Introduction

Pt–Sn bimetallic alloy catalysts have been utilized in a wide range of heterogeneous catalytic processes, namely dehydrogenation, hydrogenation, selective oxidation, and coupling reactions in both the chemical and petroleum industries. The addition of Sn as a modifier to Pt can greatly change the catalytic properties of Pt catalysts for activity, selectivity, and coking resistance in reactions of unsaturated hydrocarbons. These changes have often been attributed to the formation of alloys between Sn and Pt, with the attendant modification of the electronic structure of Pt and the geometric structure and composition of reactive sites at the surface, causing changes to surface adsorbate binding energies, bonding geometries, and energetic barriers to reaction. In order to better understand the origin of the effects of Sn modification, particularly those coming from the formation of alloy surfaces, surface science experiments have been carried out on well-defined, single-crystal model catalyst surfaces that can controllably probe different Pt–Sn alloy compositions and structures. By exposing molecules on these surfaces at low temperatures, typically at 100 K achieved by liquid nitrogen cooling, the molecules can physisorb or chemisorb (in a variety of ways) on the surface depending on the chemical properties of the molecules and the nature of the surface. Surface science experiments utilize an array of surface-sensitive spectroscopies to probe these reactions. Much of our current understanding of this chemistry has come from investigations that combine TPD and vibrational data from high-resolution electron energy loss spectroscopy (HREELS) measurements, supplemented by theoretical calculations based on density functional theory (DFT). This has led to detailed information about the adsorption energies and configurations of molecules and the formation of intermediates in the adsorption and reaction of unsaturated hydrocarbons on Sn/Pt alloys.

Structure of Surface Alloys of Sn/Pt

Pt and Sn form ordered binary bulk alloy phases that have five common compositions, e.g., PtSn(cub), Pt₃Sn(hex), Pt₂Sn₃(hex), PtSn₂(hex), and PtSn₄(orth). The surface structures of the low index faces (111, 110, and 100) of the bulk Pt₃Sn alloy have been well characterized by low-energy electron diffraction (LEED), low-energy alkali ion scattering (ALISS), and scanning tunneling microscopy (STM). For example, annealing a bulk Pt₃Sn(111) single crystal at different temperatures in ultrahigh vacuum (UHV) leads to the formation of two ordered structures, a ( \sqrt{3} \times \sqrt{3} )R30° structure ( abbreviated herein as the \sqrt{3} structure), and a p(2 × 2) or more simply the (2 × 2) structure. The (2 × 2) surface is a bulk truncated structure, while the \sqrt{3} surface is due to a single-layer, surface alloy reconstruction caused by Sn surface segregation from the subsurface. Conveniently, ordered surface alloys of Pt–Sn have also been prepared by Sn deposition on Pt single crystal surfaces, followed by modest annealing in UHV. Similar to the Pt₃Sn(111) bulk alloy surfaces, Sn/Pt(111) surface alloys with (2 × 2) and (\sqrt{3} \times \sqrt{3})R30° superstructures can be formed on Pt(111) by controlling the amount of Sn deposited and the annealing temperature. Sn is incorporated into the first layer.
of Pt atoms in the surface alloy, but slightly protrudes (0.02 nm) above the surface. Schematic drawings of these two ordered surface alloys are given in Fig. 1.

Other ordered alloy surfaces can be similarly obtained by Sn deposition, such as the \( (\sqrt{3} \times \sqrt{3}) R 30^\circ \) and \((\sqrt{3} \times \sqrt{3}) R 30^\circ \) \( \times \) \( \sqrt{3} \times \sqrt{3} \) \( \times \) \( \sqrt{3} \times \sqrt{3} \) \( R 30^\circ \) \( \times \) \( \sqrt{3} \times \sqrt{3} \) \( R 30^\circ \) surfaces on a Pt(100) substrate and the \( (4 \times 1) \) termination of a Pt\(_3\)Sn near-surface ordered alloy on a Pt(110) substrate.

