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Highly selective hydrogenation of butadiene on Pt/Sn alloy elucidated by first-principles calculations

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ABSTRACT

Reaction pathways have been explored with periodic DFT calculations in order to understand the origin of the high selectivity for the hydrogenation of 1,3-butadiene on the $Pt_2Sn/Pt(1\,1\,1)$-$(\sqrt{3} \times \sqrt{3})R30^\circ$ surface alloy. The adsorption structures of butadiene, 1- and 2-butenes and all the intermediate species have been studied. Compared to the reference catalyst Pt(1 1 1), there is a change both in geometries and in relative energies: for instance, the best adsorption mode of butadiene is *cis* 1,4-di-σ-2,3-π, while it is *trans* 1,2,3,4-tetra-σ on Pt(1 1 1). On the alloy, all the adsorption energies are reduced compared to pure platinum, and the adsorption structures implying many Pt—C bonds are more destabilized. The different pathways leading to partial hydrogenation products (1-butene, 2-butene) or other intermediate surface species (1,3- and 1,4-metallacycles) have been explored. The first hydrogenation step is clearly preferred at a terminal carbon, and the further hydrogenation to 1-butene has by far the lowest barrier. Other pathways exhibit larger activation barriers, particularly those leading to metallacycles, which is the key to explain the high selectivity to butene, in contrast to Pt(1 1 1). The role of tin is dual: a role of site blocking that forces unselective pathways to adopt distorted, high-energy transition states and a role of ligand that weakens the molecular adsorption and allows decoordination of double bonds prior to the hydrogenation, which decreases the energy barriers for the selective pathway to butene.

1. Introduction

The selective hydrogenation of dienes into mono-olefins is an important industrial process for the purification of the alkene streams used in polymerization. Group VIII metals like platinum or palladium have been used for a long time as hydrogenation catalysts for this reaction. Most of the studies are devoted to the partial hydrogenation of the simplest diene, 1,3-butadiene, into butene. In order to elucidate the origin of the selectivity (formation of butene rather than butane), many experimental studies have been carried out for two decades on the adsorption and hydrogenation of butadiene and butene on metallic single crystals [1–7] or on metal particles dispersed on silica or alumina [8–11]. The following conclusions arose from these various works: Pd is almost totally selective in butene, whereas Pt leads to a mixture of butene and butane, the latter being partly formed as primary product of the reaction. Depending on the experimental conditions and on the percentage of conversion, the selectivity to butenes is in the range 65–87%, with about 70–80% of 1-butene and 30–20% of 2-butenes. The most commonly admitted interpretation of this different behavior rests on the different competitive adsorption energies of butadiene and butene on the two metals. To verify this assumption, the adsorption structures of 1,3-butadiene and of butenes (1- and 2-butene) have been investigated by theoretical calculations [12–14]. In the two latter papers, the difference between the adsorption energies of butadiene and butenes has been found very similar on Pt and Pd and hence it cannot account for the observed selectivity. Moreover, the formation of butane as a primary product cannot be explained by considering only reaction thermodynamics.

To solve this question, a theoretical study of the hydrogenation mechanism on Pt and Pd has been tackled recently [15]. In this work, the role of dihydrogenated C_4H_8 metallacycle intermediate species, obtained by 1-3 or 2-3 hydrogenation, is underlined. These species cannot desorb from the surface and can evolve to butane by hydrogenation. The activation barriers for the formation of such species are high on Pd(1 1 1) and they cannot compete with the formation of butene. Conversely on Pt(1 1 1), their formation is as probable as that of butene, which explains the lower selectivity toward this compound and the formation of butane as a primary product.

To enhance the selectivity toward butene, other types of catalysts have been tested, namely alloys of platinum or palladium. It is well known that alloying these metals with another one deeply modifies their catalytic properties. Tin is often used as second metal. For example, one can cite PdSn particles deposited on alumina

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[16,17], the (1 1 1) surface of the Pt_3Sn alloy [18] or ordered Pt_xSn/Pt(1 1 1) surface alloys [19]. These model catalysts are less active than the pure metal but more selective toward butene. In the case of the Pt/Sn alloys, the selectivity to butenes ranges from 98% to 100%, with about 80% of 1-butene. The same behavior has also been found for the Pd/Au alloy [20]. These results raise the question of the role of the second metal in the selectivity enhancement.

In order to answer this question, we have explored the pathways for butadiene hydrogenation on the Pt/Sn surface alloys, more precisely on Pt_2Sn/Pt(1 1 1)-($\sqrt{3} \times \sqrt{3}$)R30° on the basis of density functional theory (DFT) calculations. In the present paper, we first report on the adsorption structures of butadiene, 1- and 2-butenes, and hydrogen on this surface. In a second part, we address the mechanism of the butadiene partial hydrogenation and compare it with the one found for Pt(1 1 1) and Pd(1 1 1). More particularly, we compare the formation of the various C_4H_8 species that we have shown to be the key of the selectivity on these two metals.

2. Computational details

The calculations were performed in the framework of the density functional theory (DFT) using the Vienna *Ab Initio* Simulation Program (VASP) [21–23]. The one-electron functions are developed on a basis of plane waves. The electron–ion interactions were described by the projector-augmented wave method (PAW) introduced by Blöchl [24] and adapted by Kresse and Joubert [25]. A tight convergence of the plane-wave expansion was obtained with a cutoff of 400 eV. The exchange–correlation energy and potential were described by the generalized gradient approximation (Perdew–Wang 91) [26].

