A DFT sight of oxygen and carbon monoxide coadsorption on Pt-alloy surfaces

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***Abstract*— Coadsorption of oxygen (O) and carbon monoxide (CO) on Platinum-alloy (Pt-alloy) surfaces is investigated by using density functional theory (DFT). Simultaneous coadsorption and alloying are considered in order to get more realistic picture of the electrode condition, i.e., in relation with surface CO tolerant. Significant changes on the most stable configuration for coadsorption of O and CO on PtRu- and PtRuMo-alloy surfaces to that of individual atomic O or pure CO chemisorption are observed. It is found that the pre-covered O surface weakens the adsorption strength of CO on surfaces. However, the influence of coadsorbed O, i.e., bifunctional effect, is significant on monometallic Pt surface and reduces by alloying Pt with Ru. Further alloy with Mo forming PtRuMo causes the bifunctional effect is very similar to that of electronic effect, i.e., pure CO chemisorption on PtRuMo-alloy surfaces.**

Keywords- O and CO Coadsorption; Pt-alloy surfaces; DFT; bifunctional and electronic effect

I. INTRODUCTION

One of the most important catalytic reactions and the simplest reactions is CO oxidation. The importance of such reaction can be seen in major reactions of car exhaust catalytic converters and issue of poisoning effects in catalysis, which is usually observed on fuel cells containing CO species, e.g., direct methanol fuel cells (DMFCs), or the cell designed to operate on reformed methanol. CO poisons many catalytic reactions involving transition metal active sites due to its strong bonding with such sites. Accumulation of CO on the catalysts thus impedes the cycle processes on the related reactions and finally reduces the device performance. Hence, it is not surprising that CO removal from metal catalysts by CO oxidation attracted many researchers to study such catalytic reactions [1-3]. A general technique to catalyze the CO removal from surfaces is the use of alloy catalysts such as PtRu [4] or PtNi [5] alloys, called electronic effect by alloying, which are believed to increase CO tolerance. Considering technological applications such as anode DMFCs, where CO is formed and further oxidized, a recent study showed that PtRuMo give better performance for this process [6]. In relation with this work, we focus on the fundamental part of CO oxidation, i.e., the interaction of CO + adsorbed oxidant with surface catalysts. It is believed that oxygen (O) responsible for facilitating CO oxidation [7], which is then called bifunctional mechanism.

The CO oxidation is one of the heterogeneous reactions and can be regarded as a benchmark system. The generally accepted mechanism of CO oxidation is called Langmuir-Hinshelwood mechanism [8]. In this mechanism, both reactants adsorb on surface followed by diffusion toward each other (or one reactant to the other) to form products, and finally the product desorption from the surface. One of the elementary reaction steps in this mechanism with respect to the CO oxidation is the surface reaction between CO and O, i.e., the case of CO oxidation with O. This CO oxidation resulted in desorbed carbon dioxide (CO_2). It is well known that reaction between CO and an adsorbed oxidant on the surface depend on adsorption energy of both species [2, 9-11]. Therefore, it is necessary to discuss the adsorption energy of the species under the presence of coadsorbates. In this work, we focus on the stable structure of CO and O coadsorption on Pt, PtRu, and PtRuMo surfaces before CO oxidation reaction. The role of Ru and Mo in determining the stable configuration is observed.

This paper is organized as follows. Section 2 presents computational details relevant to this work. Results mainly with regard to interaction of CO/O/surfaces are presented in Section 3. Finally, Section 4 gives concluding remarks.

II. COMPUTATIONAL DETAILS

Periodic plane-wave DFT calculations are carried out to explore the coadsorption of O and CO on surfaces. The inner cores and electronic states are modeled with pseudopotentials within the framework of the projector augmented wave (PAW) method [12]. A plane wave basis set with cutoff kinetic energy of 400 eV is used in order to get total energy convergences. A generalized gradient approximation (GGA), with the exchange-correlation functional of Perdew, Burke, and and Ernzerhof (PBE) [13, 14], is used. Brillouin-zone integration is performed by Monkhorst-Pack [15] sampling mesh of (5x5x1) k-points using Methfessel-Paxton smearing [16] of $\sigma = 0.2$ eV.