**Geometric (Ensemble) Effects and Ligand (Electronic) Effects in Alloy Surface Chemistry and Catalysis**

Commonly, the enhanced catalytic properties of bimetallic catalysts are discussed as arising from two different effects: geometric (ensemble) effects and ligand (electronic). Electronic or ligand effects arise when the electronic structure of the first metal is modified by the second, added metal. In many cases of interest, the filling of the d-band of the more reactive metal is changed, i.e., the chemical and physical properties of the reactive metal are affected by the depletion or addition of d electrons. Geometric or ensemble effects occur when the number and arrangement of contiguous reactive metal atoms comprising the active sites on the surface are changed due to dilution by the second less-active metal component. However, it is not easy to separate these two effects since some change in electronic properties by alloying with another metal always occurs and the small size (one or a few atoms) of active sites also makes it difficult to independently probe this influence. For the most studied \( (2 \times 2) \) and \( (\sqrt{3} \times \sqrt{3}) \) surface alloys of Sn/Pt(111), the addition of Sn dilutes the contiguous ensemble of Pt atoms on the Pt(111) surface and leaves only twofold pure-Pt sites on the Sn alloy surface. Sn in the \( (2 \times 2) \) alloy structure still allows 50% of the pure-Pt threefold sites compared to Pt(111), but eliminates all adjacent pure-Pt threefold sites that are often considered as active sites for molecular dissociation. These different ensembles influence how adsorbates bind to the surface and subsequently react or decompose and thus strongly define the surface chemistry of unsaturated hydrocarbons on these alloys. Still, the unique catalytic activity of Pt–Sn alloys likely originates from both ensemble and electronic effects.

**Alkenes (Olefins)**

Olefins are unsaturated aliphatic hydrocarbons that contain a carbon–carbon double bond in the molecule. Due to the saturated nature of alkanes, i.e., the valencies of the carbon atoms in the molecule are fully satisfied by hydrogen atoms, alkenes are more reactive than alkanes. The first member of the alkene series is ethene, \( \text{CH}_2=\text{CH}_2 \).

**Ethene (Ethylene, \( \text{C}_2\text{H}_4 \))**

As the simplest alkene, ethene can be the starting material in or product from hydrocarbon transformations and it serves as a model molecule for alkene adsorption on Pt and Sn/Pt alloys. The chemistry and reactivity of ethene on the \( (2 \times 2) \) and \( (\sqrt{3} \times \sqrt{3}) \) surfaces have been investigated by TPD, UPS, HREELS, and DFT calculations. Ethene is reversibly adsorbed at temperatures below 150 K on both ordered Sn/Pt(111) surface alloys under UHV conditions: no ethene decomposition occurs upon heating either surface to above
600 K. These surfaces are much less reactive than Pt(111), where 40% of adsorbed ethene decomposes upon heating. Chemisorbed ethene on the \( (2/3) \) surface forms a \( (2/3) \)R30° \( (2/3) \) ordered structure, which corresponds to a saturation monolayer coverage of 0.25 monolayer (ML; referenced to the Pt(111) surface atom density \( ¼ 1 \) ML) of ethene, similar to the \( \text{C}_2\text{H}_4 \) coverage on Pt(111).

Fig. 2 shows the ethene desorption temperature (hence the desorption activation energy \( E_{\text{des}} \)), and for such molecules, the adsorption energy \( E_{\text{ads}} \) decreases with increases in the Sn concentration in the surface alloy, from 284 K on Pt(111) to 236 K on the \( \sqrt{3} \) alloy and 183 K on the \( \sqrt{3} \) alloy. This change could be due to an electronic effect of Sn on Pt, causing a weaker binding strength of ethene to Pt. HREELS measurements indicate that ethene can bind to the Pt sites of the alloy surface and Pt(111) similarly either through both \( \pi \)-bonding and di-\( \sigma \)-bonding coordination (Fig. 2) at 100 K. Thus, the electronic changes from alloying with Sn have little effect on the adsorption configuration of ethene. DFT calculations comparing \( \pi \)-bonded ethene on Sn/Pt alloy and Pt(111) surfaces concluded that the significantly deceased adsorption energy due to alloying could be attributed to the varying local relaxation of the different metal surfaces. A large difference in the hydrogenation of ethene on the Pt(111) and \( \sqrt{3} \) alloy surfaces was revealed by TPD after coadsorption of H adatoms and ethene. Preadsorption of H adatoms on the \( \sqrt{3} \) alloy effectively blocks sites for ethene adsorption and decreases the ethene desorption activation energy from 46 to 41 kJ mol\(^{-1}\).

