

## Computational Study on Reduction Potential of $[\text{CoP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$ as a Super-Efficient Catalyst in Electrochemical Hydrogen Evolution

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Hydrogen is considered as a unique choice for future world's resources. The important parameter in the process of hydrogen production is the value of reduction potential for the used catalyst, in direct contact with consumed energy in process. The application of computational methods to design and modify molecular catalysts is highly regarded. This study sought to explore *Density Functional Theory* (DFT), employing an effective core potential basis set (LanL2DZ) for metals, as an applicable method used to calculate molecular geometries and electronic structures of the redox forms of two new super-efficient catalysts,  $\text{CoP}_4\text{N}_2$  and  $\text{FeP}_4\text{N}_2$ . The reduction potential related to  $\text{CoP}_4\text{N}_2$  catalyst in the presence of water solvent is measured using a reference isodesmic reaction. The calculated data revealed that obtained theoretical value for the reduction potential of catalyst, -0.58V, is in an excellent agreement with its experimental value, -0.50 V. The results confirmed that water molecules coordinated with Co or Fe core in catalyst structure play the main role in  $\text{H}_2$  gas production.

**Keywords:** Theoretical reduction potential, Hydrogen evolution, Isodesmic reaction, Molecular catalyst

### INTRODUCTION

In the recent era, limited resources of fossil fuels and their polluting effect on the environment have induced scholars to conduct a series of studies in search for alternative renewable resources [1,2]. Among these alternatives, hydrogen with a high energy density and as a clean energy carrier is proposed to be one of the best candidates to be used as future fuel [3-7]. One the best ways to produce hydrogen with no sulfur or carbon pollution is found to be Electrolysis [8,9]. Additionally, one of the most noticeable topics in the electrolysis system is presumed to be decreasing the value of consumed electrical energy, which is directly related to over-potential value in production process. A great deal of studies, therefore, focused on introducing efficient materials employed for decreasing the performed electrical potential [10-12].

Platinum is a unique catalyst for hydrogen evolution

reaction. However, the high price and limited sources of platinum are serious obstacles to employ it in large-scale production process. To overcome these limitations, molecular catalysts based on the earth-abundant materials, *i.e.* non-precious metal complexes, have been employed [13-15]. These catalysts were used in various solvents including non-aqueous and aqueous solutions [16-18]. Recently, cobalt complexes such as, cobaloximes [19] and cobalt dithiolene complexes [20-22] have been detected to evolve hydrogen with low over-potential.

Theoretical investigations can be performed to calculate the reduction potentials and to shed light on the mechanism of production reactions [19,23-26]. Electronic structure methods can indicate the thermodynamic values with a good accuracy. For a reduction reaction shown in Eq. (1), the standard potentials can be obtained using frequency calculations and discovering the Gibbs free energies related to the evolution reaction given in Eq. (2),

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$$E^0 = - \frac{\Delta G_{solv}^0}{nF} \quad (2)$$

where  $Ox_{solv}$ , and  $Red_{solv}$  are oxidized state and reduced forms of catalyst in solvent phase and  $\Delta G_{solv}^0$ ,  $F$ , and  $n$  are the Gibbs free energy difference of species related to Eq. (1), Faraday constant and the number of electron transferred, respectively [27,28].

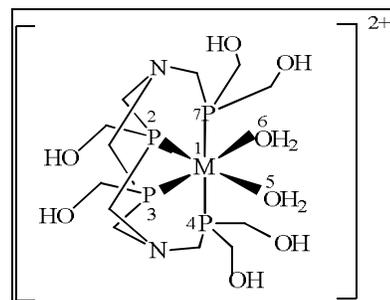
The experimental reduction potentials are reported based on a reference electrode, usually Normal Hydrogen electrode. Hence, to calculate the theoretical reduction potentials, the absolute value for the reduction potential of reference electrode, Eq. (3), is needed [19].



The Gibbs free energies for electron and proton come from Fermi-Dirac in which usually the absolute values for electron and proton are -0.868 and -266.5 kcal mol<sup>-1</sup>, respectively [29,30]. Because of inexact values considered for electron and proton free energies, the results obtained through the aforementioned direction seems to be unsatisfactory. To overcome this problem, one can model a suitable isodesmic reaction as a reference reaction and calculate the reduction potential values by using one of the experimental values as a reference value. Employing this approach yields more exact values due to elimination of the electron and proton effect [30].

