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Heterogeneous Catalysis

Geometric Requirements for Hydrocarbon Catalytic Sites on Platinum Surfaces**

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Abstract: *Vibrational spectroscopic measurements and density functional calculations were used to identify a preferential catalytic mechanism for the transformation of acetylene, HC–CH, to vinylidene, C–CH$_2$, on surfaces of Pt-Sn ordered alloys. In this mechanism, two adjacent Pt atoms adsorb an acetylene molecule and a third neighboring Pt atom is required for stabilizing the reacting H atom during the transformation. Therefore, unlike a direct H shift along the C–C bond in organometallic compounds with a single transition-metal atom, this mechanism has a geometric site requirement of three adjacent Pt atoms in the form of a three-fold site. The same geometric site requirement is identified for preferential C–H bond cleavage of acetylene with the formation of adsorbed C–CH and H species. In the absence of three-fold Pt sites, the reaction mechanism changes, and reactions of H transfer and C–H bond cleavage are suppressed.*

Pt-based catalysts are used for hydrocarbon transformations in diverse industrial applications. There is also a renewed research interest in catalytic properties of Pt owing to multiple promising new applications, ranging from fuel cells[1] to production of renewable transportation fuels and chemical feedstocks based on biomass conversion.[2]

The transformation of acetylene, HC–CH, into vinylidene, C–CH$_2$, on Pt and other catalytic metal surfaces has attracted significant attention because the chemistry of C$_2$ hydrocarbons on Pt surfaces has historically served as a bridge between surface science and heterogeneous catalysis studies and because acetylene hydrogenation is an important industrial reaction.[3] Acetylene impurities in ethylene feedstocks are unacceptable in polymerization and, therefore, are reduced to trace levels using selective hydrogenation over metal catalysts. The formation of C–CH$_2$ species from acetylene adsorbed on a Pt(111) surface has been directly observed microscopically.[4] Furthermore, spectroscopic studies with isotope labeling have shown that the transformation into C–CH$_2$ is the first acetylene reaction on a Pt(111) surface.[5] The reaction mechanism for this transformation on Pt and other metal surfaces, however, has always been assumed to be a direct "through space" H shift along the C–C bond (direct 1,2-H shift), similarly to the HC–CH to C–CH$_2$ transition identified in organometallic compounds with a single transition-metal atom. For example, in organometallic complexes with a single Ru atom, the direct 1,2-H shift has been found to be preferable to an indirect 1,2-H shift where the reacting H atom binds to both the metal and C atoms and to the pathway with a hydride–alkynyl intermediate where the reacting H atom binds only to the metal atom.[6]

In contrast to organometallic compounds with a single metal atom, metal surfaces offer multiple catalytic sites. Using vibrational spectroscopic measurements and density functional theory (DFT) calculations with well-defined ordered Pt-Sn alloys, we here identify a new mechanism for the catalytic transformation of acetylene into C–CH$_2$ species on Pt surfaces that involves surface stabilization of the reaction H atom, which is preferential to the direct 1,2-H shift pathway. We further determine that this preferential mechanism is limited by a geometric requirement: the availability of at least three adjacent surface Pt atoms (three-fold Pt sites). The same geometric site requirement is identified for preferential C–H bond cleavage of acetylene with the formation of adsorbed C–CH and H species. In the absence of three-fold Pt sites, the reaction mechanism changes, and reactions of H transfer and C–H bond cleavage are suppressed.

Catalytic metals, such as Pt, are often modified by adding a promoter, such as Sn, to enhance their performance. Catalytic promoter effects are usually classified as electronic and geometric.[7] The presence of a promoter changes the electronic structure and, therefore, the reactivity of neighboring Pt atoms. Furthermore, the presence of promoter atoms breaks the original Pt surface into ensembles of adjacent Pt atoms and, therefore, restricts the geometry of Pt catalytic sites. On a single-crystal surface of Pt(111), there are three main geometric types of catalytic sites: atop (single atom), bridge (two adjacent atoms), and three-fold (three adjacent atoms in a triangle), as shown in Figure 1a. For an ordered Pt$_3$Sn (2×2)-Sn/Pt(111) alloy surface in Figure 1b, all the

