

Differentiating electro-catalytic reaction of hydride with respect to a non-Pt catalyst morphology based on first-principles: extended surfaces versus nanoparticles

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ABSTRACT

We conducted first-principles electronic structure calculations and *ab-initio* molecular dynamics (MD) based on density functional theory (DFT) to obtain the fundamental electrocatalytic properties of a hydride (borohydride) adsorption on a non-Pt catalyst (Osmium) with respect to catalysts' facet and morphology. We found that the binding energy and the structure of the borohydride change with respect to the Os-2nm facets: $(10\bar{1}0)$, $(1\bar{1}00)$, (0001) . These fundamental properties can predict the reactivity of such facets under electrochemical environment. We note that the electro-catalytic activity of the Os decreases in the following order: $(10\bar{1}0) > (1\bar{1}00) > (0001)$ following the same trend in the binding energies. With respect to the catalyst morphology (extended surface vs nanoparticle), the reactivity is predicted by the combined effect of the strength of interaction of both the borohydride and the water molecule. On the otherhand, the size of the nanoparticle is found to affect the binding energy of the borohydride via the significant change in the nanoparticle structure due to temperature. These results are seen to provide valuable insights in the design of new catalysts systems for borohydride oxidation as well as in the modeling of nanoparticle catalysts under electrochemical conditions.

Keywords: non-Pt catalyst, borohydride oxidation, density functional theory, electronic structure and molecular dynamics calculations, electrocatalytic activity

1 INTRODUCTION

One of the attractive hydride compounds is the borohydride, which exhibits high hydrogen content in the NaBH_4 form (i.e. ~10.6 wt%) [1]. Thus, significant number of research has been devoted to investigate its applicability for energy conversion and storage, both in terms of direct electricity generation from the borohydride anodic fuel in the direct borohydride fuel cell (DBFC), which is a promising alternative microfluidic device to batteries and to direct methanol fuel cell (DMFC) and in terms of hydrogen generation via the hydrolysis reaction: $\text{BH}_4^- + 4\text{H}_2\text{O} =$

$\text{B(OH)}_4^- + 4\text{H}_2$, where the hydrogen can be supplied to a polymer electrolyte fuel cell (PEFC). Recently, a non-Pt catalyst (Osmium) for borohydride is used in the DBFC anode, yielding very high mass-specific activity of about 1240 A g^{-1} [2,3]. The wide application of this hydride in energy and catalysis and the feasibility of using non-Pt metal as catalyst necessitate atomic level information regarding surface-bound structures of borohydride and electrochemical reactions such as oxidation. To obtain this information, we performed first-principles calculations based on density functional theory (DFT).

In the implementation of the first-principles electronic structure calculations and *ab-initio* molecular dynamics (MD) [4-6], the fundamental information on the hydride structure as a function of catalysts' morphology and facets are determined. Moreover, we discuss important features of computational methods used in modeling nanoparticles under electrochemical environment.

2 COMPUTATIONAL PROCEDURES

The theoretical work conducted to study the electrocatalytic activity of borohydride molecule on different Os nanoparticle (NP) planes is based on DFT, which is implemented in Vienna Ab-initio Simulation Package (VASP) [7-10]. The exchange-correlation function is described by the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [11] and the ion-valence electrons interaction is treated using projector augmented wave method (PAW) method [12, 13]. Plane-wave expansions are conducted within kinetic energy cut-off of 400eV.

Regular polyhedral structures such as cuboctahedral, icosahedral, octahedral and hexagonal closed packed or HCP are the most commonly used models for 5d transition metals [14-17]. Due to the hcp structure of Os, the hexagonal closed packed (HCP) is considered. Moreover, because of the higher probability of existence and stability of closed shell structures with the magic number of atoms, then the Os NP with magic numbers: 57, 89 and 214 corresponding to a diameter of ~1.0nm, ~1.5nm, ~2.0nm are used. Using these sizes to represent the NPs, the nanoparticles are labeled as Os-1nm, Os-1.5nm and Os-2nm. The NPs are optimized using supercells with very

large vacuum of $\sim 25\text{\AA}$, which separates the nanoparticle from that of the neighboring cells. The Γ -point is employed for the Brillouin zone integration. All binding energies are obtained using the following expression:

$$E_{b-NP} = E_T - (E_{NP} + E_a) \quad (1),$$

where E_T is the total energy of the adsorbed system, E_{slab} is the total energy of the bare nanoparticle and E_a is the total energy of the molecule in gas phase.

