

Influence of Coadsorbed Hydrogen on Ethylene Adsorption and Reaction on a $(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Sn/Pt(111)}$ Surface Alloy

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The effect of surface-bound hydrogen adatoms on adsorption, desorption, and reaction of ethylene ($\text{CH}_2=\text{CH}_2$) on a $(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Sn/Pt(111)}$ surface alloy with $\theta_{\text{Sn}} = 0.33$ was investigated by using temperature-programmed desorption (TPD) and Auger electron spectroscopy (AES). Preadsorbed H decreased the saturation coverage of chemisorbed ethylene and less H was required to completely block ethylene chemisorption on this alloy than that on Pt(111). This is also the first report of extensive H site-blocking of ethylene chemisorption on Pt(111). Preadsorbed H also decreased the desorption activation energy of ethylene on the alloy surface. The reaction chemistry of ethylene on this Sn/Pt(111) alloy is dramatically different than on the Pt(111) surface: the H-addition reaction channel taking ethylene to ethane on Pt(111) is totally inhibited on the alloy. This is important information for advancing understanding of the surface chemistry involved in hydrogenation and dehydrogenation catalysis.

1. Introduction

Hydrogenation of ethylene (C_2H_4) to ethane (C_2H_6) over Pt(111) has been studied by a number of investigators as a model system for understanding the surface science of catalytic hydrogenation reactions.^{1–6} On Pt(111) at 52 K under UHV conditions, ethylene chemisorbs molecularly via nearly complete rehybridization from extensive back-bonding to eliminate the C–C π -bond and form two Pt–C σ -bonds.² This di- σ -bonded ethylene species is sp^3 -hybridized⁷ and resides in a fcc 3-fold hollow site on the Pt(111) surface, as determined by low-energy electron diffraction (LEED).³ Heating the surface causes di- σ -bonded ethylene to begin to dehydrogenate to form surface-bound ethylidyne (CCH_3) species at 240 K⁹ via a pathway that includes isomerization to ethylidene (CHCH_3) as first proposed by Koel and co-workers^{10,11} and later supported by others.^{9,12} Coadsorption of hydrogen adatoms and C_2H_4 on Pt(111) weakens the chemisorption bonding of ethylene to the surface and greatly increases the production of ethane in TPD experiments.^{3,13} Somorjai and co-workers¹⁴ have studied ethylene hydrogenation at 300–370 K with the total pressure of 110 Torr and proposed that the reaction mechanism of ethylene hydrogenation over Pt(111) does not involve ethylidyne, which is a spectator species or is

involved in a decomposition pathway. They also reported that relative hydrogenation rates of species adsorbed on Pt(111) at 295 K during ethylene hydrogenation at 1 atm are in the order of π -bonded ethylene \gg di- σ -bonded ethylene \gg ethylidyne.⁸

Commercially, other metal or metals are added as promoters to supported Pt catalysts. Pt–Sn bimetallic catalysts using a neutral (chemically inactive) support have been reported to exhibit high selectivity and catalyst stability for the dehydrogenation of light paraffins at elevated temperatures.^{15–17} Model studies of ethylene hydrogenation on unsupported Pt–Sn bimetallic surfaces reported that the reaction rate, i.e., ethylene turnover frequency (TOF), at 15 Torr and 300 K reached a maximum at $\theta_{\text{Sn}} = 0.1$. This corresponded to an activity enhancement of 75% over that of clean Pt(111).¹⁸ Verbeek and Sachtler¹⁹ reported years ago that ethylene chemisorption was weakened on polycrystalline Pt/Sn alloys compared to that on Pt. Later, surface science studies probed ethylene adsorption on well-defined, ordered Pt–Sn alloys.^{20,21} Alloying Sn and Pt weakens the interaction between ethylene and Pt at the surface, and ethylene is less strongly chemisorbed and less rehybridized from the gas phase on both a $(2 \times 2)\text{Sn/Pt(111)}$ surface alloy with $\theta_{\text{Sn}} = 0.25$, with a composition corresponding to the (111) face of a bulk Pt_3Sn crystal and a $(\sqrt{3} \times \sqrt{3})R30^\circ\text{Sn/Pt(111)}$ surface alloy with $\theta_{\text{Sn}} = 0.33$ and a composition corresponding to a Pt_2Sn surface. While the nature of the chemisorbed species can still be regarded as di- σ -bonded ethylene, no decomposition of ethylene occurs on either of these two alloys during heating in TPD.²⁰

