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Adsorption of Complex Molecules from Vibrational Spectroscopy: A Joint Theoretical and Experimental Approach

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Studies on heterogeneous catalysis such as the selective hydrogenation of α,β-unsaturated aldehydes on transition metal surfaces represent a challenge to both experimentalists and theoreticians. Although numerous studies have been dedicated to systems like acrolein or prenal on Pt(111) in recent years, the details of the molecule-surface bonding still remain under debate. Yet the selectivities of such processes depend crucially on the structure of adsorption complexes. Their characterization is even more complicated when alloy surfaces, which are often used to optimize the properties of the catalyst, are considered.

Here we present a joint experimental and theoretical study on molecule-surface bonding of prenal on Pt(111) and two Pt-Sn surface alloys based on the interpretation of HREEL spectra using *ab initio* density-functional theory (DFT). HREELS experiments carried out on the three model-catalysts show highly complex spectra of the adsorbed prenal at low temperatures. By comparing the HREEL spectra with the results of the vibrational analysis obtained from the DFT calculations, we are able to identify stable adsorption geometries, interpret the normal modes corresponding to the measured loss peaks and point to likely reaction paths.

1 Introduction

Investigations of reaction mechanisms, selectivities or activities in catalytic processes require a profound understanding of the interactions of the reactants, intermediates and products with the catalyst itself. Since the surface structures of industrial catalysts are usually highly complex, model systems with defined surface structures have to be used to perform such investigations. Besides using mono- and multimetallic single-crystaline samples, also alloying the surface of a monometallic substrate with a second metal can be used to create well defined model catalyst surfaces.

A considerable number of studies have been performed to understand the hydrogenation process and the adsorption properties of α,β-unsaturated aldehydes on single crystal surfaces and alloys (See Refs. 1–4 and references therein). Most of these studies are dedicated to the close-packed Pt(111) surface and well-ordered Pt-Sn/Pt(111) surface alloys as model catalysts.

The hydrogenation of α,β-unsaturated aldehydes can lead to three different products. Saturated aldehydes (Fig. 1), which represent the thermodynamically favoured hydrogenation products, the saturated alcohols and unsaturated alcohols, which are of particular interest for the chemical and pharmaceutical industry. The selectivity of this reaction depends

strongly on the aldehyde itself as well as the catalyst[1,3]. For instance it is known, that the substitution of methyl-groups on the β-carbon of the C=C bond, leading from acrolein (propenal) to crotonaldehyde (2-butenal) and to prenal (3-Methyl-2-butenal), increases the selectivity towards the unsaturated alcohol. Similarly alloying the catalyst with other metals can increase the selectivity, which is in fact observed, when one alloys a Pt catalyst with Sn[1]. Generally it is expected, that double bonds interacting with the surface are more easily hydrogenated. Therefore, changes in the adsorption modes on the various model catalysts could help to explain the observed selectivities.

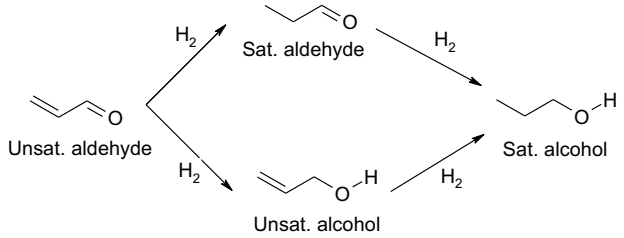


Figure 1. Possible hydrogenation reactions of α,β-unsaturated aldehydes.

We employ high resolution electron energy loss spectroscopy (HREELS) in conjunction with density functional theory (DFT) to gain deeper insights into molecule-surface interactions, surface processes and modifications by alloying effects.

In particular, the Pt(111) surface and two ultra-thin Pt-Sn surface alloys have been chosen as model catalysts. For the experiments and the density functional theory calculations in the present project, emphasis has been placed on the examples of crotonaldehyde and prenal. Extending previous studies[3], in this work all possible adsorption geometries on Pt(111), Pt_2Sn(111) and Pt_3Sn(111) have been investigated. In addition to the total energy calculations we report the computation of the vibrational spectra (HREELS, RAIRS) in comparison with recent experiments performed in Bonn.

Here we focus on the adsorption of prenal. The varity of the conceivable adsorption complexes of prenal on the three model-catalysts is increased by the fact, that prenal exists in two rota-isomers, namely (s)-trans prenal and (s)-cis prenal. Both isomers differ in the relative orientation of the C=C and C=O double bonds. In the gas phase both isomers are energetically very similar, cis prenal being by 3.5 kJ/mol less stable.