Recently,  $CoP_4N_2$  and  $FeP_4N_2$  complexes, schematically shown in Fig. 1, were discovered as two efficient catalysts for hydrogen evolution reaction in neutral water. The  $CoP_4N_2$  catalyst with an over-potential as low as 89 mV was recognized to be a super-efficient catalyst for the  $H_2$  generation [22].

The current study attempts to present a theoretical investigation of hydrogen production reaction in the Presence of  $CoP_4N_2$  and  $FeP_4N_2$  catalysts. The electronic structures of two catalysts,  $CoP_4N_2$  and  $FeP_4N_2$  were calculated in different possible spin states to find the most stable spin state. Then, their corresponding production reactions were closely studied in an attempt to find out whether or not water molecules coordinated to the center metals play the main role in production process of hydrogen gases. The reduction potential of hydrogen evolution



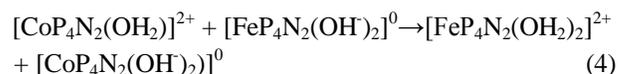
**Fig. 1.** Schematic representation of  $CoP_4N_2$  and  $FeP_4N_2$  structures,  $M = Co$  or  $Fe$ .

reaction, catalyzed by  $CoP_4N_2$ , was calculated using the Gibbs free energies which is dependent on the redox species of these two catalysts and modeling an isodesmic reaction which is compatible with this system.

## COMPUTATIONAL DETAILS

Quantum mechanical calculations were carried out with the Gaussian program series 2003 [31]. Hybrid Hartree-Fock density functional scheme, the adiabatic connection method, and Becke three-parameter with Lee-Yang-Parr (B3LYP) functional [32-34] of *Density Functional Theory* (DFT) were employed to optimize all redox species using LanL2DZ (Los Alamos National Laboratory 2 double  $\zeta$ ) as effective core potential basis set for transition metals and 6-31G basis set for all other atoms. The optimized geometries of catalysts in gas phase were re-optimized in solvent phase with the conductor-like polarizable continuum model (C-PCM) [35,36] using Bondi radii [37] for comparison of the structures in gas and solvent phase. Frequency calculations were performed on optimized structures to take/calculate the Gibbs free energies of redox species. The reduction potential was calculated using Gibbs free energies as given in Eq. (1). All calculated Gibbs free energies include zero-point energy and thermal correction contributions.

To reach the accurate value of reduction potential for hydrogen evolution reaction catalyzed by  $CoP_4N_2$ , an isodesmic reaction (Eq. (4)) was modeled using two reactions related to reduction of catalysts (Eqs. (5) and (6)).





Considering isodesmic reaction is suitable for accounting systematic errors and providing quantitatively accurate reduction potentials. In addition, calculation of reduction potentials using an isodesmic reaction has an advantage which avoids us to consider the determining quantities such as the free energies of the gas-phase electron and proton and the solvation free energy of the proton [38,39].

## RESULTS AND DISCUSSION

### Geometry Optimization of Redox Specious

The oxidized structures of catalysts,  $[\text{CoP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$  and  $[\text{FeP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$ , were fully optimized at different spin states, without imposing any symmetry constrain, at the UB3LYP/6-31G/LanL2DZ level. Different possible spin states of core metals might be very critical point that should be considered in optimization step. Figure 2 illustrates the optimized structures of 4 redox specious including  $[\text{CoP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$ ,  $[\text{FeP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$ ,  $[\text{CoP}_4\text{N}_2(\text{OH})_2]^0$ , and  $[\text{FeP}_4\text{N}_2(\text{OH})_2]^0$ . The structural details of  $[\text{CoP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$  and  $[\text{FeP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$  catalysts are reported in Table 1.