We consider three surfaces, i.e., a pure Pt-, a PtRu-, and a ternary PtRuMo- surface. All these surfaces are fcc (111), represented as three layer slabs, which has been tested to be sufficient in describing Pt bulk system. Each slab was

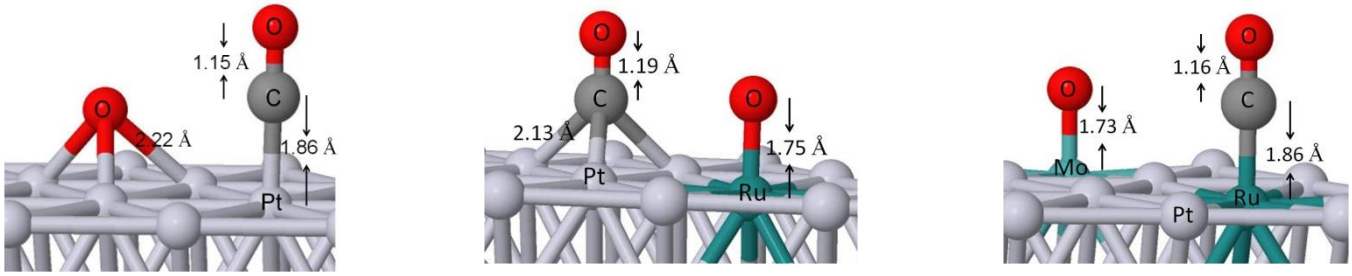
separated by a vacuum of 15 Å in order to minimize the interaction among neighboring slab. Each layer is consisted of 16 atoms in a (4 x 4) unit cell. Preliminary calculation with respect to convergence test of slab thickness and k-points is established. Geometry optimizations (relaxation) are converged to a maximum 0.05 eV/Å of residual atomic force. Because adsorption is made on one side of the slab, we considered also dipole moment correction through calculations [17]. Considering the Pt:Ru:Mo atomic ratio in the experiments [18] and a theoretical study of surface segregation energy of alloys' components [19] with Pt host metal; we construct alloy surfaces by substituting Pt atom on the Pt surface by Ru and Mo [20] which will be used as catalyst materials in this work. All calculations are performed by using the Vienna ab initio Simulation Package (VASP) [21-23].

III. Results and Discussions

We use the large surface model in simulating coadsorption of O and CO since experimental results showed that CO is observed on *p*(4x4) or *p*(8x8) of Pt(111) surfaces at low CO coverage [24]. In the smaller cell it is reported to provide dilution to calculate the isolated CO adsorption energy [25]. Thus we use (4x4) cells with total coverage of 1/8 ML, i.e., the same coverage of 1/16 ML for both O and CO. These large unit cells are also required to provide more adsorption sites for O and CO coadsorption on binary PtRu and ternary PtRuMo surfaces. Both coadsorbates and all atoms in the first layer are allowed to relax in describing coadsorption processes in order to find their preferential sites. Based on previous research, interaction of O and CO is more pronounced due to the effect of surface relaxation [26]. However, under coadsorption of O and CO, both of coadsorbates pull out the surface atom on which they adsorbs, the surfaces become flatter (see **Fig**. **1**).

CO on O/surface is 1.58 eV, i.e., 0.34 eV weaker than that of CO single molecule on Pt-surface. In our calculation, firstly, individual atomic oxygen is located at all possible adsorption sites, but it is stable only on top, hcp-, and fcc- hollow sites. At bridge site, it is unstable and tends to move to other stable site, i.e., fcc-hollow site. Our calculation shows that the most favorable site for oxygen adsorption on Pt(111) is the fcc, with binding energy of 4.81 eV, which is in an excellent agreement experiment [29] and other DFT calculations [26, 30]. Furthermore, on the O/Pt-surface, CO absorbs preferentially atop Pt site. The most stable position of CO adsorption on O/Pt-surface is different with adsorption on the clean Pt using GGA approximation, i.e., hcp-hollow site.

Alloying Pt with Ru causes the preferential binding configuration of O and CO coadsorption is changed to a position as shown in **Fig**. **1** (**b**), i.e., O and CO prefer atop Ru and fcc-holow site respectively. CO binding energy in this coadsorption system is 1.61 eV. Indeed, the coadsorption affects the weakening of CO binding energy by 0.26 eV relative to the alloying effect[31]. However, our calculation shows that alloying Pt with Ru weakens the Pt-C interaction by 0.05 eV. This result gives smaller effect than the reduction of Pt-CO binding energy obtained by Ge et al[32]. This may be caused by the choice of Ru coverage. The oxygen adsorption site in this system is different with individual atomic oxygen adsorption on the same PtRu surface, while CO binding site is still maintain the original site. For individual O on PtRu, the oxygen favors on bridge Pt-Ru site, while individual CO molecule adsorbs on the Pt-Pt-Pt fcc-hollow site. The calculated adsorption energy of individual atomic oxygen on PtRu surface is 5.16 eV. Furthermore, on the PtRuMo surface, the most favorable site for O and CO coadsorption is as depicted in **Fig. 1** (**c**). Several possible coadsorption sites are examined, and the minimum energy of the system is obtained for CO atop Ru



(**a**) (**b**) (**c**)

Fig. 1 The most stable configuration of O and CO coadsorption on (**a**) Pt, (**b**) PtRu, and (**c**) PtRuMo surfaces

