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## Adsorption of Simple Alkenes on Pt(111) and Pt–Sn Surface Alloys: Bond Strength versus Heat of Adsorption

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In heterogeneous catalysis, bond activation caused by hybridization of the adsorbed reactants is a crucial phenomenon. It is commonly believed that the hybridization of adsorbed molecules, which is closely connected to the reactivity, is directly related to the heat of adsorption on alloy surfaces. We have investigated the adsorption of two prototypical alkenes on Pt(111) and Pt–Sn surface alloys using density functional theory. This approach allowed the determination of the bonding geometries and the degree of hybridization of the adsorbed molecules on the respective surfaces. It has been found that the final geometries, and thus the hybridization, of the adsorbed species do not change as a function of the surface composition. The observed strong decrease of the heat of adsorption on the Pt–Sn alloys is mainly attributed to relaxation effects of the metal surface and is not linked to a decrease in bond strength.

Alloys are widely used as heterogeneous catalysts due to an enhanced selectivity and reactivity in catalytic reactions. In this context chemisorption on alloy surfaces is one of the decisive steps determining the performance of the catalyst. Even though numerous studies have been devoted to this problem, a detailed (atomic scale) understanding of energetics of chemisorption is still missing. In this letter, we address the question of the relationship between the heat of adsorption of alkenes on Pt–Sn surface alloys and the bond strength of the chemisorbed molecule. Even though we have observed the effects, which we discuss here, in three previous studies devoted to the adsorption of cyclopentene,<sup>1</sup>  $\alpha,\beta$ -unsaturated aldehydes,<sup>2</sup> and ethene<sup>3</sup> on Pt(111) and ordered Pt–Sn surface alloys we here restrict our analysis to the case of simple alkenes, which adopt a  $\eta^2$ -di $\sigma$ (CC) coordination on the Pt(111), Pt<sub>3</sub>Sn/Pt(111), and Pt<sub>2</sub>Sn/Pt(111) surfaces.

Ethene and cyclopentene experience a comparable lowering of the desorption temperature ( $T_{\text{des}}$ ) on the Pt–Sn surface alloys as compared to Pt(111) (Table 1). This can be interpreted as a decrease of the heat of adsorption  $E_{\text{ads}}$ , which is commonly explained in terms of a lowering the d-band center of the substrate by alloying.<sup>4</sup> This particular model explains chemisorption in terms of a frontier orbital approach, in which the metal d-band is represented by a single energy level at its center of gravity, which shifts due to alloying. Hence, this model describes only the initial state of the chemisorption system and so the consequences arising from the relaxation of the metal or the molecule are not explicitly included. Nevertheless, the d-band model often successfully explains the lowering of the

**TABLE 1: Comparison of the Desorption Temperatures and Adsorption Energies of Ethene and Cyclopentene on Pt(111) and Pt–Sn Surface Alloys**

	$T_{\text{des}}/\text{K}$		$E_{\text{ads}}/\text{kJ mol}^{-1}$	
	C <sub>2</sub> H <sub>4</sub>	C <sub>5</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>5</sub> H <sub>8</sub>
Pt(111)	273	278	−100.4	−94.0
Pt <sub>3</sub> Sn/Pt(111)	226	243	−65.8	−42.0
Pt <sub>2</sub> Sn/Pt(111)	184	192	−57.1	−30.0

heat of adsorption on alloys and bimetallic systems from the phenomenological point of view. However, it does not provide a thorough description of the evolution of the intrinsic energetic properties of the final (adsorbed) state (e.g., molecular and substrate vibrational shifts).

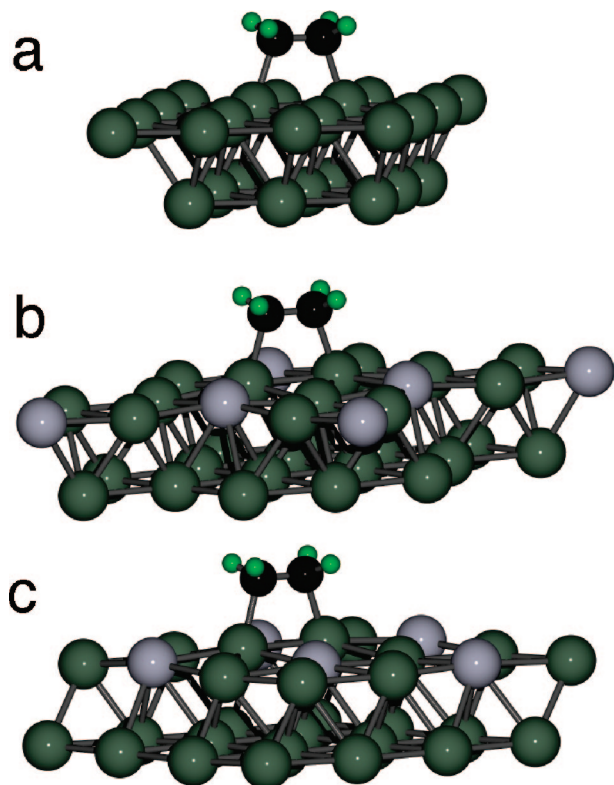
We have used density functional theory (DFT) calculations in conjunction with vibrational spectroscopy<sup>1,3</sup> to elucidate the atomistic details of the chemical bonding of ethene and cyclopentene on Pt(111) as well as on the ordered Pt<sub>3</sub>Sn/Pt(111) and Pt<sub>2</sub>Sn/Pt(111) surface alloys. This approach allows us to directly validate the results of the DFT calculations by comparing the calculated vibrational spectra with the experimental ones.