While a large amount of ethane is produced by hydrogenation of ethene on Pt(111), this reaction pathway is completely shut off under UHV conditions on the \( \sqrt{3} \) alloy.

**Propene (Propylene, \( \text{C}_3\text{H}_6 \)) and Butene (Butylene, \( \text{C}_4\text{H}_8 \)) Isomers**

The adsorption and thermal decomposition of other alkenes have been studied on Pt(111) and the \( (2 \times 2) \) and \( \sqrt{3} \) surfaces at 100 K. Right: Optimized geometries for ethene on (A) Pt(111), (B) Pt\(_3\)Sn/Pt(111), and (C) Pt\(_2\)Sn/Pt(111). Left: Reprinted with permission from Adapted from Tsai, Y.-L.; Xu, C.; Koel, B. E. (1997) Chemisorption of Ethylene, Propylene and Isobutylene on Ordered Sn/Pt (111) Surface Alloys. *Surf. Sci.* **385**, 37–59. Copyright 1997 Elsevier. Right: Reprinted with permission from Becker, C.; Haubrich, J.; Wandelt, K. et al. (2008) Adsorption of Simple Alkenes on Pt(111) and Pt–Sn Surface Alloys: Bond Strength Versus Heat of Adsorption. *J. Phys. Chem. C* **112**, 14693–14695. Copyright 2008 American Chemical Society.

600 K. These surfaces are much less reactive than Pt(111), where 40% of adsorbed ethene decomposes upon heating. Chemisorbed ethene on the \( (2 \times 2) \) surface forms a \( (2/3) \times 2(\sqrt{3}) \)R30° ordered structure, which corresponds to a saturation monolayer coverage of 0.25 monolayer (ML; referenced to the Pt(111) surface atom density \( ¼ 1 \) ML) of ethene, similar to the \( \text{C}_2\text{H}_4 \) coverage on Pt(111).
Cyclopentene (C₅H₈)

Adsorption and reaction of cyclopentene on Pt(111) and Sn/Pt alloy surfaces has been studied by TPD, HREELS, UPS, and DFT calculations. Cyclopentene is di-σ-bonded and occupies twofold pure-Pt bridge sites on all these surfaces. On Pt(111), the strong interaction between Pt and the β-H causes facile dehydrogenation of cyclopentene. This interaction is much weaker on the alloy surfaces, and no dehydrogenation occurs during TPD on the alloys. The decrease in the adsorption energy of cyclopentene on the Sn/Pt alloys compared to Pt(111) has been attributed to a ligand effect from alloying. However, DFT studies of adsorption on Pt(111) and Sn/Pt surface alloys, considering the vibrational frequencies and bond length of the adsorbed molecules, indicate that the decrease in the adsorption energy of cyclopentene, as for ethene, is mainly caused by the relaxation of the alloy surfaces. The normal d-band model, considering only initial states and attributing the weakening of the adsorption energy (ΔE_{ads}) to the downshift of the d-band center by alloying, is not adequate to predict the similarity in the bonding changes of alkenes on Pt(111) and the Sn/Pt(111) alloys.

Cyclohexene (C₆H₁₀)

Adsorption and reaction of cyclohexene is of interest as an intermediate in the dehydrogenation of cyclohexane to benzene. On Pt(111), cyclohexene is di-σ-bonded to the surface with chair and boat configurations with desorption temperature peaks at 240 and 280 K in TPD. The high temperature peak (280 K) disappears when adsorbed on the (2 × 2) alloy, and the monolayer coverage at 180 K drops from 0.18 ML on Pt(111) to 0.12 ML on the alloy. Cyclohexene only forms a weak H-bonded state on the √3 alloy, with desorption peak temperature of 208 K. A combination of HREELS and DFT suggests that the adsorption of cyclohexene on the √3 alloy is a mixture of several chemisorption bonding modes, including di-σ and π-bonding, and a physisorbed state.