Fig. **1** shows the most stable configuration of O and CO coadsorption on Pt, PtRu, and PtRuMo surfaces, i.e., structure with the minimum energy. On the pure Pt surface, the preferential sites for CO and O coadsorption are atop Pt and fcc site, which is in a good agreement with experiment [27] or theoretical calculation [28]. In the case of coadsorption of O and CO on surfaces, the binding energy of CO on O-covered surface is formulated as $E_{CO/surface+O} = E_{tot} - (E_{surface+O} + E_{CO})$, where E_{tot} is the total energy of the whole system, $E_{surface+O}$ indicates the total energy of surface with individual chemisorbed O, and E_{CO} represents the CO free energy in the gas phase. The calculated adsorption energy of

and O atop Mo. The CO binding energy on O-covered PtRuMo is 2.09 eV. This binding energy is weaker by 0.09 eV compared to the case of single CO molecule on PtRuMo with CO adsorption site moves from hollow to top Ru by the presence of O/surface. On the other hand, O adsorption site in the coadsorption system is not move from the original position of individual O on PtRuMo. Here, the adsorption energy of oxygen on PtRuMo is 5.97 eV. From the structural geometry, the shorter bond distant between O and surface is very apparent on the PtRuMo, indicating the stabilization of atomic O by Mo.

In order to understand the CO chemisorptions on O/surfaces(111), we calculated a local density of states at CO from Pt-(O+CO), PtRu-(O+CO), and PtRuMo-(O+CO). **Fig. 2** displays the LDOS around CO on three O/surfaces. The solid black line represents the two π-bonds of isolated CO molecule. Interaction of the 2p-states of Carbon with metal d-states plays important role in the chemisorptions systems. Upon interactions, this state hybridized with the surface sp- and d-band. The two main broad peaks are observed in the presented LDOS which can be attributed to bonding and anti-bonding states.

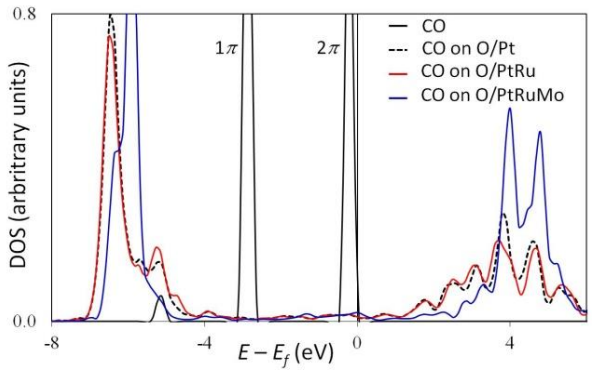


Fig. 2 LDOS around CO on O/surfaces

Derived anti-bonding states shifts further to right with the alloying, i.e., the position with higher energy, implying more vacant in this state caused by electron transfer to the bonding metal-C region. This explains why the bonding strength between CO and O/PtRuMo is higher than that of O/PtRu. Thus, compared to the LDOS of individual CO on PtRu and PtRuMo surfaces, the intensity of Mo anti-bonding states in coadsorption system is much higher than that of single molecule adsorption. This tells us less charge vacancy to be transferred to the metal-C bonding region resulting in weaker binding energy. It may be caused by atomic O, because of its high electronegativity, withdraw some electrons. Further analysis with Bader charge difference[33], oxygen in the coadsorption system plays significant role in withdrawing charge. In CO/O/Pt, atomic O gets 0.70e^- while CO is only transferred by 0.06 e^- of charge. Thus, in the system of CO/O/PtRu, atomic O obtains 0.73e^-, while the charge transferred to CO is only 0.28e^-. Furthermore, CO/O/PtRuMo, atomic O gains 1.12 e^- and the charge transferred to CO is 0.30e^-. This situation may explain the bond distant of Mo-O is shorter by 0.02 Å than Ru-O in the O and CO coadsorption. In general, the presence of oxygen in the coadsorption affect more significant to the CO binding energy on monometallic surface, and does not weaken significantly on alloying metal surface. These results drive to the conclusion that bifunctional mechanism is more effective in the pure Pt surface.

IV. CONCLUSION

Coadsorption of O and CO on Pt, PtRu, and PtRuMo (111) surfaces has been investigated. The most stable configuration of O + CO on these three metal surfaces is obtained. The effect of O coadsorption on the weakening CO binding energy on the surfaces is clarified. The presence of atomic O may cause some electron attraction in the coadsorbed systems, resulting in the weakening CO-surfaces binding energy. However, the influence of coadsorbed O is significant on monometallic Pt surface and it reduces by alloying Pt with Ru. The addition of Mo forming ternary PtRuMo surfaces causes the effect of coadsorbed O, called "bifunctional effect", is very similar to that of "electronic effect", i.e., pure CO chemisorption on PtRuMo.

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