This approach yields qualitatively the correct trend in the lowering of the adsorption energies  $E_{\text{ads}}$  (Table 1), which is reflected in the lowering of the desorption temperatures. However, a closer look on the detailed structure of the adsorbed molecules reveals striking similarities between the adsorption complexes on Pt(111) and the two surface alloys (Figure 1). Table 2 summarizes two important geometrical parameters of adsorbed ethene and cyclopentene. Despite the significant decrease of  $E_{\text{ads}}$  on the surface alloys the adsorption geometries do not change. In particular, the C–C bond length of the bonding carbon atoms varies only slightly indicating a similar

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**Figure 1.** Optimized geometries for ethene on (a) Pt(111), (b) Pt<sub>3</sub>Sn/Pt(111), and (c) Pt<sub>2</sub>Sn/Pt(111). Only the two topmost surface layers are shown.

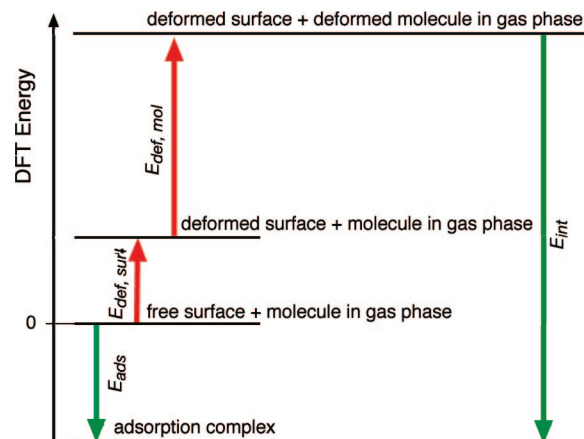
**TABLE 2: Characteristic Bond Lengths for Adsorbed Ethene and Cyclopentene. Outward Relaxation (Pt<sup>†</sup>) of the Bonding Pt Atoms for the Case of Ethene Adsorption**

	Pt–C/pm		C–C/pm		Pt <sup>†</sup> / pm
	C <sub>2</sub> H <sub>4</sub>	C <sub>5</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>5</sub> H <sub>8</sub>	
Pt(111)	212.3	213.7	148.9	150.4	18
Pt <sub>3</sub> Sn/Pt(111)	213.5	214.5	148.7	149.7	28
Pt <sub>2</sub> Sn/Pt(111)	213.2	213.8	148.7	150.4	42

bond order, which points to a similar hybridization on all three surfaces. This is corroborated by the vibrational frequencies of ethene and cyclopentene on Pt(111) and the Pt–Sn surface alloys, which vary only slightly.<sup>1,3</sup> In particular the  $\nu(\text{PtC})$  stretching vibrations vary only little (see Supporting Information), which seems to suggest that alloying does not alter the bond strength (force constant) of the Pt–C bond.

This is obviously at variance with the observed strongly lowered heat of adsorption on the alloy surfaces. In fact the only structural parameter affected by the surface stoichiometry is the outward relaxation (Pt<sup>†</sup>) of the Pt dimer (Table 2) that is involved in the formation of the adsorption complex. This value increases with the Sn fraction in the surface. It should also be noted that for Pt<sub>2</sub>Sn additional in-plane displacements are found. Therefore, the change in adsorption energy seems to be strongly related to the surface relaxation.

In order to study this effect in detail, we decomposed the calculated adsorption energies into three terms describing the deformations of the molecule and of the surface as well as the interaction between molecule and surface.<sup>5</sup> As depicted in Figure 2, the energies required to deform the surface ( $E_{\text{def, surf}}$ ) and the molecule ( $E_{\text{def, mol}}$ ) are positive. These values are calculated by comparing the electronic energies obtained by single point calculations of the separated components (surface



**Figure 2.** Schematic representation of the energetic contributions involved in the chemical bonding of a molecule on a solid surface.