There are no reports of ethylene and hydrogen coadsorption on Pt/Sn alloys, but one might expect copious production of ethane on the two Sn/Pt(111) surface alloys in coadsorption experiments. This could arise from a

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confluence of the large increase in ethane production observed in TPD after H + C₂H₄ coadsorption on Pt(111), the higher relative hydrogenation rate reported for π -bonded ethylene over that of di- σ -bonded ethylene on Pt(111) along with the decrease in rehybridization of chemisorbed ethylene on Pt/Sn alloys back toward that in the gas phase, and the slightly weaker Pt–H bond on Pt/Sn alloys,²² which should create a more-labile H adatom.

To probe experimentally the influence of chemisorbed hydrogen on ethylene chemistry on Pt/Sn alloys, we have investigated the effect of hydrogen adatoms on adsorption, desorption, and reaction of ethylene on a ($\sqrt{3} \times \sqrt{3}$)R30°-Sn/Pt(111) surface alloy by using TPD and Auger electron spectroscopy (AES). We report these results herein. Because H₂ does not adsorb on this alloy under UHV conditions,²² an H-atom source was used to generate the hydrogen-precoverages investigated.

2. Experimental Methods

Experiments were performed in a three-level UHV chamber at a typical background pressure of 1×10^{-10} Torr, as described earlier.²³ The Pt(111) crystal (Atomergic; 10 mm diam, 1.5 mm thick) was prepared by using 1-keV Ar⁺-ion sputtering and oxygen treatments (5×10^{-7} Torr O₂, 900 K, 2 min) to give a clean spectrum using AES and a sharp (1 × 1) pattern in LEED.

The ($\sqrt{3} \times \sqrt{3}$)R30°Sn/Pt(111) surface alloy was prepared by evaporating two monolayers of Sn onto the Pt(111) crystal surface and subsequently annealing the sample to 830 K for 20 s. On this surface prepared as above, Sn is incorporated substitutionally into the surface layer to form an ordered alloy with $\theta_{\text{Sn}} = 0.33$, corresponding to a Pt₂Sn surface. This surface is relatively “flat”, but Sn atoms protrude 0.02 nm above the surface-Pt plane.^{24,25} Importantly, forming this alloy structure eliminates all pure-Pt, 3-fold sites. For brevity herein, we will refer to the ($\sqrt{3} \times \sqrt{3}$)R30°-Sn/Pt(111) surface alloy as the $\sqrt{3}$ alloy.

A Pt-tube doser was constructed, based on the design of Engel and Rieder,²⁶ as a pyrolytic source of gas-phase hydrogen atoms. The principal component is a bent Pt tube (1 mm o.d., 0.8 mm i.d.) into which a hole of 0.1 mm diameter was mechanically drilled. The tube was resistively heated to 1275 °C while water-cooling kept an adjacent Cu block cold. The temperature of the Pt tube was directly measured by an optical pyrometer that was calibrated by the temperature of the Pt(111) crystal sample, as measured by a Cr/Al thermocouple. The estimated relative accuracy of the pyrometer reading was ± 5 °C. The flux of H atoms obtained from this source with the Pt tube at 800 °C, and the H₂ pressure increased in the Pt tube until a background pressure of 5×10^{-8} Torr was measured in the UHV chamber was estimated to be 3×10^{13} atoms cm⁻² s⁻¹. This value was obtained by assuming that the initial sticking coefficient of H atoms on Pt(111) at 100 K was unity and using the H adatom coverage and subsequent H₂ yield in TPD produced from the well-known decomposition of ethylene on Pt(111).¹⁰

H₂ (Matheson; 99.99%) was introduced via a variable leak valve (Granville-Phillips) into the Pt-tube doser after passing through a liquid-nitrogen-cooled, U-tube trap. C₂H₄ (Matheson; 99.99%) was introduced via a microcapillary array doser connected to the gas line through a leak valve. All of the exposures reported here are given simply in terms of the pressure measured by the ion gauge in the UHV chamber. No attempt was made to correct for the flux enhancement of the doser or ion gage sensitivity. Mass spectrometry performed in the UHV chamber showed no appreciable concentration of impurities in the source gases.

