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The role of the chiral modifier on the enantioselective hydrogenation of methyl pyruvate on Pt(111)

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Using density functional calculations we have investigated the enantioselective hydrogenation of methyl pyruvate (MP) to methyl lactate over Pt(111). Chirality was induced to the surface by adsorption of the chiral modifier naphthyl-ethylamine (NEA). In our calculations, we have investigated both the role of hydrogen in the formation of the observed docking complex and the role of the functional group of the modifier. As a result, we could identify the importance of the amine group for the interaction between reactant and modifier and propose that the observed docking complex is formed between semihydrogenated MP and NEA.

KEY WORDS: heterogeneous catalysis; hydrogenation; chiral; enantioselective.

Heterogeneous catalytic processes which mediate asymmetric reactions are of high technological importance, e.g. for the fabrication of pharmaceuticals. Achiral surfaces may become enantioselective by introduction of an adsorbate, the chiral modifier. The modifier either forms a template structure exposing chiral, reactive spots of the surface or constitutes part of the reactive site and forms chiral docking complexes (DC) with the reactant [1–3]. The enantioselective hydrogenation of α-keto esters on platinum (111) surfaces, i.e. the Orito-reaction [4], is one of the most successful and at the same time most intensively studied processes of this class. In extensive NEXAFS and STM-studies [5–7] as well as TPD studies [8], the reaction mechanism, the temperature dependence, the effect of the coadsorption of hydrogen and the role of the chiral modifier, chinchona alcaloid or naphthyl-ethylamine (NEA) has been investigated. These studies resulted in detailed information about the adsorption geometries of the reactant and the modifier as far as experimentally accessible. The most important result for a more general understanding of the process, however, is the direct observation of 1:1 DC [7] which rules out earlier assumptions about the reaction mechanism in form of a template model.

In this work, we present for the first time a detailed DFT-investigation of the thermochemistry of MP and NEA at Pt(111). We identify the observed DC between MP and NEA and have characterized the reaction intermediates towards the two enantiomers of methyl lactate (ML). To achieve the highly desired enantiomeric excess of the chiral reaction product ML, an understanding of the role of the various parts of the chiral modifier is crucial. By substituting the functional group of NEA with several other chemical functions, i.e. using a hydroxyl or a phosphine group instead of the amine group, we identified the importance of the amine group for the formation of DCs with enantiodifferentiating activity.

Calculations were performed using the plane wave based code DACAPO [9]. (4×4×2) and (5×5×2) surface slabs with a (2×2×1) k-point sampling, periodic boundary conditions and the PW91 parameterization of the xc-functional together with an energy cut-off of 25 Ryd were used to model the atomic structures. All atoms except the lowest Pt-layer were allowed to relax during geometry optimization. Test calculations with three Pt-layers have been performed, resulting in a merely constant shift of all configurations to 0.05–0.07 eV higher binding energies.

Due to the periodic boundary conditions, the intermolecular distance becomes 11.3 Å, which agrees with the experimental conditions with a spacing of 8–12 Å [7].

In agreement with the findings in recent cluster calculations [10], we find the MP molecule to adsorb strongly distorted at the Pt(111) surface. Figure 1 shows the complete reaction scheme for the hydrogenation of MP. Starting with the ideal Pt(111)-surface and MP as well as H_2 in the gas phase, the total energy of the system is lowered during the first three steps: adsorption of H_2 to two separated H-atoms on Pt (1.0 eV), adsorption of MP (0.65 eV) and the first hydrogenation step (0.26 eV). The latter has to occur at the keto-oxygen of MP. Hydrogenation of the carbon atom in the first hydrogenation step would, instead, increase the energy by 0.48 eV. Note, that in the gas phase the semihydrogenated MP with the H attached to the carbon would

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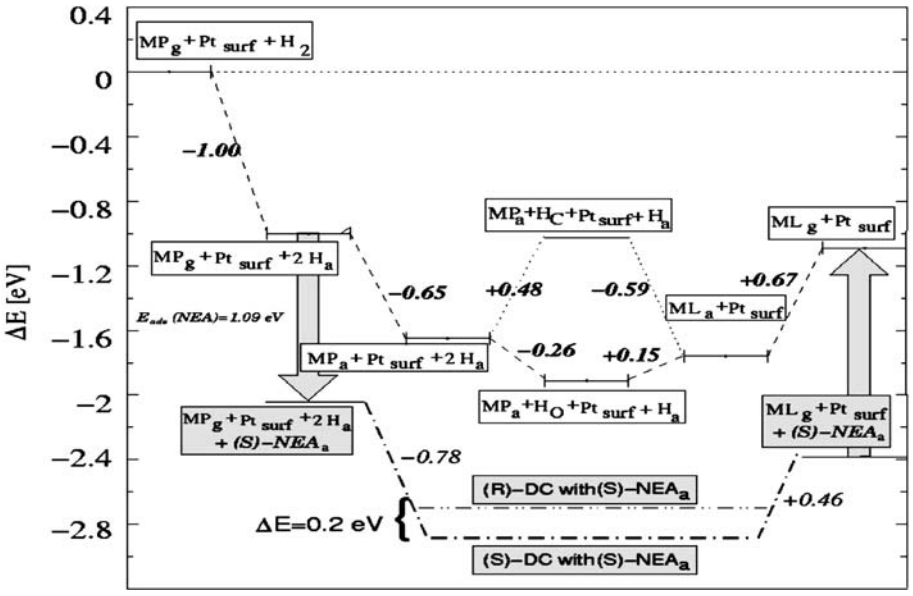

