

# Study of acetylene adsorption and reactivity on Pt and Pt-Sn alloys with HREELS, TPD and DFT calculations

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## Introduction

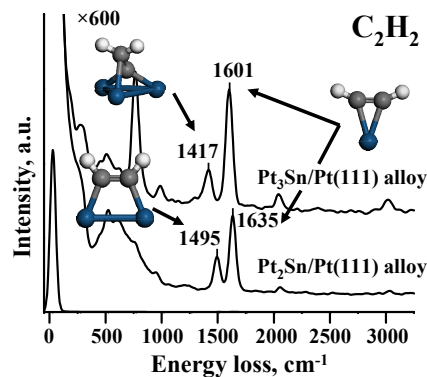
Platinum-based catalysts are used in a wide variety of industrial hydrocarbon reactions, for example, in hydrogenation, isomerization and oxidation. Sn is frequently added to Pt catalyst formulations as a promoter that suppresses hydrocarbon decomposition and improves reaction selectivities. Unlike pure Pt, which is known to catalyze only acetylene decomposition, Sn/Pt(111) alloys have been shown to enable cyclotrimerization of acetylene to benzene [1]. 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 obtained with high resolution electron energy loss spectroscopy (HREELS) and evolution of products from temperature desorption (TPD).

## Materials and Methods

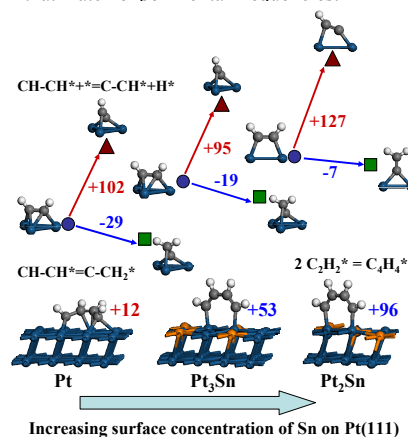
Acetylene adsorption with regular ( $C_2H_2$ ) and deuterated acetylene ( $C_2D_2$ ) was studied on two ordered surface alloys:  $Pt_3Sn/Pt(111)$  and  $Pt_2Sn/Pt(111)$  with HREELS and TPD at 90-1000 K. The alloys were prepared by evaporating Sn onto a Pt(111) single crystal surface and subsequently 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 [2]. Gradient-corrected periodic DFT calculations with the DMol3 code in Materials Studio software by Accelrys were used to obtain geometries, adsorption energies and vibrational frequencies for various  $C_2H_2$  and  $C_2H$  adsorbed species.

## 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 indicate 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. In contrast to pure Pt,  $\pi$ -bonded acetylene on the alloys transforms to a di- $\sigma$ -bonded configuration ( $\nu_{CC}$  peak at  $1495\text{ cm}^{-1}$  in Figure 1) on annealing to higher temperatures. 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



**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.** Reaction energies for acetylene transformation to C-CH+H and C-CH<sub>2</sub> (top) and acetylene dimerization (bottom), kJ/mol.

## References

- Xu, C., Peck, J.W., and Koel, B.E., *J. Am. Chem. Soc.* 115, 2 (1993).
- Overbury, S.H., Mullins, D.R., Paffett, M.T., and Koel, B.E., *Surf. Sci.* 254, 1-3 (1991)

rearrangement to adsorbed vinylidene species is not observed on the  $Pt_3Sn$  alloy due to the absence of pure-Pt three-fold sites.

The DFT models calibrated based on adsorption experiments were used to explore acetylene reactivity by evaluating reaction barriers and energies. Reaction energies illustrated in Figure 2 indicate that the presence of Sn changes reaction pathways for adsorbed acetylene. The destabilizing effect of Sn alloying is more significant for C-CH<sub>2</sub> and C-CH+H species than for acetylene. This change in relative stability of C<sub>2</sub> species suppresses acetylene decomposition and rearrangement reactions on Pt-Sn. On the other hand, the presence of Sn makes the formation of dimers, C<sub>4</sub>H<sub>4</sub> species, more energetically favorable. The combined effect of Sn alloying, therefore, is suppression of dissociative reactions and promotion of associative reactions. The close integration of experimental and computational results allowed us to develop a molecular-level explanation of why benzene formation, as a product of acetylene trimerization, is experimentally observed on Pt-Sn alloys and not on pure Pt.

## Significance

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