Dehydrogenation of cyclohexene on ordered Sn/Pt(111) surface alloys

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Abstract

The adsorption and dehydrogenation of cyclohexene on Pt(111) and two Sn/Pt(111) surface alloys has been studied since cyclohexene is a likely intermediate in the dehydrogenation of cyclohexane to benzene, a prototypical reaction for catalytic reforming. Our investigations used TPD, AES, LEED, and sticking coefficient measurements. The two ordered, Pt–Sn surface alloys were prepared by annealing monolayer amounts of Sn vapor-deposited onto Pt(111). Depending upon the conditions used, the annealed surface exhibited a $p(2 \times 2)$ or $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern corresponding to the (111) face of Pt$_2$Sn or a surface alloy of composition Pt$_x$Sn, respectively. Sticking coefficient measurements showed that the initial sticking coefficient, $S_0$, was equal to unity on all three substrates and determined a saturation coverage of 0.14 ML for the cyclohexene monolayer on all three substrates at 180 K; Sn in these surface alloys has no measurable effect on the adsorption kinetics and the monolayer coverage compared to Pt(111) at 180 K. Precursor mediated adsorption kinetics on all three surfaces are indicated by the constant initial sticking coefficient up to cyclohexene coverages of at least 0.02 ML. However, the cyclohexene binding energy decreases with increasing Sn concentration in the surface layer, indicating that Sn has a substantial electronic effect on cyclohexene adsorption on the Pt(111) surface. The di-$\sigma$-bonded cyclohexene on the Pt(111) surface is changed to hydrogen-bonded cyclohexene on the $(\sqrt{3} \times \sqrt{3})R30^\circ$Sn/Pt(111) surface. This change is attributed to the stronger influence of Sn on the surface capacity for forming di-$\sigma$ bonds than hydrogen bonds. At small cyclohexene coverages, the alloying of Pt with Sn increases both the activity and selectivity of gas phase benzene production under UHV conditions. At higher cyclohexene coverages, the self-poisoning of the surface by cyclohexene or reaction intermediates becomes the determining factor in the reactions of cyclohexene and the addition of Sn to the surface only slightly increases the selectivity of gas phase benzene production. However, carbon deposition on the surface is strongly suppressed.

1. Introduction

The dehydrogenation of cyclohexene on Pt (111) surfaces has been the subject of many studies as a model catalytic system [1–10]. Generally it is thought that cyclohexene adsorbs molecularly at 100 K on the Pt(111) surface. TPD and HREELS show two different states of molecularly adsorbed cyclohexene in the first adsorbed layer [8,10]. At least one of these states is correlated to di-$\sigma$-bonded cyclohexene as revealed by HREELS and XPS [8,10]. Upon heating, cyclo-
hexene begins to dehydrogenate at 180–220 K. A C₆H₉ reaction intermediate has been identified on the surface using laser-induced thermal desorption (LITD) combined with Fourier transform mass spectrometry (FTMS) [9], and HREELS and bismuth-postdosing thermal desorption spectroscopy (BPTDS) [10]. Benzene is formed on the surface at temperatures near 300 K. Further heating causes a fraction of the benzene formed to desorb from the surface at 400–500 K and the remaining benzene to decompose to hydrogen and adsorbed carbon. The thermochemistry of these reactions on Pt(111) has also been described [11].

The poisoning of heterogeneous Pt catalysts by carbon (coke) that accumulates on the Pt metal surfaces during reforming is a serious problem. In order to increase the resistance against this coking or poisoning, and thus prolong the lifetime of the catalyst, a second metal component such as Re [12], Ir [13], or Sn [14–18] is added to reforming catalysts. These bimetallic catalysts show improved selectivity for producing aromatic hydrocarbons and increased resistance to coking. An interesting question remains regarding the importance of alloy formation or direct Pt–Sn interaction as a component of the improved performance of Pt–Sn bimetallic catalysts.

Motivated to better understand the fundamental chemistry of bimetallic surfaces, we have started a systematic investigation of a series of hydrocarbon molecules on well-defined Sn/Pt(111) alloy surfaces. Paffett and Windham [19] showed that evaporating Sn onto a Pt(111) surface followed by annealing to 1000 K produces two well-ordered surface layers. Later, angle-dependent low energy ion scattering spectroscopy (LEISS) studies [20] confirmed that surface alloys were produced and these surfaces were very stable. Bulk Pt–Sn alloy surfaces, in contrast, often show reconstruction and/or surface concentration changes induced by adsorbates and heating. The Sn/Pt(111) surface alloys used herein offer outstanding new opportunities for fundamental surface science and catalysis investigations. Previously, we have studied the adsorption of CO, H₂ and O₂ [21], C₂H₄ [22] and C₂H₆ [23]. Recently, we have explored the adsorption of butane, isobutane and isobutylene [24], cyclohexane and benzene [25], and toluene and methylcyclohexane [26] on these surfaces. In this paper, we report our investigation of the adsorption and decomposition of cyclohexene on Sn/Pt(111) surface alloys using AES, TPD, LEED, and sticking coefficient measurements. The presence of Sn has a strong influence on cyclohexene reactions on Pt(111). Particularly at low cyclohexene coverages, the presence of Sn increases both the activity and selectivity of gas phase benzene production under UHV conditions.

2. Experimental

The experiments were performed in a stainless steel UHV chamber equipped with instrumentation for AES and LEED, a shielded UTI 100C quadrupole mass spectrometer (QMS) for TPD, and a directed beam doser for making sticking coefficient measurements. The system base pressure was 6 × 10⁻¹¹ Torr.

AES spectra were recorded using a Perkin Elmer 10-360 hemispherical analyzer and a glancing incidence electron gun. The typical incident electron beam current used was 20 nA, and so electron beam induced effects in AES were negligible. The amount of carbon left on the surface after each TPD experiment was calibrated by AES using the known C₂H₄ saturation coverage on clean Pt(111) at 300 K, θC = 0.5 [27], as a reference.