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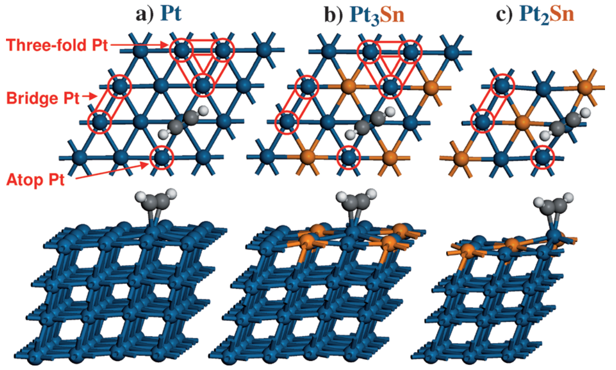

Figure 1. Catalytic Pt sites on a) Pt(111), b) Pt$_3$Sn/Pt(111), and c) Pt$_2$Sn/Pt(111) single-crystal surfaces: atop (single atom), bridge (two adjacent atoms), and three-fold (three adjacent atoms in a triangle). The Pt$_2$Sn surface does not have three-fold Pt sites. Surfaces are shown with π-adsorbed acetylene on atop Pt sites. The top row shows a top view of only the surface layer for each single crystal for clarity.

initial main geometric Pt sites are preserved. However, at a higher Sn concentration in an ordered Pt$_2$Sn $(\sqrt{3}\times\sqrt{3})$R30°-Sn/Pt(111) alloy surface in Figure 1c, the arrangement of Sn atoms eliminates all three-fold Pt sites. The Pt surface in this case is broken into ensembles of only one or two neighboring Pt atoms. As the concentrations of Sn in the Pt$_3$Sn and Pt$_2$Sn alloys are not much different, electronic promoter effects should be comparable. Differences in activity between these two Pt-Sn alloy surfaces should, therefore, be mostly due to the geometric effect of eliminating three-fold Pt sites.

DFT calculations for the transformation of HC−CH into C−CH$_2$ species on the Pt$_3$Sn surface are summarized in Figure 2a. Acetylene initially preferentially adsorbs on a bridge Pt site (Figure 2a,b-1) with a C−H bond distance of 0.11 nm, which is nearly the same as in gas-phase acetylene. During the reaction, the C−H distance increases to 0.16 nm, and the reacting H atom stabilizes on a neighboring Pt atom of a three-fold Pt site (Figure 2a,b-3) with an estimated reaction barrier of 167 kJ mol^{-1}. This transition state, therefore, requires a three-fold Pt site. The hydrocarbon then rotates around the reacting H atom, which remains stabilized by the Pt atom, with just a small decrease in the energy from 167 to 164 kJ mol^{-1} (Figure 2a-4). This rotation allows the hydrocarbon to transfer the H atom from one C atom to another energetically efficiently. Once a bond between the reacting H atom and the second C atom is established, this H atom starts breaking the initial bond with the Pt surface. After that, the distance for the newly formed H−CH bond decreases to 0.11 nm, completing the formation of C−CH$_2$ surface species accompanied by a rapid decrease in the system energy (Figure 2a-5). This new mechanism thus consists of three parts. In the first part, the C−H bond distance increases, the H atom is stabilized by a surface Pt atom, and the system energy increases. In the second part, the hydrocarbon rotates around the surface-stabilized H atom and transfers it from one C atom to another, with the energy being at the highest plateau. Finally, in the third part, the second C atom "picks up" the reacting H atom from the surface, and the energy decreases. In summary, the adsorbed hydrocarbon uses a Pt atom of a three-fold Pt site for transitional stabilization of the reacting H atom while it is transferred between the two C atoms, making this transfer more energetically efficiently than a direct H shift "through space" along the C−C bond, that is, without establishing a bond between the H atom and the Pt surface.

