Water dissociation on multimetallic catalysts

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ABSTRACT

DFT based calculations were employed in the study of the dissociation of the water molecule onto copper and nickel (110) and (111) surface models, incorporating two additional metallic elements, because it was found previously that metal alloying leads to strong synergic effects in the catalysis of this reaction. The dissociation reaction was studied on the Pt/Ru/Ni, Pt/Ru/Cu, Rh/Ru/Cu, Ni/Ru/Cu and Al/Zn/Cu combinations, in a total of 25 trimetallic surfaces. Very low activation energy barriers for the dissociation of water were calculated on several of the surface models, suggesting that multimetallic surfaces can be interesting alternatives for catalyzing the dissociation of the water molecule, which is a crucial elementary step in the water gas shift reaction. Encouragingly, the calculations predict a facile dissociation of the water molecule onto the (AlZn)@Cu(111) catalyst model which is in agreement with recent experimental studies where it was found that a $Cu_{0.5}Zn_{0.5}Al_2O_4$ spinel oxide catalyst holds improved activity for the water gas shift reaction.

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1. Introduction

The catalysts used nowadays in industry, which have been developed mostly by trial and error approaches, are still presenting several drawbacks that must be solved urgently, namely, low activity or selectivity and environmental problems caused by the toxicity of the catalyst components or by the formation of reaction byproducts. In some cases, these byproducts are pollutants that contribute to the greenhouse effect. In addition to the environmental problems, the high cost of catalysts, the high energy consumption and the low reaction yields associated with the catalytic process or difficulties in catalyst recycling are economic factors motivating the search of new catalysts or the optimization of the characteristics of catalysts already in use; this should be done through a rational design of nanostructured materials with improved selectivity and activity for industrial processes.

Novel catalysts based on multicomponent active phases were suggested for catalytic reactions with interesting activity and selectivity. For instance, the steam reforming of acetic acid toward the H_2 generation was studied on monometallic, bimetallic and trimetallic catalysts by Hu et al. [1]. It was found that the trimetallic catalyst based on Cu-Zn-Co is more active than bimetallic and monometallic catalysts composed by these metals because of a synergic effect between the three elements. The better performance of the trimetallic catalyst is due to the suppression of side reactions and avoidance of coke formation [1]. The authors proposed different roles for the metals: Cu suppresses CO formation, possibly via WGS reaction; Zn promotes the enhancement of the catalytic activity especially at low temperature; Co is the main active species in the reforming process [1].

In the case of the CO oxidation, where the O_2 dissociation assumes a critical role, a Pt-Ru-Sn ternary catalyst [2] was found to have larger CO tolerances than previous platinum based catalysts. Sn is deposited by chemical vapor deposition and found to be mostly in an oxide form and located in the vicinity of Pt and of Ru regions. It was suggested that Sn aids the formation of oxygenated species from water dissociation, which migrate to the Pt and Ru rich regions where the CO is strongly adsorbed (CO is not adsorbed on Sn) [2]. Despite these experimental evidences, the exact mechanism at the microscopic level is unknown. In these situations, computational studies are tremendously important since it is possible to compare the energetics of reactions under similar conditions which is ideal to check the most favorable adsorption, diffusion and reaction steps allowing to elucidate the reaction mechanism. High-throughput and combinatorial approaches were used to find multicomponent catalysts for the CO oxidation and water gas shift (WGS) reactions. Using such approaches, it was derived and optimized a new Ru-Co-Ce catalyst for the CO oxidation reaction and also a new Pt-Fe-Ce catalyst with synergic effect among the three components for the WGS reaction [3]. Pt-Ru-Co catalysts [4] were

also checked for the WGS reaction but it was found that the surface composition and the chemical states of the elements in the catalyst drastically change with the reaction moisture and, therefore, improvements are required.

Computational methods are thought for obtaining knowledge in this area of research because they can be used to interpret data arising from on-going experimental studies or to screen new catalysts for a given reaction; this was assumed to be a priority in research by the USA government [5]. This is because computational methods allow with satisfactory accuracy the study, at the atomic level, of active sites on the catalyst models, reaction mechanisms, coverage effects, among other factors that are important to understand the catalytic activity [6,7]. Reactions on solid surfaces have a quite localized character which often allows the representation of particular catalysts with small molecular models, making the problem tractable from a computational point of view. Furthermore, recent advances in computing power enable the study of catalytic reactions on more complex and realistic catalytic models with increasing accuracy [8–11]. Such advances also enable the calculation of full reaction profiles, upon location of intermediate and transition state structures, which is very crucial to understand the activity of a specific catalyst.

Unfortunately, when applied to a large number of systems, such calculations require significant computation times which prevent their use for catalyst screening purposes. Brønsted-Evans-Polanyi (BEP) relationships between the activation energy barrier for a chemical reaction on a catalytic system and a descriptor were suggested for several reactions [6,12–17] occurring both on single transition metal [6,7,12–18] or multimetallic [8,19] surfaces and look very appropriate for fast elimination of low catalytic activity catalyst candidates. Recently, a general relationship was derived for the O—H bond breakage on transition surfaces based on calculations for the O—H bond break in water, alcohols and organic acids [20,21]. The descriptors used in such BEP relationships are quantities that are calculated much more easily than the activation energies, *i.e.*, they require less computational effort with a concomitant speed increase. Thus, descriptors and BEP relationships are thought to be very convenient for the screening of catalysts. Examples of descriptors are the adsorption energies of the reaction products or even the reaction energy (e.g. difference between the energies of the products and the reactants).