Details regarding the theoretical calculations and the experiments are presented in Sec. 2. The follwing discussion in Sec. 3 gives important results of the studies of prenal on three model catalyst surfaces. Finally some conclusions will be drawn in Sec. 4 showing the potential and also limits of this joint theoretical and experimental approach.

2 The Theoretical and Experimental Approaches

2.1 Computational Details

The DFT calculations have been performed using the VASP program[5] at the general gradient approximation (GGA, Perdew-Wang 91[6]) with PAW pseudopotentials[7]. A tight

convergence of the plane-wave expansion is obtained with a cut-off of 400 eV. For both the Pt(111) and Pt_2Sn(111)/Pt(111) surfaces a 3×3 cell of the adsorbate was considered (coverage of 1/9 monolayer, ML), consisting of a 4 layer metallic slab and a 5 layer thick vacuum with adsorption of the molecules on one side of the slab. For the Pt_3Sn(111)/Pt(111) surface a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ adsorbate periodicity was used. In the cases of the Pt_2Sn(111)/Pt(111) and Pt_3Sn(111)/Pt(111) surface, a single alloy layer is modeled above a Pt(111) bulk[8,9]. For the geometry optimizations, only the two uppermost metal layers and the molecule are relaxed whereas the two lowest metal planes are kept frozen. 2D Brillouin zone integration is performed on a sufficiently converged $3 \times 3 \times 1$ k-point grid. The vibrational frequencies are calculated by numerical computation of the 2^{nd} derivatives of the potential energy surface, neglecting any coupling between molecular modes and surface phonons lying in the 0-200 cm^{-1} range (see Ref. 4 for more details). Therefore only the harmonic modes with frequencies above 320 cm^{-1} will be given. The HREELS loss intensities are calculated from the 1^{st} derivatives of the z-component of the dynamical dipole moments[4]. Due to the large number of possible adsorption structures of prenal and crotonaldehyde on the three chosen surfaces and the size of the supercells, this project turned out to be computationally highly demanding. Numerous of the calculations have been performed at the computer center (ZAM) of the Forschungszentrum Jülich utilizing the newly established massively-parallel IBM supercomputer JUMP.

2.2 Experimental Details

The experiments were performed in an ultrahigh vacuum chamber (base pressure 10^{-8} Pa) equipped with a high resolution electron energy loss spectrometer (HREELS, VSW IB2000), a back-view LEED optics, an Auger electron spectrometer (AES) and a quadrupole mass spectrometer (QMS)[9]. The HREEL spectra were recorded with a primary electron energy of 4.7 eV in a specular geometry 60° off normal incidence. The Pt(111) sample was cleaned by repeated cycles of Ar^+ sputtering at 900K (2 keV) and annealing to 1150K.

The ordered Pt_nSn(111)/Pt(111) surface alloys have been prepared by depositing Sn films at 300K onto the Pt(111) and subsequent annealing[9]. The amount of Sn deposited was characterized by Auger electron spectroscopy. After annealing the Sn films to 600K, a LEED pattern with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ symmetry indicates the formation of a Pt_2Sn(111) surface alloy (Fig. 2). At higher temperatures of 1000K, the $p(2 \times 2)$ symmetry of a Pt_3Sn(111) surface alloy was found.

To characterize the thermal stability and reactivity of prenal on these surfaces, additionally TPD and LEED experiments of prenal adsorbed at 100K were performed. On Pt(111) the desorption of the prenal multilayer is detected at 160K followed by a desorption state at 199K. Furthermore decomposition reactions are observed giving rise to desorption of H_2 and CO. The HREELS experiments carried out between 100K and 500K on Pt(111) show highly complex spectra of the adsorbed prenal and its fragments, which form above 300K. On Pt_2Sn/Pt(111) and Pt_3Sn/Pt(111) this fragmentation process is suppressed. The HREELS experiments on these surfaces show only intact prenal species on the surface.