Evaluation of multiple pathways for C−H bond cleavage on the same Pt$_3$Sn surface shows that this reaction also preferably proceeds through stabilization of the reacting H atom on a Pt atom of a three-fold Pt site. This pathway is summarized in Figure 2b. The estimated transition state on a three-fold Pt site is the same for both the H transfer and C−H cleavage (Figure 2a,b-3) within the accuracy of the employed search method. After the initial increase in the C−H bond distance and stabilization of the reacting H atom on a Pt atom of a three-fold Pt site, the C−H distance continues to increase (Figure 2b-4), and the H atom moves away from the C−CH surface species (Figure 2b-5). This pathway has a lower barrier compared to H stabilization on another neighboring Pt atom or on the Pt atom that binds the reacting C atom.

In the absence of three-fold Pt sites on the Pt$_2$Sn surface, the mechanism of H transfer with surface stabilization becomes impossible because Sn atoms do not bind either H or C atoms nearly as strongly as Pt. As a result, the only possible mechanism in this case is a direct "through space" H shift between the two C atoms (direct 1,2-H shift), which is summarized in Figure 3a. The hydrocarbon in this mechanism remains stationary as the reacting H shifts and forms C−CH$_2$ species. In the transition state, the C−H bond distance increases from the 0.11 nm initial value to 0.13 nm, and the reacting H is bonded to both carbon atoms (Figure 3a-3). As the reacting H in this transition is not stabilized by the catalytic surface, the calculated barrier for this

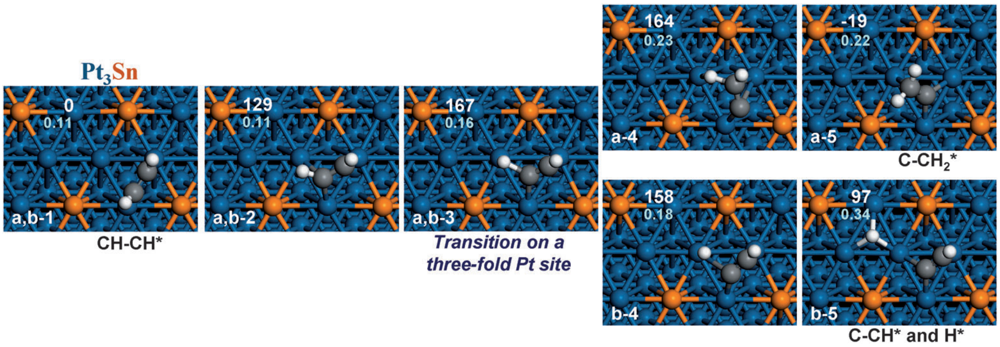

Figure 2. Acetylene reaction pathways in the presence of three-fold Pt sites on the Pt$_3$Sn surface with the formation of a) C−CH$_2$ and b) C−CH and H surface species. The top number for each configuration shows the energy relative to adsorbed acetylene (kJ mol^{-1}) and the lower number shows the C−H distance (nm).

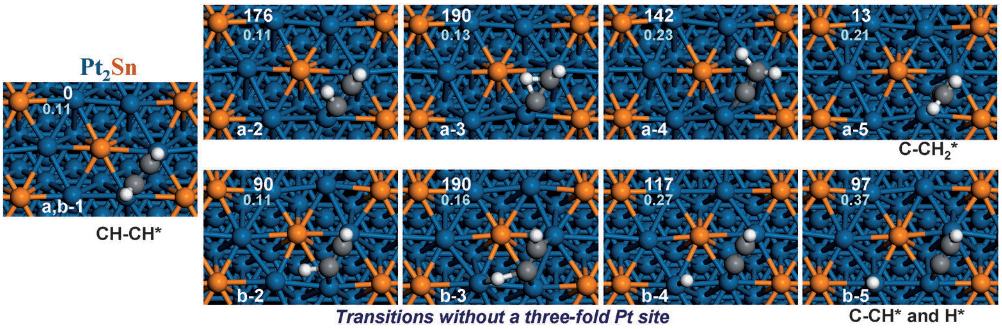

Figure 3. Acetylene reaction pathways in the absence of three-fold Pt sites on the Pt_2Sn surface with the formation of a) C–CH_2 and b) C–CH and H surface species. The top number for each configuration shows the energy relative to adsorbed acetylene (kJ mol^{-1}) and the lower number shows the C–H distance (nm).