TPD measurements were made using the QMS in line-of-sight with the sample surface and using a linear heating rate of ~ 4 K/s. The crystal was always positioned very close (~ 1 mm) to the entry aperture of the QMS shield. The contribution of the crystal back and edges to the TPD spectra was negligible as indicated by the complete suppression of H₂ desorption in TPD after benzene or cyclohexane exposures on the Sn/Pt(111) surface alloys [25], even though the crystal back and edges were not covered with Sn. We have recently reported the strong effects of electrons on the decomposition of hydrocarbon multilayers [28]. To suppress low energy electrons coming out of the QMS and to remove the
attendant artifacts in TPD, a screen biased by −55 V was placed between the QMS ionizer and the sample.

The Pt(111) crystal could be 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. [29].

Cyclohexene (Fischer, 98%) was used as received after several freeze–pump–thaw cycles. The purity was checked by gas chromatography (GC) and in situ mass spectrometry. Cyclohexene was exposed on the sample either by using a microcapillary array-directed beam doser and a leak valve or by a similar doser that was connected to a calibrated leak and high pressure (1–10 Torr) gas line. Exposures for TPD studies are given in langmuir (1 L = 10⁻⁶ Torr · s) and are reasonable estimates for the true exposures on the sample given the uncertainties associated with the doser enhancement, ion gauge sensitivity, and other factors. The relative exposures are precisely reported.

The sticking coefficient was determined using a simple kinetic uptake method which was previously described [30]. Using the known saturation coverage of C₆H₁₀ on clean Pt(111) at 100 K, \( \theta_{C₆H₁₀} = 0.25 \) [27], the cyclohexene coverage, \( \theta_{C₆H₁₀} \), was calibrated with the following equation [31]:

\[
\theta_{C₆H₁₀} = \frac{P_{C₆H₁₀}}{P_{C₂H₆}} \left( \frac{M_{C₆H₁₀}}{M_{C₂H₆}} \right)^{1/2} \int \frac{S_{C₆H₁₀} \, dt}{S_{C₂H₆} \, dt} \theta_{C₂H₆},
\]

where \( \theta, P, M \) and \( S \) represent the coverage, backing pressure in the gas line behind the leak, molecular weight, and sticking coefficient for cyclohexene and ethylene, respectively.

Adsorbate and adatom coverages in this paper are referenced to the Pt(111) surface atom density, i.e., \( \theta = 1 \) is defined as \( 1.505 \times 10^{15} \text{ cm}^{-²} \).

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 subse-

![Fig. 1. Structures of the \( (2 \times 2) \) and \( (\sqrt{3} \times \sqrt{3})R30° \) Sn/Pt(111) surface alloys.](image)
for Sn, the Sn/Pt(111) surface alloys must be newly prepared for each experiment. Sn was removed by sputtering at 1000 K for 15 min. The sputtered surface was then heated at 800 K in $2 \times 10^{-8}$ Torr O$_2$ and annealed to 1200 K. The cleanliness and order were checked by AES and LEED.

3. Results

3.1. Adsorption and decomposition of benzene

Since benzene is the expected product of cyclohexene dehydrogenation, we first studied the adsorption and decomposition of benzene on the two Sn/Pt(111) surface alloys. These results are published together with our cyclohexane studies in a separate paper [25]. Here we only briefly summarize the major results in order to put our cyclohexene studies in the proper context. Upon alloying of Pt with Sn, the decomposition of benzene was completely suppressed under UHV conditions: no H$_2$ desorption was detected from the Sn/Pt(111) surface alloys at any of the benzene coverages (up to several condensed layers) used in our experiments. At small benzene coverages, the molecular desorption of benzene from a strongly chemisorbed state on the Sn/Pt(111) surface alloys increased because of the suppression of benzene decomposition. At higher benzene coverages, benzene desorption from chemisorbed states decreases with increasing Sn concentration. At the expense of the chemisorbed states, a weakly bonded benzene, probably a physisorbed state, was formed in the first adsorbed layer. These results show a destabilization of $\pi$-bonded, chemisorbed benzene species and a strongly decreased reactivity of benzene on the Sn/Pt(111) surface alloys relative to the Pt(111) surface.

3.2. Adsorption and decomposition of cyclohexene

3.2.1. Adsorption and desorption

Fig. 2 shows cyclohexene TPD spectra after several cyclohexene exposures on the Pt(111) surface. Our TPD data are in good agreement with those reported previously by Rodriguez and Campbell [8] with the one exception that all of the desorption peaks in our spectra are shifted to lower desorption temperatures by $\sim 15$ K (which can be attributed mostly to the different heating rates used in the two experiments). At small cyclohexene coverages, no molecular cyclohexene desorption was visible and all adsorbed cyclohexene suffers dehydrogenation. Increasing the cyclohexene dose to 0.2 L, we first populate two peaks at 239 and 281 K and a small peak at 177 K. With further increases in cyclohexene exposure, the peak at 177 K gains intensity. Finally a peak at 145 K is seen at high cyclohexene exposure. The four peaks were previously assigned by Rodriguez and Campbell [8] to desorption from the multilayer ($\alpha$, 145 K), second layer ($\beta$, 177 K) and two different states ($\gamma$ and $\lambda$, 239 and 281 K) in the first layer. Based on their TPD results they had assigned these latter two states to di-$\pi$-bonded and H-bonded cyclohexene. In recent
HREELs measurements, Henn et al. [10] reassigned both of these states to di-σ bound cyclohexene but in different conformations, proposed to be in the chair and boat configurations.