Dienes

Dienes are unsaturated hydrocarbons containing two C=C bonds. Selective hydrogenation of dienes is an important heterogeneous catalysis process for the purification of the alkene streams used in polymerization. Dehydrogenation of dienes is also an intermediate step to the synthesis for more complex chemicals, e.g., synthesis of benzene from the dehydrogenation of cyclohexadiene.

Butadiene (C₄H₆)

Adsorption, desorption, and dehydrogenation of 1,3-butadiene on Pt(111) and the (2 × 2) and √3 alloys have been investigated by TPD, HREELS, and DFT calculations. Adsorption of 1,3-butadiene on Pt(111) has been considered to occur in two possible adsorption configurations: di-σ-bonding of both C=C bonds in the molecule in a tetra-σ-bonding configuration, or in a 1,4-di-σ-bonding configuration accompanied by the formation of a new C=C bond at the center of the molecule. Due to the strong interaction with Pt(111), chemisorbed butadiene decomposes completely and only H₂ is evolved in TPD. On the alloys, dehydrogenation of butadiene is completely inhibited and chemisorbed butadiene molecularly desorbs from both alloy surfaces during TPD. The desorption activation energy for 1,3-butadiene on the (2 × 2) and √3 alloys is 88 and 75 kJ mol⁻¹, respectively. The monolayer coverage of chemisorbed butadiene on all three of these surfaces is the same at 0.15 ML.

Alloyed Sn in the surface layer opens a new hydrogenation reaction pathway compared to that on Pt(111). Butadiene hydrogenation by coadsorbed hydrogen occurs with 100% selectivity to produce butene (C₄H₈) in TPD, and no fully hydrogenated product (butane, C₄H₁₀) was observed. The activation energy barrier for hydrogenation of strongly bound 1,3-butadiene was estimated to be 91 and 72 kJ mol⁻¹ on the (2 × 2) and √3 alloys, respectively. In batch reactor kinetics measurements, hydrogenation of butadiene was zero order in butadiene and the (2 × 2) and √3 alloys exhibited one order of magnitude lower activity, but much higher selectivity to form butene, in comparison with Pt(111).

DFT calculations give meaningful insights for the butadiene adsorption energy, adsorption configuration, and hydrogenation reaction mechanism. Butadiene bonds to the √3 alloy through a weaker cis 1,4-di-σ-2,3-π bonding configuration, instead of the strong trans-1,2,3,4-tetra-σ-bonding to the Pt(111) surface. Alloying with Sn modifies the hydrogenation selectivity by tuning

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Pt(111)</th>
<th>(2 × 2)</th>
<th>√3</th>
</tr>
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<tr>
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<td>59, 63</td>
<td>45, 49</td>
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<tr>
<td>Propene</td>
<td>73</td>
<td>58, 62</td>
<td>45, 49</td>
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<tr>
<td>1-Butene</td>
<td>73</td>
<td>67</td>
<td>56</td>
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<tr>
<td>cis-2-buten</td>
<td>71</td>
<td>65</td>
<td>50</td>
</tr>
<tr>
<td>Isobutene</td>
<td>71</td>
<td>63</td>
<td>46</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>79</td>
<td>72</td>
<td>61</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>73</td>
<td>62, 66</td>
<td>49, 55</td>
</tr>
</tbody>
</table>

Table 1: Summary of alkene desorption activation energies on Pt(111) and two Sn/Pt(111) alloys
the reaction pathway to avoid the formation of a 1-3-metallacycle that could be hydrogenated to butane. The preferred hydrogenation site is at a terminal carbon, and the hydrogenation of the central carbon is a highly activated process. Sn functions not only as a site blocker to suppress unfavorable adsorption structures, but also modifies the electrometric property of the surface to lower the Pt–C bond strength and reduce the activation energy barriers to form butenes.

