Use of chemical descriptors approach and DFT to analyze the C—C bond cleavage on Pt$_3$Re$_1$ alloy in the ethanol oxidation reaction for fuel cells

Alejandro E. Pérez, Rafael Ribadeneira *

Departamento de Procesos y Energía, Universidad Nacional de Colombia, Medellín, Colombia

A B S T R A C T

Design of selective catalysts able to cleave C—C bond in ethanol oxidation reaction at low temperatures is primordial for improving the direct ethanol proton exchange membrane fuel cells (DEFCs). Pt—Re mixture could be an appropriate alloy for the C—C bond cleavage in ethanol decomposition, but yet, it has not been studied in detail the reactivity of this alloy for this step. In this work, the reactivity of Pt$_3$Re$_1$ surface for the C—C bond cleavage is studied and compared with pure metal surfaces Pt and Re, using chemical descriptors through density functional theory (DFT) calculations. The adsorption energies of CHCO, CO and CH molecules are the chemical descriptors investigated and the results are analyzed with respect to the electronic structure of the surface in order to understand the nature of the active sites. It is found that the addition of Re to Pt leads to form an active site with a Re atom, which is more reactive for the C—C bond cleavage in CHCO, but the sites without Re become less reactive for this step. Then the addition of Re to Pt has not a significant effect on the promotion of full oxidation of ethanol, since not all sites at the Pt$_3$Re$_1$ surface are more active towards C—C bond cleavage.

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1. Introduction

Direct ethanol-proton exchange membrane fuel cells (DE-PEMFCs) are promising clean energy converters, ethanol is an interesting fuel due to its high energy density, renewability, its easy production in large quantities, and the availability of the infrastructure for its transportation and storage [1–5]. However, its efficiency is still far from that obtained with hydrogen fuel cells, which can be partly attributed to the incomplete conversion of ethanol to CO$_2$.

Currently, it is observed that the preferred ethanol oxidation pathway is the partial oxidation to acetic acid. This pathway just releases four electrons, while the complete oxidation to CO$_2$ would release twelve electrons, increasing the faradaic efficiency of the cell [2,5–8]. Unlike partial oxidation, complete oxidation involves the C—C bond cleavage, which is pointed out as the limiting step in the complete ethanol oxidation [7]. Then, the development of catalysts with higher specific activity for C—C bond cleavage is required [1,9].

Authors have proposed to combine different metals with Pt to improve the activity for ethanol oxidation reaction (EOR). It is found that the addition of oxophilic metals such as Sn [10–14] improves the activity for ethanol oxidation by activating water molecules, which provides OH species that oxidizes the adsorbed intermediates species, which is

called the bifunctional mechanism [15,16]. But these catalysts do not promote the oxidation to CO$_2$ [17–19]. However, it is suggested that addition of metals as rhodium [20], iridium [21], and rhenium [22] at specific compositions help in C—C breakage at low temperatures (below 100 °C).

Mixtures of platinum (Pt) and rhenium (Re) could be a good catalyst for C—C bond cleavage, they are mostly used in petroleum-reforming [23–25]. Some studies on PtRe catalysts for hydrocarbons suggest that this alloy is more active for C—C bond cleavage than pure Pt and Re [26], also the Re sites facilitate CO oxidation promoting the bifunctional mechanism [26–28]. Mixtures with Re have been tested in fuel cells, for instance a Pt-Re alloy with Re atomic composition of 25%, finding that this catalyst is more active for CO oxidation than Pt [29]. Also, it is found that the addition of Re to Pt-Sn anodes leads to a superior performance [22,30]. DE-PEMFCs using PtSnRe anodes show higher power density than PtSn, PtSnHf, PtSnOs and PtSnIr anodes [30].

These evidences indicate that Pt-Re is suitable modifying C—H and C—C bonds. However, the reactivity of this alloy for the EOR and the C—C bond cleavage step is not studied in detail. Thus, it is of interest to model this reaction step on Pt-Re catalysts in order to determine the usefulness of Re for promoting C—C bond cleavage in the EOR. An approach that would allow the description of C—C bond cleavage and the understanding of determining factors in catalytic activity of materials is a theoretical approach using ab-initio atomistic modeling. This approach allows the calculation of electronic structure of the system and related properties as the adsorption energy, which can be utilized as descriptors of the surface reactivity for a given reaction [31–33].

* Corresponding author.
E-mail addresses: aleperezme@unal.edu.co (A.E. Pérez), reribade@unal.edu.co (R. Ribadeneira).

Theoretical studies using Density Functional Theory (DFT) have been carried out for ethanol decomposition on different transition metals as Au [34,35], Pd [36,37], Rh [38], Pt [39–41], PtSn [17,42], PtRu [17], PtPd, PtRh, PtRe [43,44] and Iridium alloys [45]. In some of these studies the potential energy surface and the activation energies for the ethanol decomposition processes are calculated. In this way, the comprehensive mechanism for ethanol decomposition on Pd(111) [36], Rh(111) [38] and Pt(111) [39,40] is investigated, finding that the most favorable step for the C—C bond cleavage is CHCO → CH + CO [36,38,40]. This is found using linear relationships between activation and reaction energy, called Brønsted-Evans-Polanyi (BEP) correlation, which is also appropriate for the ethanol decomposition reaction steps on metallic surfaces, including C—C dissociation reaction [36,40].

Moreover, these BEP correlations are suitable to provide qualitative trends in activity and selectivity for ethanol decomposition on different catalytic surfaces (Pt, Pd, Ir, Rh, Re, Ru and Ni) [46]. It is found that for all metals studied the predicted rate-determining step (RDS) for C—C cleavage is the cleavage through the CHCO intermediate. Likewise this approach is utilized by Curtuois et al. [45] for screening iridium based catalysts, calculating adsorption energies of CO, CH and CHCO with DFT on different surfaces and using the BEP relation to calculate the activation energies for C—C bond cleavage in CHCO.