As clearly seen in geometries of species, Fig. 2 and Table 1, the structures appear to be similar to an octahedral structure. According to the structural details of two catalysts, the bond distances between Co or Fe metal and phosphors corroborate our findings in previous experimental studies [40,41]. Meanwhile, the values of P-Co-P, O-Co-P, and O-Co-O binding angles, which were about  $90^\circ$ , confirm the presence of an octahedral configuration for two catalysts.

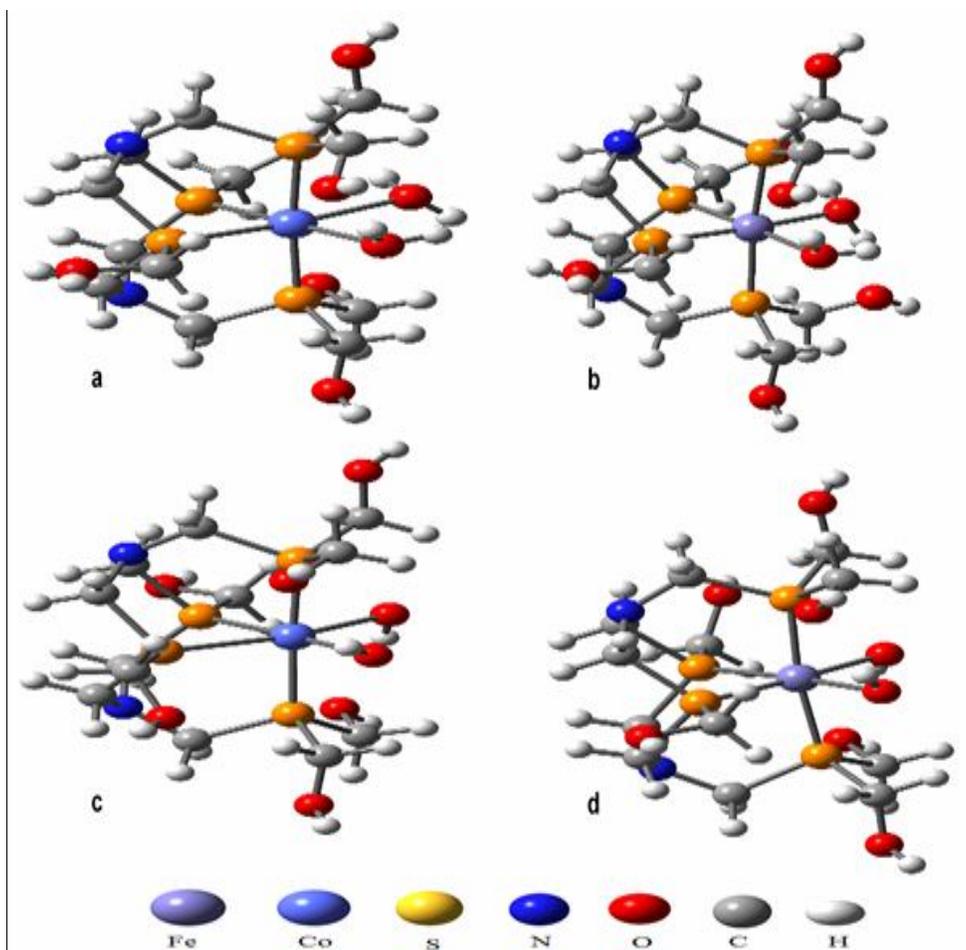
The structures optimized in gas phase were re-optimized in solvent, water, using the conductor-like polarizable continuum model [14] (C-PCM) including non-electrostatic interactions resulting from dispersion, repulsion, and cavity formation. The structural details were not changed significantly in solvent phase compared to those in the gas phase. Solvation energies of  $[\text{CoP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$  and  $[\text{FeP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$  catalysts were calculated at the UB3LYP/6-31G/LanL2DZ level. The values obtained for both

structures were found to be equal (about  $-138 \text{ kcal mol}^{-1}$ ). This closeness might imply that the solvent effect can stable both structures similarly. Hence, to reduce the CPU time, the calculations for other cases were performed only in the gas phase.

