Heterogeneous Catalysis

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Catalytic Hydrogenation of Unsaturated Aldehydes on Pt(111): Understanding the Selectivity from First-Principles Calculations**

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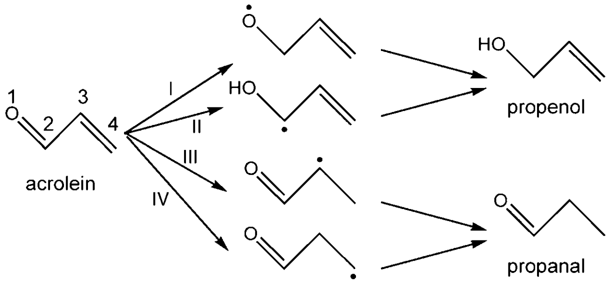
Selectivity is an essential aspect of chemistry in general and of heterogeneous catalysis in particular. It is commonly acknowledged that the C=C bond is more reactive than the C=O bond in the hydrogenation on metal surfaces of molecules with a vinyl or carbonyl bond.[1,2] Hence, according to this statement, the partial hydrogenation of α,β-unsaturated aldehydes containing conjugated C=C and C=O bonds should selectively produce the saturated aldehyde (SAL), which is the thermodynamic product, instead of the unsaturated alcohol (UOL), which is in practice the desired product in the pharmaceutical and fragrance industries. Although this rule is respected for the hydrogenation of acrolein (propenal) on Pt(111), which yields almost exclusively the SAL (93 % of propanal versus only 2 % of propenol), it is violated for prenal (methylbutenal), for which the selectivity is reversed in favor of the UOL.[2,3] Thus, understanding the selectivity requires a thorough knowledge of all the competitive steps involved in the reaction mechanism.

In this study we combine first-principles calculations for the exploration of elementary reaction steps and a kinetic model to understand how selectivity is controlled for a chemo-regioselective reaction occurring on a metallic surface. The simplest system chosen for illustration is the hydrogenation of acrolein ($CH_2{=}CH{-}HC{=}O$) on a Pt(111) catalyst which leads to the competitive formation of propanal ($CH_3{-}CH_2{-}HC{=}O$) and propenol ($CH_2{=}CH{-}CH_2{-}OH$).

The adsorption of acrolein has been previously studied on Pt(111)[4] and on Pt/Sn alloys.[5] Reaction barriers on Pt(111) and on Ag(111) have recently been proposed from an empirical approach with no connection with a kinetic model.[6] Our calculations are performed in the density-functional theory (DFT) periodic formalism. Only the hydrogenation pathways starting from the most stable adsorbed structure (the planar η^4-*trans* geometry where both C=C and C=O bonds interact with the surface) are considered here. This is not an important limitation since the molecule can easily adapt its geometry prior to hydrogenation in the approach used for calculating the reaction pathways.

Exploring the hydrogenation of such a molecule remains a complex task. There are four possibilities for the attack of the first H atom that give four surface intermediates adsorbed on the surface (Scheme 1). For each of them, there are three possibilities to add a second H atom, but the present study is limited to the formation of the unsaturated closed-shell species through further hydrogenation of the previously attacked double bond. The adsorbed propenol and propanal can then desorb, or be further hydrogenated (an event which will not be considered here).



Scheme 1. Competitive hydrogenation routes of an acrolein molecule (propenal). The first hydrogenation intermediates (allyloxy, hydroxyallyl, 1-formylethyl, and 2-formylethyl for pathways I, II, III, and IV, respectively) and the products in competition (propenol (UOL) and propanal (SAL)) are shown.

First, the four surface intermediates are optimized on the Pt surface. In all cases, both the remaining double bond and the non-hydrogenated site interact with the surface to give structures bound by three atoms (η^3,μ_3). The adsorbed hydroxyallyl intermediate is much more stable than the other ones (Figure 1). As in the final products, propenol adsorbs through the C=C bond (η^2,μ_2) without participation of the O atom, and with an adsorption energy ($104\,kJ\,mol^{-1}$) similar to that of η^4-*trans*-acrolein ($102\,kJ\,mol^{-1}$). In contrast, the adsorption of propanal is weaker ($22\,kJ\,mol^{-1}$) and can occur either through the C=O bond (η^2,μ_2) or through the O atom (η^1,μ_1).[7]

Several coadsorption geometries have been tested for a hydrogen atom and the adsorbate to be hydrogenated—either acrolein or the surface intermediates. The coadsorption states are 4 to $10\,kJ\,mol^{-1}$ less stable than the reference state (adsorbate and H atom at an infinite distance on the surface). Generally, the H atom is in a ternary site, and less commonly in a bridging or a top position. For each reaction step, one coadsorption geometry is selected as the precursor state of the reaction, depending on the considered reactant.

