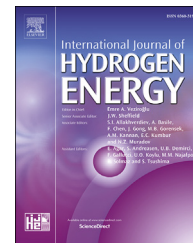




ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# Theoretical research on the H<sub>2</sub> generation mechanism on Pt<sub>6</sub>, Pt<sub>5</sub>Sn<sub>5</sub> and Pt<sub>3</sub>Sn<sub>6</sub> clusters by density functional theory

Chao Kong<sup>a,\*</sup>, Yan-Xia Han<sup>a,b</sup>, Li-Jie Hou<sup>a</sup>, Bo-Wan Wu<sup>a</sup>,  
Zhi-Yuan Geng<sup>b</sup>

<sup>a</sup> School of Chemistry & Chemical Engineering, Longdong University, Qingyang 745000, China

<sup>b</sup> School of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

## ARTICLE INFO

### Article history:

Received 2 March 2017

Received in revised form

10 May 2017

Accepted 11 May 2017

Available online 12 June 2017

### Keywords:

Pt<sub>5</sub>Sn<sub>5</sub> cluster

Pt<sub>3</sub>Sn<sub>6</sub>

H<sub>2</sub> generation

Potential barrier

Mechanism

DFT

## ABSTRACT

In this paper, the mechanisms of H<sub>2</sub> evolution on Pt<sub>6</sub>, Pt<sub>5</sub>Sn<sub>5</sub>, and Pt<sub>3</sub>Sn<sub>6</sub> clusters were respectively investigated by the B3LYP method of density functional theory (DFT). The B3LYP functional with non-local dispersion corrections (B3LYP-D3) method were performed to investigate the adsorption of H and H<sup>+</sup> on clusters. The calculation results indicated that the adsorption energy of H on Pt reduced due to the interaction of Sn and Pt, which promoted H desorption from Pt to form H<sub>2</sub>. Meanwhile, Sn atom of Pt<sub>5</sub>Sn<sub>5</sub> and Pt<sub>3</sub>Sn<sub>6</sub> clusters had strong interaction with H<sup>+</sup> due to the existence of Pt, which was benefit for the reduction of H<sup>+</sup> on Sn atom. As a consequence, Pt<sub>5</sub>Sn<sub>5</sub> and Pt<sub>3</sub>Sn<sub>6</sub> showed lower potential barrier and higher activities than Pt for H<sub>2</sub> evolution. The potential barriers of H<sub>2</sub> formation over Pt<sub>3</sub>Sn<sub>6</sub> clusters was only 11.1% of that over Pt cluster.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

The replacement of non-renewable fossil fuel by the clean renewable energy will be an inevitable trend with the development of clean-energy frame technologies. As a clean renewable energy source, solar energy is inexhaustible that can be used directly to driven hydrogen evolution reactions from water splitting over semiconductor photocatalysts. Therefore, storing solar energy in the form of clean and high-energy density hydrogen has been pursuing as the most ideal way to solve the energy and increasing environmental problems [1–13].

To achieve a high-efficiency hydrogen generation, a co-catalyst that is active, stable, and cost-efficiency is typically required in photocatalytic systems. Noble metal Pt has been identified as the most active hydrogen evolution catalyst due to its low overpotential for proton reduction and high stability for long-term utilization [11,14]. However, the scale-up application of the Pt cocatalyst is still hard because of their scarceness and high-cost, and the searching for the potential substitutes of Pt and the increase of Pt activity became the main approach to solve this problem [15,16]. Our previous study displayed that PtSn and PtSn<sub>2</sub> alloy co-catalysts had higher hydrogen evolution activity than Pt. Due to the low adsorption energy of H and H<sup>+</sup> on Sn, the reduction of H<sup>+</sup> on

\* Corresponding author.

E-mail address: [kongchao010@163.com](mailto:kongchao010@163.com) (C. Kong).