The above methods pertain to the electronic structure part of the computation. In the case of the *ab-initio* molecular dynamics approach conducted to draw implications of temperature on adsorption, we performed simulated annealing via *ab-initio* molecular dynamics (MD). Here, the systems are equilibrated at high temperature of 1100K and cooled to 300K. The equilibration is conducted using microcanonical MD with timestep of 2 fs and MD steps of 2000. The residual minimization method (RMM-DIIS) [18,19] is used for the electronic minimization. The relaxation of the electronic degrees of freedom is terminated with 10^{-4} energy change is attained.

3 RESULTS AND DISCUSSIONS

The initial borohydride adsorption is first evaluated for (0001) plane of Os-2nm. Using reaction (2) below, the final adsorption configuration of the generated specie (molecular borohydride) associated with (0001) plane can be obtained.



Here, we note that at this facet, the most stable configuration is molecular. The reaction equation (2) also indicates that an e^- charge is transferred to the electrode upon borohydride adsorption. Next, by taking into account a solution phase, we can modify this reaction by allowing solvation of the ion, $BH_4^-_{aq}$ and also water molecule substitution upon oxidative adsorption as given in the following:



to obtain the change in the Gibbs free energy of the initial oxidative adsorption as a function of electrode potential:

$$\Delta G_{ads} = G_{BH_4^*} + G_{H_2O_{aq}} - G_{BH_4^-_{aq}} - G_{H_2O^*} - eU \quad (4)$$

where U is the electrode potential on the vacuum scale.

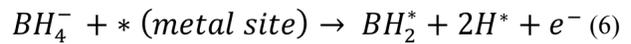
The free energy of the adsorbed species, G_{A^*} (where $A^* = BH_4^*, H_2O^*$) is the ground state energy, E_{DFT} adjusted by adding zero-point vibrational energy (E_{ZPVE}) and vibrational entropy ($S_{vib}T$) terms:

$$G_{A^*} = E_{DFT} + E_{ZPVE} - S_{vib}T \quad (5)$$

where $T = 298K$

Next, the free energy of the solvated species, A_{aq} (i.e. $BH_4^-_{aq}, H_2O_{aq}$), is obtained by the inclusion of solvation, ΔG_{sol} as taken from literature [20, 21].

The initial oxidative adsorption in the other facets entails determination of the change in the Gibbs free energy for different adsorption configuration of borohydride (dissociated). For instance, in the (10 $\bar{1}$ 0) and (1 $\bar{1}$ 00) planes of the Os-2nm, the reaction (2) becomes:



and the G_{A^*} for equation (5) is adjusted consistent with the E_{DFT} , E_{ZPVE} and $S_{vib}T$ for the $BH_2^* + 2H^*$ structure. We note that the binding energy of borohydride on all planes (or facets) of Os-2nm are: -5.71eV (10 $\bar{1}$ 0) > -5.61eV (1 $\bar{1}$ 00) > -5.33eV (0001). We further note that the adsorption configuration on (0001) is different from that of (10 $\bar{1}$ 0) and (1 $\bar{1}$ 00) planes yielding some differences in E_{ZPVE} and $S_{vib}T$. Thus, there is a significant influence of the strength and outcome of the interaction of the planes with the borohydride (i.e. binding energy and final configuration) on the ΔG_{ads} . The figure below shows the differences in the change in Gibbs free energy as a function of electrode potential for different facets of Os-2nm.