Henn et al. also [10] showed that the β state desorption can be eliminated by using an aluminum focusing cone to discriminate against desorption from the back and edges of the crystal. Therefore, the β state was attributed to desorption from the crystal back and edges, a possibility that was suggested also in Ref. [8]. Further support for this assignment comes from a careful investigation of the multilayer desorption. The inset to Fig. 2 shows an expanded view of cyclohexene TPD spectra below 230 K. A peak at 145 K begins to develop after saturation of the β, γ, and λ states. With increasing cyclohexene coverage, the peak at 145 K shifts to higher temperature, a typical behavior for zero-order desorption kinetics. At larger cyclohexene exposures, we see a new peak at 143 K which has not been reported previously. Similar results were seen for cyclohexene on both the (2 x 2) and √3 alloy surfaces (e.g., see the inset to Fig. 4). Therefore, we assign the previously-labeled α state to desorption from the second layer and the α' state to desorption from the third and additional layers. We also conclude that cyclohexene grows initially in a layer-by-layer mode on Pt(111) and both alloy surfaces.

Cyclohexene TPD spectra after several cyclohexene exposures on the (2 x 2) and √3 alloy surfaces are provided in Figs. 3 and 4. On the (2 x 2) alloy, the four desorption peaks on the Pt(111) surface are reduced to 3 peaks as shown in Fig. 3. The peak at 146 K cannot be saturated with increasing cyclohexene coverage and is attributed to the second layer and multilayer desorption. The peaks at 239 and 281 K on Pt(111) are reduced to one peak at 236 K on the (2 x 2) alloy, while the β state remains with the same desorption temperature. In addition, a small shoulder near 200 K is also visible. As for Pt(111), we attribute all peaks above 160 K to desorption from different bonding states in the first adsorbed layer.

On the √3 alloy, we first populate a peak at 208 K with increasing cyclohexene exposure as shown in Fig. 4. The second layer peak at 147 K begins to develop at cyclohexene doses higher than 0.3 L. As mentioned before, we see a pair of peaks near 145 K at even higher cyclohexene coverages, as shown in the inset to Fig. 4, due to desorption from the second and subsequent layers. We assign the peak at 176 K to p state desorption. A small peak at 236 K is seen at all coverages used in our experiments.

The presence of Sn in the Pt(111) outermost surface layer changes both the desorption peak shape and the amount of desorbed (reversibly adsorbed) cyclohexene from the first chemisorbed layer. This is more clearly shown in Fig. 5 where the TPD spectra of cyclohexene on Pt(111) and the (2 x 2) and √3 alloy surfaces are directly compared. The highest desorption temperature of cyclohexene decreases gradually with increasing Sn concentration in the surface. At the same time, the amount of cyclohexene desorption above...
160 K and thus the amount of reversibly adsorbed cyclohexene in the monolayer, increases with the increasing Sn concentration in the surface.

A direct measurement of the sticking coefficient of cyclohexene on Pt(111), (2 x 2) alloy and \( \sqrt{3} \) alloy surfaces at 180 K was made using a beam reflection method as described previously [30,31]. The results are shown in Fig. 6. The initial sticking coefficient of cyclohexene on all three surfaces is near unity: Sn has no significant influence on the cyclohexene initial sticking coefficient. On all three surfaces, the sticking coefficient stays constant up to a cyclohexene coverage of 0.02 ML and then gradually decreases to zero at saturation coverage. These results imply precursor-mediated adsorption kinetics of cyclohexene on all three surfaces, with no measurable changes in the adsorption kinetics due to the presence of Sn. The cyclohexene monolayer saturation coverage at 180 K was determined to be

0.14 ML on Pt(111), and 0.13 ML on the (2 x 2) and 0.12 ML on the \( \sqrt{3} \) alloy surfaces. This slight reduction is within the normal experimental un-
certainties, but also arises because the adsorption energetics vary somewhat for the three surfaces and we chose a constant adsorption temperature of 180 K for all three surfaces. Thus, there is no significant effect of Sn on the monolayer saturation coverage of cyclohexene on Sn/Pt(111) sur-

Fig. 7. H₂ TPD spectra after several C₆H₁₀ exposures on Pt(111), and the (2×2) and (\sqrt{3}×\sqrt{3})R30°Sn/Pt(111) surfaces.

Fig. 8. C₆H₆ TPD spectra after different C₆H₁₀ exposures on Pt(111), and the (2×2) and (\sqrt{3}×\sqrt{3})R30°Sn/Pt(111) surfaces.
face alloys compared to Pt(111). These results are also consistent with our interpretation that the cyclohexene TPD peaks at 239 and 281 K on Pt(111) are reduced to one peak on the Sn/Pt (111) surface alloys.

Finally, we also used LEED to study the adsorption of cyclohexene on the Sn/Pt(111) surface alloys. Monolayer cyclohexane coverages are disordered and caused only an increase in the diffuse background intensity on both of the Sn/Pt(111) surface alloys. The (2 × 2) and (√3 × √3)R30° LEED patterns were still clearly seen, showing that adsorption of cyclohexene does not alter the structure of these surface alloys.

3.2.2. Dehydrogenation, hydrogenation, and decomposition

TPD spectra showing H₂ evolution and C₆H₆ formation from adsorbed cyclohexene are summarized in Figs. 7 and 8. On Pt(111), H₂ TPD spectra after cyclohexene exposures show a strong coverage dependence as shown in Fig. 7a. For small exposures, the H₂ TPD spectra have an almost identical shape as those for H₂ evolution from cyclohexane [25,32]. Similar to that for cyclohexane, the peak at 353 K can be attributed to cyclohexene dehydrogenation to benzene and the peaks at 523 and 630 K to benzene decomposition. With increasing cyclohexene coverage, a much more complicated H₂ TPD spectrum develops, which is consistent with previous results reported by Rodriguez and Campbell [8]. At least five peaks at 294, 397, 439, 523 and 630 K are visible in Fig. 7a. The H₂ peaks below 450 K are correlated to cyclohexene dehydrogenation and the peaks above 450 K are due to the decomposition of benzene formed from cyclohexene.

