



# Generalized Brønsted–Evans–Polanyi relationships and descriptors for O–H bond cleavage of organic molecules on transition metal surfaces



José L.C. Fajín<sup>a</sup>, M. Natália D.S. Cordeiro<sup>a</sup>, Francesc Illas<sup>b,\*</sup>, José R.B. Gomes<sup>c,\*</sup>

<sup>a</sup> REQUIMTE, Faculdade de Ciências, Universidade do Porto, P-4169-007 Porto, Portugal

<sup>b</sup> Departament de Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain

<sup>c</sup> CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

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## ABSTRACT

Periodic density functional theory (DFT) based calculations were used to explore the relationship between the activation energy corresponding to RO–H bond cleavage of organic compounds on catalytically active transition metal surfaces and other simpler quantities which can be used as descriptors. Taking data for methanol on various surfaces, several Brønsted–Evans–Polanyi (BEP)-like relationships linking the activation energy barrier to the reaction energy, the adsorption energy of the reaction products or to the adsorption energy of an oxygen atom were explored. The general validity of these relationships has been explored by considering cases not included in the database used to extract the BEP relationships. For the more promising BEP relationship, the database for methanol was combined with results corresponding to O–H bond breaking of ethanol, formic acid and water on a sufficiently broad number of transition metal surfaces. This extended database provided a more general and statistically meaningful general BEP type relationship connecting the activation energy for the O–H bond breakage of general RO–H compounds on catalytic transition metal systems to the adsorption energy of the reaction products. Finally, a protocol is presented that allows one to determine good candidates for bond breakage of general RO–H compounds on metallic and bimetallic surfaces limiting the explicit calculation of the activation energy barriers to a few, previously detected, interesting cases only.

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## 1. Introduction

Chemical processes often consist of a number of elementary reaction or steps where bond making and bond breaking occur. One of the important elementary steps concern the cleavage of RO–H functional group since this is present in many common compounds such as alcohols, organic acids or even water. Due to the well-known polar character of the O–H bond, displaying higher electron density in regions around oxygen atom than in regions close to the H atom [1], compounds with OH groups are usually involved in quite intricate intra and/or intermolecular hydrogen bond networks which give them peculiar behaviors, with water, either liquid but especially as ice, being a paradigmatic example.

Likewise, there are several heterogeneous catalytic processes where the elementary steps involving the cleavage of O–H bonds either in reactants or intermediate species play a key role. The water–gas shift reaction (WGS:  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ) is essential

in the production of clean hydrogen and the ability of the catalyst to ease dissociation of the O–H bonds in the water molecule becomes crucial. In fact, the dissociation of the first O–H bond in water was shown to be the rate determining step on planar and stepped Cu surfaces [2,3]. The scission of O–H bonds is also involved in the selective oxidation of alcohols to carboxylic compounds over heterogeneous recyclable catalysts, another important industrial process which is also relevant to green organic chemistry [4–6]. In fact, various experimental studies agree that, in general, the mechanism for alcohol oxidation involves the formation of an adsorbed alkoxy species [4–12]. In the case of Au surfaces, this is also supported by recent model density functional theory (DFT) based calculations and experiments [13].

For the case of O–H bond scission of water catalyzed by metallic surfaces, recent DFT based computational studies [14–16] using periodic models suggested to relate the energy barrier for the reaction of O–H bond dissociation to the energy of the reaction leading to the well-known Brønsted–Evans–Polanyi (BEP) relationships [17,18] but also to relate this energy barrier to the adsorption energy of the products of the reaction (e.g.,  $\text{H} + \text{OH}$ ) or to the adsorption energy of an oxygen adatom leading to even simpler descriptors of the

\* Corresponding authors. Fax: +34 93 402 1231 (F. Illas). Fax: +351 234 370 004 (J.R.B. Gomes).

E-mail addresses: [francesc.illas@ub.edu](mailto:francesc.illas@ub.edu) (F. Illas), [jrgomes@ua.pt](mailto:jrgomes@ua.pt) (J.R.B. Gomes).

catalytic activity of these surfaces toward O–H bond dissociation in water. The BEP relationships were determined for the reaction of water dissociation on pure [14] or on bimetallic transition metal surfaces [15] and also on platinum nanoparticles [16]. In these studies, similarities between the relationships arising from the calculations involving different catalyst models, either based on different transition metals or having different shapes, clearly emerged. Additionally, the energy barrier for the reaction on the platinum nanoparticles of increasing size tends to the value calculated for the infinite Pt(111) surface providing an internal check of the computational method and models. The relationships for O–H bond dissociation of the water molecule catalyzed by transition metal catalysts strongly suggest that it is possible to find more general relationships in O–H group containing compounds such as alcohols or organic acids. This idea is supported by the universal relation for hydrogenation and dehydrogenation reactions over transition metals recently suggested by Wang et al. [19].