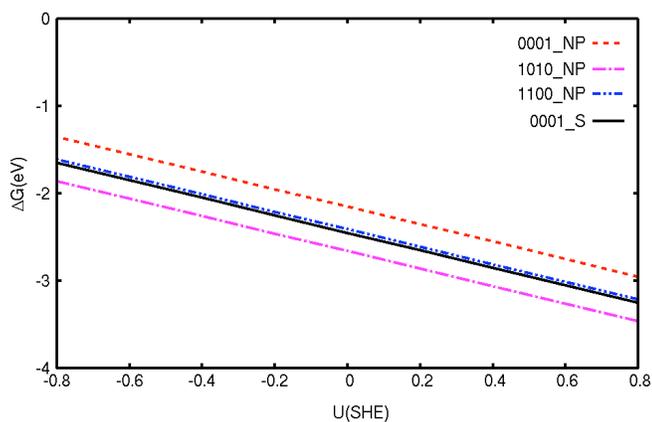


Figure 1: The change in Gibbs free energy as a function of electrode potential shifted with respect to standard hydrogen electrode (SHE) for different facets of Os-2nm. Also included is the plot of such change in Gibbs free energy for extended surface morphology.

It can thus be noted that the most active facet is the $(10\bar{1}0)$, followed by the $(1\bar{1}00)$ and then the (0001) . This trend follows the same binding energy sequence for the borohydride on the nanoparticle facets. Therefore, it can be noted that the initial oxidative adsorption defined in reaction (2) or (6) can be well predicted by the adsorption energy of the borohydride. Further, it can be argued that the initial oxidative adsorption of borohydride on an entire nanoparticle can be properly described or modeled by either the combined effect of all the planes or by the effect of one or two planes which exist in greater proportion. The sole use of clean metal slab of a particular facet (no defects such as kink or steps) to model initial oxidative adsorption process on a nanoparticle may not be fully adequate.

Another important feature of the conduct of the study on the fundamental properties of the initial oxidative adsorption of borohydride on the Os is the difference between the modeling methods employing slabs and that of the cluster. In Figure 1, we note that the relationship of the change in Gibbs free energy with the electrode potential for the surface of Os $\{(0001)$ is chosen} does not coincide with that of the (0001) of the nanoparticle. The mere binding energy of the borohydride also does not explain this difference since, as we have noted, the adsorption is stronger for the nanoparticle than on the surface. Further investigation into the initial oxidative adsorption on borohydride as described in reaction (3) indicates that another specie (water) played an important role. We found that an increase in the water-metal interaction strength leads to a decrease in the change in the Gibbs free energy for the reaction (3) despite a strong borohydride binding energies. This case is observed for the Os nanoparticle vs extended

surface of the same facet. Thus, we propose looking into the effects of both the facets (for the nanoparticle) and the morphology (nanoparticle vs extended surface) in describing theoretically the reactivity of a catalyst under electrochemical environment.

Lastly, using the *ab-initio* MD to draw the effect of temperature on the catalysts morphology, we note that after annealing to 1100K and cooling down to 300K, the structure of all the nanoparticles : Os-1nm, Os1.5nm and Os-2nm has changed significantly as compared to the DFT-optimized structure, which is at 0K. To wit, these changes include the protrusion of the corner atoms and buckling (or bending) of bonds formed from the corner and the edge atoms. One of the conjectures of these observations is the enhancement of the reactivity due to the protrusion of the corner atoms. Also we note that these changes in the geometry of the nanoparticles due to temperature is more profound for the smaller sized ones.

4 CONCLUSION

We conducted first-principles electronic structure calculations and *ab-initio* molecular dynamics (MD) based on DFT to obtain the fundamental information on the hydride electrocatalytic activity as a function of catalysts' morphology and facet. We found that the binding energy of the borohydride on the Os-2nm facets can predict the reactivity of such facets under electrochemical environment. We note that the electrocatalytic activity of the Os, described by the initial oxidative adsorption reactions above, decreases in the following order: $(10\bar{1}0) > (1\bar{1}00) > (0001)$. With respect to the catalyst morphology (extended surface vs nanoparticle), the reactivity is predicted by the combined effect of the strength of interaction of both the borohydride and the water molecule. These results are seen to provide valuable insights in the design of new catalyst systems for borohydride oxidation as well as in the modelling of nanoparticle catalysts under electrochemical conditions.

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