H₂ evolution in TPD studies of cyclohexene adsorption on the (2 × 2) and √3 alloy surfaces are shown in Figs. 7b and 7c. With the help of previous studies by Paffett et al. [21] of the desorption of H₂ following H atom exposures on the Sn/Pt(111) surface alloys, we can assign our H₂ TPD peaks after cyclohexene dosing. Similar to the behavior on Pt(111), the (2 × 2) alloy in Fig. 7b has two peaks below 450 K. Both peaks have to be correlated with the dehydrogenation of cyclohexene to benzene. The low temperature desorption peak is very similar to the H₂ TPD from hydrogen adatoms [21] both in the desorption temperature and shape. We assign this peak to an H₂ desorption-limited process. The desorption peak at 441 K is therefore reaction rate-limited. On the √3 alloy, the peak at 339 K is also attributed to an H₂ desorption-limited process. The higher temperature peaks at 410 and 442 K are reaction rate-limited and correlate with the dehydrogenation of cyclohexene or some reaction intermediates to benzene or some benzene-like species.

From Fig. 7b it can be seen that an appreciable amount of H₂ desorbs above 450 K on the (2 × 2) alloy. We know from our previous studies of benzene adsorption on these two Sn/Pt(111) surface alloys that benzene is only reversibly adsorbed on these surfaces [25]; no benzene decomposition occurs at either small or high benzene exposures. Fig. 7b indicates that either the benzene formed from cyclohexene is more reactive than benzene from benzene adsorption (highly unlikely) or else cyclohexene can also decompose through a different pathway than through benzene, such as C–C bond cleavage or loss of two hydrogen atoms from one carbon atom prior to benzene formation. The lineshape of the H₂ desorption peaks above 450 K are similar to the profile for H₂ evolution after benzene exposure on Pt(111). Thus, we assume that some benzene-like species is formed on the surface. However, species produced by these routes are more strongly bonded to the surface than benzene and decompose with further heating.

Consistent with the H₂ TPD results, AES shows a strong decrease in the amount of carbon left on the surface after each TPD experiment with increasing Sn concentration. On the √3 alloy surface, no significant carbon signal was ever detected after TPD experiments for any cyclohexene coverages used. This indicates that the presence of θ_{Sn} = 0.33 in the Pt(111) surface completely suppresses decomposition of cyclohexene to adsorbed carbon and hydrogen.

C₆H₆ TPD spectra following cyclohexene exposure on the Pt(111) surface are shown in Fig. 8a. These are in good agreement with the results published by Rodriguez and Campbell [8]. For
cyclohexene exposures of less than 0.05 L, no benzene desorption from the Pt(111) surface was observed. By contrast, benzene desorption from the two Sn/Pt(111) surface alloys was observed at the smallest cyclohexene exposures that were used as shown in Figs. 8b and 8c. At 0.05 L cyclohexene exposure, benzene also desorbs from the Pt(111) surface. However, unlike C₆H₆ TPD spectra after benzene dosing, the desorption of benzene formed from cyclohexene shows a very sharp onset at low temperature. Rodriguez and Campbell [8] attributed this difference to an autocatalytic process and poisoning of the surface by adsorbed hydrogen. The dehydrogenation of cyclohexene to benzene is inhibited by site-blocking from coadsorbed cyclohexene and reaction intermediates, so no benzene desorption is seen below 385 K. Above this temperature, hydrogen desorbs and additional benzene can be formed and desorbed. Benzene formed from cyclohexene desorbs at much lower temperatures on both Sn/Pt(111) surface alloys compared to Pt(111). Both the desorption temperature and the shape of the benzene TPD spectra are similar to those obtained after benzene exposure [25]. Therefore, benzene desorption must be the rate-limiting step in benzene production on the Sn/Pt(111) surface alloys. This result is consistent with the fact that much more cyclohexene desorbs from these surfaces at low temperatures leaving sites for benzene formation prior to H₂ desorption.

In order to get more insight into the role of Sn in altering cyclohexene dehydrogenation, we compared H₂, C₆H₆ and C₆H₁₀ TPD spectra on Pt(111) and the two alloy surfaces for the same cyclohexene exposures. This comparison is shown in Fig. 9 for spectra taken after a small cyclohexene dose that produces ~20% of one monolayer coverage of cyclohexene. At this small coverage, self-site-blocking has a negligible effect on the chemistry of cyclohexene; cyclohexene dehydrogenation is mainly dictated by the surface of the substrate. In this case, the presence of Sn increases molecular cyclohexene desorption and suppresses H₂ evolution, especially the high temperature H₂ desorption states. The most interesting result is that benzene production shows a maximum on the (2 × 2) alloy.

Fig. 9. C₆H₁₀ (a), H₂ (b) and C₆H₁₀ TPD spectra following 0.05 L cyclohexene exposures on Pt(111), and the (2 × 2) and (√3 × √3)R30°Sn/Pt(111) surfaces.
We can explain the enhanced benzene formation on the \((2 \times 2)\) alloy as follows. The decomposition of benzene and the dehydrogenation of cyclohexene to benzene is suppressed with increasing Sn concentration in the Pt(111) surface. But, Sn is more effective in suppressing benzene decomposition compared to cyclohexene dehydrogenation. Decomposition of benzene is eliminated on the \((2 \times 2)\) alloy as shown in our studies of benzene adsorption [25] and by the absence of an \(\text{H}_2\) TPD peak in Fig. 9 near 500 K on the \((2 \times 2)\) alloy. The dehydrogenation of cyclohexene decreases only slightly on the \((2 \times 2)\) alloy compared to Pt(111) as indicated by the large \(\text{H}_2\) desorption peaks below 450 K which are accompanied by only a small molecular cyclohexene desorption peak. As a result, the gas phase benzene production strongly increases from Pt(111) to the \((2 \times 2)\) alloy. Increasing \(\theta_{\text{Sn}}\) from the \((2 \times 2)\) to the \(\sqrt{3} \times \sqrt{3}\) alloy causes the activity of the surface to be reduced further. The dehydrogenation of cyclohexene is now greatly decreased as indicated by the large molecular cyclohexene desorption peak and the small \(\text{II}_2\) desorption peak below 450 K. Reversible adsorption of cyclohexene on the \(\sqrt{3} \times \sqrt{3}\) alloy causes a decrease in benzene production.

