalysts and may explain aspects of this catalysis.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research.

#### **References and Notes**

(1) Davis, S. M.; Somorjai, G. A. In The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1984; Vol. 1, Chapter 7.

- (2) Sinfelt, J. H. In Catalysis, Science and Technology; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: Berlin, 1981; Vol. 1, Chapter 5.
- (3) Tsai, M. C.; Friend, C. M.; Mutterties, E. L. J. Am. Chem. Soc. 1982, 104, 2539.

(4) Hitchcock, A. P.; Newbury, D. C.; Ishii, I.; Stöhr, J.; Horsley, J. A.; Redwing, R. D.; Johnson, A. L.; Sette, F. J. Chem. Phys. 1986, 85, 4849.

- (5) Stöhr, J.; Sette, F.; Johnson, A. L. Phys. Rev. Lett. 1984, 53, 1684. (6) Firment, L. E.; Somorjai, G. A. J. Chem. Phys. 1977, 66, 2901.
- (7) Demuth, J. E.; Ibach, H.; Lehwald, S. Phys. Rev. Lett. 1978, 40,

1044 (8) Kang, D. B.; Anderson, A. B. J. Am. Chem. Soc. 1985, 107, 7858.

(9) Rodriguez, J. A.; Campbell, C. T. J. Phys. Chem. 1989, 93, 826.

(10) Parker, D. H.; Pettiette-Hall, C. L.; Li, Y. Z.; McIver, R. T., Jr.; Hemminger, J. C. J. Phys. Chem. 1992, 96, 1888.

- (11) Land, D. P.; Pettiette-Hall, C. L.; McIver, R. T., Jr.; Hemminger, J. C. J. Am. Chem. Soc. 1989, 111, 5970.
- (12) Pettiette-Hall, C. L.; Land, D. P.; McIver, R. T., Jr.; Hemminger, J. C. J. Am. Chem. Soc. 1991, 113, 2755.
- (13) Bussell, M. E.; Henn, F. C.; Campbell, C. T. J. Phys. Chem. 1992, 96, 5978.
- (14) Karpinski, Z.; Clarke, J. J. Chem. Soc. Faraday Trans. II 1975, 71, 893.
- (15) Davis, B. H. J. Catal. 1977, 46, 348.
- (16) Meitzner, G.; Via, G. H.; Lytle, F. W.; Fung, S. C.; Sinfelt, J. H. J. Phys. Chem. 1988, 92, 2925.
  - (17) Xu, C.; Koel, B. E. Surf. Sci., accepted for publication.
  - (18) Paffett, M. T.; Windham, R. G. Surf. Sci. 1989, 208, 34.
- (19) Paffett, M. T.; Gebhard, S. C.; Windham, R. G.; Koel, B. E. J. Phys. Chem. 1990, 94, 6831
- (20) Paffett, M. T.; Gebhard, S. C.; Windham, R. G.; Koel, B. E. Surf. Sci. 1989, 223, 449.
  - (21) Xu, C.; Peck, J. W.; Koel, B. E. J. Am. Chem. Soc. 1993, 115, 751.
  - (22) Jiang, L. Q.; Koel, B. E.; Falconer, J. L. Surf. Sci. 1992, 273, 273.
- (23) Windham, R. G.; Bartram, M. E.; Koel, B. E. J. Phys. Chem. 1988, 92, 286.
  - (24) Xu, C.; Koel, B. E. Surf. Sci. 1993, 292, L803.
- (25) Griffiths, K.; Lennard, W. N.; Mitchell, I. V.; Norton, P. R.; Pirug, G.; Bonzel, H. P. Surf. Sci. Lett. 1993, 284, 398.
- (26) Campbell, C. T.; Ertl, G.; Kuipers, H.; Segner, J. Surf. Sci. 1981, 107, 220.
- (27) Overbury, S. H.; Mullins, D. R.; Paffett, M. T.; Koel, B. E. Surf. Sci. 1991. 254. 45.
- (28) Jiang, L. Q.; Koel, B. E. J. Phys. Chem. 1992, 96, 8694.
- (29) Campbell, J. M.; Seimanides, S.; Campbell, C. T. J. Phys. Chem. 1989. 93, 815
- (30) Tsai, M. C.; Mutterties, E. L. J. Am. Chem. Soc. 1982, 104, 2534. (31) Abon, M.; Bertolini, J. C.; Billy, J.; Massardier, J.; Tardy, B. Surf. Sci. 1985, 162, 395
- (32) Garfunkel, E. L.; Farias, M. H.; Somorjai, G. A. J. Am. Chem. Soc. 1985, 107, 349
- (33) Land, D. P.; Wulf, E.; Ibach, H. Surf. Sci., submitted for publication. (34) The following paper reviews this literature: Rodriguez, J. A.; Goodman, D. W. Surf. Sci. Rep. 1991, 14, 1.
  - (35) Lehwald, S.; Ibach, H.; Demuth, J. E. Surf. Sci. 1978, 78, 577.
  - (36) Somers, J.; Bridge, M. E.; Lioyd, D. R.; McCabe, T. Surf. Sci. 1984,
- 181. L167.
- (37) Herz, R. K.; Gillespie, W. D.; Petersen, E. E.; Somorjai, G. A. J. Catal. 1981, 67, 371
- (38) Davidsen, J. M.; Henn, F. C.; Rowe, G. K.; Campbell, C. T. J. Phys. Chem. 1991, 95, 6632.
- (39) Xu, C.; Koel, B. E. J. Chem. Phys., in press.