

# Investigation of Benzene Formation from Acetylene on Pt-Sn Alloys with HREELS, TPD and DFT Calculations

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## Introduction

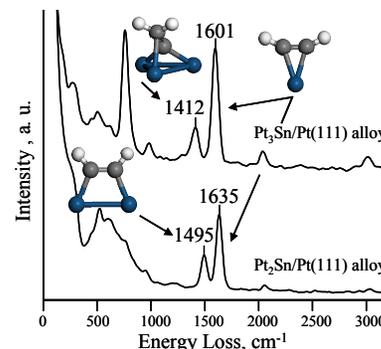
Pt-based catalysts are used in a wide variety of industrial hydrocarbon reactions, for example, in hydrogenation, reforming and oxidation. Sn is frequently added to Pt catalyst formulations as a promoter that suppresses hydrocarbon decomposition and improves reaction selectivities. Unlike pure Pt(111) in ultra-high vacuum (UHV), which is known to catalyze only acetylene decomposition [1, 2], Sn/Pt(111) alloys have been shown to enable cyclotrimerization of acetylene to benzene [2]. The current investigation provides molecular insight into differences in acetylene adsorption and reactivity on Pt and Pt-Sn alloys by combining density functional theory (DFT) calculations with vibrational analyses to explain vibrational spectra from high resolution electron energy loss spectroscopy (HREELS) and evolution of products from temperature programmed desorption (TPD).

## Materials and Methods

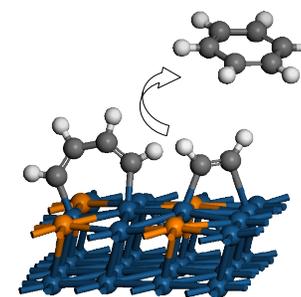
Benzene formation from regular ( $C_2H_2$ ) and deuterated acetylene ( $C_2D_2$ ) was studied on two ordered surface alloys:  $Pt_3Sn/Pt(111)$  and  $Pt_2Sn/Pt(111)$  with HREELS and TPD in UHV at 90-1000 K. The alloys were prepared by evaporating Sn onto a Pt(111) single crystal surface and subsequently annealing the sample to 1000 K for 10 s. Depending on the initial amount of Sn, the annealed surface exhibited either a  $(2 \times 2)$  or  $(\sqrt{3} \times \sqrt{3})R30^\circ$  pattern in LEED. Sn was incorporated only in the top surface layer to form, respectively,  $Pt_3Sn/Pt(111)$  and  $Pt_2Sn/Pt(111)$  surface alloys [3]. Gradient-corrected periodic DFT calculations were performed with the DMol3 code in Materials Studio by Accelrys.

## Results and Discussion

HREELS spectra for the  $Pt_3Sn$  alloy at the dosing temperature of 90 K exhibit a single  $\nu_{CC}$  peak at  $1601\text{ cm}^{-1}$ . This peak and the corresponding peak at  $1635\text{ cm}^{-1}$  on the  $Pt_2Sn$  alloy are assigned to acetylene species  $\pi$ -bonded to a single Pt atom (Figure 1). DFT calculations suggest that the most stable acetylene configuration on Pt(111) is a di- $\sigma/\pi$ -bonded species in a three-fold site with  $\nu_{CC}$  of  $1310\text{ cm}^{-1}$ . This di- $\sigma/\pi$ -bonded configuration is not observed on the Pt-Sn alloys because it is less stable in the presence of Sn compared to the di-



**Figure 1.** HREELS spectra for acetylene on Pt-Sn alloys at 200 K and DFT models of stable adsorbates with vibrational modes that match experimental frequencies.



**Figure 2.** DFT models of  $C_4H_4$  (acetylene dimer) and  $C_2H_2$  as intermediates in benzene formation on  $Pt_3Sn/Pt(111)$  alloy. Preferential hydrocarbon bonding is to Pt only.

$\sigma$ -bonded configuration on a Pt-Pt bridge site. On annealing to higher temperatures,  $\pi$ -bonded acetylene on the alloys transforms to a more stable di- $\sigma$ -bonded configuration ( $\nu_{CC}$  peak at  $1495\text{ cm}^{-1}$  in Figure 1). In addition,  $\pi$ -bonded acetylene isomerizes to vinylidene ( $C-CH_2$ ) species di- $\sigma/\pi$ -bonded to three Pt atoms on the  $Pt_3Sn$  alloy ( $\nu_{CC}$  peak at  $1412\text{ cm}^{-1}$  in Figure 1). Such a rearrangement of adsorbed vinylidene species is not observed on the  $Pt_2Sn$  alloy due to the absence of pure-Pt three-fold sites.

HREELS, TPD and DFT results suggest that acetylene forms a cyclic  $C_4H_4$  dimer on the Pt-Sn alloys. This  $C_4H_4$  intermediate is predicted to produce benzene by reacting with an additional surface acetylene (Figure 2). The destabilizing effect of Sn alloying is more significant for acetylene than for the  $C_4H_4$  intermediate, and as a result, the reaction of  $C_4H_4$  formation is estimated to change from being endothermic on pure Pt to being exothermic, *i.e.* energetically favorable, on the Pt-Sn alloys. Benzene, thus, does not form on pure Pt due to the strong bonding of adsorbed acetylene, which decomposes instead of producing the  $C_4H_4$  intermediate. On both Pt-Sn alloys, formed benzene readily desorbs, and the amount of produced benzene is higher over the  $Pt_2Sn$  alloy with a higher Sn concentration.

## Significance

Adsorption modes of acetylene on Pt-Sn surface alloys have been identified for the first time. The presence of Sn changes preferential hydrocarbon adsorption sites, decreases stability of adsorbed species and favors associative reactions, thus, enabling benzene production. A molecular reaction mechanism for benzene formation has been developed by consolidating HREELS and TPD experimental results with DFT calculations.

## References

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