1,3-Cyclohexadiene (C₆H₈)

Adsorption and dehydrogenation of 1,3-cyclohexadiene on Pt(111) surfaces can be used to probe possible intermediate steps in catalytic conversion of cyclohexane to benzene. Cyclohexadiene irreversibly chemisorbs on Pt(111), strongly chemisorbing on the surface in a quadra-σ-bonding configuration. At low coverages (25% of the monolayer) of cyclohexadiene, complete decomposition of adsorbed molecules during heating in TPD only evolves H₂ while producing surface carbon. At higher coverages, chemisorbed cyclohexadiene dehydrogenates to desorb some benzene upon heating. Alloying of Sn at the Pt(111) surface strongly alters the selectivity of 1,3-cyclohexadiene dehydrogenation on these surfaces such that 100% selectivity for producing gas-phase benzene was observed under UHV conditions due to the complete elimination of benzene dehydrogenation on these alloys. As shown in Fig. 3, 1,3-cyclohexadiene dehydrogenation produces a benzene product whose desorption temperature is lowered from 310 K on Pt(111) to 225 K on the \((\sqrt{3})\) alloy due to site-blocking by Sn and coadsorbed H atoms from the dehydrogenation reaction. This greatly reduces the activation energy for benzene desorption, which is the rate-determining step for producing gas-phase benzene under these conditions.

DFT calculations of the adsorption of 1,3-cyclohexadiene on Pt(111) and these Sn/Pt(111) alloys found that the adsorption energies of 1,3-cyclohexadiene and relevant intermediates decrease with an increase of the Sn concentration. Alloying Sn prohibits further dehydrogenation of benzene, enhancing the catalytic properties of these Sn/Pt alloys for highly selective 1,3-cyclohexadiene dehydrogenation to gaseous benzene.

Aromatics

Aromatic molecules are unsaturated hydrocarbons that are especially stable, lower reactivity, having planar cyclic (ring) structures with “resonance stabilized” bonding in the ring that is a hybrid (average) of resonance forms given by a conjugated system of alternating single and double bonds within the ring. Many aromatic molecules are derivatives of benzene (C₆H₆), which has a simple six-membered ring of carbon atoms. Adsorption and reactions of aromatics on metal and alloy surfaces have been
investigated for a wide range of fundamental and applied interests. Because of the delocalization of the pi system of the molecule around the ring, chemisorption of aromatic molecules often involves bonding with the ring plane nearly parallel to the surface.

Benzene (C6H6)

Pt catalysts are used in the production of benzene from dehydrogenation of cyclohexane and in the hydrogenation of aromatic compounds in the petrochemical industry. Adsorption and reaction of benzene on Pt single-crystal surfaces has been investigated by TPD, HREELS, and UPS. On Pt(111), benzene is π-bonded to the surface with its ring parallel to the surface. Below 350 K, benzene is molecularly chemisorbed. Significant dehydrogenation of benzene on Pt(111) occurs at 525 K during TPD and causes H2 desorption with the concomitant formation of adsorbed hydrocarbon products. Further heating to 800 K dehydrogenates these intermediates to adsorbed carbon, desorbing hydrogen between 525 and 800 K. At high initial coverages of benzene, molecular benzene desorbs at 320 and 480 K, corresponding to desorption activation energies of 82 and 117 kJ mol⁻¹, respectively. Addition of Sn to Pt(111) weakens the bonding between benzene and the substrate and also completely inhibits dehydrogenation pathways under UHV conditions. Benzene is more weakly bonded to the alloy surfaces than on Pt(111), with a desorption energy of 50 kJ mol⁻¹ on the (2x2) alloy and 47 kJ mol⁻¹ on the (sqrt(3)x(sqrt(3))) alloy. Vibrational spectra obtained from HREELS, as shown in Fig. 4, provide information on the geometry of adsorbed benzene molecules, by determining whether enhancement is observed of vibrational modes with atomic motion parallel or perpendicular to the ring plane, and the adsorption bond strength on the surfaces, by observing shifts in the vibrational frequencies for the monolayer compared to those for the physisorbed, condensed multilayer spectra. The largest peak in the HREELS spectrum for the multilayer in Fig. 4 is the out-of-plane C–H bonding mode at 84 meV. Benzene monolayers on both Sn/Pt(111) surface alloys have vibrational spectra similar to this multilayer spectrum on Pt(111), which indicates that benzene is physisorbed on the alloys. It has been reported that the minimum ensemble for chemisorption of benzene on Pt(111) is about six adjacent Pt atoms and more Pt atoms are needed in the ensemble for dehydrogenation of benzene. Thus, the Sn/Pt surface alloys do not contain the Pt ensembles needed for benzene to chemisorb and/or dehydrogenate. Similar effects of Sn on the chemistry of benzene on Sn/Pd alloys have also been observed.

