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Simple model to study heterogeneous electrocatalysts

Edison Franco-Junior, Ana Carolina G. Lopes, Hugo B. Suffredini, Paula Homem-de-Mello*

Centro de Ciências Naturais e Humanas, Universidade Federal do ABC (UFABC), Av. dos Estados, 5001, 09210-580 Santo André, SP, Brazil

HIGHLIGHTS

- Simple DFT-based methodology for studying morphologically heterogeneous catalysts.
- Model has good correlation with previous simulations and experimental data.
- Adsorption on "valleys" or cavities with both Pt and Pb atoms involved.

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ABSTRACT

New electrocatalyst materials have been proposed to increase the performance of fuel cells. Experimental studies show that Pt and Pb metallic and oxide materials are quite efficient in the oxidation of alcohols and small organic molecules such as formic acid in advanced fuel cells. This work proposes a model for studying morphologically heterogeneous catalysts through quantum chemistry methods such as density functional calculations. For testing the model, we have experimentally studied the adsorption of small organic molecules, namely formic acid and methanol, on Pt and Pb electrodes. All methodologies we have tested can be employed for this kind of study, but M06 functional results correlate best with previous simulations of homogeneous catalysts and with experimental data obtained for homogeneous and heterogeneous electrodes. Our model indicates that the presence of a Pt–Pb interface is responsible for higher adsorption energies of these molecules, most likely due to the orientation of the organic molecules that should facilitate the oxidation process.

1. Introduction

The search for new energetic sources is fundamental to the near future of society; in this context, fuel cells are being widely studied. Fuel cells are devices with the ability of turning chemical energy into electric energy using electrocatalysts.

Studies by Suffredini et al. [1–5] for heterogeneous catalysts based on Pt, Pb, PbO_x and other metallic oxides have shown excellent performance for formic acid oxidation. The authors proposed that platinum poisoning can be avoided by the presence of lead and its oxides, which might curb the adsorption of some undesired intermediates in the reaction, such as acetic acid and acetaldehyde. These type of electrodes were synthesised by the sol–gel method, using acetates, carboxylates, acetylacetonates or metal alkoxides, among other salts. The electrodes obtained using the synthetic route presented in Ref. [5] are composed of distinct phases of Pt and Pb and nanometric islands of Pt, which are heterogeneously dispersed on the carbon support. Some Pb particles are spread over the support, as shown in microscopy studies [5].

Computational simulations have been extensively applied in catalyst studies, including reactions related to fuel cells [6–17]. These simulations, however, are based on the periodic properties of morphological homogeneous electrodes. In our previous work [5], in addition to experimental results, we presented a simple method to investigate the behaviour of heterogeneous electrodes and their adsorption sites. In the present study, we validate the chosen computational methodology and extend the calculations to study methanol adsorption onto heterogeneous catalysts.

2. Computational details

Two main approaches are usually employed for *ab initio* simulations of adsorption processes: plane wave periodic techniques or cluster calculations. Both employ crystal parameters obtained for solids whose atoms are homogeneously distributed. Defects are

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* Corresponding author.
E-mail address: paula.mello@ufabc.edu.br (P. Homem-de-Mello).

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introduced by the addition, removal or replacement of an atom of the crystal lattice.

As extensively discussed in previous publications [5,18], electrodes synthesised by sol–gel methodology present heterogeneous distributions of atoms what showed to improve their catalytic activity. The enhancement in the catalytic activity is attributed to the presence of active sites consisting of defects and/or interphases regions. Aiming to find geometries and composition for active sites, we built a very small model of the system, with metallic atoms (Pt and Pb) bonded to a carbon chain, and performed full geometry optimisations without symmetry restrictions with and without fuel molecule. Since our electrode model is a kind of molecule rather than a cluster, we employed quantum chemistry methods of simulation, namely gaussian-based DFT.

The electrode model employed in this work was inspired by the Dipped Adcluster Model [14,16,17], consisting of only four metallic atoms in different proportions of Pt and Pb. Thereby, cluster and adcluster geometry were fully optimised, with the only restriction imposed by the presence of a saturated carbon chain (with 7 carbon atoms and 12 hydrogen atoms) over the metallic atoms to induce them together. By this procedure, we intend to obtain optimal sites for adsorption.

We have performed a methodological study using the functionals M05 [19], M06 [20], M05-2X [21], B3LYP [22–24] and the LANL2DZ pseudopotential basis set [25–27]. The convergence criterion for the electronic self-consistent iterations was 1×10^{-8} a.u. The results obtained were compared to the interaction energy obtained in previous works [7,11,28] for the adsorption of formic acid on a homogeneous platinum surface.

We subsequently investigated the adsorption of formic acid and methanol on electrodes containing platinum and lead. We studied various electrode compositions, varying the relative atomic positions.