Considering the previous ideas, in this work is studied the reactivity of Pt_3Re_1 alloy for the C—C bond cleavage step in EOR, using DFT calculations to describe adsorption of key molecules as CO, CH and CHCO, which are the molecules involved in the reaction identified as the most favorable for the C—C bond cleavage:

$$CHCO \rightarrow CH + CO \qquad (1)$$

The adsorption energies of these molecules are utilized in BEP relationship to estimate the activation energy for C—C bond cleavage in the reaction step proposed (Eq. (1)). The adsorption is described using electronic structure calculations and the "d-band model" [47], since the adsorption energy depends on the electronic interaction between the molecule and the surface, this approach facilitates the understanding of the reactivity of Pt-Re and the effects of Re addition on the activity for C—C bond cleavage.

2. Methods

2.1. Computational details

DFT calculations were performed with Quantum Espresso package, which is based on plane waves and pseudopotentials [48]. The exchange correlation functional as described by the Generalized Gradient Approximation (GGA) by Perdew and Wang (PW91) [49]. Core-electrons were represented using ultrasoft pseudopotentials [50]. Convergence was tested with respect to total energy both for the Brillouin sampling and also for the kinetic energy cut-off in the plane waves expansion. Brillouin zone integration was done on a $3 \times 3 \times 1$ Monkhorst-Pack k-mesh [51] and the kinetic energy cut-off for the plane waves was 544 eV. A denser grid of $6 \times 6 \times 1$ was utilized for electronic properties calculation (e.g. DOS). In order to find the minimum energy geometry, the slabs with five and six layers were fully relaxed without constraints until the force was less than 0.03 eV/Å, the total energy of the optimized structures was used to calculate the different properties of the system.

2.2. Surface model

The (111) facet of the face-centered cubic metals (Pt and Pt_3Re_1) and also the (0001) facet of the hexagonal close-packed metals (Re) were studied. The surface was modeled with the slab approach, with a 2×2 super cell under periodic boundary conditions which corresponds to a surface coverage of 0.25 mL. Five and six layers of atoms were employed for representing the portion of solid and empty space of 9.00 Å was left above of the atomic surface to avoid self-interaction of the slab. If 15.00 Å was left above atoms the adsorption energy changed only 0.02 eV, indicating that the top of one slab has essentially no effect on the bottom of the next.

A reasonable representation of adsorption is achieved using five material layers, as can be checked, if these results are compared with the results of calculations using six layers. Using the later, the adsorption energy of CH is decreased approximately 0.02 eV, adsorbed CH bond distance is the same, and distance between rhenium and carbon atom is decreased 0.01 Å. Besides, adsorption energy of CO is decreased approximately 0.03 eV, adsorbed CO bond distance and the distance between rhenium and carbon atom is the same. Finally, the adsorption energy of CHCO is decreased approximately 0.03 eV, C—C bond distance in adsorbed CHCO is the same, and distance between rhenium and CH is increased 0.01 Å. This comparison between the systems of five and six layer shows that the approximation with just five layers is enough for the study of the system and demonstrates the accuracy of the calculations using DFT.

The slab for each system was constructed using the lattice parameters obtained using DFT. The lattice constants calculated are consistent with the experimental values, for Pt was obtained a value of 3.998 Å, in comparison the experimental value is 3.924 Å. For Re, a = 2.766 Å c = 4.439 Å, while the experimental values are a = 2.761 Å c = 4.431 Å. For the Pt_3Re_1 alloy, the DFT-obtained lattice parameter is 3.967 and the experimental value is 3.895 Å. The DFT calculations overestimate this parameter, which is expected if GGA functional as PW91 or PBE are used, nevertheless, these values are similar to those found in other theoretical work [52–54]. The values calculated involve relative errors of 1.93%, 0.18% and 1.85% for Pt, Re and Pt_3Re_1 respectively.

2.3. Properties calculation

The adsorption energy was calculated as the total energy of the slab with the i-species adsorbed $E_{i/s}$ minus the total energy of clean slab E_s and the energy of the i-species in gas phase E_i these energies were estimated through relaxation calculations allowing the free movement of all atoms.

$$E_{ads-i} = E_{i/s} - E_s - E_i \qquad (2)$$

According to transition state theory, the rate of an elemental reaction step can be estimated from the activation energy for this reaction, which is calculated with transition energies E_{TS}. In this work was utilized the transition state scaling relationship proposed in [46] to calculate the transition energies of catalytic reactions in ethanol decomposition.

$$E_{TS} = \alpha E_P + \beta \text{ with } \alpha = 0.87 \text{ eV and } \beta = 1.07 \text{ eV} \qquad (3)$$

E_{TS} is the energy of the transition state relative to the energy of initial state (reactants) in gas-phase E_i and the energy of clean slab E_s. And E_P is the energy of the final state (products) with the same reference. Then for catalytic C—C bond cleavage reaction (Eq. (1)) the E_P can be write as follows:

$$E_P = E_{\frac{CH}{s}} + E_{\frac{CO}{s}} - 2E_s - E_{CHCO} = E_{ads-CH} + E_{ads-CO} \qquad (4)$$
$$+ E_{diss-CHCO} \text{ with } E_{diss-CHCO} = E_{CH} + E_{CO} - E_{CHCO}$$

In the previous equation the clean slab energy E_s is multiplied by two because the dissociation reaction needs two sites at the surface. The activation energy E_a was calculated as the difference between the transition state and the initial state relative to the energy of initial state