For the family of the alcohols, methanol and ethanol interactions with transition metal surfaces are the most studied due to their use as combustible in fuel cells [20] and as industrial feedstock for obtaining other chemicals [21]. Methanol and ethanol steam reforming [22,23] or dehydrogenation reactions [24] provide well known and important examples. In these processes, the first reaction step after alcohol adsorption at the catalyst surface involves the cleavage of the O–H bond (*cf.* [25–27] and references cited therein). In fact, compared to the case of the water molecule, the O–H bond cleavage in these alcohols is much more facile and the (m)ethoxy radicals are the dominant surface intermediates at low temperatures on most catalyst surfaces studied [27]. Several theoretical works, most of them based on the DFT approach, have focused on the decomposition of alcohols on surfaces of pure transition metals [28–32], metal oxides [33,34], metal sulfides [35] and multicomponent solid catalysts [36–39]. These computational works have shown that the reaction path leading to O–H bond scission path is usually that with lower energy barrier for the methanol decomposition. Nevertheless, one must be aware that other reaction pathways become possible when the process takes place under realistic conditions. For instance, a microkinetic modeling study based on DFT activation energy barriers for methanol decomposition on Pt(111) has shown that methanol will preferably suffer C–H rather than O–H bond cleavage [40]. It is also worth mentioning the work of Wang et al. [32] concerning the reaction of ethanol reforming on nine different transition metal surfaces, all with the (111) Miller index, using the PW91 functional and the periodic slab approach. They found that an initial decomposition step starting with O–H bond breaking was clearly preferred on most of the surfaces studied with activation energy barriers between 0.44 eV for Co(111) and 1.94 eV for Ag(111). In the cases of Rh(111) and Ir(111), the O–H bond cleavage energy barrier (~0.6 to 0.7 eV) was found to be slightly higher than that associated with the C–H bond rupture (~0.5 eV). Additionally, they found that the ethanol dissociation barriers for the different elementary steps in the full reforming mechanism for converting ethanol in molecular hydrogen are lower on Rh, Co, Ir and Ni surfaces than those on Cu, Ag and Au surfaces [32]. Obviously, a different mechanism is also likely to hold when considering a different substrate as in the case of oxide surfaces. For instance in the interaction of methanol with  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>(100) [33], three different reaction paths were proposed from a combined DFT/cluster model study depending on the local surface chemical composition. On the surface without oxygen vacancies, the methanol molecule suffered an oxidative decomposition yielding formaldehyde and surface hydroxyls or carbon dioxide, water and surface hydroxyls. In the case of the surface with oxygen vacancies, methanol adsorbs intact (non-dissociative adsorption), except in a single situation where the Ga<sub>2</sub>O<sub>3</sub>(100) surface has two neighbor vacancies on tetrahedral

gallium sites, and dissociative adsorption yielding methoxy and hydroxyl species was found [33]. Non-dissociative and dissociative methanol adsorption on the defective surface were identified experimentally [33]. On the TiO<sub>2</sub>(110) surface, the adsorption of methanol was found to be more difficult when water was present [41]. However, the dissociation barrier was found to be low in the case of the stoichiometric surface [42] and the reactivity increased when step edges were present [43].

The interaction of organic acids with metallic surfaces has also been subject of quite intensive research. In particular, the interaction of formic acid with solid catalysts has been widely studied both from experimental [44–47] and theoretical [48–52] points of view. Often, formic acid dehydrogenates to formate (HCOO), which is a quite stable intermediate [2,48,53]. In the recent comparative DFT study of Luo et al. [48], it was found that formic acid decomposes to formate species on Ni(111) [48], with an activation energy barrier of about 0.4 eV, which is smaller than barriers calculated for the reaction on Pd(111), Pt(111) or MgO(001) surfaces. The evolution of the dehydrogenation product (HCOO) toward CO<sub>2</sub> and H is limited by a high energy barrier (1 eV). This is precisely the elementary step that is the rate determining one in the case of formic acid decomposition on Ni(111) [48]. Formate is known to be a common intermediate in the synthesis of methanol mediated by several transition metal surfaces or oxide-supported transition metals [54–56] and has also been identified in the hydrogenation of CO<sub>2</sub> on Ni(110) [57] and on Au/TiC based model catalysts [58].

In spite of the rather large number of theoretical studies above commented dedicated to the interaction and reactivity of alcohols and, to a lesser extent, organic acid on metallic surfaces, a clear general picture which can help to rationalize the vast number of available results is still missing. Herewith, we present a density functional theory based study aimed to fill this gap. To this end, a series of systematic calculations have been carried out to obtain the activation energy barrier and reaction energy for the dissociation of the O–H bond of methanol, ethanol and formic acid on several different transition metal surfaces with the main aim to derive meaningful BEP relationships which can be used as predictive tools. For comparative purposes, results will be evaluated against those already reported for the dissociation of the first O–H bond in the water molecule [14]. The existence of simpler descriptors such as adsorption energies of selected species will be also analyzed.

## 2. Catalyst surfaces models and computational details

The metallic surfaces selected in this systematic study are represented by periodic slab models with the repeated slabs separated, as usual, with a vacuum region of ~10 Å, which is large enough to avoid interactions with neighboring replicas. Different surface sites were systematically explored which are schematically depicted in Fig. 1. A total of eleven different surfaces have been considered, namely: Ni(111), Cu(111), Pt(111), Pd(111), Ag(110), Ir(111), Cu(110), Cu(321), Ni(110), Ni(211) and Rh(211). The choice includes catalytically active surfaces such as those of Pt or Rh and less active ones such as those of Cu and Ag. This choice also allows one to make a meaningful comparison with results calculated previously for the water dissociation on various transition metals (TM) surfaces [14].

For the TM(111) and TM(110) surfaces, the slab models are based on a 2 × 2 unit supercell with four atomic layers thickness. In the case of the TM(211) surfaces, the slabs were built from repetition of the 2 × 1 unit cells while the slabs considered for the TM(321) surfaces were constructed from the repetition of 1 × 1 unit cells. The lattice vectors for each of the bulk metals have been

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