Alkynes

Alkynes are unsaturated aliphatic hydrocarbons that undergo reactions similar to alkenes, but are more reactive than alkenes because they contain a carbon–carbon triple bond in the molecule. The first member in the series of alkynes is ethyne, HC≡CH.

Ethyne (Acetylene, C2H2)

Unlike Pd(111), which is capable of catalyzing acetylene coupling (cyclotrimerization) to benzene at low temperatures, Pt(111) and Ni(111) favor complete decomposition of acetylene into surface carbon and hydrogen upon heating. The catalytic properties of Pt(111) for acetylene coupling are strongly modified by alloying with Sn. TPD measurements after adsorption of acetylene found
that adding Sn to the Pt(111) surface strongly suppressed D\textsubscript{2} evolution from C\textsubscript{2}D\textsubscript{2} decomposition. Significantly, benzene and butadiene products from the direct coupling of adsorbed acetylene on the Sn/Pt(111) alloy surfaces form and desorb into the gas phase, while these products are barely detected for Pt(111). The alloy shows the highest yield of benzene and butadiene. The acetylene monolayer saturation coverage on the \(\sqrt{3}\) alloy is 0.16 ML, and about 10\% of the adsorbed acetylene forms benzene by cyclotrimerization. This chemistry of the alloy surfaces was also probed in catalytic reactor studies at moderate pressures (10–100 T). The \(\sqrt{3}\) surface alloy showed four to five times more activity for acetylene di- and trimerization than Pt(111). Only \(C_4\) and \(C_6\) products were observed from the di- and trimerization reactions, and the reaction kinetics indicated that the ring \(C_6\) products from acetylene cyclotrimerization proceed through a metalloccyclopentadiene intermediate.

Sn/Pt alloy surfaces with 0.5 and 0.67 ML surface Sn atoms can be prepared on a Pt(100) single crystal and form \(c(2 \times 2)\) and \((3\sqrt{2} \times \sqrt{2})R45^\circ\) (abbreviated herein as the \(3\sqrt{2}\) structure) Sn/Pt(100) surface alloy structures. This surface alloy system is interesting for several reasons. First, the \(c(2 \times 2)\) alloy reconstruction removes all pure-Pt fourfold hollow and pure-Pt twofold bridge sites, leaving only isolated Pt surface atoms, which causes large changes in acetylene adsorption and reaction. However, an equivalent coverage of Sn adatoms, rather than alloyed Sn atoms nearly coplanar with top layer Pt atoms, also can form a \(c(2 \times 2)\) Sn adlayer structure, which is completely inert for chemisorption due to severe repulsive interactions with the adlayer that inhibit sufficiently close approach of reactive molecules to surface Pt atoms needed for strong chemisorption bonding. Also the \(3\sqrt{2}\) alloy reconstructs locally within several atom-wide long terraces into a \(p(2 \times 2)\) alloy structure that leaves available (for higher reactivity) pure-Pt twofold bridge sites even though the surface Sn coverage is higher than for the \(c(2 \times 2)\) surface alloy. Alloying with Sn decreases the initial sticking coefficient of C\textsubscript{2}H\textsubscript{2}, such that it drops from 1 on Pt(100) to 0.6 on the \(c(2 \times 2)\) alloy at 100 K. The monolayer saturation coverage of C\textsubscript{2}H\textsubscript{2} is also reduced from 0.5 ML on Pt(100) to 0.32 ML on the \(c(2 \times 2)\) alloy and 0.25 ML on the \(3\sqrt{2}\) alloy. The acetylene chemisorption bond energy, determined by the acetylene desorption activation energy measured in TPD, decreases by 45\%–65\% as the alloyed Sn concentration increases. Cyclotrimerization of acetylene to benzene is structure sensitive and is observed only on the \(3\sqrt{2}\) alloy on this substrate.