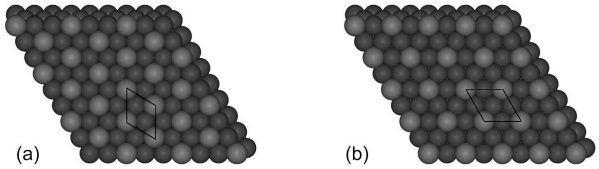


Figure 2. (a) Model of the $Pt_2Sn(111)/Pt(111)$ $(\sqrt{3}\times\sqrt{3})R30°$ surface. This surface shows only platinum top and brigde adsorption sites. (b) Model of the $Pt_3Sn(111)/Pt(111)$ $p(2\times 2)$ surface. On this surface pure platinum threefold hollow sites are present, too.

3 Identification of the Adsorption Modes of Prenal

3.1 Prenal/Pt(111)

The HREEL spectrum of prenal on Pt(111) shown here (Fig. 3) was obtained after adsorption at 100K and subsequent annealing to 205K in order to desorb the multilayer phase as determined by TPD experiments. It is highly complex and the loss signals measured show characteristic intensity changes and shifts compared to the signals of a prenal multilayer. The latter can be well described using the frequencies obtained from the calculation of prenal in the gas phase.

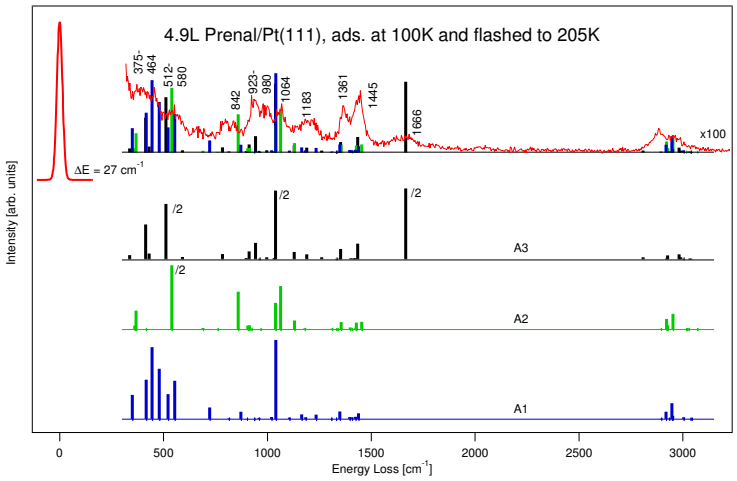


Figure 3. HREELS experiments and DFT calculations of prenal/Pt(111).

The theoretical modelling of the HREEL spectrum of the monolayer of prenal/Pt(111) requires the calculated spectra of η^4-(s)-trans-diσ(CC)+diσ(CO) (59 kJ/mol, A1), η^3-(s)-cis-diσ(CC) (49 kJ/mol, A2) and η^2-(s)-trans-diσ(CC) (54 kJ/mol, A3) binding sites. Two additional adsorption sites, η^4-(s)-cis-π(CC)+diσ(CO) (47 kJ/mol) and η^2-(s)-cis-diσ(CC)

(48 kJ/mol) can also not be excluded, neither from their adsorption energies nor from their vibrational fingerprints.

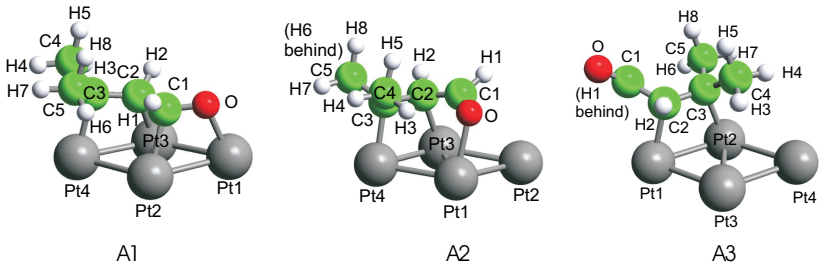


Figure 4. The identified adsorption geometries of prenal on Pt(111): η^4-(s)-trans-diσ(CC)+diσ(CO) (59 kJ/mol, A1), η^3-(s)-cis-diσ(CC) (49 kJ/mol, A2) and η^2-(s)-trans-diσ(CC) (54 kJ/mol, A3).

As seen from the superposition of these computed HREEL spectra with the experimental spectrum, the agreement of the frequencies is excellent in the region between 300 and 2000 cm^{-1} with errors of ca. 1%. Below 300 cm^{-1} the neglect of the surface phonons during the vibrational analysis and the limited thickness of the 4 layer metal slab leads to slightly larger errors (ca. 3%). In the CH-stretching region above 2500 cm^{-1} also sizeable errors are induced in the calculations. These are due to the anharmonicity of the potential and Fermi-couplings, which are ignored in the numerical frequency analysis.

