



Evaluating Pd–Ni layered catalysts for selective hydrogenation of 1,3-butadiene: A theoretical perspective



Guillermina Gómez, Patricia G. Belelli*, Gabriela F. Cabeza, Norberto J. Castellani

Grupo de Materiales y Sistemas Catalíticos, Departamento de Física (IFISUR) Universidad Nacional del Sur, Av. Alem 1253, Bahía Blanca B8000CP, Argentina

ARTICLE INFO

Article history:

Received 13 August 2013

Received in revised form 24 June 2014

Accepted 30 June 2014

Available online 5 July 2014

Keywords:

1,3-Butadiene
Partial hydrogenation
Pd–Ni surfaces
Periodic DFT

ABSTRACT

The partial hydrogenation of 1,3-butadiene (13BD) to several C_4H_8 products, including 1-butene (1B), 2-butene (2B) and butan-1,3-diyol (B13R), on both Pd/Ni(1 1 1) and Pd₃/Ni(1 1 1) bimetallic surfaces was theoretically investigated using DFT methods. For that purpose, different intermediates C_4H_7 and C_4H_8 radical species were evaluated according to the Horiuti–Polanyi mechanism performed in two sequential steps. The whole process was found to be exothermic on Pd/Ni(1 1 1) and endothermic on Pd₃/Ni(1 1 1). Furthermore, the former surface, where the intermediate adsorptions are more favorable, exhibits lower activation barriers than Pd₃/Ni(1 1 1). On both surfaces, the B13R formation is associated with high transition state energies through the pathways studied here; for this reason, it is extremely improbable to obtain B13R. Our calculations predict that on the Pd/Ni(1 1 1) catalyst model, the products would be mainly the butene isomers, with a little more selectivity toward 2B, in contrast to the pure Pd surface and in agreement with experimental data.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

1,3-Butadiene (13BD) is the simplest alkene containing conjugated bonds, that is why it can be considered as a model molecule to study the factors controlling the activity and selectivity in partial hydrogenation over a catalyst. In particular, the selective hydrogenation of 13BD is not only an important reaction in the purification of light alkenes in polymerization processing [1], but also it is a good prototype in probing the catalytic properties and electronic structures of metal catalysts [2,3]. Specifically, if we know what controls selectivity toward the formation of *cis* versus *trans* olefins [4], it will have significant practical applications; for instance, it is desirable to reduce the production of *trans* fatty acids during the partial hydrogenation of natural oils to edible fats [5]. However, hydrogenation will lead to either *trans*- or *cis*-2-butene products since there are *trans*- and *cis*-isomers in the 1,3-butadiene molecule.

The Pd and Pt metallic systems have been the focus of most studies because they play a great role in heterogeneous catalysis devoted to hydrogenation. In the last few years, the developments in the field of computational chemistry have made feasible the theoretical investigations of realistic catalytic systems. Thus, the

adsorption of representative molecules such as ethylene, propylene, butadiene, etc, on these surfaces has been covered with a large range of experimental techniques (such as LEED, EELS, STM, or TPD) [6–8] as well as theoretical calculations [9–13].

Specifically, in experimental studies carried out on Pt(1 1 1) surface by Lee et al. [14], the selectivity for *cis/trans*-2-butene isomerization was investigated by measuring their kinetics in the presence of a small amount of hydrogen. The corresponding results indicated that the *trans*-2-butene isomerization to its *cis* isomer is easier than the opposite *cis*-to-*trans* conversion on Pt(1 1 1) single-crystal surface. The kinetic study on the butene catalytic conversion also suggested different selectivities on Pt(1 1 1) and Pt(1 0 0) surfaces. In a further study, the ratios of *trans*-to-*cis* vs. *cis*-to-*trans* conversion rates on both tetrahedral and cubic supported Pt particles as a function of the temperature were investigated [15]. Results show that the selectivity of the reaction may be controlled by using supported catalysts with appropriate metal particle shapes. Pd deposited on Ni(1 1 1) is an interesting catalytic situation to study for the 1,3-butadiene hydrogenation is when. In previous experimental work [16], the very poor activity of Ni(1 1 1) surface ($\sim 10^{14}$ molecules converted/cm² s at 300 K and under $P_{H_2} = 35$ Torr) evidenced a strong increase after deposition of 0.5 ML Pd at 300 K under UHV conditions, reaching an average value between Pd(1 1 1) and Pd(1 1 0) activities ($\sim 10^{15}$ mol/cm² s). Selectivity ratio toward butene isomers always remained close to unity.