Finally, the hydrogenation of cyclohexane was detected by monitoring cyclohexane desorption. For small cyclohexene coverages, no significant cyclohexane desorption was observed from any of the three surfaces investigated. Cyclohexene desorption was detectable after cyclohexene exposures higher than 0.4 L which produce a complete cyclohexene monolayer, but only on Pt(111) as shown in Fig. 10. On both Sn/Pt(111) surface alloys, no cyclohexane formation was observed at any coverage. (The small peaks in the TPD spectra in Fig. 10 for the Sn/Pt(111) alloy surfaces have the same peak temperature and shape as cyclohexene and are attributed to cyclohexene hydrogenation within the QMS ionizer.) The cyclohexene peak temperature in Fig. 10 for Pt(111) is well above the cyclohexene desorption temperature after dosing cyclohexane [25] indicating that the desorption peak in Fig. 10 is a reaction rate-limited process. The hydrogenation of cyclohexene is obviously dictated by the concentration of hydrogen on the surface. Since Pt(111) has the highest reactivity for dehydrogenation of cyclohexene and produces the most adsorbed hydrogen on the surface, it also has the most cyclohexane production.

4. Discussion

4.1. Adsorption of cyclohexene on Pt(111) and Pt–Sn alloys

Cyclohexene can be adsorbed onto the Pt(111) surface in two different binding states: bonded to the surface with the double bond analogous to ethylene in a \(\pi\) or di-\(\sigma\) configuration, and bonded to the surface with the alkane ring as in cyclohexane where hydrogen bonding plays an important role. The relative strength of these alternative bonding interactions dictates how cyclohexene is
bonded to the surface. On the Pt(111) surface, di-σ-bonding is a more favored configuration over hydrogen bonding for small alkenes such as ethylene. For large molecules like cyclohexene, the hydrogen bond becomes important because of the increasing amount of hydrogen bonded to the surface in one molecule. Also physisorption forces are larger in the hydrogen-bonded configuration where cyclohexene is “lying down” than in the di-σ-bonded form where the molecule is “standing up”. But, cyclohexene is still bonded to the surface in a di-σ configuration on Pt(111) as viewed by HREELS. This is also consistent with the TPD peak temperatures (T_P) of ethylene [22] and cyclohexane [25], showing that ethylene (T_P = 280 K) has a much higher binding energy than cyclohexane (T_P = 228 K). Thus, from TPD one expects the di-σ bond to be the favored binding configuration for cyclohexene. In fact, cyclohexene desorbs from the Pt(111) surface at 281 K, the same desorption temperature as ethylene, indicating a similar binding energy. This also shows that the additional alkyl ring of cyclohexene has almost no influence on the strength of the di-σ bond to Pt. The same results have also been found by Avery and Sheppard [35] for the adsorption of different alkenes on the Pt(111) surface: ethylene, propene, butene and pentene all have the same molecular desorption temperatures. These results indicate that the alkyl group does not have a significant electronic influence on the di-σ-bonding interaction, i.e., the Pt–C covalent bond strength, D(Pt–C). However, steric effects of the alkyl groups can be appreciable in certain cases (see below).

The presence of Sn on the Pt(111) surface changes the situation described above. The strength of di-σ and hydrogen bonding interactions are both decreased with increasing Sn concentration on the Pt(111) surface, but to different degrees. The influence of Sn on the di-σ bond strength is more dramatic than on that of the hydrogen bond. In Fig. 11, we compare the desorption temperatures of cyclohexene, cyclohexane [25], isobutane [24], isobutylene [24], and ethylene [22] on the three surfaces studied. It is obvious that all of the alkanes show a very similar dependence of the desorption temperature on the Sn concentration. (This is also true for other alkane molecules that we have investigated like methylcyclohexane [26], butane [24], and heptane [34], but these results are not shown here.) On the other hand, ethylene and isobutylene show a similar dependence. The decrease in the desorption temperature with increasing Sn concentration is more dramatic for alkenes than alkanes. Cyclohexene is an exception to this observation. In going from the Pt(111) surface to the (2 × 2) alloy, the decrease of the cyclohexene desorption temperature is similar to other alkenes. But a further increase in the Sn concentration to form the \( \sqrt{3} \) alloy only causes a small decrease in the cyclohexene desorption temperature, much smaller than one would expect from the weakening of the di-σ bond strength in ethylene or isobutylene by the presence of Sn. In order to understand this, we must first take a more detailed look at
the behavior of ethylene and cyclohexane. On the Pt(111) surface, the desorption temperature of ethylene is much higher than cyclohexane, and with increasing Sn concentration on the Pt(111) surface, the desorption temperature of both ethylene and cyclohexane decreases. But the decrease of the di-σ bonding energy is larger than that of the hydrogen bonding energy as indicated by the larger reduction of $T_p$ for ethylene in comparison to cyclohexane. On the $\sqrt{3}$ alloy, cyclohexane desorbs at a higher temperature than ethylene. This result indicates that hydrogen-bonded cyclohexene becomes a more favored configuration than the di-σ-bonded cyclohexene on the $\sqrt{3}$ alloy. As a consequence of the change in adsorption geometry and the nature of the chemisorption bond, the decrease in desorption temperature from Pt(111) to the $\sqrt{3}$ alloy is small, simply because H-bonded cyclohexene has a higher desorption temperature than di-σ bonded cyclohexene on the $\sqrt{3}$ alloy. As shown in Fig. 11, hydrogen-bonded cyclohexene has a higher desorption temperature than H-bonded cyclohexene, indicating that the C=C double bond contributes to the adsorption energy in this geometry.