The first hydrogenation on a C atom of the C=C bond has an energy barrier of 91 and $89\,kJ\,mol^{-1}$ (see pathways III and IV, respectively, in Figure 1). This barrier is lowered to $60\,kJ\,mol^{-1}$ for the attack on the C=O bond (see pathway I in Figure 1). The hydrogenation on the O atom (pathway II) occurs in three steps. First, the H atom migrates from one ternary site to another one closer to the molecule while the C=O bond decoordinates from the surface to give a (η^2,μ_2) precursor state (not shown in Figure 1). Then the H atom migrates again to a top position from which the hydrogenation occurs. The overall barrier associated with pathway II is $40\,kJ\,mol^{-1}$, hence the lowest one.

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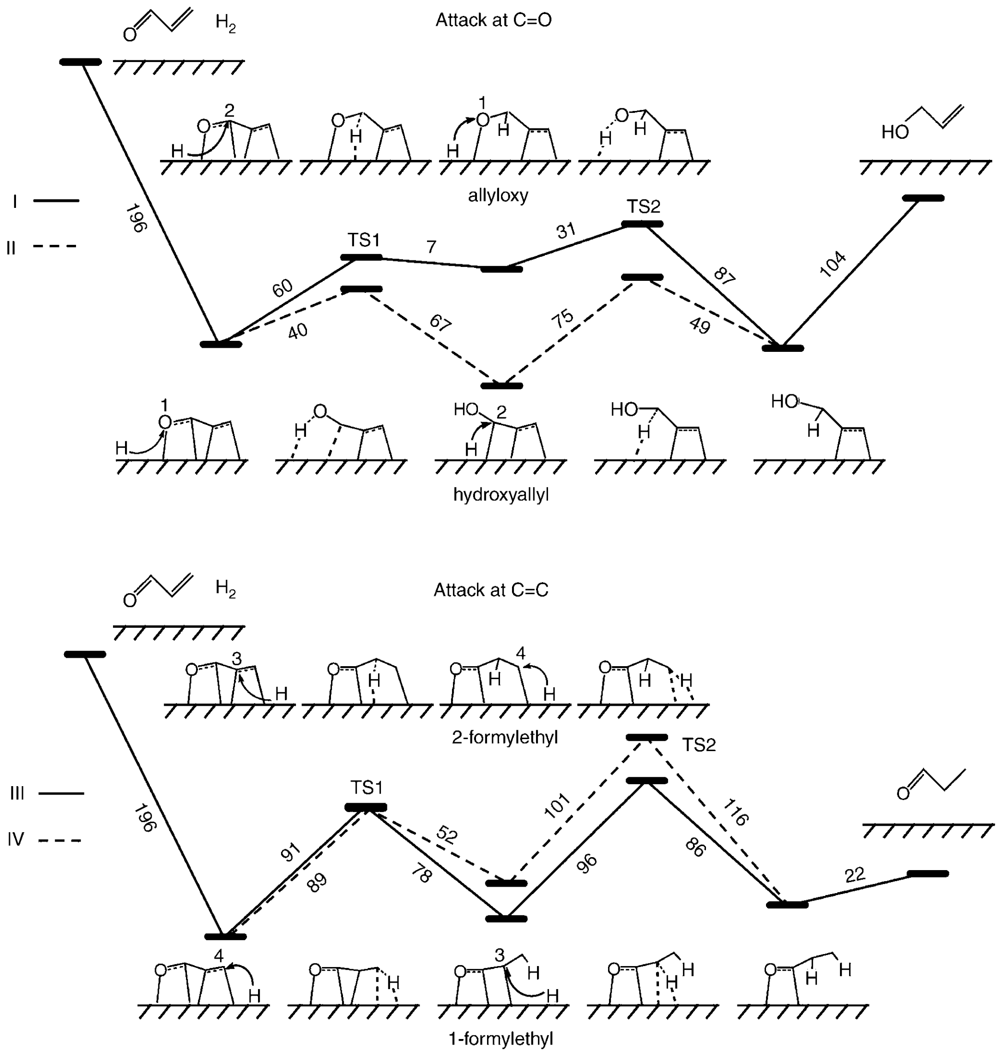

Figure 1. Energy profiles of hydrogenation pathways for acrolein on Pt(111): attack on the C=O bond (pathways I and II) and on the C=C bond (pathways III and IV). The energies (kJ mol^{-1}) refer to the initial state (H_2+acrolein, gas phase). The adsorption energies of acrolein and two hydrogen atoms are summed in the initial coadsorption state. The transition states are labeled TS1 and TS2 for the first and the second hydrogenation, respectively.