The inputs related to the interaction between clusters and fuels were chosen such that the distance between the adsorbate and the metal, composing the adcluster, was constant. However, the relative positions of the organic molecules were different, identified as A, B, C and D (as shown in Figs. 2 and 4). Frequencies were calculated to guarantee a minimum in the potential energy surface. Atomic charges derived from electrostatic charges (ESP) were obtained using the ChelpG scheme [29]. All calculations were carried out with the Gaussian 09 package [30].

3. Results and discussion

3.1. Cluster characterisation

The geometry of isolated adsorbate systems, formic acid and methanol, and catalysts, was first optimised using M05-2X, M05, M06 and B3LYP functionals with the LANL2DZ basis set (Table 1).

From these results, we can compare electrodes with the same number of electrons. When just one different atom is present (*b* and *c* or *h* and *i*), the cluster for which this atom is on the border (*b* and *i*) is generally more stable (except for the M05 functional). For the 2:2 Pt/Pb proportion (clusters *d*, *e*, *f* and *g*), the results for all functionals are consistent; the most stable cluster is that with Pb in the borders and 2 Pt in the middle (cluster *f*), followed by cluster *g*, in which Pt and Pb are intercalated, cluster *d*, with Pt in the borders, and cluster *e*, with two separated domains.

Fig. 1 presents the final conformations of the electrodes obtained with M06. In each electrode, there have been modifications in relation to the input structure, but all functionals predict similar structures. Distances between Pt atoms are approximately 2.6 Å and between Pb atoms 3.2 Å, smaller than the distances observed in crystal structure of the pure metal (respectively, 2.8 Å and 3.5 Å). Pt–Pb distances range from 2.6 to 2.8 Å. The more stable structures with only one different atom, clusters *b* and *i*, have a zigzag structure, while clusters *c* and *h* are in arc form. For 2:2 clusters, the stability order, $f > g > d > e$, also follows the same geometric criteria, for which cluster *g* is in arc form and *e* is almost linear. For cluster *d*, there is a greater separation between Pb atoms.

Our previous works [5,18] demonstrated that these heterogeneous catalysts present different phases, with characteristics of both pure metal and alloy. In the present work, the electrode is represented as small clusters, which do not allows us to use band theory but enables us to compare changes in the electronic properties of electrodes by evaluating frontier molecular orbitals. In Table 2, the energies of frontier orbitals, HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), as well as the difference between them (gap energy), are listed. The data were obtained with the M06 functional. DFT generally underestimates gap values [31]; however, qualitative comparisons between conformations can indicate general trends.

The electrode composed of pure lead presents a small gap value as do structures with a higher proportion of this atom (3:1). The cluster Pt–Pt–Pb–Pb has a quite low gap value. The other structures have behaviour closer to the pure Pt electrode but with higher values.

As the aim of this work is to assess the response of the catalysts to the oxidation of organic molecules, we have analysed the LUMO energies for several compositions. The pure clusters, formed by only one kind of element, have a very low LUMO energy that indicates the facility to receive electrons. The LUMO energy of Pt–Pt–Pb–Pb is slightly more negative than the same for a pure cluster of platinum and 0.01 a.u. (approximately 0.27 eV) lower than that of a pure cluster of lead.

After these initial calculations, we began to study the interaction between fuel molecules and clusters, thus obtaining the adclusters presented in the following sections.

3.2. Formic acid

In the previous work [5], we have proposed some models to study formic acid electrooxidation, but the main focus was experimental results. Here, we present the theoretical methodology and models employed in a more detailed study of this system. Initial adcluster conformations (inputs) with formic acid are shown in Fig. 2. The intramolecular hydrogen bond of formic acid was avoided, as our aim is confirming the difference between both oxygen atoms. This system was fully optimised.

Based on total energies ($E_{\text{adcluster}}$) (Fig. SI1, Supplementary information), obtained after optimising adcluster geometry (including all possible combinations of Pt and Pb and also considering every possible initial position for formic acid), we have calculated adsorption energies (E_{ads}) by the following equation:

$$E_{\text{ads}} = E_{\text{adcluster}} - E_{\text{cluster}} - E_{\text{fuel}}.$$

As noted previously [5], our calculations with the M06 functional, even with a simplistic approach, were able to reproduce qualitatively well the results of plane wave calculations for formic acid adsorption on a Pt electrode [7,11].

As a general bias, we can observe that the adsorption energy of formic acid onto different clusters is about −0.3 to −0.4 eV, as predicted by all functionals (Fig. SI1 in Supplementary information). We can compare the M06 functional with its predecessors M05 and M05-2X (parameterised to weak interactions and non-metallic systems) and B3LYP, widely used among chemists. Our model provided the following mean values for the