The next question concerns how cyclohexene is bonded on the (2 x 2) alloy. Starting from the desorption temperature of cyclohexene on the Pt(111) surface and on the $\sqrt{3}$ alloy, and using the ethylene $T_p$-dependence on the Sn concentration for the di-σ bonding configuration and the cyclohexane $T_p$-dependence on Sn concentration for the hydrogen bonding configuration, we can estimate the desorption temperature of di-σ-bonded cyclohexene on the (2 x 2) alloy to be around 237 K and the desorption temperature of hydrogen-bonded cyclohexene to be 218 K on the (2 x 2) alloy. Therefore, we predict that on the (2 x 2) alloy, cyclohexene is also di-σ-bonded. In fact, cyclohexane on the (2 x 2) alloy desorbs at 236 K, very close to our predicted value of di-σ-bonded cyclohexene on the (2 x 2) alloy. Therefore, cyclohexene should still remain in the di-σ bonding configuration on this alloy surface, but this needs to be verified spectroscopically. Ethylene is di-σ-bonded on both alloy surfaces [22].

In addition to the molecular cyclohexene desorption at 281 K ($\lambda$ state) on the Pt(111) surface, a desorption peak at 239 K (γ state) has been observed always. Rodriguez and Campbell [8] originally assigned this γ state to H-bonded cyclohexene. Using the desorption temperature of H-bonded cyclohexene on the (\sqrt{3} x \sqrt{3}) alloy and the cyclohexane desorption temperature dependence on the Sn concentration, we estimate that H-bonded cyclohexene would desorb from the Pt(111) surface at 251 K, similar to the desorption temperature we observed for the γ state. However, H-bonded cyclohexene will cause a well-known softening of the C-H bond stretch frequency and can be easily identified in the HREELS measurements. The HREELS results of Ref. [10] showed no indication of a C-H bond softening. Henn et al. [10] reassigned this state to a di-σ-bonded form of cyclohexene, but in a less stable configuration than that responsible for the TPD peak at 281 K. These authors speculate that the chair and boat conformations account for the two states. We show our model for these adsorbed conformers in Fig. 12a. The Newman projection along the original double bond for both chair and boat conformations is provided in this figure. It is well known that conformational isomerism in the gas phase takes place readily at the desorption temperature of the γ state (239 K) [36]. It is reasonable to assume that such isomerism can also occur on the surface. An alternative explanation for the different di-σ-bonded desorption states involves the cis and trans isomers. Newman projections of these two isomers of cyclohexene are shown in Fig. 12. We expect both cis forms to be higher in energy than the trans form. In the cis boat configuration, cyclohexene is in the so-called eclipsed configuration which has about 7 kcal/mol higher energy than the trans configuration. In the cis chair configuration, the alkyl ring is at a very short distance from the surface and we expect a repulsive interaction between the surface and the alkyl ring. In the case of the trans configuration there are no large steric effects. This difference in the cis and trans configurations could be the origin of the two di-σ-bonded cyclohexene states. It is also important to mention that isomerization between the cis and trans forms requires one C-Pt or C-H bond to be broken, so that this transformation is
difficult and requires an additional Pt site. High cyclohexene coverages could block sites for this transition and cause two distinct desorption peaks. By contrast, the transformation between the chair and boat conformations does not require breaking any bonds and therefore is much easier. One can argue that the cis configuration is the kinetically more favorable product. One might never make trans-cyclohexene on the surface. In fact, the syn addition of cyclohexene is the general rule. However, anti addition is sometimes also observed. For example, hydrogenation of 1,2-dimethylcyclohexene over palladium gives trans-1,2-dimethylcyclohexane as the major product [43]. A definitive assignment of the adsorption geometry of cyclohexene will require additional, fairly difficult, spectroscopic studies.

Further support for this explanation comes from the TPD investigation of different alkenes including cis- and trans-2-butene on the Pt(111) surface. Avery and Sheppard [35,37] have found that propene, 1-butene, trans-2-butene and 1-pentene all have the same desorption temperature, but that cis-2-butene desorbs at a temperature 10 K lower than trans-2-butene. This is expected from our simple steric effect arguments. In Fig. 13a, Newman projections of butene isomers are provided. It is obvious from Fig. 13a that only cis-2-butene has a CH₃ group directed towards the surface. If one tries to go to the eclipsed configuration avoiding the interaction of the CH₃ group with the surface, one increases the interaction between two CH₃ groups in the cis configuration as shown in Fig. 13b. As a result, cis-2-butene has a lower desorption temperature than all of the other alkene molecules. Isobutylene, which always has a CH₃ group near the surface, also has a lower desorption temperature than linear alkenes as shown in Fig. 11. However, the difference in desorption temperature between adsorbed cis- and trans-2-butene (10 K) is much smaller than the difference between the adsorbed cis- and trans-cyclohexene (42 K). A possible explanation is that the configuration provided in Fig. 12a does not exist on the surface, although it is the most stable configuration in the gas phase. In order to build a more stable bond to the surface and avoid repulsive steric interactions with the surface, a configura-
tion like the eclipsed configuration provided in Fig. 13b might exist on the surface. These configurations certainly have reduced steric effects and a reduced difference between the binding energy of the cis and trans configurations. It is much easier to have the transition from the configuration depicted in Fig. 13a to those in Fig. 13b for 2-butene than for cyclohexene. (The energy difference between two different eclipsed butanes in the gas phase corresponding to trans- and cis-butene on the surface is 0.7 kcal/mol, while the energy difference for the gas phase chair and boat cyclohexane configurations corresponding to the trans- and cis-cyclohexene in the eclipsed configuration on the surface is 10.7 kcal/mol [43].) Therefore, the difference between the binding energy of adsorbed cis- and trans-cyclohexene is also larger.

Of course, these two peaks could simply correspond to cyclohexane adsorbed on different sites. For example, two different adsorption states have also been found for ethylene which has a temperature difference in TPD spectra of 20 K. A definitive decision between the above mentioned alternatives is not possible at the present time. Additional spectroscopic investigations are planned to resolve this issue.