Figure 1. Reaction scheme of the hydrogenation of MP and effect of the chiral modifier.

already be chiral, while it remains only prochiral if the oxygen is hydrogenated first. A slight energy increase (0.15 eV) takes place during the second hydrogenation step, and finally a larger increase in energy (0.67 eV) leads to the desorption of the reaction product in the gas phase. The complete system lowers its energy during this process by 1.09 eV. This study shows already the catalytic effect of the Pt-surface: in the gas phase, the first hydrogenation step is endothermic and, additionally, requires the energy costly dissociation of the H_2-molecule. Nevertheless, the process will result in a racemic mixture of (S)-ML and (R)-ML, and it is the task of the chiral modifier to filter out one of the enantiomers. Such an enantiomeric excess can be achieved if the chiral modifier forms preferentially DCs with the reactant in a certain adsorption geometry. The modifier can only interact with MP by forming one strong H-bond with its functional group to one of the three oxygens of MP. Therefore, six principally different complexes of MP and NEA can be formed, three of which lead to (R)-ML, three to (S)-ML.

Our calculations of the adsorption geometry of (S)-NEA agrees with the NEXAFS data [6], such as we find a tilted adsorption with the naphtalene-part of the molecule serving to anchor the molecule on the surface and the amine group within the functional group pointing towards the surface. The calculated tilting angle is with 33° slightly smaller than the measured angle ($46° \pm 5°$). We have calculated various structures for DCs between MP and (S)-NEA. It turned out that these complexes are stable against dissociation, but due to only weak hydrogen bonds between the two molecules, NEA did not act as a preferred adsorption site for MP. From the experimental data it is, however, not clear, at which time the first hydrogenation step takes place. At the temperatures used in the experiments, i.e. below 370 K [7], the Pt-surface is covered with hydrogen. For the applied hydrogen pressure during the measurements, temperature programmed reaction (TPD) yields the first peaks above 410 K. This is confirmed by our modeling showing full hydrogen coverage of the Pt(111) surface below 390 K when comparing calculated H-coverage dependent surface free energies as a function of the temperature following Refs. [11,12].

However, considering the third step in the reaction diagram in figure 1, it becomes clear that the semihydrogenation step towards the keto-oxygen of MP will lower the energy of the system and will, thus, be favorable whenever H and MP are co-adsorbed. It is, therefore, likely that the observed DC is not formed between NEA and MP but between NEA and the semihydrogenated MP. Consequently, we have calculated possible models for DCs between these two species. Our results show that (S)-NEA serves as a preferential adsorption site for semihydrogenated MP in all six principally different orientations of the molecules towards each other.

Table 1 shows the binding energies of the respective structures, which serve as precursors for the (R)- or (S)-enantiomer of ML in the subsequent hydrogenation step. The interaction of the amine group of the modifier with the keto-oxygen of the semihydrogenated MP is clearly favored over an interaction with the two ester-oxygens. Furthermore, this (S)-precursor is favored by 0.2 eV over the resp. (R)-precursor. This energy difference determines the probability and efficiency of the enantiodifferentiation step. Checking this value with one Pt-layer added in our calculation, we obtain slightly higher

Table 1
Binding energies (in [eV]) of the six possible DCs between the semi-hydrogenated MP and (S)-NEA

	-O– (ester)	=O (ester)	-OH (keto)
(R)-precursor	1.20	1.22	1.40
(S)-precursor	0.81	1.28	1.60

binding energies of 1.46 eV for the (R)-precursor and 1.68 eV for the (S)-precursor, respectively, while the energy splitting that is crucial for the enantiodifferentiation step remains ≈0.2 eV.

The energetics of the modified reaction are shown in figure 1, as indicated by the grey shaded arrows. The system with the most stable DC adsorbed to the Pt(111) surface and one further H adsorbed to the surface has been calculated to be 0.78 eV lower in energy than a system consisting of the Pt(111)-surface with two pre-adsorbed H-atoms and NEA plus MP still in the gas phase. Compared to the final system consisting of NEA adsorbed on the surface and ML in the gas phase, the DC is 0.46 eV lower in energy.

Due to the higher number of degrees of freedom in the states where one of the involved molecules is in the gas phase, raising the temperatures changes the free energy of the systems asymmetrically, i.e. affects the gas phases considerably stronger than the adsorbate states. It will, thus, lead to a strong lowering of the free energies of both the initial and the final state, but will only have a weak effect on the state with the DC. Due to the energy splitting between the (S)- and the (R)-precursor, (S)-ML derived from the most stable (S)-precursor will be produced in excess.

