



Adsorption and desorption of propane on Pd (111): A van der Waals density functional study. Energy binding sites and geometries

Tadeu Leonardo Soares e Silva, Martin Schmal*

Federal University of Rio de Janeiro, Chemical Engineering Program/COPPE/NUCAT, Cidade Universitária- CP: 68502, Rio de Janeiro, RJ, CEP-21941-972, Brazil



ARTICLE INFO

Keywords:

Adsorption
Pd (1 1 1) surface
vdW-DF
Propane

ABSTRACT

Palladium supported catalysts used for the partial oxidation of propane reaction aiming the H_2 production deserves specific characterizations and theoretical modeling for the explanation of the transition phase and energy needed for the adsorption and desorption of propane on top of the palladium atoms. On the other hand, the product distribution will depend on the adsorption and desorption capacity of the different compounds present during the reaction. In this work, the adsorption of propane on a Pd (111) surface was studied by using different approximations. A periodic method based on the Density Functional Theory (DFT) formalism employing vdW-DF functional was investigated for determining preferred binding sites of propane on palladium. The results show that the adsorption on hcp site is more stable than on top site and predictions fit well the experimental results.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

There are many processes hydrogen production, such as steam reforming or partial oxidation of hydrocarbons and alcohols, biomass, electrolysis of the water or as by-product of the oil refining. Among them, steam reforming is probably the most common and cheapest way for hydrogen production [1]. The oxidative steam reforming or auto thermal reforming has the main advantage that the initial oxidation reaction is extremely exothermic, generating heat for the subsequent endothermic reforming reactions [2]. Propane is drawing attention in hydrogen production studies primarily because it is a constituent of LPG [3,4]. LPG is a commercial gas that is easily transported and stored on site [5]. This gas has short aliphatic C3-C4 chains and absent of sulphur or other electronegative atoms. LPG is reported to present some significant advantages compared to heavier feedstock, mainly in terms of catalyst deactivation and resistant to carbon deposition during reforming [6]. Moreover, propane is produced in relative high amounts from natural gas and oil crude refining.

Kinetics and surface adsorption and desorption studies for the partial oxidation and auto thermal reforming of hydrocarbons are scarce in the literature, in particular for propane [7]. Ribeiro and co-workers [8–10] studied the kinetic parameters for the partial oxidation reaction; however, the reported reaction mechanisms for these reaction conditions are inadequate when comparing with experiments. Most reaction mechanisms for the partial oxidation and reforming of methane were extrapolated for the propane reaction without sufficient evidence about the surface reaction structure under different reaction conditions. In par-

ticular, palladium supported catalysts used for the partial oxidation of propane reaction aiming the H_2 production deserve specific characterizations and theoretical modeling for the explanation of the transition phase and energy needed for the adsorption and desorption of propane on top of the palladium atoms. On the other hand, the product distribution will depend on the adsorption capacity of the different compounds present during the reaction.

The determination of surface structure and reactivity is generally grounded on experimental studies. There is an immense arsenal of available surface techniques that are used nowadays as routinely tool in surface science. However, theoretical studies based on quantum mechanics are also of fundamental importance in molecular and materials modeling, since they permit to confirm or discard hypothesis concerning structure and reactivity. The recent developments of both ab-initio wave function and density functional theory (DFT) based methods and the ever growing computational facilities make it possible to use total energy methods to compute the structure of reactants and products in a chemical reaction, to predict thermal properties or reaction rates or to obtain spectroscopic properties. In particular, for most applications, the Kohn–Shan implementation of DFT permits to include electronic correlation effects at a reasonable computational cost. Modern DFT is less computational demanding than ab-initio wave function based methods and is also accurate enough so as to permit the study of rather complicated systems, especially in condensed matter. Understanding the fundamental interactions that bind organic molecules to noble metal substrates is of crucial importance in molecular scale electronics and self-assembly, where the competition between molecule substrate and inter-

* Corresponding author.

E-mail addresses: tajo33@gmail.com (T.L.S. e Silva), schmal@peq.coppe.ufrj.br (M. Schmal).

molecular interactions can lead to template arrangements with specific spectroscopic and transport properties [15,16]. As the forces driving the formation of these organic-inorganic assemblies often include both local chemical bonding and non-specific long range interactions, it is essential to have an accurate description of both contributions [17].

In the present paper the adsorption/desorption energies, binding site preferences and geometries of propane on the Pd (111) surface are determined by means of DFT calculations, employing the method vdW-DF. The main purpose of the present study is precisely to determine and compare the geometry, binding site preference and adsorption energies of propane (C_3H_8) on the Pd (111) surface catalysts by mean suitable DFT calculation, by using two different approximations. Consequently, an accurate characterization of the adsorption site, adsorption modes and packing arrangement appear to be a necessary step towards understanding the subsequent surface processes, because unfortunately, to the best of our knowledge there is no structural information available for propane on Pd (111) mainly employing the method vdW-DF. It is expected that this structural information will help to understand the reactivity of propane on metal surface. Experimental results on Pd supported catalysts were reported in the literature [7] support our theoretical predictions.

2. Surface model

The reliability of the DFT approach depends on the approximation of the exchange-correlation (XC) functional. Recent studies, usually go beyond the well-known local density approximation (LDA) and are based either on the generalized gradient approximation (GGA) or on hybrid functionalism [11–14].