The second hydrogenation takes place at a C atom for pathways II–IV. There is again a high barrier to the second attack at the C=C bond (96 and 101 kJ mol^{-1} for pathways III and IV, respectively) while the final saturation of the C=O bond is easier (75 kJ mol^{-1}, pathway II). The barrier for the attack at the O atom (pathway I) is again the lowest one (31 kJ mol^{-1}), with a mechanism similar to the one calculated for the first hydrogenation step. One important comment is that the barriers calculated by DFT differ significantly from the empirical results reported previously, with a maximum deviation of 100 kJ mol^{-1}.[6]

In agreement with the Hammond principle, the activation energy is small when the step is exothermic. This is the case for the hydrogenation on oxygen where the transition states are similar to the initial states with long OH bonds (1.60–1.63 Å, see Figure 2). In contrast, attack on the C=C

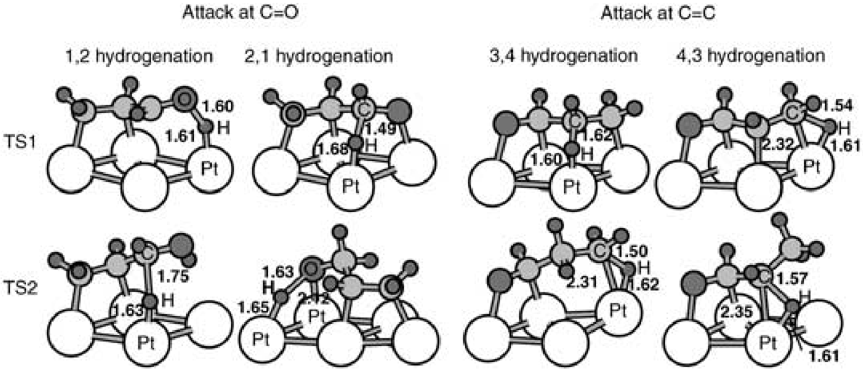

Figure 2. Geometries of the transition states for the first (TS1) and second (TS2) hydrogenation steps of acrolein on a Pt(111) catalyst. In each case, the lengths of the formed C–H or O–H bonds and the broken Pt–H bonds are given in Å.

bond is mainly endothermic and the CH bonds formed are short (1.50–1.62 Å) in the corresponding transition states.

In summary, all the surface reaction barriers for hydrogenation of the C=O bond (pathways I and II) are smaller than those for hydrogenation of the C=C bond (pathways III and IV), which is opposite to the generally assumed hypothesis. These low energy barriers might suggest that the formation of propenol on the surface is a facile process, which is in apparent disagreement with the selective formation of propanal found experimentally. However, desorption of the product from the surface is a necessary last step. This step, which is found to be non-activated, is much easier for propanal (22 $\mathrm{kJ\,mol^{-1}}$) than for propenol (104 $\mathrm{kJ\,mol^{-1}}$). The key of the selectivity therefore resides in the competition between the surface reaction barriers and the desorption endothermicity.

The determination of the final balance between these two effects and of the product mixture thus requires a kinetic treatment. The fundamental assumptions of our model have been developed in the literature previously.[8] The elementary steps considered in the model are depicted in steps 1–7.

$$(1)\quad \mathrm{H_{2(gas)}} \Leftrightarrow \mathrm{2H_{(ads)}}$$

$$(2)\quad \mathrm{propenal_{(gas)}} \Leftrightarrow \mathrm{propenal_{(ads)}}$$

$$(3)\quad \mathrm{propenal_{(ads)}} + \mathrm{H_{(ads)}} \Leftrightarrow \begin{cases} \mathrm{allyloxy_{(ads)}} \\ \mathrm{hydroxyallyl_{(ads)}} \\ \text{1-formylethyl}_{\mathrm{(ads)}} \\ \text{2-formylethyl}_{\mathrm{(ads)}} \end{cases}$$

$$(4)\quad \left.\begin{matrix} \mathrm{allyloxy_{(ads)}} + \mathrm{H_{(ads)}} \\ \mathrm{hydroxyallyl_{(ads)}} + \mathrm{H_{(ads)}} \end{matrix}\right\} \Leftrightarrow \mathrm{propenol_{(ads)}}$$

$$(5)\quad \left.\begin{matrix} \text{1-formylethyl}_{\mathrm{(ads)}} + \mathrm{H_{(ads)}} \\ \text{2-formylethyl}_{\mathrm{(ads)}} + \mathrm{H_{(ads)}} \end{matrix}\right\} \Leftrightarrow \mathrm{propanal_{(ads)}}$$