The presence of Sn reduces the two cyclohexene desorption peaks at 239 and 281 K on the Pt(111) surface to only one desorption peak, indicating an easier transition between the two cyclohexene states. This change might be due to the reduced binding energy of cyclohexene on the Sn/Pt(111) surface alloys.

Lastly we come to the desorption state at 177 K (β state). As mentioned before, the amount of the β state desorption is always very small, especially in our TPD curves. From the TPD area, we can estimate that the β state desorption is less than 5% of the cyclohexene monolayer coverage. In separate experiments, we have shown that the presence of carbon, oxygen or other contamination on the surface strongly increases the intensity of this peak. Therefore, we assign this peak to cyclohexene desorption from contaminated regions of the surface. This assignment is consistent with the finding by Henn et al. [10]. They assigned this peak to desorption from the back and edges of the sample. The edges and back of the sample were unsputtered and probably carbon-covered.

4.2. Dehydrogenation and decomposition of cyclohexene on Pt(111) and Pt–Sn alloys

The influence of Sn on the dehydrogenation and decomposition of cyclohexene on Pt(111) is best demonstrated in Fig. 14 in which the activity and selectivity for gas phase benzene production at low and high cyclohexene coverage is plotted. The selectivity has been calculated by division of the H₂ TPD areas below 470 K by the total H₂ TPD areas, because the H₂ desorption below 470 K primarily represents cyclohexene dehydrogenation and the H₂ desorption above 470 K is from decomposition of benzene or benzene-like species. For the activity for gas-phase benzene production, we simply plot the benzene TPD areas against Sn concentration.

It is obvious from Fig. 14 that Sn has a different influence on cyclohexene dehydrogenation depending on the cyclohexene coverage. After a small cyclohexene exposure (0.05 L), the (2 × 2) alloy shows the highest activity for benzene production, while the selectivity for gas-phase benzene production is highest on the Pt–Sn alloy. At high initial cyclohexene coverages, the selectivity for benzene production increases only slightly.

![Fig. 14. The influence of Sn on the activity and selectivity of gas phase benzene production.](image-url)
with increasing concentration of Sn, but the activity for gas-phase benzene production decreases strongly with increasing Sn concentration.

How can we understand this dependence on the cyclohexene coverage? At small cyclohexene coverages, the Pt(111) surface has a very high reactivity for both dehydrogenation of cyclohexene and decomposition of benzene. The benzene formed from cyclohexene suffers further decomposition and is converted to carbon and hydrogen. Therefore, no benzene desorption is observed at small cyclohexene coverages. In order to get benzene desorption, the reactivity of Pt must be decreased. There are two possible ways to reach this effect: blocking sites (ensemble effects) and altering the electronic structure (ligand effects). At small cyclohexene coverages, the presence of Sn reduces the reactivity of Pt(111) towards cyclohexene and benzene through both electronic and site-blocking effects. At small Sn concentrations, the suppression of benzene decomposition (which promotes benzene desorption) dominates and, at high Sn concentrations, the decrease in cyclohexene dehydrogenation (which poisons benzene formation) also becomes important. As a result of these two opposite influences, a maximum in the gas-phase benzene production occurs on the \((2 \times 2)\) alloy. Turning now to the situation for high cyclohexene coverages, coadsorbed cyclohexene and other hydrocarbon intermediates block sites for the decomposition of benzene. The presence of Sn causes additional decreases in the reactivity of the surface, which has a much larger effect on cyclohexene dehydrogenation than on benzene decomposition. As a consequence, the Sn/Pt(111) surface alloys show a reduced activity for benzene production at high cyclohexene coverages.

![Proposed pathways of cyclohexene decomposition.](image_url)
Another interesting question is why are there large amounts of $\text{H}_2$ desorption on the $(2 \times 2)$ alloy above 470 K, even though benzene does not decompose on the alloy at any benzene coverage used in our experiments. Some strongly bonded benzene-like intermediate must be formed on the surface at high cyclohexene coverage. There are two possibilities which can account for this intermediate. One is a $\text{C}_6\text{H}_3$ species. A $\text{C}_6\text{H}_5$ species can be produced if two hydrogen atoms are lost from the same carbon atom before the dehydrogenation of cyclohexene to benzene is completed. A possible precursor could be species (B) as shown in Fig. 15, which has often been found in organometallic complexes and is known to be very stable. The second possibility is also illustrated in Fig. 15 as species (c). The di-o-bonded cyclohexene can break a C–H or C–C bond with increased sample temperature. Both are exothermic reactions and thermodynamically favorable. At low cyclohexene coverage, C–H bond cleavage is kinetically more favorable and therefore it is the major reaction process on the surface. With increasing cyclohexene coverage, because of site-blocking effects on the C–H bond breaking rate or a relatively larger increase in the activation energy for C–H bond breaking C–C bond cleavage may also become important and competitive with C–H bond cleavage. Then, substantial amounts of species (C) could be formed at high cyclohexene coverages. Species (B) and (C) are very strongly bonded to the surface and probably undergo further dehydrogenation and decomposition upon heating in TPD. In addition to other effects, these species also cause a strong decrease in the activity and selectivity of benzene production on the Sn/Pt(111) surface alloys. The presence of Sn obviously does not suppress decomposition of species (B) or (C) as efficiently as for benzene. Finding a way to suppress formation of these species would improve the selectivity and activity of gas-phase benzene production and the catalyst lifetime. This may be a fine balancing act of tuning the C–H cleavage rate constant to make sure that benzene formation occurs, but that no benzene dehydrogenation occurs subsequently.

