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Atomic scale insights into ethanol oxidation on Pt, Pd and Au metallic nanofilms: A DFT with van der Waals interactions

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ABSTRACT

In this work, we use dispersion corrected DFT calculations (DFT + D3) to explore the ethanol decomposition on Pt, Pd and Au metallic nanofilms. The structural and energetic properties of ethanol and the most common intermediate products in ethanol oxidation were investigated, namely acetaldehyde, acetic acid, acetyl and CO. Our results suggests that even when starting from an initial condition very close to the equilibrium geometry it is not possible to obtain the correct adsorption properties from standard DFT calculations; the system is trapped in a local minimum geometry and the correct adsorption geometry cannot be accessed. Therefore, the inclusion of vdW interactions is fundamental to assure correct adsorption properties and agreement with experimental data. By analyzing the adsorption of ethanol and its oxidation products on metallic nanofilms we found that Pt (1 1 1), Pt/Pd (1 1 1), Pt/Au (1 1 1) and Pd/Pt (1 1 1) nanofilms present enhanced adsorption properties and seem to be good candidates for ethanol catalysis.

1. Introduction

Direct alcohol fuel cells (DAFC) are interesting electrochemical devices for a clean and renewable energy production, due to their high energy density, low pollutant emission, no need of a external reformer and low operating temperature (60–100°) [1,2]. Among the available alcohols, ethanol has attained a large attention, because of its high energy density by mass, nontoxicity, and its availability from renewable biomass sources. Moreover, ethanol is liquid at ambient conditions, easy to store and handle, and a distribution network is well established. The high energy density in ethanol is a result of the 12 electrons available during the complete electrochemical oxidation to CO_2; as a consequence, the use of the total available energy is closely related to the selectivity of the catalyst toward CO_2 production. However, even for the most effective catalysts, the total oxidation is not observed and the search and development of new catalysts for efficient ethanol oxidation is required [3–6].

Additionally to its use in fuel cells, ethanol has a number of important applications in the chemical industry, including hydrogen production and synthesis of organic products as aldehydes and ketones [4,7–9]. During the reforming process of ethanol, hydrogen can be obtained from the two main reactions [8]:

(i) *Steam reforming*: $CH_3CH_2OH + 3\,H_2O \rightarrow 6\,H_2 + 2\,CO_2$ ($\Delta H = 41.6$ kcal/mol);
(ii) *Partial oxidation:* $CH_3CH_2OH + 3/2\,O_2 \rightarrow 3\,H_2 + 2\,CO_2$ ($\Delta H = -132.0$ kcal/mol).

These reforming reactions have been extensively studied in several metallic catalysts, such as Co, Ni, Cu, Ru, Rh, Pd, Pt, Ir and Rh/CeO_2, which demonstrate that if ethanol can be efficiently converted to hydrogen with an appropriated catalyst it can be an interesting candidate to solve the crucial problem of the costly hydrogen production and storage [7–9].

The kinetics for ethanol oxidation is very slow because several reaction intermediates states (acetaldehyde, acetic acid, acetyl and CO) are generated and the oxidation to CO_2 is incomplete [6]. The completely electrochemical oxidation of ethanol to CO_2 is only possible if a C–C bond cleave and a oxygen addition to adsorbed CO happen, which usually occurs by following two different reaction pathways, namely acetic acid and CO pathways. In the acetic acid pathway there is no C–C bond breaking and acetaldehyde is produced, which can desorb from the catalyst surface yielding two electrons. This is the less desirable product since it results in the lowest energy output. If acetaldehyde is reabsorbed, it can undergo further oxidation to acetyl that combined to an OH^- group can lead to acetic acid production and four electrons. On the other hand, in the CO pathway, acetaldehyde can suffer reabsorption accompanied by a C–C bond breaking, producing adsorbed intermediates such as CH_x and CO, that eventually oxidize to CO_2.

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In order to clarify the performance of catalysts, theoretical and experimental studies of ethanol decomposition and oxidation were carried out on several metallic surfaces, including Ni (1 1 1), Rh (1 1 1), Pt (1 1 1), Pt (1 1 0), Cu (1 1 0), Ag (1 1 0), Pd (1 1 1), Pd (1 1 0), Co (1 1 1), Rh/CeO_2 (1 1 1), and Ru/ZrO_2 (1 1 1) [7–13]. Additionally, first principles calculations based on the density functional theory (DFT) had been performed to explore the origin of the low CO_2 selective in Pt catalysts. Kavanagh et al. [5] have shown that a pure Pt-based catalyst is not sufficiently active for CO_2 production, and highlights the need for careful control of the oxidant surface coverage (O^- and OH^-) during the oxidation process of ethanol to facilitate the C–C bond cleavage and still provide sufficient levels of CO oxidation. Although experimental results suggests that for Pt-based catalysts the acetic acid pathway is usually preferred and even for very low applied potentials a considerable amount of CO_2 is not observed [10].

The divergence between theoretical and experimental results for Pt based catalysts may be related to the lack of van der Waals (vdW) interactions in standard DFT calculations, which has been shown to be extremely important to determine the interaction between organic compounds and metallic surfaces [14–16]. Especially for ethanol adsorption on transition metal surfaces, dispersion corrected DFT calculations have shown a considerable change of the adsorption properties. Inclusion of vdW interactions drastically changes the orientation of the C–C bond with respect to the metallic surface. DFT calculations yield an almost perpendicular orientation of the C–C bond and adsorption occurs at the top site, while for dispersion corrected DFT calculations the C–C bond is almost parallel to the surface and adsorption occurs in a hollow site very close to the top site [16].