For all TPD experiments, the heating rate was 3.6 K s⁻¹ and all exposures were given with the surface temperature at 100 K.

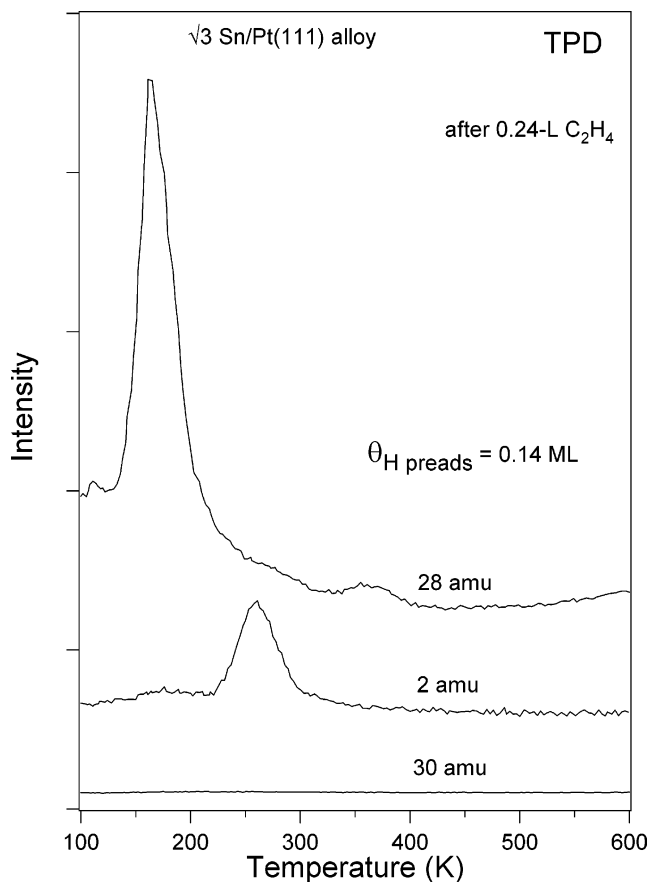


Figure 1. H₂ (2 amu), ethylene (28 amu), and ethane (30 amu) TPD spectra following 0.24-L ethylene exposures on a ($\sqrt{3} \times \sqrt{3}$)R30° Sn/Pt(111) surface alloy with 0.14-ML preadsorbed H at 100 K.

AES measurements were made with a double-pass cylindrical mirror analyzer (CMA). The electron gun was operated at 3-keV beam energy and 1.5- μ A beam current. Coverages, θ_i , reported herein are referenced to the surface atom density of Pt(111) such that $\theta_{\text{Pt}} = 1.0$ ML is defined as 1.505×10^{15} cm⁻².

3. Results

TPD was used to probe monolayer (saturation) coverages of ethylene on a clean and H-precovered $\sqrt{3}$ alloy at 100 K. Possible gas-phase reaction products formed during TPD were monitored at 2, 26, 28, 30 amu, but only the desorption of H₂ (2 amu) and ethylene (28 amu) were identified, as shown in Figure 1. The most significant finding of this investigation is that *the reaction pathway that is so prominent on Pt(111)^{3,13} between coadsorbed H adatoms and ethylene resulting in the evolution of gas-phase ethane upon heating is totally blocked on the $\sqrt{3}$ alloy.*

Desorption spectra for the H₂ and C₂H₄ products are shown in Figures 2 and 3. The desorption spectra of H₂ were not perturbed to any significant extent by the subsequent coadsorption of 0.24-L ethylene, as shown in Figure 2. This ethylene exposure exceeds by at least 30% the amount required to saturate a “clean” $\sqrt{3}$ alloy surface, i.e., with $\theta_{\text{H}} = 0$, at 100 K. H₂ desorption at low θ_{H} occurs at 265 K in a peak that shifts to 253 K with increasing θ_{H} . Upon saturation of this peak, a second peak at 215 K evolves at higher θ_{H} . The features below 200 K are in part from the cracking of ethylene in the mass spectrometer. The H₂ desorption peaks are about 15 K lower than D₂ desorption peaks reported previously on the $\sqrt{3}$ alloy,²² which is attributed to kinetic isotope effects (in addition