One striking effect on surface chemistry is that alloying with Sn significantly increases the coking resistance, a probe by the thermal decomposition of C\textsubscript{2}H\textsubscript{2} in TPD. This resistance to coke formation shows a strong nonlinear dependence on the Sn concentration at the surface, indicating key ensembles of pure-Pt sites are involved, as shown in Fig. 5. The \(c(2 \times 2)\) Sn/Pt(111) alloy with 25\% Sn prevents 25\% of the C\textsubscript{2}H\textsubscript{2} decomposition, while the \(c(2 \times 2)\) Sn/Pt(100) nearly completely shuts off this reaction pathway.

The adsorption energy and geometry of chemisorbed C\textsubscript{2}H\textsubscript{2} has been investigated by HREELS measurements and DFT calculations. C\textsubscript{2}H\textsubscript{2} adsors on Pt(111) to form strongly bound di-\(\sigma/\pi\)-bonded acetylene species. Alloying with Sn weakens the adsorption interactions and modifies the nature of available sites to bind C\textsubscript{2}H\textsubscript{2}, which forms more weakly adsorbed \(\pi\)- and di-\(\sigma\)-bonded species on the surface. Destabilization of adsorbed acetylene on the alloys enhances the formation of dimers (\(C_4\) hydrocarbons) and trimers (benzene) by coupling reactions over dehydrogenation reactions that are the dominant reaction pathways on Pt(111). The nature of the chemisorbed C\textsubscript{2}H\textsubscript{2} species is dependent on the availability and geometry of Pt surface atoms. Facile isomerization of acetylene, HC–CH\textsubscript{2}, occurs on Pt(111) and the \(c(2 \times 2)\) Sn/Pt(111) alloy since this reaction requires three adjacent Pt atoms in the form of a pure-Pt threefold site. Acetylene adsorption modes and reactions on Pt catalytic surfaces can, therefore, be controlled by alloying with Sn in a somewhat simple manner, since all hydrocarbon species bind

\[\text{Fig. 5  Fractional decomposition of acetylene in the monolayer (normalized to the saturation monolayer coverage on each surface) during TPD from Pt (111) and Sn/\text{Pt}(111) surface alloys (\textcircled{1}) and from Pt(100) and Sn/\text{Pt}(100) surface alloys (o). Reprinted with permission from Panja, C.; Saliba, N. A.; Koel, B. E. (2000) Coking Resistance of Pt–Sn Alloys Probed by Acetylene Chemisorption. Catal. Lett 68, 175–180. Copyright 2000 Springer.}\]
preferentially only to Pt sites. In this tuning of reactivity, the concentration of Sn needs to be held at an intermediate, optimal level for the highest catalytic activity and selectivity.

**Propyne (Methylacetylene, C₃H₂)**

Exposure of methylacetylene on the Pt(111) surface leads to irreversible adsorption of the chemisorbed molecule, and no molecular methylacetylene desorption occurs in TPD. Propene is formed as the main desorption product, with a yield corresponding to 20% of the adsorbed methylacetylene. The monolayer saturation coverage of methylacetylene on Pt(111) is 0.25 ML, similar to that for C₂H₂ adsorption. Alloying with Sn greatly reduces the amount of decomposition of adsorbed methylacetylene and increases the amount of molecular methylacetylene desorbed. The desorption energy of methylacetylene is 119 kJ mol⁻¹ on the (2 x 2) alloy and 96 kJ mol⁻¹ on the √3 alloy, compared to an estimated 161 kJ mol⁻¹ on Pt(111). The main desorption product from these alloys is also propene. This is very different behavior from C₂H₂ surface chemistry on the alloys, where C₄ and C₆ products were formed by di- and trimerization reactions. This can be explained by the more reactive α-H in methylacetylene, compared to acetylenic hydrogens, that leads to facile dehydrogenation of methylacetylene on the surface. Formation of strongly bound surface intermediates as a result of this dehydrogenation suppresses the coupling reactions.