The Sn/Pt(111) surface alloys that we investigated are more reactive toward cyclohexene than ethylene. As reported previously by us [22], the dehydrogenation of ethylene is completely suppressed (no $\text{H}_2$ desorption was observed in TPD studies) on either of the $(2 \times 2)$ or $\sqrt{3}$ surface alloys. However, cyclohexene shows significant reactivity on the $(2 \times 2)$ alloy as shown in Figs. 7 and 9. The higher reactivity of cyclohexene in comparison to ethylene cannot be attributed to a difference in adsorption energies since both ethylene and cyclohexene desorb at the same temperature. Rather, a difference in activation energy for reaction must be responsible for this. Campbell et al. have shown previously that the differences between the activation energies for the dehydrogenation of different adsorbed hydrocarbons is nearly equal to the difference in their gas phase C–H bond dissociation energy [38–40]. It is well known that a $2^\circ$ C–H bond has a lower bond dissociation energy (94.5 kcal/mol) than a vinylic C–H bond (108 kcal/mol) for molecules in the gas phase [41]. Therefore, we expect a higher reactivity of cyclohexene compared to ethylene. Although the C–C double bond is extensively rehybridized to nearly a C–C single bond for both alkenes on Pt(111) (and to a lesser extent on Sn/Pt(111)), hydrogen atoms bonded to sp$^3$-hybridized carbon atoms in cyclohexene are likely to still have a lower dissociation activation energy than hydrogen atoms bonded to the partially rehybridized, sp$^2$–sp$^3$ carbons bonded to the surface. We have also found that toluene and ethylbenzene are more reactive than benzene, and this can be attributed to the lower dissociation energy of alkyl hydrogens compared to aromatic hydrogens.

4.3. Comparisons with related results on other bimetallic Pt surfaces

The dehydrogenation and decomposition of cyclohexene on Bi-precovered Pt(111) surfaces under UHV conditions was previously studied by Rodriguez and Campbell [8] using TPD. Because of the weak interactions between Bi and Pt and Bi and hydrocarbons [8,10,32,38,39,42], Bi has been thought to simply act as a site-blocker in this type of experiment. It has been used to
attempt to isolate the site-blocking effect from the electronic effect which is a very difficult task. The influence of alloyed Sn atoms incorporated into the surface layer on the H₂ and benzene TPD spectra after cyclohexene exposures is very similar to the influence of Bi adatoms. Both the change in desorption temperature and the shape of the H₂ and benzene TPD spectra are almost the same for addition of either modifier. This is consistent with our proposal that the influence of Sn on benzene adsorption and reaction is mainly by site-blocking and the finding by Paffett et al. [21] that the H₂ desorption temperature (following H adsorption) is only decreased slightly by the presence of Sn on the surface. Since the desorption of benzene and H₂ formed by cyclohexene dehydrogenation to benzene is limited by the desorption rate of benzene and H₂ both on Sn/Pt(111) and Bi/Pt(111), and the hydrogen desorption at higher temperatures is limited by benzene decomposition, we have similar H₂ and benzene TPD spectra after cyclohexene exposures on Sn/Pt(111) and Bi/Pt(111).

In contrast, the adsorption and desorption of cyclohexene is influenced differently by Sn and Bi. The presence of Bi simply suppressed the adsorption of cyclohexene on Pt(111) and a peak in TPD correlated to desorption from Bi appeared [8]. No significant shifts of the TPD peak for cyclohexene desorption from the Pt(111) surface was observed. This indicates that Bi mainly has a site-blocking effect and almost no electronic effect in cyclohexene adsorption and desorption. The addition of Sn to form the surface alloys does not simply suppress desorption from the Pt(111) surface, but rather gradually shifts the desorption temperature of cyclohexene to lower temperatures. As opposed to Bi/Pt(111), the Sn/Pt(111) surface alloys show a uniform behavior in the adsorption and desorption of cyclohexene, i.e., no separate peaks associated with Sn and Pt were observed. Similar effects have also been observed for ethylene [22] and cyclohexane [25] on Sn/Pt(111) surfaces. These results indicate that surface Sn can act merely as a site-blocker or can have a substantial electronic influence depending on the molecule and/or the reaction probed. A partial explanation is that different molecules and reactions probe different parts of the surface electronic structure. Upon alloying Pt with Sn some Pt bands are non-bonding and retain the character of Pt essentially unchanged. If this part of electronic structure is responsible for adsorption and reaction, a site-blocking effect of Sn is expected. However, some of the Pt bands strongly interact with Sn and form new bands. If this part of the electronic structure is responsible for the adsorption and reaction, we expect significant electronic effects in addition to site-blocking effects.

5. Conclusions

Cyclohexene adsorption and desorption kinetics are not sensitive to the individual Pt and Sn sites available on the Sn/Pt(111) surface alloys, but rather show a gradual decrease of the cyclohexene desorption temperature with increasing Sn concentration and no significant influence of the monolayer saturation coverage by the addition of Sn in the surface layer. The presence of Sn decreases the adsorption energy for chemisorbed benzene much more strongly (by eliminating a strongly bound state) than for di-σ-bonded cyclohexene, which is more strongly decreased than for hydrogen-bonded cyclohexene. With increasing Sn concentration, the decomposition of benzene is suppressed faster than the cyclohexene dehydrogenation and di-σ-bonded cyclohexene on Pt(111) is largely converted to H-bonded cyclohexene on the Pt₂Sn surface alloy. As a result, the gas-phase benzene production in TPD is strongly promoted and the surface carbon buildup during TPD is strongly suppressed at small cyclohexane coverages on the Sn/Pt(111) surface alloys. A competitive pathway is also clearly important on the Pt–Sn alloys. The presence of Sn does not suppress this pathway as efficiently as it does benzene decomposition. At high cyclohexene coverages, the self site-blocking by the adsorbed cyclohexene and the dehydrogenation intermediates formed becomes important. Cyclohexene dehydrogenation decreases with increasing Sn concentration, and as a result, the selectivity of benzene production is only
slightly increased by alloying with Sn and the reactivity is strongly decreased. Comparisons with related experiments using Bi show that Sn has a substantial electronic effect on cyclohexene adsorption and desorption.

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7. References