While density functional theory (DFT) provides a many-particle framework that, in principle, incorporates both local and non-local interactions, common semi-local approximations to DFT neglect long-range attractive contributions to van der Waals interactions, so-called “London dispersion forces”. In recent years, progress has been made towards including London dispersion corrections within standard DFT. Among these methods, a fully first-principles van der Waals density functional (vdW-DF) [18,19] has been developed to accurately include the effects of London dispersion forces. This method has been shown to be relatively accurate as well as computationally tractable. The concept “vdW forces” includes forces due to permanent-dipole-dipole interactions, permanent-dipole and induced-dipole interactions, and instantaneous induced-dipole interactions, also called London dispersion forces. The most widely used implementations of DFT do not include the non-local London dispersion forces. The lack of vdW forces could be problematic in studies of propane, since that propane is a hydrocarbon. Such molecules are believed to have a considerable part of the binding due to vdW forces [20–34].

The cluster model approach is thought to capture the essential features of the chemisorption bond and to be able to predict local properties such as adsorption geometries and vibrational frequencies in the limit of extremely low coverage [35,36]. The alternative is the super cell approach based on the use of periodic slabs constructed to exploit the translational symmetry of the system.

An advantage of super cell models is connected to the fact that they are well suited to study the influence of the adsorbate coverage on the surface. The study of low coverage situations with slab models requires the use of large super cells with a concomitant increase in the computational cost.

To describe the adsorption of propane on palladium, an organic molecule interacting with a surface, it is imperative that the vdW forces are well described.

The vdW force originates primarily from the most loosely bound electrons, which for molecular monomers are in states modified by chemical bonding. It is not directed through nuclear centers, as assumed by some semi-empirical methods. In the vdW-DF method the vdW interaction is

correctly described as an effect originating in the tails of the electron distribution, and it is well suited to include effects of image planes [27].

The GPAW code is an all-electron DFT code based on projector augmented waves [41] (PAW) and using finite differences. In several of our previous vdW-DF applications we used self-consistent calculations with the generalized gradient approximation (GGA) to determine the electron density and part of the total energy followed by non-self-consistent calculations to determine the total energy within vdW-DF. This allowed us to focus on either the GGA need for accuracy in choice of computational parameters and methods such as for example the need of a fixed amount of vacuum in the total system [42–44] or the vdW-DF need for accuracy in other parameters and methods (for example the need for fixing the local electron density grid [45,46]). When carrying out self-consistent calculations for vdW-DF all of these requirements must be met in all calculations. We choose the real-space grid for representing the wave functions in the PAW procedure to have a distance less than 1.1 nm between nearest-neighbor (nm) grid points. The (valence) electron density is represented on the same grid with additional grid points at half the nm distance, values obtained from interpolation of the electron density grids is important for the quality of the evaluation of the nonlocal correlation contribution [45].

Brillouin zone integrations were performed on a grid of $4 \times 4 \times 1$ Monkhorst-Pack special k -points [47–52]. In this case a Methfessel-Paxton smearing of width $\sigma = 19.3$ kJ/mol was used [53].

3. Results and discussions

It is important to stress that the calculations predicted for well-structured model crystallites were observed on the real metal supported particles. The XRD experiments in situ were performed previously aiming to match the predicted surface properties. The XRD experiments on the supported Pd/Al₂O₃ under different pretreatments conditions are described elsewhere [7] where the reduction was performed using H₂/He flow and ramping the temperature up to 773 K. Notwithstanding is that after reduction the band corresponding to metallic Pd⁰ at $2\theta = 39.8^\circ$ appeared with reference to the plane $\langle 111 \rangle$, with simultaneous decreasing intensity of band at $2\theta = 34^\circ$, suggesting the reduction of PdO. It suggests that the reference plane $\langle 111 \rangle$ is the predominant plane on the supported catalyst. Therefore, resulting structure is in a good agreement with the geometry suggested by experimental XRD data.

The accuracy of density functional theoretical methods for the prediction of binding and adsorption energies is typically within 21.50 to 33.50 kJ/mol of the reported experimental values [37–40]. Much less is known about the activation energies, but they too appear to fall within this range. This is not within the 1 kcal/mol accuracy that might be necessary for engineering models. The predictions, however, are quite useful in that they typically provide the correct trends, even when the energy differences are relatively small. While we expect that there will be some deviations from the exact quantitative accuracy of the results reported herein, the comparison of binding energies, and overall reaction energies and activation barriers for different steps should be fairly reliable.

The Pd (111) surface of the FCC catalysts was represented with a slab containing four atomic metal layers. The effect of the slab thickness was tested considering slabs containing up to six atomic layers. The results showed that a slab with four layers provides converged results, with accuracy higher than 3.85 kJ/mol. Therefore, a slab with four atomic layers should be appropriate to the present study. A three dimensional periodic cell was constructed including a vacuum gap of ~ 1 nm in the perpendicular direction to the metallic surface. The thickness of this vacuum region was found to be adequate to eliminate any interaction between adjacent metal slabs. The DFT-optimized lattice constant for Pd was used to define the surface. This lattice constant, 0.396 nm, is in good agreement with the experimental value of 0.389 nm [51].

We calculated the total energies of the adsorption E_{ads} and E_a system using the DFT program GPAW [54] with vdW-DF [55,56] in a Fast-

Download English Version:

<https://daneshyari.com/en/article/5421115>

Download Persian Version:

<https://daneshyari.com/article/5421115>

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