reaction mechanism at 190 kJ mol^{-1} is higher than that on a three-fold Pt site at 167 kJ mol^{-1} (Figure 2 a,b-3). After completion of the H shift on the Pt_2Sn surface, the final step in the reaction involves a change in the surface binding of C–CH_2 species. The C–CH_2 molecule "stands up", changing from a configuration where each C atom binds to one of the Pt atoms of a Pt–Pt bridge site (Figure 3 a-4) to a configuration where only one C atom binds to the Pt–Pt bridge site and the CH_2 group is not bonded directly to the surface, with the C–C bond being oriented normal to the surface (Figure 3 a-5). The geometries for all the structures in Figure 2 and Figure 3 are provided in Tables S1–S4. Differences in the calculated energy barriers provide a comparison of alternative reaction pathways.

C–H cleavage in the absence of three-fold Pt sites can proceed only through H stabilization on a neighboring Pt atom or on the Pt atom that binds the reacting C atom. The stabilization on a neighboring Pt atom, shown in Figure 3 b, is energetically preferable. The C–H bond distance in the transition state is estimated at 0.16 nm (Figure 3 b-3), the same as on a three-fold Pt site (Figure 2 b-2). The calculated reaction barrier in the absence of a three-fold Pt site, however, is higher at 190 kJ mol^{-1} compared to 167 kJ mol^{-1}. Thus, the geometry of a three-fold Pt site allows better stabilization of the transitional configuration for C–H cleavage. In summary, the presence of three-fold Pt sites reduces the energy barriers for both H transfer and C–H cleavage reactions. Moreover, the presence of three-fold Pt sites opens a new mechanism for H transfer reactions involving H stabilization by the surface.

The changes in the reaction mechanism that are due to the absence of three-fold Pt sites were validated experimentally by comparing transformations of adsorbed acetylene as a function of temperature on exactly the same Pt_3Sn/Pt(111) and Pt_2Sn/Pt(111) surfaces that were used in the computational studies (Figure 1 b,c). These two Pt-Sn ordered surface alloys were prepared by evaporating Sn onto a Pt(111) single-crystal surface and subsequently annealing the samples to 1000 K. This high annealing temperature generated surfaces that were stable (no surface reconstruction) under all subsequent testing conditions. Sn was incorporated only in the top surface layer by substituting for Pt atoms,[8] and the amount of introduced Sn determined the composition and structure of the alloys. The (2×2) pattern for the Pt_3Sn surface and the $(\sqrt{3}\times\sqrt{3})R30°$ pattern for the Pt_2Sn surface were confirmed with low-energy electron diffraction (LEED) measurements.

Acetylene was dosed at 90 K, and its transformations on the Pt-Sn surfaces upon annealing to 500 K were monitored with high-resolution electron energy-loss spectroscopy (HREELS). The HREELS spectra are presented in Figure 4 with vibrational peak assignments, which were made in our previous study of adsorption energies, preferential adsorption sites, and normal vibrational modes of regular and deuterated C_2 hydrocarbon species.[3j] The computational surface models were also used successfully in our previous studies of ethylene oxide and cyclohexanone adsorption.[9] Along with spectroscopic measurements, evolution of gas-phase products after acetylene adsorption was monitored by a quadrupole mass spectrometer in temperature-programmed desorption (TPD) experiments.