Metallic layered supported thin films have received increasing attention in the past few years. The deposition of atomic layers onto metallic crystalline surfaces can modify their catalytic or electrocatalytic properties by a systematic modification of the electronic structure, which offers the opportunity to design catalysts of greatly improved activity and selectivity for several applications [17–20]. Particularly, Pt, Pd and Au nanofilms present enhanced adsorption properties for H, O and OH, and seems to be interesting catalysts for ethanol electrochemical oxidation [21]. Based on this, we use dispersion corrected DFT calculations to explore the ethanol decomposition on Pt, Pd and Au metallic nanofilms. The structural and energetic properties of ethanol and the most common intermediate products in ethanol decomposition were investigated, for instance acetaldehyde, acetic acid, acetyl and CO. In a first step we analyze the effects of vdW interactions on the CH_3CH_2OH, CH_3CHO, CH_3COOH, CH_3CO and CO adsorption on Pt (1 1 1) surface, which is usually chosen as model catalysts. Following, we use dispersion corrected DFT calculations to investigate how the structural, energetic and electronic properties change for the different types of nanofilms and adsorbates.

2. Methodology

Standard DFT and dispersion corrected DFT (DFT + D3) calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) [22,23]. The exchange and correlation terms are treated in the Generalized Gradient Approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [24], and projector-augmented wave pseudopotentials [25,26] are used. Mean-field dipole corrections along the direction perpendicular to the surface and spin polarization is also considered [27,28]. Convergence was tested for supercell size effects, Brillouin sampling, and energy cutoff. Plane waves with kinetic energy cutoff of 400 eV are used and the Brillouin zone integration is done on a $4 \times 4 \times 1$ Monkhorst-Pack k-point mesh.

In order to include vdW interactions to standard DFT calculations, we consider the dispersion correction D3 approach proposed by Grimme [14]. Therefore, the total energy will be given by

$$E_{DFT+D3} = E_{DFT} + E_{disp}, \tag{1}$$

where E_{DFT} is the standard DFT energy and E_{disp} is a semi-empirical dispersion energy correction of the form

$$E_{disp} = -\frac{1}{2}\sum_{AB}\left[s_6 \frac{{C_6}^{AB}}{{r_6}^{AB}} f_{d,6}(r_{AB}) + s_8 \frac{{C_8}^{AB}}{{r_8}^{AB}} f_{d,8}(r_{AB})\right]. \tag{2}$$

In the dispersion energy the pairwise interactions are summed over all atoms within a cutoff radius of 50 Å. The dispersion coefficients (C_{AB}), the scaling factor (s_n) that ensures asymptotic exactness of the approximation, and the damping function ($f_{d,n}$) have been directly taken from Ref. [14].

In our calculations we consider Pt, Pd and Au nanofilms composed by one atomic monolayer deposited over Pt (1 1 1), Pd (1 1 1) and Au (1 1 1) substrates, as proposed in Ref. [21]. A generic metallic nanofilm (MF) supported by a metallic substrate (MS), defined as MF/MS (1 1 1), is represented by a supercell ($3 \times 3 \times 1$) containing a five-layer slab separated by 18 Å of vacuum. To determine and refine the atomic structures we perform a full ionic relaxation of the adsorbed species, nanofilm layer and the uppermost layers of the substrate, while the two bottommost layers of the substrate are fixed at bulk values, using the conjugate gradient method until all forces on the system are bellow to 0.04 eV/Å. The calculated DFT lattice parameter for bulk Pt is 3.99 Å and DFT + D3 lattice parameters for the bulk Pt, Pd and Au are 3.93, 3.90 and 4.12 Å, respectively. Values for DFT + D3 agree well with the experimental data of 3.92, 3.89 and 4.08 Å, and have been employed throughout the paper. Calculations for the isolated gas phase molecules have been carried out in a large supercell to avoid interaction between the molecule and its images, and the Brillouin zone was sampled on the Γ point. As expected, no considerable change of the molecular structure was observed after inclusion of vdW interactions.

The chemical adsorption energy of a generic metallic nanofilm (MF) supported by a metallic substrate (MS) with one adsorbed molecule in the supercell is defined as

$$E_{ads} = E_{Mol:MF/MS(1\ 1\ 1)} - E_{MF/MS(1\ 1\ 1)} - n_{Mol}E_{Mol}, \tag{3}$$

where $E_{Mol:MF/MS\,(1\,1\,1)}$ and $E_{MF/MS\,(1\,1\,1)}$ are the total energy of the MF/MS (1 1 1) system with and without an adsorbed molecule, and E_{Mol} is the total energy of the isolated molecule in the gas phase.

The calculated trends in the adsorption energies are also analyzed with respect to the electronic structure. To this aim, we use the d-band center model proposed by Hammer and Nørskov, where a single electronic level can represent the whole d-band of a transition metal. In this model, the location of the d-band center (ε_d), is given by [29]

$$\varepsilon_d = \frac{\int_{-\infty}^{\infty} \varepsilon\rho(\varepsilon - \varepsilon_F)d\varepsilon}{\int_{-\infty}^{\infty} \rho(\varepsilon - \varepsilon_F)d\varepsilon}, \tag{4}$$

where $\rho(\varepsilon)$ is the projected density of states of the d-band of nanofilm surface atoms, ε is the energy and ε_F is the Fermi level energy. According to this model, the position of the d-band center with respect to the Fermi level is linearly correlated to the adsorption energy [30]. Generally, a d-band center position close to the Fermi level results in stronger adsorption. If this model is valid for a given adsorbate, then it would be possible to predict the catalytic active for a given surface before the adsorbate adsorption by verifying the clean surface' d-band center (unadsorbed d-band center). This model has proved to be very useful to describe trends in H, O and OH adsorption energies on Pt, Pd and Au nanofilms. For these systems, because of the misfit between the lattice