* Corresponding author. Tel.: +54 291 4595141; fax: +54 291 4595142.
E-mail address: patricia.belelli@uns.edu.ar (P.G. Belelli).

Based on these previous results, the Pd–Ni system was brought to our attention. Firstly, the study of the structural, electronic and magnetic properties of multilayer bimetallic systems Pd_n/Ni(1 1 1), with $n=0$ to 4 Pd layers over a Ni(1 1 1) substrate, was performed [17]; and then the 13BD adsorption on Pd/Ni(1 1 1) and Pd₃/Ni(1 1 1) surfaces were rigorously evaluated [18].

In the present theoretical approach, the partial hydrogenation of 1,3-butadiene (13BD) to several C₄H₈ species on both Pd/Ni(1 1 1) and Pd₃/Ni(1 1 1) bimetallic surfaces using DFT methods is further investigated. This study is organized as follows: Section 2 gives an overview of the methodology used; in Section 3, the adsorption structures and relative stabilities of different intermediates (C₄H₇ and C₄H₈ radical species) are examined; specifically, the possible reaction pathways of 13BD partial hydrogenation performed on both metal surfaces are presented in Section 3.3. Finally, the conclusions are drawn in Section 4.

2. Computational details and surface models

The calculations reported in this work were carried out in the framework of density functional theory (DFT) using the Vienna ab initio simulations package (VASP) [19–21]. Electron exchange and correlation effects are described by the generalized gradient approximation (GGA) using the functional proposed by Perdew–Wang (PW91) [22,23]. The Kohn–Sham one-electron wave functions were expanded on the basis of plane waves with kinetic energy below 450 eV. A (3 × 3 × 1) Monkhorst–Pack grid of special k points was adopted for integration in the reciprocal space. The projector augmented wave (PAW) method developed by Blochl [24] was used to reproduce the atomic core effects in the electronic density of the valence electrons. The PAW is essentially an all-electron frozen core method combining the accuracy of all electron methods, such as the full potential linearized plane wave method, and the computational simplicity of the pseudopotential approach, especially in the implementation of Kresse and Joubert [25]. The Methfessel–Paxton method [26] with a smearing width of 0.20 eV was used to determine how the partial occupancies are set for each one-electron wave function. The calculations were performed at the spin polarized level to take into account the magnetic properties of the systems.

For all the calculations, a FCC stacking layered structure was assumed. The (1 1 1) metallic surfaces were represented with a slab containing four layers of atoms separated in the normal direction by a vacuum region. The width of this gap was optimized to avoid the interaction between slabs. For that purpose, we observed that a distance of ~15 Å is adequate. Our investigations were focused in the 13BD partial hydrogenation on two multilayered bimetallic surfaces Pd_n/Ni(1 1 1) with $n=1$ and 3 Pd layers over a Ni(1 1 1) substrate, i.e. Pd/Ni(1 1 1) and Pd₃/Ni(1 1 1), respectively. The structural, electronic and magnetic properties of both surfaces were previously analyzed considering the ferromagnetic condition acquired by the Pd overlayer epitaxially deposited on the Ni(1 1 1) surface [17]. For Pd/Ni(1 1 1) and Pd₃/Ni(1 1 1), the Pd–Pd interatomic distances in the first layer were optimized to 2.57 Å and 2.75 Å, respectively.