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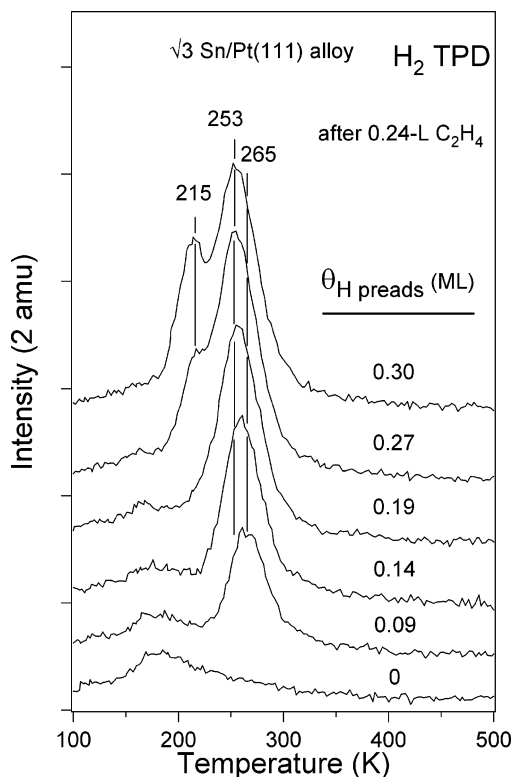


Figure 2. H_2 TPD spectra following 0.24-L ethylene exposures on a $(\sqrt{3} \times \sqrt{3})R30^\circ$ Sn/Pt(111) surface alloy at 100 K that has been precovered with varying amounts of H adatoms.

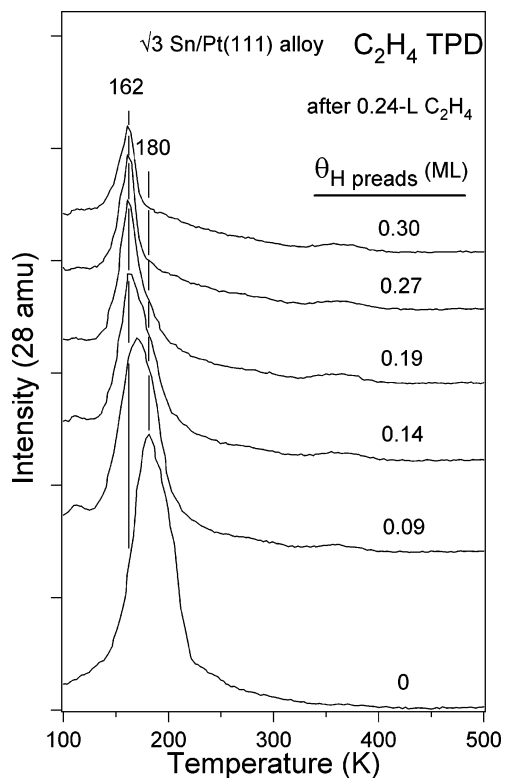


Figure 3. Ethylene TPD spectra following 0.24-L ethylene exposures on a $(\sqrt{3} \times \sqrt{3})R30^\circ$ Sn/Pt(111) surface alloy at 100 K that has been precovered with varying amounts of H adatoms.

to different heating rates). As shown in Figure 3 for small precoverages of H adatoms, subsequent ethylene exposures produced ethylene desorption in TPD in a peak at 170 K, which is 10 K lower than that from a clean $\sqrt{3}$ alloy. With increasing θ_H , ethylene desorption shifted to