These results raise the question about a more general understanding of the interaction. Of particular interest is here the influence of the chemical character of the functional group of the modifier. In NEA, this group consists of an amine group, a methyl group and a hydrogen, all attached to the carbon atom which is the chiral center of the molecule. In the DC, particularly the amine group but also the single hydrogen serve as hydrogen donors in bonds to the oxygen atoms of the reactant. A substitution of these functions can, therefore, be expected to cause the strongest changes.

Figure 2 shows top- and side views of the most stable DC that can be formed with the original modifier, NEA, and with three slight variations of the modifier. Although no strong changes in the adsorption geometry are observed, the energetics of the system change considerably. If the NH_2 group is substituted with an OH-group (upper right panel), the intermolecular hydrogen bonds shorten by 0.01 A and the most stable DC is stabilized by further 0.11 eV, but the energy splitting between the most stable (S)- and (R)-precursor is reduced to 0.17 eV. An OH-group instead of the single H (lower left panel) strengthens the H-bond between this group and the doubly bonded ester-oxygen of MP. Since on the other hand the N–H...O bond is elongated

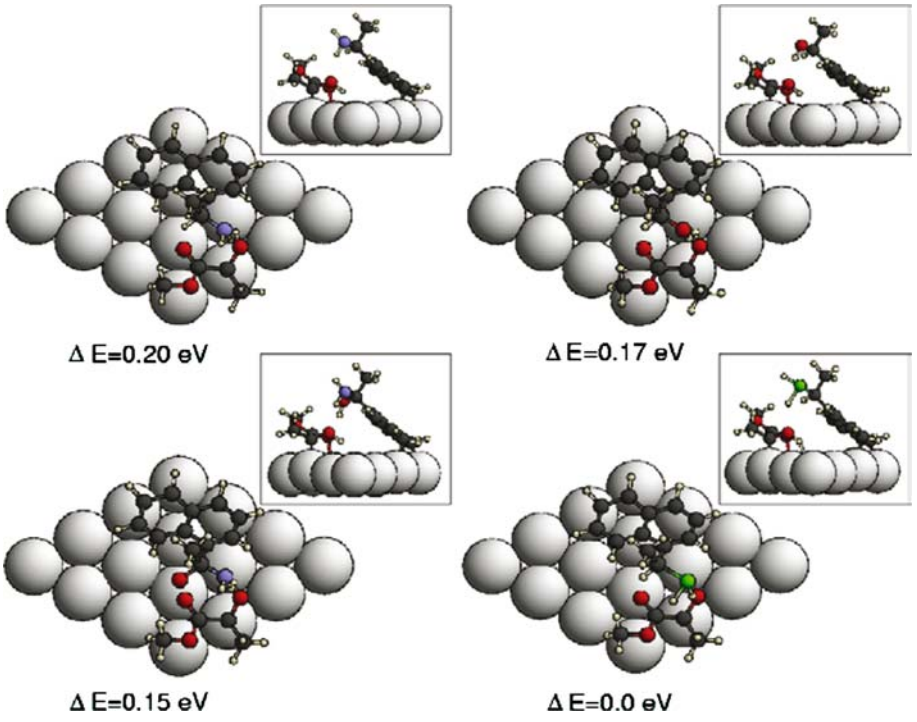

Figure 2. The most stable DCs between semihydrogenated MP and the modifier. ΔE is the energy splitting for enantioselectivity. Four different functional groups are considered on the modifier. Upper left: NEA. Upper right: NEA with NH2 substituted with OH. Lower left: NEA with H substituted with OH. Lower right: NEA with P instead of N.

by 0.1 A and the bond of the ester-O to the Pt-surface by 0.16 A, only a slight stabilization of 0.16 eV compared to the DCs with the original modifier occurs. The energy splitting decreases further to 0.15 eV. Finally, if the NH_2-group is replaced by a PH_2-group (lower right panel), the system becomes destabilized by 0.18 eV, and the energy splitting vanishes completely. This can be understood, since P-H is known to be a very weak hydrogen bond donor [13]; the P–H...O bond has only a strength comparable to that of a C–H...O bond.

Thus, among these modifiers, the NEA-molecule has obviously the highest enantiodifferentiating potential. Although reducing the energy splitting by 0.03 eV, a substitution of the amine group with an OH-group might be of technological interest, since the complete system is stabilized and allows the reaction to be driven at higher temperatures. In summary, we have identified the DC which under UHV-conditions has been observed in STM-studies for NEA and MP with an atomistic model. Our calculations of the binding energies of various configurations yield an explanation of the enantioselectivity of the reaction.

Furthermore, we have shown the importance of the amine group by varying the functional group of the modifier. In future work, additional studies considering also the kinetics of the involved processes have to be performed. Instead of studying the system under UHV-conditions, it remains a future task to investigate the process under operational conditions, where e.g. NEA acts only a precursor for the acting modifier [14].

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