The hydrogenation of 1,3-butadiene (13BD) can lead to different products: partial hydrogenation yields to butene, while total hydrogenation leads to butane. The Horiuti–Polanyi mechanism [27,28] implies the initial formation of a C₄H₇ moiety and its subsequent hydrogenation to a C₄H₈ species. The determination of the transition state energies (ΔE_{TS}) and the activation barriers were performed by the nudged elastic band method (NEB) [29]. This method, as implemented in VASP, allows finding the minimum energy path of reaction and the transition state (TS). The validity of transition states so obtained was checked by a full vibrational

frequency analysis, achieved by calculating the Hessian matrix, followed by a diagonalization procedure to obtain the eigenmodes. The corresponding transition states present only one negative force constant. Then, we checked that the eigenvector associated with this negative force constant was related to the reaction pathway considered. This procedure allows us to obtain accurate transition states energies and activation barriers.

Relative reaction energies (E_{rel}) taking both isolated 13BD ($E_{C_4H_6(g)}$) and H₂ ($E_{H_2(g)}$) molecules in gas phase as energy references were calculated according to the equation:

$$E_{rel} = E_{C_4H_x/surf} + (8 - x)E_{H/surf} - (9 - x)E_{surf} - E_{C_4H_6(g)} - E_{H_2(g)} \quad (1)$$

where C₄H_x corresponds to 13BD, to 13BD in co-adsorption with H, to one of the possible intermediates as well as to the latter in co-adsorption with another H; $E_{H/surf}$ is the adsorption energy of an isolated hydrogen atom, E_{surf} is the energy of bare surface and x is the amount of H atoms in the reaction ($x=6,7,8$). The corresponding adsorption energies were calculated as the difference between the energy of the adsorbed molecule on the surface and the sum of the bare surface (E_{surf}) and the gas phase molecule energies. A negative value indicates an exothermic chemisorption process. A large box of (20 × 20 × 20) Å³ was used to obtain the gas phase molecule energy. The binding site preference and the adsorption energies of 13BD on both bimetallic surfaces were already published [18]. The geometries of adsorbates together with the two uppermost layers of the surface were fully optimized.

Energy profiles associated with the reaction pathways were plotted from the reactants to provide the products adsorbed on the surface, assuming certain energy as zero reference. In our case, this reference corresponds to the sum of the energies of 13BD and two H atoms adsorbed at infinite distance (without interaction). Non-zero-point-energy (ZPE) corrections were made because it was found that the ZPE contributions to relative reaction energies and the activation energies were below 0.01 eV.

3. Results and discussion

In a previous work we proved theoretically that the most stable adsorption mode for 13BD on Pd/Ni(1 1 1) and Pd₃/Ni(1 1 1) surfaces is the 1,2,3,4-tetra- σ one [18]. 13BD shows in this geometry the *trans* configuration, with each of their four C atoms linked to a different surface Pd atom through a σ -bond. From this result, in the present paper the 13BD hydrogenation on both surfaces was considered following the Horiuti–Polanyi mechanism, where the co-adsorbed H atom is added into one of the C=C double bonds of the 13BD to produce two C₄H₇ intermediates: 1-buten-4-yl (CH₂=CHCH₂CH₂•, 1B4R) and 2-buten-1-yl (CH₂•CH=CHCH₃, 2B1R), which are formed by H addition on the C₂ (or C₃) and C₁ (or C₄), respectively. The subsequent incorporation of another H atom produces the C₄H₆ products: 1-butene (1B), 2-butene (2B) and the diradicals butan-1,3-diyl (B13R) and butan-1,4-diyl (B14R) [30]. Taking into account the different steps necessary to describe reaction pathways in the Horiuti–Polanyi mechanism, we present in following subsections first the intermediate species (1B4R and 2B1R), afterward, the co-adsorptions (13BD + H, 1B4R + H and 2B1R + H), and finally the reaction pathways and transition states.

3.1. Intermediate species on Pd/Ni(1 1 1) and Pd₃/Ni(1 1 1) surfaces

Figs. 1 and 2 show the optimized geometries of the intermediate species on Pd/Ni(1 1 1) and Pd₃/Ni(1 1 1), respectively. Both monoradicals produced after the first hydrogenation, 1B4R and 2B1R, have the C=C double bonds lengthened with respect to the free diene in gas phase (1.34 Å) and the Pd–C bonds also change

Download English Version:

<https://daneshyari.com/en/article/65422>

Download Persian Version:

<https://daneshyari.com/article/65422>

[Daneshyari.com](https://daneshyari.com)