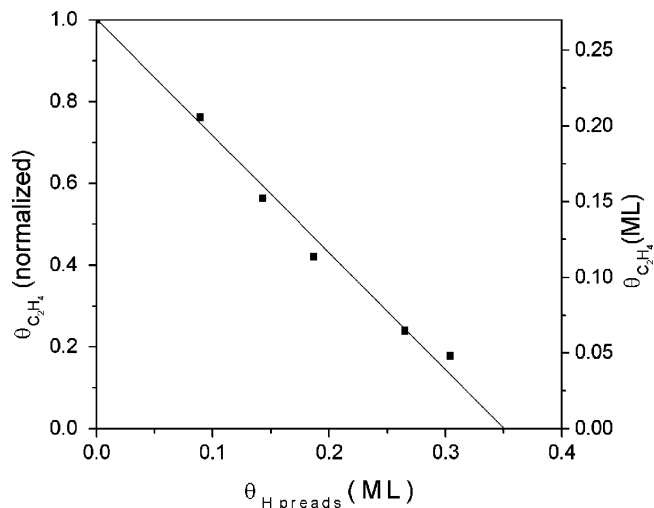


Figure 4. Influence of preadsorbed H adatoms on the monolayer (saturation) coverage of ethylene on a $(\sqrt{3} \times \sqrt{3})R30^\circ$ Sn/Pt(111) surface alloy at 100 K.

lower temperatures, and eventually ethylene desorbed in a peak at 162 K for $\theta_H \geq 0.19$ ML. An important observation shown in Figure 3 is that the intensity of the ethylene desorption peak decreases with increasing θ_H , and we will expand on this observation below. The small desorption feature observed between 350 and 400 K in Figure 3 is from CO desorption from adsorbed CO ($\theta_{CO} < 0.02$ ML) accumulated from the background gas. Assuming first-order kinetics with a preexponential factor of 10^{13} s^{-1} , the Redhead method²⁷ can be used to estimate a desorption activation energy E_d for ethylene. A value of $E_d = 45.5 \text{ kJ mol}^{-1}$ was found for C_2H_4 adsorbed on the clean $\sqrt{3}$ alloy, and this was decreased to 40.8 kJ mol^{-1} on the larger H precoverages on the $\sqrt{3}$ alloy. In cases such as this where no appreciable barrier to adsorption is expected to exist, the desorption activation energy is equal to the adsorption energy and one sees that hydrogen weakens slightly ($\sim 10\%$) the bonding interaction of coadsorbed ethylene to the alloy surface.

Figure 4 summarizes the influence of preadsorbed H adatoms on the ethylene monolayer (saturation) coverage on the $\sqrt{3}$ alloy, as obtained by integration of the ethylene TPD peak areas. The saturation coverage of ethylene on the clean $\sqrt{3}$ alloy was set to 1.0 on the left axis, and this corresponds to an actual coverage of 0.27 ML.²¹ The actual ethylene coverages are provided on the right-hand axis. Ethylene coverage was decreased linearly with increasing amounts of preadsorbed H adatoms. For $\theta_H = 0.30$ ML, the ethylene saturation coverage is reduced to only 18% of that on the clean $\sqrt{3}$ alloy. Extrapolation of the line given in Figure 4 indicates that the chemisorption of di- σ -bonded ethylene will be completely blocked when 0.35 ML of H adatoms is preadsorbed on the $\sqrt{3}$ alloy surface.

To understand the quantitative aspects of the decrease in the saturation coverage of ethylene with increasing coverages of preadsorbed H on the $\sqrt{3}$ alloy, we also carried out one coadsorption experiment on Pt(111). AES was used to measure the amount of adsorbed ethylene on the surface with and without preadsorbed hydrogen. Figure 5 shows two AES spectra, one obtained after a saturation exposure of ethylene on clean Pt(111) (bottom) and the other after the same ethylene exposure on a Pt(111) surface that had been precovered by 0.6-ML H (top). The C(272):Pt(237) ratio shown for the bottom spectrum corresponds to $\theta_C = 0.50$ ML ($\theta_{C_2H_4} = 0.25 \text{ ML}^{10}$) on clean Pt(111). This ratio