The surface alloy was modeled by a periodic four-layer slab, where only the first layer contains Sn atoms in a stoichiometry Pt_2Sn. Indeed, by Sn vapor deposition on Pt(1 1 1) followed by annealing, two structures are formed depending on the amount of Sn, namely (2 × 2) with stoichiometry Pt_3Sn and ($\sqrt{3} \times \sqrt{3}$)R30° with stoichiometry Pt_2Sn [27]. XPD data have shown that these compounds are two-dimensional surface alloys [28]. Each slab is separated from its periodic image in the z direction by a sufficiently large vacuum space corresponding to five layers (11.5 Å). 3 × 3 supercells containing nine atoms per layer are used (see Fig. 1). The 2D Brillouin zone integrations have been performed on a 3 × 3 × 1 Monkhorst–Pack grid since it was found to be accurate as well as computationally efficient for this cell size. The Pt–Pt distance optimized from Pt bulk calculations (2.82 Å) has been used for the frozen part of the slab. This is justified by the fact that experimentally the lattice parameter is imposed by the underlying Pt bulk, and the Sn atoms in the uppermost layer accommodate this constraint by an outward displacement, inducing a Pt–Sn distance of 2.86 Å.

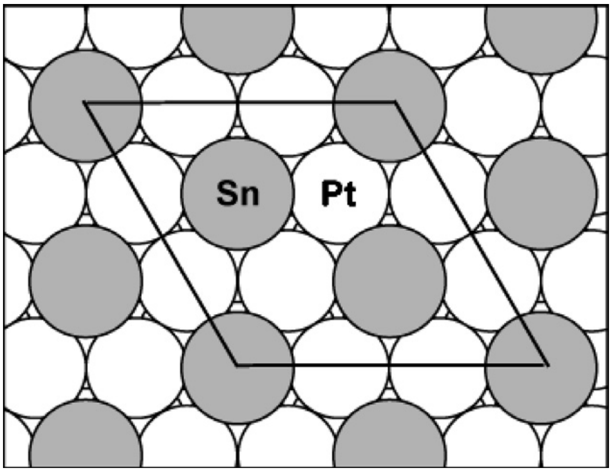

Fig. 1. Top view of the ($\sqrt{3} \times \sqrt{3}$)R30° Pt_2Sn/Pt(1 1 1) surface alloy. Platinum and tin are colored in white and gray, respectively. The subsurface layers only contain platinum. The diamond represents the 3 × 3 unit cell.

Adsorption and reaction were performed on one side of the metal slab with one molecule adsorbed per unit cell, which gives a coverage $\theta = 1/9$. The geometries of the two uppermost layers of the surface together with the adsorbate (C_4H_x , $x = 6$–8 species) were fully optimized, whereas the two lowest metal planes were kept fixed. The adsorption modes and the corresponding adsorption energies for all the C_4H_x moieties were determined. The reaction intermediates were studied on different adsorption sites. For sake of simplicity, only the most stable structures are reported here. Coadsorption with hydrogen has also been explored in detail by comparing various possible situations.

The energy along the reaction (E_{react}) was calculated using butadiene and H_2 in the gas phase as the energy reference with the following expression:

$$E_{react} = E_{syst/surface} - E_{surface} - E_{C_4H_{6(g)}} - E_{H_{2(g)}}$$

A negative value indicates an exothermic chemisorption process. The system is a C_4H_x species and $(8 - x)$ hydrogen atoms ($x = 6, 7, 8$) adsorbed on the surface. If we consider that the hydrogen atoms and the hydrocarbon do not initially interact, the $E_{syst/surface}$ term is then obtained by combining the results from independent slab calculations for the molecular species and the hydrogen atoms:

$$E_{syst/surface} = E_{C_4H_x/surface} + (8 - x)(E_{H/surface} - E_{surface})$$

In order to directly compare with previous results, the adsorption energy for the species existing in the gas phase has also been reported ($E_{ads} = E_{C_4H_x/surface} - E_{surface} - E_{C_4H_x}$). The energies of the transition states (E_{TS}) were calculated with respect to adsorbed butadiene and two adsorbed hydrogen atoms without interaction.

In order to obtain more detailed insights into the changes of adsorption energy, it is decomposed in deformation energy and interaction energy terms following the equation:

$$E_{ads} = E_{Int} + E_{Def,Mol} + E_{Def,Surf}$$

where $E_{Def,Mol}$ and $E_{Def,Surf}$ are the deformation energies of the molecule and of the surface, respectively, calculated as the difference between the energies of the optimized geometry of the considered moiety and of the geometry it has in the adsorbed system. E_{Int} is the interaction energy between the two moieties in their deformed geometry.

The Nudged Elastic Band method (NEB), developed by Jónsson and coworkers [29], has been used to determine the transition states, with sets of 8 or 16 intermediate images along the reaction pathways. The obtained approximate transition states have been refined by minimizing residual forces below 0.01 eV/Å with the *quasi*-Newton algorithm implemented in VASP. To validate the saddle points, a vibrational analysis including adsorbate and relaxed substrate degrees of freedom has been performed. The presence of a single imaginary frequency (negative force constant) and the consistency of the corresponding normal mode with the reaction path have been checked.

The prediction of atomistic thermodynamics in reaction conditions is crucial here. A simple way to estimate the stability of the reactant and the products on the catalytic surface is the prediction of the Gibbs free adsorption energy ΔG_{ads}, according to the following formula (see [30] and references therein for the elaboration of the corresponding model):