All of the measured loss peaks in the HREEL spectra can be assigned from the DFT calculations. The most important assignments are presented in table 3.1.

Experimental: [cm^{-1}]	Assignment from DFT [cm^{-1}]:
1666	ν(C=O) of η_2-(s)-trans (1686).
	ν(C2=C3) of η_2-(s)-trans (1189), inactive.
1445	sym. and asym. δ'(CH$_3$),
1361	δ"(CH$_3$) and u(CH$_3$) of all ads. sites.
1181	ν(C2=C3) of η_3-(s)-cis (1181).
1183, 1164	ν(C2=C3) and ν(C=O) of η_4-(s)-trans, both weak.
1064	ν(C1-C2) of η_3-(s)-cis (1063),
	ν(C1-C2) of η_2-(s)-trans (1039) and
	γ_s"(C4H$_3$, C5H$_3$) of η_4-(s)-trans (1040).
923-980	mainly γ_{as}(C1H1, C2H2) of η_2-(s)-trans (943).
842	γ_s(C1H1, C2H2) of η_3-(s)-cis (859).
512-580	ν(Pt-C3) of η_2-(s)-trans (511), ν_{as}(Pt-CC) of
	η_3-(s)-cis (539), ν_{as}(Pt-CC) (554) and
	δ(O-C1-C2) (521) of η_4-(s)-trans.
464, 375	δ(C2=C3-C4,C5) (444), ν_s(Pt-CC) (417) of
	η_4-(s)-trans and δ(C3-C4,C5) of η_2-(s)-trans (413).

To highlight the sensitivity of the double bond stretching frequencies to the various adsorption modes, their positions shall be compared at this point. At 1666 cm^{-1} the ν(C=O) vibration of the η^2-(s)-trans-diσ(CC) agrees with the experiment. It is only slightly shifted compared to the gas phase value of 1677 cm^{-1} since it is not directly involved in the interaction to the substrate. The corresponding ν(C=C) vibration of this site is shifted strongly to 1189 cm^{-1} in agreement with its diσ(C=C) bonding configuration. In the case of the η^3-(s)-cis-diσ(CC) geometry both vibrational normal modes are computed with sizeable shifts at 1453 cm^{-1} (ν(C=O), inactive) and 1181 cm^{-1} (ν(C=C)). The frequency of the latter mode again indicates the diσ(C=C) bonding configuration. At 1183 cm^{-1} the ν(C=C) normal mode of the η^4-(s)-trans-diσ(CC)+diσ(CO) site is calculated with weak intensity in agreement with the measured spectrum. Its ν(C=O) vibration is computed at 1164 cm^{-1}.

3.2 Prenal/Pt_3Sn(111)

Also in the case of prenal on the Pt_3Sn/Pt(111) surface alloy a model can be deduced by combining the HREELS experiments with the DFT calculations (Fig. 5). Experimentally it is seen in TPD and HREELS, that prenal adsorption is completely reversible on this surface and that the adsorption strength of the monolayer species is sizeably decreased compared to Pt(111).

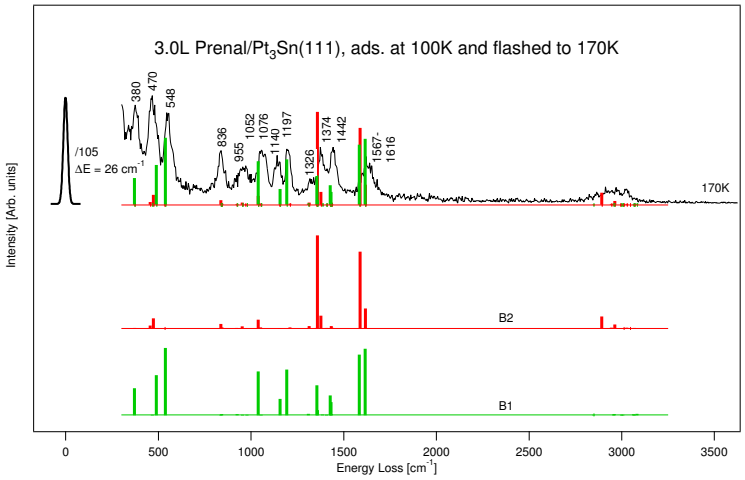


Figure 5. HREELS experiments and DFT calculations of prenal/Pt_3Sn(111).