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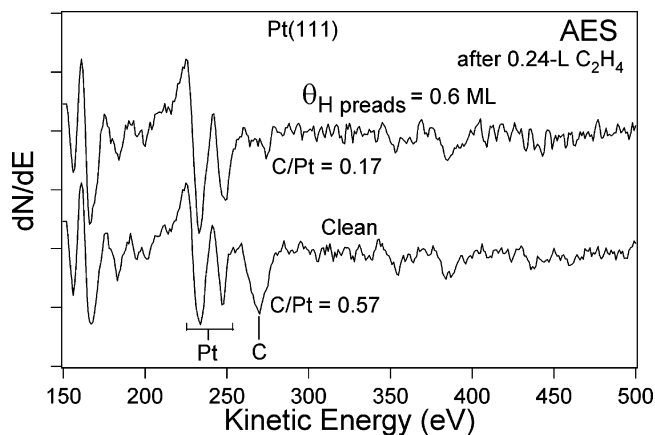


Figure 5. AES spectra obtained following adsorption of a monolayer (saturation) coverage of ethylene on clean Pt(111) (bottom) and a 0.6-ML H precovered Pt(111) surface (top).

decreases dramatically from that on Pt(111) to that of C(272):Pt(237) = 0.17 for ethylene adsorbed on 0.6-ML H precovered Pt(111). This ratio corresponds to $\theta_C = 0.15$ ML ($\theta_{C_2H_4} = 0.07$ ML). These data suggest that H adatoms effectively block ethylene access to Pt sites on both Pt(111) and the $\sqrt{3}$ alloy. Such site blocking effects of preadsorbed H have also been observed for benzene²⁸ and 1,3-butadiene²⁹ chemisorption on Pt(111). Preadsorbed hydrogen on Pt(111) also blocks ethylene chemisorption sites, but more hydrogen than on the alloy is required to eliminate chemisorbed ethylene on Pt(111) at 100 K. On the $\sqrt{3}$ alloy, preadsorbed $\theta_H = 0.30$ ML blocked 82% of ethylene adsorption sites while twice as much hydrogen, $\theta_H = 0.60$ ML, only blocked 70% of the ethylene adsorption sites on Pt(111). This means that ethylene cannot chemisorb on Sn sites or on many of the remaining Pt sites on the $\sqrt{3}$ alloy. On the $\sqrt{3}$ alloy, Sn only occupies 33% of the surface area and 67% is still available as Pt sites. Our results show that only 0.35 ML of preadsorbed H, which occupies one-half the available Pt sites, will totally block the adsorption of ethylene. This indicates that two Pt atoms are required for ethylene adsorption.

4. Discussion

Hydrogen coadsorption weakens the interaction between ethylene and the $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Sn/Pt(111) alloy surface. One effect is to cause a decrease in the adsorption energy of coadsorbed di- σ -bonded ethylene, but this perturbation is rather small. The most significant, and unexpected, effect of hydrogen coadsorption is to cause a nearly 1:1 “site-blocking” of ethylene chemisorption. *Preadsorption of 0.3-ML H is sufficient to eliminate population of di- σ -bonded ethylene on the $\sqrt{3}$ alloy surface.*

There is a direct, large repulsive interaction between coadsorbed H adatoms and ethylene molecules on the $\sqrt{3}$ alloy.²⁹ Such a geometric or site-blocking effect has often been invoked to explain the action of a second metal atom, such as Sn or Bi, or other adatoms, such as S, O, or C, on transition metal chemistry, but such an effect is rarely used in explaining the action of the relatively “small” H adatoms. The site-blocking behavior of H on the $\sqrt{3}$ alloy and Pt(111) is similar, although one might expect small differences to arise from the weaker, and thus longer, Pt–H bond on the alloy which allows the H adatom to sit higher at the surface or perhaps have a little additional

negative charge, and thus larger diameter, interfering with the close approach of ethylene to Pt atoms at the surface needed to facilitate strong bonding interactions. The large difference in the amount of H needed on the $\sqrt{3}$ alloy and Pt(111) to completely eliminate sites for ethylene to chemisorb arises from the influence of alloyed Sn. These surface Sn atoms directly eliminate Pt sites by their physical presence and also affect the electronic structure of neighboring Pt sites.^{30,31}