The breakage of the first O—H bond in water is the rate determining step (RDS) of the WGS reaction on copper surfaces [18,22]. Here however, the reader should be aware that an elementary reaction step having the highest activation energy barrier is not always granted to be the RDS since several other factors, such as coverage effects, amount of available active sites on the surface, and propensity to occur the reverse reaction, play also important roles in the overall reaction mechanism [23]. The RDS can be defined from the evaluation of the degree of rate control for all the reaction steps as proposed by Campbell et al. in refs. [24,25]. Therefore, the water dissociation may not be the RDS of the WGS on some of the trimetallic surfaces considered in this work.

Under industrial conditions, the WGS reaction proceeds at high and low temperatures on iron oxide stabilized by chromium oxide and on copper catalysts in the form of metal nanoparticles dispersed onto a support [26], respectively. This reaction is very important in the synthesis and steam reforming of alcohols, and can be also useful for cleaning the hydrogen gaseous stream used in fuel cells [27–30]. But the need of high temperatures and the usage of chromium oxide are triggering the search of more convenient catalysts for the WGS reaction. Recently, a ternary catalyst based on the combination of Al/Zn/Cu demonstrated high activity for the WGS reaction at low temperature [31]. In fact, Boumaza et al. found that the $Cu_{0.5}Zn_{0.5}Al_2O_4$ spinel oxide catalyst, because

of its easy reduction, presents a reactivity higher than bimetallic catalysts based on the mixture of copper with other metals.

So, based on these advances, we studied the performance of trimetallic surfaces in the catalysis of the water dissociation reaction. The trimetallic surfaces considered are based on the Pt/Ru/Ni, Pt/Ru/Cu, Rh/Ru/Cu, Ni/Ru/Cu and Al/Zn/Cu ternary combinations because pure Pt, Ru, Ni and Rh were proposed as very reactive metals for the water dissociation [6] and Cu, a cheap metal, is the active metal in the industry catalysts for the WGS at low temperature.

2. Catalyst surfaces models and computational details

2.1. Slab models

Trimetallic catalyst models were generated by the substitution of atoms of a monometallic surface slab (matrix), either from copper or nickel, with atoms of two other metals. In the case of the copper and nickel slabs, (111) and (110) surface terminations were chosen as examples of flat and combed surfaces, respectively. The (111) Miller index is the most stable for the surfaces of these two metals. The (110) surfaces present low coordinated atoms which usually increase the surface reactivity toward water dissociation [6,8,20]; thus, the effect of the low coordinated atoms will be also determined for the trimetallic catalysts. Substitutions of matrix atoms by dopant atoms of the elements Pt, Ru, Rh, Al and Zn were done only in the top layer to yield the Pt/Ru/Ni, Pt/Ru/Cu, Rh/Ru/Cu, Ni/Ru/Cu and Al/Zn/Cu ternary combinations. For comparison purposes, a surface slab corresponding to the (100) Miller index was also considered for the most reactive Al/Zn/Cu ternary combination.

The surfaces of these trimetallic catalysts were based on 3×3 slabs (with respect to the minimal unit cell of Cu(111), Ni(111), Cu(110) or Ni(110) surfaces), with thickness corresponding to four metallic layers. In the case of the (111) flat termination, two different models were obtained for each combination of trimetals, *i.e.*, a slab where the dopant atoms are in direct contact (Fig. 1a) or surrounded by atoms of the matrix (Fig. 1b), while in the case of the combed (110) termination, three different catalyst models were considered, *i.e.* models with the two dopant atoms separated in different combs (Fig. 1c) or with the two dopant atoms separated (Fig. 1d) or in direct contact (Fig. 1e) in the same comb. Therefore, for each combination of three metals, five different catalyst possibilities were explored in this work. The different possibilities for molecular adsorption on each model are shown in Fig. 1.

2.2. Computational details

Adsorption energies, activation energy barriers and reaction energies for the water dissociation reaction ($H_2O^* \rightarrow OH^* + H^*$) on the trimetallic catalyst models considered in this work were determined from spin-polarized periodic DFT calculations with the VASP [32–34] computer code. The PW91 generalized gradient approach (GGA) exchange correlation potential [35] was used to compute the electron density and the projected augmented-wave (PAW) method [36,37] was considered to take into account the effect of core electrons in the valence electron density. Valence electronic states were described using a set of plane waves with a cutoff set to 415 eV. A $7 \times 7 \times 1$ Monkhorst-Pack grid of special k-points [38] was considered for the numerical integration in the reciprocal space. The convergence of the results with respect to plane wave cutoff and Monkhorst-Pack grid was checked for some selected adsorption positions on the different catalyst models. PW91 density functional was chosen to permit a direct comparison with results obtained for the water dissociation on monometallic and bimetallic catalysts [6,9] and also due to its good performance in the study of the RO—H bond cleavage on metallic surfaces [21]. Also, the PW91