The analysis of this model system leads to the identification of two η^1-(s)-trans-top-OSn adsorption structures (Fig. 6), in which prenal interacts solely with the oxygen of the aldehydic function with Sn atoms on the surface. Both related sites differ only by the relative orientation of the molecule. Due to the alloying with Sn the adsorption energies decrease strongly: With 39 (B1) and 31 kJ/mol (B2) the adsorption energies are only 66% of those on pure Pt(111).

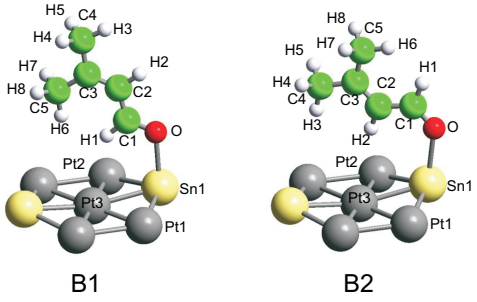


Figure 6. The two identified η^1-(s)-trans-top-OSn adsorption geometries of prenal on $Pt_3Sn(111)$.

Again a full vibrational assignment can be given from the DFT calculations. Importantly, the ν(C=O) and ν(C=C) vibrations of the two η^1-(s)-trans-top-OSn adsorption structures lead to an intensive loss signal between 1567 and 1616 cm^{-1}. The DFT calculations indicate as expected, that the ν(C=O) normal modes (1616/1615 cm^{-1}) of these adsorption complexes show larger shifts compared to the gas phase due to the interaction with the surface than the ν(C=C) vibrations (1588/1583 cm^{-1}). In the gas phase calculations, the ν(C=O) and ν(C=C) vibrations appear at 1677 and 1633 cm^{-1} respectively.

3.3 Prenal/$Pt_2Sn(111)$

For adsorption of prenal on Pt_2Sn/Pt(111), only small shifts and slight changes in relative loss intensities are found in the HREEL spectra for all the considered exposures. This suggests that prenal is weakly bound on this surface alloy, which is being supported by the calculated adsorption energies ($<$ 20.0 kJ/mol). Using only the most stable sites such as η^3-(s)-trans-π(CC)-OSn, we are not only unable to reproduce the HREEL spectra satisfactorily, but even find several signals that are not present experimentally. On the other hand, the best correspondence is achieved by considering the calculated spectra of η^2-(s)-trans-diσ(CC) and η^2-(s)-trans-π(CC) (both ca. 1.5 kJ/mol). These calculated spectra show the smallest difference compared to the gas phase frequencies. By fixing prenal at a distance of 4 Å parallel to the surface in the calculations, it is not only possible to reproduce the gas phase frequencies in agreement with the measured HREEL spectra, but also the computed intensities are well in agreement with the loss intensities detected.

Here both the theory and the experiment have difficulties to reach a convincing explanation when considered on their own. Yet the combination of the results from both approaches allows to reach the conclusion, that prenal is physisorbed in this case.

4 Conclusions

In the present study, the interactions of a multifunctional molecule (prenal) with mono- and bimetallic model catalyst surfaces has been investigated with combined experimental (HREELS) and theoretical (DFT) studies. Besides the adsorption on Pt(111), also the key

role of alloying the Pt surface with a second metal (Sn) on the adsorption of such complex molecules is adressed. Although qualitatively a larger number of possible adsorption complexes can be conceived on the Pt-Sn surface alloys, the presence of Sn simplifies the number of competitive stable adsorption states, hence leading to less complex HREEL spectra.

In terms of the adsorption energy, Sn induces a direct destabilization of the molecule-surface interaction. While on $Pt_3Sn(111)$ prenal is still chemisorbed, it only physisorbs when the surface concentration of Sn is increased like in the case of the $Pt_2Sn(111)$ surface alloy. According to the change of adsorption sites from flat geometries like η^4 and η^3 on Pt(111), in which both double bonds are interacting with the surface, to the vertical η^1-top-OSn sites on $Pt_3Sn(111)$, an increase of selectivity may be expected, since on this alloy surface the interacting C=O bond will probably be preferred for hydrogenation.

This study shows how a joint experimental and theoretical approach not only provides a good understanding of the vibrational spectra of the adsorbed prenal but also leads to a deeper understanding of the adsorption complexes on the pure Pt(111) and the discussed model-catalyst surfaces $P_3Sn/Pt(111)$ and $P_2Sn/Pt(111)$.

Acknowledgments

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