**Crotonaldehyde (CH₃CH═CHCHO), an α,β-Unsaturated Aldehyde**

Selective hydrogenation of α,β-unsaturated aldehydes produces important intermediates (e.g., unsaturated alcohols) for the fine chemical industry. Since hydrogenation of the C=O bond is more thermodynamically favorable than the hydrogenation of the C=C bond in these molecules, selective hydrogenation of the C=O functional group relies on kinetic control by the utilization of selective catalysts. Sn/Pt bimetallic catalysts have demonstrated promising selectivity for this reaction, and research efforts have attempted to understand the origin of this catalytic selectivity. A crucial question for supported practical catalysts is the role of cationic Sn in Sn oxide phases and the role of Sn/Pt alloy phases in this chemistry and catalysis. Surface science studies have focused on the Sn/Pt alloys since interfacial Sn oxide phases in contact with Pt are quite unstable at modest conditions. Compared to the simple unsaturated hydrocarbons discussed above, adsorption and reaction of unsaturated aldehydes is complicated by the existence of multiple isomers and the potential for interactions with the surface involving either or both C=C and C=O groups.

Surface science experiments and DFT calculations provide useful information on how such unsaturated aldehydes adsorb and react differently at model catalyst surfaces of Pt(111) and ordered Sn/Pt surface alloys. Crotonaldehyde, (but-2-enal, C₄H₆O), irreversibly chemisorbs on Pt(111) in multiple stable adsorption configurations involving different combinations of di-σ-C=C-, di-σ-C=O-, or σ-O-bonding to the surface. Alloying with Sn decreases the adsorption energy by 40%–50% and reduces the number of stable adsorption configurations. Due to the oxophilicity of Sn, the oxygen atom of the carbonyl group forms a strong σ bond with Sn instead of Pt on both of the (2 x 2) and √3 alloys. The main stable adsorption configurations at high coverages of crotonaldehyde are mixtures of different di-σ-C=C-bonding structures at Pt sites and σ-O-bonding structures at Sn sites. At low coverages, more “flattened” structures with higher hapticity such as di-σ-C=C/di-σ-C=O, or di-σ-C=C/σ-O(Sn) bonding also become stable. Similarly, the adsorption energy of prenal (3-methyl-2-butenal) is also significantly smaller on Sn/Pt(111) alloys than on Pt(111). The substitutional effect of the methyl group on the β-carbon is attributed as the origin of the weakened

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**Fig. 6** Decomposition of the adsorption energies into the constituting deformation energies required to distort the adsorbate and the surface in order to form the geometry for optimal bonding, and the resulting interaction energies between them. Reprinted with permission from Haubrich, J.; Loffreda, D.; Delbecq, F. et al. (2009) Adsorption and Vibrations of α,β-Unsaturated Aldehydes on Pt(111) and Pt–Sn Alloy (111) Surfaces. 3. Adsorption Energy versus Adsorption Strength. *J. Phys. Chem. C* **114**, 1073–1084. Copyright 2009 American Chemical Society.
adsorption, and this results in σ-O-bonding species to Sn being the dominant configurations on the alloy surfaces. However, observations that the vibrational and geometrical properties of the surface-bound complexes are very similar for both Pt(111) and the alloys indicate that the decreased adsorption energy is not simply related to the interaction energy between the complexes and alloy surfaces. The interaction energy obtained after the adsorption energy is corrected for the relaxation energy of surface metal atoms and adsorbed molecules, as shown in Fig. 6, is more consistent with the vibrational features of the adsorbates. The 10% decrease in the interaction energy observed for both adsorbed crotonaldehyde and pren on the Sn/Pt(111) alloys compared to Pt(111) correlates well with the small downshifting of the d-band center due to the formation of the alloys.

See also: Formation of Surface Alloys and Related Applications; Hydrazine Electro-Oxidation at Epitaxial Ir(110) Alloys; Understanding the Corrosion of Mg and Mg Alloys.

Further Reading


