DFT Study on the Hydrogen Evolution Reaction on CoP(110) Surface

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Abstract. Hydrogen evolution reaction (HER) through water splitting depends on the development of efficient non-noble catalysts, among which the cobalt phosphide has been considered as one of the promising catalyst. Herein, the Gibbs free energy towards HER on CoP(110) surface was studied with density functional theory (DFT) calculation. It can be found that the crystal parameters calculated with both GGA-PBE and GGA-PW91 functionals consist well with the experimental result. The CoP(110) may possess good HER activity since it has good conductivity and appropriate Gibbs free energy (∆G_H) for hydrogen adsorption.

1. Introduction
The generation of hydrogen fuel from water as an alternative to fossil oils has been considered as a promising green technology with the ongoing energy crisis and climate change[1]. Hydrogen evolution reaction (HER) through electrolytic water splitting has been received increasing worldwide concern. Platinum is considered as state-of-the-art electrocatalysts for HER. However, the scarcity and high price hamper their large-scale applications compared with the traditional natural gas reforming method. Thus it is of high priority to research earth-abundant and cost-effective catalysts as possible alternatives to noble metals[2]. Recently, transition metals (Mo, Co, Ni, Fe, etc.) sulfides and phosphides have been testified that they own good catalytic activity toward HER[3]. Transition metal phosphides (TMPs) which own similar structure with hydrogenase are considered as promising electrocatalysts for the HER, since they possess both good corrosion resistance and good electrical conductivity as an electrode[4]. It has been established that CoP has presented good catalytic activity towards HER, however, most of studies were focused on the experimental researches, but the deep and comprehensive understanding of the relationship between the catalytic activity and the electronic and geometric structures of CoP was rarely reported.

Herein, DFT calculations were performed to study the properties of the CoP(110) surface. It has been found that the surface formation energy of CoP(110) was a little bit positive. However, the Gibbs free energy for H adsorption on CoP(110) was comparative with that on Pt. Thus the CoP(110) may perform good catalytic activity towards HER.

2. Methodology
A preliminary screening of different functionals suggested that both PW91 and PBE functional are suitable to describe accurately the structural and electronic properties of CoP bulk. Thus the DFT calculations were performed with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional for the properties of CoP(110)[5]. The (110)
facet was modeled through cutting from the optimized bulk structure. The k-point meshes were set to 2×2×1 and the core electrons were treated with ultrasoft pseudopotentials[6]. A cutoff energy of 340 eV was used for all calculations. The convergence criterion for the structural optimizations was a maximum force of 0.05 eV/Å and a maximum displacement of 0.002 Å. A vacuum layer of 15 Å thickness was used along the z-direction to eliminate totally the interaction among different surfaces.

The surface formation energy (E_s) was calculated according to equation (1):

$$E_s = \frac{(E_{slab} - N^*E_{bulk})}{2A}$$

where $E_{slab}$ is the energy of the optimized CoP surface and $E_{bulk}$ is the energy of CoP bulk. N is the number of CoP bulk contained in CoP surface and A is the surface area of CoP(110).

The Gibbs free energy ($\Delta G_H$) of H adsorption on CoP(110) surface was calculated according to the method proposed by Nørskov et al[7].

$$\Delta G_H = E_{total} - (E_{surface} + \frac{1}{2}E_{H_2}) + \Delta E_{ZPE} - T\Delta S$$

where $E_{total}$ is the total energy for the adsorption state, $E_{surface}$ is the energy of the pure surface, $E_{H_2}$ is the energy of hydrogen molecule, $\Delta E_{ZPE}$ is the zero-point energy change and $\Delta S$ is the difference in entropy between H that is adsorbed and in the gas phase, at 101325 Pa.

3. Results and discussion

3.1. The calculation of bulk CoP

Table 1. The computed bond lengths between Co and its six coordinated P atoms with different exchange-correlation functionals, respectively.

| Functionals | Bond length of Co-P (Å) |
|-------------|-------------------------|
|             | a           | b           | c           |        |
| LDA-CAPZ    | 2.335       | 2.316       | 2.316       | 2.196  |
| GGA-PW91    | 2.392       | 2.361       | 2.359       | 2.246  |
| GGA-PBE     | 2.387       | 2.373       | 2.371       | 2.234  |
| GGA-WC      | 2.361       | 2.346       | 2.344       | 2.217  |

Table 2. Computed lattice parameters and volumes of CoP with different exchange-correlation functionals

| Functionals | Parameters (Å) | Volume (Å³) |
|-------------|----------------|-------------|
| LDA-CAPZ    | 3.261          | 4.926       | 5.366       | 86.200  |
| GGA-PW91    | 3.327          | 5.024       | 5.484       | 91.664  |
| GGA-PBE     | 3.325          | 5.024       | 5.482       | 91.580  |
| GGA-WC      | 3.299          | 4.980       | 5.423       | 89.093  |
| Ref [8]     | 3.281          | 5.077       | 5.587       | 93.100  |
As shown in figure 1, the computationally optimized lattice structure of bulk CoP has a monoclinic structure where Co atoms are 6-fold coordinated to P atoms, and the P atoms are also 6-fold coordinated to Co atoms. In order to identify the best method for the description of CoP, four different exchange-correlation functionals have been screened in this paper. As listed in table 1 and table 2, the bond lengths of Co-P vary not too much with different functionals. All the functionals give lattice parameters within about 8% deviation with respect to the available experimental data[8]. However, the GGA-PBE and GGA-PW91[9] functionals perform a lower deviation compared to GGA-WC[10] and LDA-CZAP[11]. Thus the GGA-PBE functional was chosen for the following calculations.

3.2. The calculation of CoP(110)
As shown in figure 2, it can be found that one 3-fold coordinated and two 5-fold coordinated P atoms are exposed to the vacuum, while two 4-fold coordinated and one 5-fold coordinated Co atoms are exposed to the vacuum. What’s more, the optimized surface area of CoP(110) is 33.52 Å² and the surface formation energy (Es) is only 0.124 eV/Å².

Figure 2. The optimized CoP(110) surface. Blue and pink balls represent Co and P atoms, respectively.

The band structure of CoP(110) was shown in figure 3, there is no significant band gap around the Fermi level, which represents that the CoP(110) surface possess good conductivity.

3.3. Catalytic Activity of CoP(110) toward HER
The Gibbs free energy of hydrogen reaction (ΔG_H) is a reasonable descriptor for HER catalysts. A good HER catalyst should possess a value of ΔG_H close to 0 eV, which keeps a balance between the transfer of hydrogen and the removal of adsorbed hydrogen. As shown in figure 4, the ΔG_H of HER on CoP(110) surface is found to be -0.068 eV, which is a little bit closer to thermoneutral than that of Pt (-0.09 eV), which means that the CoP(110) may perform even better catalytic activity toward HER than that of Pt.
4. Conclusions
Recent experimental works have identified CoP as a promising catalyst for HER. In order to gain insights into the surface stability and the catalytic activity toward HER, DFT study on CoP(110) surface was performed. The results suggest that the surface formation energy of CoP(110) surface is 0.124 eV/Å². The CoP(110) may possess good catalytic activity towards HER, since the CoP(110) performs good conductivity and the Gibbs free energy of HER on CoP(110) is closer to thermoneutral.

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