Another possible influence is that preadsorbed H exerts an electronic or ligand effect in which H adatoms change the local density of states at Pt sites on the $\sqrt{3}$ alloy, and this inhibits back-bonding so severely that di- σ -bonded ethylene cannot be formed. There is support for this notion. RAIRS has been used to show that di- σ -bonded ethylene on Pd(111) is converted to π -bonded ethylene when the surface is presaturated by H adatoms.³² First-principles calculation of ethylene and H coadsorption on Pd(110)³³ shows that the presence of coadsorbed H increases the four-electron repulsion between the ethylene π orbital and the d_{z^2} band of the metal and decreases the back-donation interaction between the metal d_{z^2} orbital and the ethylene π^* orbital. Because ethylene is already less rehybridized on the $\sqrt{3}$ alloy than on Pt(111), the addition of coadsorbed hydrogen could reduce the back-bonding just enough to convert di- σ -bonded ethylene to π -bonded ethylene, which is only physisorbed on the $\sqrt{3}$ alloy and therefore not adsorbed at 100 K (desorbing at 85 K on K/Pt(111)³⁴).

The other major finding of this work is the large difference in hydrogenation activity in these experiments between the Pt(111) surface and the $\sqrt{3}$ alloy. Coadsorption of H adatoms and ethylene on Pt(111) forms mostly ethane upon heating.^{3,13} *This reaction pathway is totally blocked on the $\sqrt{3}$ alloy.* This is unexpected. Alloyed Sn in Pt(111) shifts the sp^3 -hybridization of carbon atoms in di- σ -bonded ethylene in the direction of sp^2 -hybridized carbon in π -bonded ethylene,²⁰ and it has been reported that π -bonded ethylene hydrogenates to ethane much faster than di- σ -bonded ethylene under catalytic conditions on Pt(111).⁸ However, Domen’s recent IRAS findings³⁵ excluded the existence of π -bonded ethylene under similar catalytic conditions, and they concluded that the rate-determining step of hydrogenation does not involve forming either di- σ -bonded or π -bonded ethylene (they proposed that activation of hydrogen plays an important role in ethylene hydrogenation under catalytic conditions). Our finding that no ethylene hydrogenation occurs upon heating a coadsorbed monolayer of H adatoms and ethylene on the $\sqrt{3}$ alloy implies that π -bonded ethylene is not particularly reactive and ethylene simply desorbs at a temperature that is lower than that required for hydrogenation.

Our results have important implications for modeling and understanding catalytic hydrogenation over bimetallic Pt/Sn catalysts. Adding Sn to supported Pt catalysts causes a dramatic decrease in catalytic activity for the propene (C_3H_6) hydrogenation reaction.³⁶ The hydrogenation activity for ethylene and 1-hexene (C_6H_{12}) is also inhibited

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on Pt/Sn/Al₂O₃ catalysts.³⁷ Our surface science results are consistent with these observations, even though Pt/Sn alloy phases have not been identified as catalytically active in these catalysts. There has been one report in a model study that the addition of 0.1-ML Sn increased the reactivity of Pt(111) for ethylene hydrogenation.¹⁸ However, these authors themselves pointed out the difficulty of distinguishing a direct effect from changes that occurred in the amount of carbon deposition, and reaction rate decreased quickly with further increases of Sn. We conclude that adding Sn to platinum catalysts decreases the alkene hydrogenation activity by not only decreasing the interaction between alkenes and Pt but also, more importantly, by decreasing the reactivity of adsorbed alkenes at the catalyst surface.

5. Conclusions

The hydrogenation reaction pathway so prevalent on Pt(111) between ethylene and coadsorbed hydrogen is

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completely inhibited on a ($\sqrt{3} \times \sqrt{3}$)R30°-Sn/Pt(111) surface alloy with $\theta_{\text{Sn}} = 0.33$. Coadsorbed H on the alloy slightly weakens ($\sim 10\%$) the adsorption energy for ethylene on the this alloy. However, the chemisorbed monolayer saturation coverage of ethylene decreased linearly with increasing θ_{H} on the alloy due to substantial site-blocking effects, which totally eliminate ethylene chemisorption at $\theta_{\text{H}} = 0.35$ ML. This is much less hydrogen than is needed to completely block the adsorption of ethylene on Pt(111). These observations represent important information for advancing the surface science of hydrogenation and dehydrogenation catalysis and aid in explaining the decreased activity for alkene hydrogenation observed in supported bimetallic Pt/Sn catalysts.

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