<http://dx.doi.org/10.1016/j.ijhydene.2017.05.084>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Pt, H transfer from Pt to Sn, and H desorption from Sn to form H<sub>2</sub> were considered to be the main H<sub>2</sub> formation path on Pt–Sn co-catalyst [17]. Therefore, the real mechanism of hydrogen formation on Pt–Sn alloy is still undiscovered. The density functional theory (DFT) includes exchange-correlation functional showing the high computational accuracy which was close to that of CCSD (Coupled cluster singles and doubles), and is often used to study the reaction mechanism and calculate the adsorption energy [18,19]. In this paper, DFT method was employed to investigate the mechanism of H<sub>2</sub> formation on the surface of Pt<sub>n</sub>, Pt<sub>n</sub>Sn<sub>n</sub>, Pt<sub>n</sub>Sn<sub>2n</sub> clusters. The calculation found that H transfer step from Pt to Sn really existed in the channel of two H atoms desorbing from the adjacent Pt and Sn for H<sub>2</sub> generation over Pt–Sn co-catalyst, but the formation of H<sub>2</sub> by direct desorption of H on the same Pt atom was the main reaction channel. The adsorption energy of H on Pt reduced and that of H<sup>+</sup> on Sn increased in Pt<sub>5</sub>Sn<sub>5</sub> and Pt<sub>3</sub>Sn<sub>6</sub> due to the interaction of Sn and Pt, which promoted H desorption from Pt and H<sup>+</sup> reduction on Sn. The potential barriers of the main channel on Pt<sub>5</sub>Sn<sub>5</sub> and Pt<sub>3</sub>Sn<sub>6</sub> were 44.8 and 22.3 kJ/mol, which were respectively 22.4% and 11.1% of that over Pt. Therefore, Pt–Sn co-catalysts showed higher photocatalytic H<sub>2</sub> generation activity than Pt.

## Computational methods

All of the calculations were carried out with the DFT using the B3LYP method. The Los Alamos relativistic effective core potential (RECP) plus DZ basis set (LANL2DZ) was utilized for Pt and Sn atoms [20,21], and the 6-31G(d,p) basis set was used for the H atoms [22]. Pt, PtSn, and PtSn<sub>2</sub> belonged to the face-centered cubic, NiAs configuration, and CaF<sub>2</sub> configuration, respectively. According to the configuration of Pt, PtSn, and PtSn<sub>2</sub>, atom was added into the optimized cluster structure one by one as a starting point for obtaining the stable structure. Considering that the photocatalytic H<sub>2</sub> generation reactions were taking place in solution, so all the calculations were coupled with the polarizable continuum model (PCM) [23]. The harmonic vibration frequencies obtained at the

corresponding level were used to characterize the local minima and first-order saddle points. The intrinsic reaction coordinate (IRC) calculation was employed to track minimum energy paths from transition structures to the local minima points. Natural bond orbital (NBO) analysis was carried out with NBO 3.1. All calculations were carried out using the Gaussian 09 package [24–26]. For gaining the precise adsorption energies of H atom and H<sup>+</sup> on clusters, the B3LYP functional with non-local dispersion corrections (B3LYP-D3) method were performed to investigate the adsorption of H and H<sup>+</sup> on clusters [27]. The adsorption energies ( $E_{ads}$ ) were calculated according to Equation (1), and the binding energies per atom ( $E_b$ ) with Equation (2) [28,29].

$$E_{ads} = (E_{H/H^+} + E_{cluster}) - E_{cluster-H/H^+} \quad (1)$$

$$E_b = [nE_{Pt} + nE_{Sn}/2nE_{Sn} - E(Pt_nSn_n/Pt_nSn_{2n})]/(n + n/2n) \quad (2)$$

where  $E_{cluster-adsorbate}$ ,  $E_{cluster}$ , and  $E_{H/H^+}$  were the energies of the complex (cluster + H/H<sup>+</sup>), cluster, and H atom or H<sup>+</sup>, respectively. In Equation (2),  $E(Pt_nSn_n)$  and  $E(Pt_nSn_{2n})$  were the total energy of bare Pt<sub>n</sub>Sn<sub>n</sub> and Pt<sub>n</sub>Sn<sub>2n</sub> cluster, and  $E_{Pt}$  and  $E_{Sn}$  denoted the energy of Pt and Sn atom, respectively.