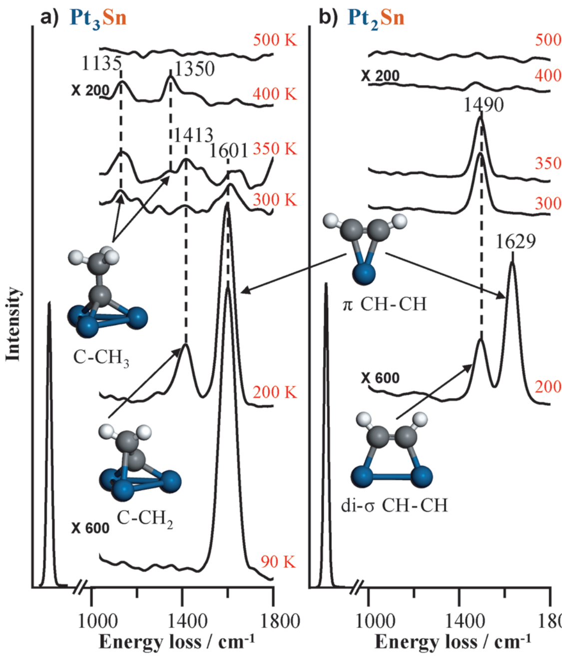

Figure 4. Evolution of HREELS spectra as a function of annealing temperature after acetylene (HC–CH) adsorption on a) Pt_3Sn surface with three-fold Pt sites and b) Pt_2Sn surface without three-fold Pt sites. The absence of C–CH_2 on the Pt_2Sn surface indicates that both the H transfer and C–H bond cleavage reactions are suppressed in the absence of three-fold Pt sites.

At a dosing temperature of 90 K, acetylene adsorbs molecularly. At this temperature on the Pt_3Sn surface (Figure 4 a), a single peak in the C–C bond stretching (ν_{CC}) region is observed at 1601 cm^{-1}, which is assigned to π-bonded acetylene on atop Pt sites. The same π-bonded HC−CH species on atop Pt sites remain on the Pt_3Sn surface after annealing to 200 K. These HC−CH species on atop Pt sites are also observed at 200 K on the Pt_2Sn surface with a similar ν_{CC} peak at 1629 cm^{-1} (Figure 4b). The peak is shifted to higher wavenumbers on the Pt_2Sn surface due to an electronic effect of the higher Sn concentration and a resulting weaker bonding of adsorbed acetylene. In addition to π-bonded HC−CH species on atop Pt sites, di-σ bonded HC−CH species on bridge Pt sites are observed on the Pt_2Sn surface at 200 K with a ν_{CC} peak at 1490 cm^{-1} (Figure 4b). In contrast, no equivalent peak is observed for the Pt_3Sn surface. Instead, there is a peak at 1413 cm^{-1}, which is due to $C{-}CH_2$ species (a coupled vibrational mode of CH_2 deformation and C−C stretching, δ_{CH_2}/ν_{CC}). Identification of $C{-}CH_2$ species is further confirmed with the observation of ethylidyne, $C{-}CH_3$ species, with characteristic peaks[3g,5,10] at 1135 and 1350 cm^{-1} at 300–400 K because $C{-}CH_2$ is a likely intermediate in $C{-}CH_3$ formation through acetylene disproportionation.[3d,4,5]

At temperatures above 200 K for the Pt_2Sn surface, π-bonded HC−CH species on atop Pt sites desorb first as evidenced by a decrease in the intensity of the peak at 1629 cm^{-1}, followed by desorption of di-σ bonded HC−CH species on bridge Pt sites with the peak at 1490 cm^{-1} (Figure 4b). Hydrocarbon desorption is substantially complete by 400 K when strong vibrational peaks are no longer observed. Importantly, however, $C{-}CH_2$ species are not detected on this surface, which must be due to a kinetic factor and a change in the reaction mechanism due to the absence of three-fold Pt sites, in agreement with the computational results.

Furthermore, the amount of desorbed acetylene molecules in TPD experiments is lower for the Pt_3Sn surface than that for the Pt_2Sn surface. This result shows that acetylene is more reactive on the Pt_3Sn surface. The amount of desorbed hydrogen, which must be formed through C−H bond cleavage, on the other hand, is higher for the Pt_3Sn surface, which is also in line with higher hydrocarbon reactivity on this surface. These TPD results, which are shown in Figure S1, provide further evidence that both the H transfer and C−H cleavage reactions are suppressed in the absence of three-fold Pt sites on the Pt_2Sn surface, in agreement with the computational results for the geometric requirements for Pt catalytic sites. As synthesis methods for custom-tailored Pt-Sn[1,11] and other Pt alloy surfaces are being rapidly developed that can control both the composition and geometric arrangements of elements, this information on the geometric requirements for hydrocarbon reactivity is critical for realizing the full potential of rational design[3i,12] for new Pt bimetallic materials.

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