**TABLE 3: Energetic Contributions Related to the Model Given in Equation 1 (kJ mol<sup>−1</sup>) for the Adsorbed Ethene and Cyclopentene Molecules**

	C <sub>2</sub> H <sub>4</sub>			C <sub>5</sub> H <sub>8</sub>		
	Pt	Pt <sub>3</sub> Sn	Pt <sub>2</sub> Sn	Pt	Pt <sub>3</sub> Sn	Pt <sub>2</sub> Sn
$E_{\text{ads}}$	−100.4	−65.8	−57.1	−94.0	−42.0	−30.0
$E_{\text{def,surf}}$	15.4	34.5	49.6	17.0	45.8	62.8
$E_{\text{def,mol}}$	138.1	142.3	143.5	146.3	157.2	152.8
$E_{\text{int}}$	−253.9	−242.6	−250.1	−257.3	−245.0	−245.6

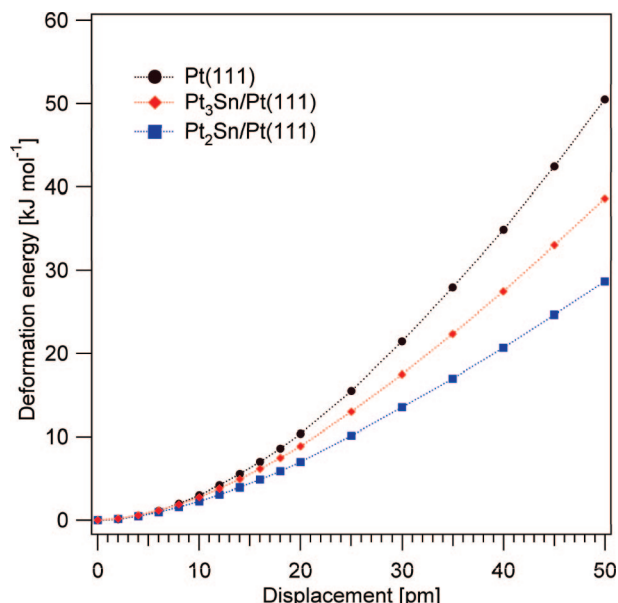
and molecule) – using the geometry of the fully relaxed adsorption complex – with those of the fully optimized clean surface and free molecule, respectively. Then the interaction energy  $E_{\text{int}}$  is derived easily from these deformation energies using eq 1

$$E_{\text{int}} = E_{\text{ads}} - E_{\text{def,surf}} - E_{\text{def,mol}} \quad (1)$$

The value of  $E_{\text{int}}$  represents the energy gain related to the formation of the molecule–surface bond once the surface and the molecule have already paid the energetic cost of distortion. Table 3 shows the detailed energy contributions obtained for adsorbed ethene and cyclopentene.

At first glance, it becomes obvious that the interaction energy  $E_{\text{int}}$  changes only marginally by less than 5 kJ/mol ( $\sim 3\%$ ) on the different surfaces. This can be interpreted in terms of a quasi-identical interaction between the associated Pt atoms and the molecule on all considered surfaces. This and the unaltered geometries of the bonding complexes immediately explain the absence of changes in the vibrational spectra. The apparently similar bond strength, which we inferred from the constant value of  $\nu(\text{PtC})$ , is indeed caused by an almost constant interaction energy. Moreover, the term, which becomes decisive for the change of the heat of adsorption  $E_{\text{ads}}$  as a function of surface composition, is the deformation energy of the surfaces. Although it is the smallest contribution in absolute values, it ultimately determines the change in  $E_{\text{ads}}$ . The total response of the system is obviously governed by the formation of the preferred adsorption complex consisting of the molecule and a Pt dimer in the surface layer. In other words, the interaction energy, which is the biggest contribution to the heat of formation, determines the geometry of the adsorption complex consisting of the molecule and the Pt dimer. The remaining surface atoms then relax in order to minimize the total energy.