## Results and discussion

### Pt<sub>n</sub>, Sn<sub>n</sub>, Pt<sub>n</sub>Sn<sub>n</sub>, and Pt<sub>n</sub>Sn<sub>2n</sub> cluster structures

The stable geometries of clusters, Pt<sub>n</sub> ( $n = 2-8$ ), Sn<sub>n</sub> ( $n = 1-6$ ), Pt<sub>n</sub>Sn<sub>n</sub> ( $n = 1-6$ ), and Pt<sub>n</sub>Sn<sub>2n</sub> ( $n = 1-4$ ) clusters were optimized, as shown in Figs. S1–S4 (in Supporting Information). The binding energy per atom ( $E_b$ ) and its variation tendency with  $n$  value are displayed in Table 1 and Fig. 1, respectively. In Fig. 1, the increase in  $E_b$  became slower when the value of  $n$  was larger than 2 for Pt<sub>n</sub>Sn<sub>n</sub> and Pt<sub>n</sub>Sn<sub>2n</sub> and larger than 3 for Pt<sub>n</sub> and Sn<sub>n</sub> clusters, indicating that Pt<sub>n</sub>Sn<sub>n</sub> and Pt<sub>n</sub>Sn<sub>2n</sub> were relatively stable at  $n > 2$  while Pt<sub>n</sub> and Sn<sub>n</sub> was stable at  $n > 3$ . For reducing the computational cost and increasing the veracity of results, the relative stable Pt<sub>6</sub>, Pt<sub>5</sub>Sn<sub>5</sub>, and Pt<sub>3</sub>Sn<sub>6</sub> clusters were selected as the co-catalyst models in following

**Table 1 – Energies (a.u.) and  $E_b$  (kJ/mol) of Pt<sub>n</sub>, Pt<sub>n</sub>Sn<sub>n</sub> and Pt<sub>n</sub>Sn<sub>2n</sub> clusters.**

| Clusters                                     | E (a.u.)     | $E_b$ (kJ/mol) | Clusters                                     | E (a.u.)     | $E_b$ (kJ/mol) |
|--|--------------|----------------|--|--------------|----------------|
| Pt <sub>1</sub>                              | -119.0627959 | –              | Pt <sub>2</sub>                              | -238.2543096 | 169.0          |
| Pt <sub>3</sub>                              | -357.4759868 | 251.7          | Pt <sub>4</sub>                              | -476.6547887 | 264.9          |
| Pt <sub>5</sub>                              | -595.8196498 | 265.5          | Pt <sub>6</sub> <sup>1</sup>                 | -715.0202234 | 281.6          |
| Pt <sub>6</sub> <sup>2</sup>                 | -714.9791417 | 263.6          | Pt <sub>6</sub> <sup>3</sup>                 | -714.9933158 | 269.8          |
| Pt <sub>6</sub> <sup>4</sup>                 | -715.0120714 | 278.0          | Pt <sub>7</sub>                              | -834.2091637 | 288.7          |
| Pt <sub>8</sub>                              | -953.3846312 | 289.5          | Sn   | -3.2985933   | –              |
| Pt <sub>1</sub> Sn <sub>1</sub>              | -122.5577721 | 257.8          | Pt <sub>2</sub> Sn <sub>2</sub>              | -245.22235   | 327.9          |
| Pt <sub>3</sub> Sn <sub>3</sub>              | -367.8807687 | 348.6          | Pt <sub>4</sub> Sn <sub>4</sub>              | -490.570675  | 369.25         |
| Pt <sub>5</sub> Sn <sub>5</sub> <sup>1</sup> | -613.1738639 | 358.9          | Pt <sub>5</sub> Sn <sub>5</sub> <sup>2</sup> | -613.167554  | 357.2          |
| Pt <sub>6</sub> Sn <sub>6</sub>              | -735.874255  | 373.2          | Pt <sub>1</sub> Sn <sub>2</sub>              | -125.9424817 | 247.2          |
| Pt <sub>2</sub> Sn <sub>4</sub>              | -252.0469861 | 318.1          | Pt <sub>3</sub> Sn <sub>6</sub> <sup>1</sup> | -378.1164479 | 331.5          |
| Pt <sub>3</sub> Sn <sub>6</sub> <sup>2</sup> | -378.1151356 | 331.2          | Pt <sub>4</sub> Sn <sub>8</sub>              | -504.1926514 | 339.7          |
| Sn <sub>2</sub>                              | -6.6758344   | 103.3          | Sn <sub>3</sub>                              | -10.1200077  | 196.2          |
| Sn <sub>4</sub>                              | -13.49247    | 195.7          | Sn <sub>5</sub>                              | -16.9510011  | 240.52         |
| Sn <sub>6</sub>                              | -20.3663168  | 251.5          | –  | –            | –              |

Download English Version:

<https://daneshyari.com/en/article/5147362>

Download Persian Version:

<https://daneshyari.com/article/5147362>

[Daneshyari.com](https://daneshyari.com)