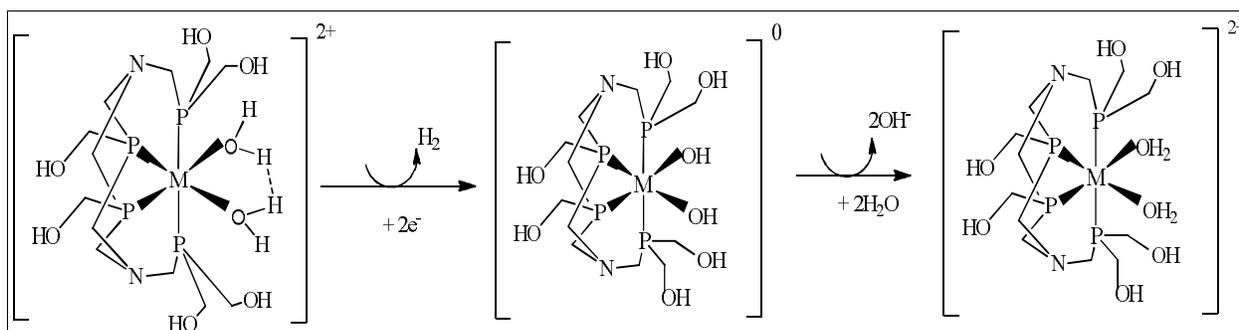
Based on assumption taken in experimental study [22] for the nature of hydrogen production in the presence of these catalysts, the water molecules coordinated to the Fe or Co core have the main role in hydrogen evolution. Regarding this assumption, it might imply that OH groups, on ligands, do not play any considerable role in production course. So, the catalyst appears to rebuild itself when the evolution process is finished. As Fig. 3 indicates, due to weak O...H bonds in water molecules, they are able to produce hydrogen gas. Every two water molecules coordinated in catalyst structure seem to participate in reaction to produce one hydrogen molecule. So, the reduced conjugates of these catalysts were optimized at the same levels used for their oxidized states (see Fig. 2). The Co or Fe core has an octahedral coordinated structure, resulted from interaction with phosphors groups of tetra dentate phosphine ligand (see Fig. 1) and two water molecules come from water solvent environment.

### Calculation of Gibbs Free Energies and Reduction Potential

Trying to find the reduction potential value for hydrogen evolution reaction, a suitable isodesmic reaction [27], based on this system, was drawn. Since type and number of bonds at two sides of the reaction should be similar, we considered the subtraction of Eqs. (5) and (6) as the reference reaction to find the reduction potential. The reduction potential values in the experimental article were referred to *Normal Hydrogen Electrode*, NHE. So, the calculated values using this isodesmic reaction was assumed to refer to the reference electrode employed in experiment, NHE. Using UB3LYP functional with mixed 6-31G and LanL2DZ basis sets, the Gibbs free energy of the employed isodesmic reaction (see Eq. (4)) was measured to be  $-20.67 \text{ kcal mol}^{-1}$ . The values of Gibbs free energies, enthalpies, and electronic energies of four redox specious which include zero-point energy and thermal correction contributions, except for reported electronic energies, are depicted in Table 2. These values are needed to calculate the Gibbs free energy of



**Fig. 2.** Optimized structures of four redox species, a)  $[\text{CoP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$ , b)  $[\text{FeP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$ , c)  $[\text{CoP}_4\text{N}_2(\text{OH})_2]^0$ , and d)  $[\text{FeP}_4\text{N}_2(\text{OH})_2]^0$  (d) using UB3LYP/6-31G/LanL2DZ method.



**Fig. 3.** The reaction of  $\text{H}_2$  evolution in the presence of catalyst in water solvent.

**Table 1.** The Structural Details of  $[\text{CoP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$  and  $[\text{FeP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$  Catalysts Using UB3LYP/6-31G/LanL2DZ Method

Connected atoms	$[\text{CoP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$		$[\text{FeP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$	
	Gas	Solvent	Gas	Solvent
Bond distances ( $\text{Å}^0$ )				
1-2	2.75	2.65	2.38	2.36
1-3	2.38	2.36	2.41	2.39
1-4	2.41	2.38	2.39	2.37
1-5	2.28	2.24	2.03	2.04
1-6	2.01	2.02	2.03	2.04
Bond angle ( $^\circ$ )				
3-1-4	91.56	91.25	89.50	91.01
4-1-5	88.08	85.43	86.80	87.38
2-1-7	89.31	91.01	91.36	91.78
6-1-7	88.91	88.71	88.71	87.73