Two complementary reasons can be considered to explain the surface deformation. First, the molecule–surface interaction modifies the electronic distribution at the surface by a partial



**Figure 3.** Energetic cost required for displacing a single Pt atom perpendicularly out of the surface. The single point calculations were done on a  $(3 \times 3)$  super cell for Pt(111) and Pt<sub>2</sub>Sn/Pt(111) and on a  $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$  unit cell for Pt<sub>3</sub>Sn/Pt(111) and compared to the energy of the respective fully optimized clean surfaces.

filling of some antibonding states.<sup>6</sup> This results in a weakening of the metallic bonds at the surface. Additionally, repulsive Pauli interactions are present between occupied orbitals of the molecule and the almost filled surface d-states.<sup>7,8</sup> The outward relaxation of the Pt dimer allows the partial relief of this repulsion by displacing the molecule away from the rest of the surface atoms. In the case of the Pt–Sn surface alloys, the increased electron density at the Pt surface atoms, induced by the electronic transfer coming from Sn atoms, should yield a stronger Pauli repulsion, as previously shown in the case of the Pt<sub>80</sub>Fe<sub>20</sub>(111) surface.<sup>9</sup> This effect will be further amplified by the buckling of the Sn atoms in the surface alloys. Consequently, a larger outward relaxation of the Pt dimer is required in the case of the alloy to compensate for this enhanced Pauli repulsion, at the expense of the energy required for the stronger surface distortion.

This effect is facilitated by an easier deformation of the alloy surfaces. Indeed, DFT calculations show that the energy required to displace a single Pt atom perpendicularly out of the clean surfaces is much smaller for the surface alloys than for the pure Pt surface (Figure 3). This result is due to the weakening of the Pt–Pt and Pt–Sn bonds in the alloys compared to the Pt–Pt bonds in the pure metal. In fact, the charge transfer from Sn to Pt found in the surface alloys<sup>10</sup> increases the Pauli repulsion between the Pt atoms. Moreover, Pt and Sn having different electronegativity, their interacting orbitals have different ener-

gies, which weakens the Pt–Sn bonds compared to pure Pt–Pt ones. Thus, for a given deformation energy, a larger outward relaxation is induced on the alloy compared to pure Pt(111). If both effects are considered the unusually large adsorbate-induced relaxation in the case of the alloys can be rationalized.

## Summary

Although the d-band model links the weakening of the heat of adsorption ( $E_{\text{ads}}$ ) to the downshift of the d-band center by alloying,<sup>4</sup> it does not predict the behavior of the true interaction energy between the adsorbate and the substrate ( $E_{\text{int}}$ ) since it does not include relaxation effects observed in the final state. In the light of this analysis, our usual interpretation and perception of the effects of alloying on the adsorption strength of simple organic molecules should be reconsidered carefully. Obviously, at least in the case of simple alkenes on Pt–Sn surface alloys, the determining factor is the deformation of the surface required for an optimal molecule-surface bond formation. These deformations and the associated energy cost are larger in the case of the alloys, resulting in a decrease of the overall adsorption energy. In contrast, the interaction energy, bond strength, and force constant between the molecule and the surface hardly change.

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**Supporting Information Available:** Computational methods. Structural and vibrational data of the adsorbed molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Becker, C.; Delbecq, F.; Breitbach, J.; Hamm, G.; Franke, D.; Jäger, F.; Wandelt, K. *J. Phys. Chem. B* **2004**, *108*, 18960.
- (2) Haubrich, J.; Loffreda, D.; Delbecq, F.; Jugnet, Y.; Sautet, P.; Krupski, A.; Becker, C.; Wandelt, K. *Chem. Phys. Lett.* **2006**, *433*, 188.
- (3) Essen, J. M.; Haubrich, J.; Becker, C.; Wandelt, K. *Surf. Sci.* **2007**, *601*, 3472.
- (4) Hammer, B. J.; Nørskov, K. *Adv. Catal.* **2000**, *45*, 71.
- (5) Morin, C.; Simon, D.; Sautet, P. *J. Phys. Chem. B* **2004**, *108*, 5653.
- (6) Loffreda, D.; Delbecq, F.; Simon, D.; Sautet, P. *J. Chem. Phys.* **2001**, *115*, 8101.
- (7) Sautet, P.; Paul, J. F. *Catal. Lett.* **1991**, *9*, 245.
- (8) Delbecq, F.; Sautet, P. *Catal. Lett.* **1994**, *28*, 89.
- (9) Delbecq, F.; Sautet, P. *J. Catal.* **1996**, *164*, 152.
- (10) Delbecq, F.; Sautet, P. *J. Catal.* **2003**, *220*, 115.
- (11) Kresse, G.; Hafner, J. *J. Phys. Rev. B* **1993**, *47*, 558. (a) Kresse, G.; Hafner, J. *J. Phys. Rev. B* **1993**, *48*, 13115.
- (12) Perdew, J. P.; Wang, Y. *J. Phys. Rev. B* **1992**, *45*, 13244.
- (13) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.

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