$$(6)\quad \mathrm{propenol_{(ads)}} \Leftrightarrow \mathrm{propenol_{(gas)}}$$

$$(7)\quad \mathrm{propanal_{(ads)}} \Leftrightarrow \mathrm{propanal_{(gas)}}$$

Steps 1 and 2 correspond to the adsorption of the two reactants, H_2 and propenal, respectively. Step 3 corresponds to the competitive first hydrogenation steps on the surface that lead to the four partially hydrogenated intermediates. In steps 4 and 5, a second H atom further hydrogenates the intermediates on the surface to yield the products (propenol and propanal); these steps are in competition. Steps 6 and 7 are the desorption steps of the products.

The partial pressures of the gas reactants are kept constant in our kinetic model. The adsorption (acrolein and H_2) and the desorption (propenol and propanal) steps are considered to be equilibrated, so the initial coverages of the reactants are imposed by the temperature and the partial pressures. The rate constants are calculated from our DFT activation barriers by using the transition-state theory,[9] and no empirical data are used. All the surface intermediate coverages are obtained by integration of the set of nonlinear differential equations with time. The selectivity is defined from the partial pressures of the desorbed products. An almost 100 % selectivity to propanal is obtained from a mixture of acrolein (30 Torr) and hydrogen (900 Torr) at 350 K, a result which is in close agreement with experiments and which can be qualitatively related to the energy profiles. The rate-limiting step in the hydrogenation of the C=O bond is the product desorption, with a barrier of 104 $\mathrm{kJ\,mol^{-1}}$, whereas for the hydrogenation of the C=C bond, it is the formation of the second C−H bond (101 $\mathrm{kJ\,mol^{-1}}$). This second pathway is thus favored and propanal is selectively formed. The hydroxyallyl intermediate and hydrogen are the main species adsorbed during the reaction. The coverage of propenol increases on the surface, while propanal rapidly desorbs without accumulation. Hence, the species which is present to the greatest extent on the surface is not associated with the most abundant gas-phase product. As a result, product desorption appears to be a key factor in determining the reaction selectivity and can be used as a tuning parameter. If the energy for the desorption of propenol is numerically decreased by 30 $\mathrm{kJ\,mol^{-1}}$ without changing the other barriers, the calculated selectivity is reversed in favor of the unsaturated alcohol. This could explain qualitatively the change of selectivity observed experimentally for other reactants such as prenal on Pt(111), for which the desorption barriers of the corresponding UOL are decreased by this amount. Clearly, the determination of the other barriers are required to provide fully reliable conclusions in these other cases.

In this study, the partial hydrogenation of the C=C or the C=O bonds of acrolein on a Pt(111) catalyst has been studied by a theoretical approach based on first-principles calculations and a kinetic model. Total energy calculations have shown that the selectivity between the two competing products is controlled by the balance between the hydrogenation steps on the surface and the desorption of the partially hydrogenated products. The surface steps favor the attack at the C=O moiety to yield propenol, whereas desorption is easier for the product arising from the attack at the C=C bond (propanal). The kinetic model shows that the desorption step controls the selectivity in this case and almost 100 % of propanal is obtained for a simulation under catalytic conditions (350 K and respective partial pressures of 30 and 900 Torr for acrolein and hydrogen reactants, respectively). Hence, the desorption energy of the product appears to be the critical tuning parameter for the selectivity.

Experimental Section

All the calculations were performed with the DFT formalism with the plane wave based VASP code.[10] The projector-augmented wave method[11] and the Perdew Wang 91 generalized gradient approximation[12] were used. The plane wave cutoff was set to 400 eV. The Pt(111) surface was modeled by a periodic four-layer slab with a vacuum region equivalent to five Pt layers. Adsorption took place on one side of the slab. A 3×3 unit cell was considered and gave a coverage of 1/9 monolayer. The Brillouin zone integration was performed on a $3 \times 3 \times 1$ grid. For the stationary points, the positions of the adsorbate and of the two uppermost layers were optimized. There are two main sources of error in the DFT adsorption energy: the systematic error arising from the limited thickness of the metallic slab, which is the largest one (10 $\mathrm{kJ\,mol^{-1}}$), and the numerical error arising from the choice of the basis set and the k-point mesh, which is smaller (5 $\mathrm{kJ\,mol^{-1}}$). The search for the transition states (TS) was performed with the climbing-image nudged elastic band method (CI-NEB).[13] The considered reaction surface intermediates did not show a spin-polarized electronic structure after adsorption. The transition-state structures were characterized by a vibrational analysis which showed one pure imaginary frequency.

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