**Table 2.** The Values of Gibbs Free Energies, Enthalpies, and Electronic Energies of Four Redox Specious in the Gas Phase Using UB3LYP/6-31G/LanL2DZ Method

System	Electronic Energy ( $\text{kcal mol}^{-1}$ )	Enthalpy ( $\text{kcal mol}^{-1}$ )	Gibbs free energy ( $\text{kcal mol}^{-1}$ )
$[\text{CoP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$	-1693356.03	-1693019.21	-1693083.71
$[\text{FeP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$	-1679786.88	-1679448.70	-1679510.79
$[\text{CoP}_4\text{N}_2(\text{OH})_2]^{0}$	-1692863.20	-1692545.24	-1692612.41
$[\text{FeP}_4\text{N}_2(\text{OH})_2]^{0}$	-1679272.88	-1678953.39	-1679018.81

considered isodesmic reaction. The Gibbs free energy of isodesmic reaction along with one of the experimental values of reduction potential of two catalysts, Co or Fe complex, can be applied to calculate the reduction potential of other species Using the Gibbs free energy of Eq. (4) and the experimental reduction potential of Fe based catalyst, -1.03 V, the reduction value for the Co based catalyst was

found to be -0.58 V vs. NHE, which was an indication of a good agreement with the experimental value (-0.50 V).

This study also attempts to carry out absolute approach to two aforementioned catalysts,  $[\text{CoP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$  and  $[\text{FeP}_4\text{N}_2(\text{OH}_2)_2]^{2+}$ . In this step, the reduction potentials were calculated without considering any isodesmic reference reaction. The resulted reduction potentials obtained using

Eq. (2), were referred to the absolute reduction potential of reference electrode used in experiment [22], NHE. Using recommended values in articles for proton and electron's absolute Gibbs free energies which were about -0.868 and -266.5 kcal mol<sup>-1</sup> [29,30], respectively, the calculated value for NHE at UB3LYP/6-31G level, was found to be 4.40 V. Reduction potentials achieved through this approach were not compatible enough with experimental values. This contradiction might be due to (1) applied computational method, and (2) inaccurate value of the proton Gibbs free energy employed in the measurements. When employing these catalysts in experimental condition, hydrogen gas was generated without the presence of any proton. So, the reaction was performed in neutral water. Obviously, in the half reaction related to the reference electrode, NHE, one proton adsorbed an electron and formed H<sub>2</sub> gas (see Eq. (3)).

However, in the half-reactions related to Eqs. (5) and (6), no proton was identified to participate in reduction process. Thus, it could be concluded that subtraction of the absolute potential of half-reactions (Eqs. (5) and (6)) from absolute potential of NHE might not omit the effect of inaccuracy related to the proton Gibbs free energy.

## CONCLUSIONS

The reduction potential of [CoP<sub>4</sub>N<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> as a super-efficient catalyst for electrochemical hydrogen production was calculated theoretically. An isodesmic reaction was designed to eliminate the electron and proton effect and account for the employed computational method errors. Gibbs free energies of the redox species, [CoP<sub>4</sub>N<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>, [CoP<sub>4</sub>N<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>0</sup>, [FeP<sub>4</sub>N<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> and [FeP<sub>4</sub>N<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>0</sup> were measured using frequency calculation for the optimized structures. UB3LYP/6-31G/LanL2DZ level employed to optimize the structures sounds to be appropriate due to the satisfying resulted structures and reduction potential. The obtained reduction potential using this approach for [CoP<sub>4</sub>N<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> catalyst amounted to -0.58 V using UB3LYP/6-31G/LanL2DZ computational method, in agreement with experimental value, -0.50 V.

The outcomes confirmed that the water molecules coordinated to Co or Fe core, in catalyst structure, played a main role in H<sub>2</sub> gas production. Additionally, it seems

notable that obtaining values close to those in experimental studies might reveal a promising idea about designing new inexpensive efficient catalysts which could provide materials for hydrogen production with low over-potential.

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