Hydrogen generation from water molecule with Pt₇ clusters

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ABSTRACT: The reaction paths of hydrogen generation from water molecule with Pt₇ cluster are presented, based on the density functional theory with the generalized gradient approximation. The 12 stable complex structures of the H₂O@Pt₇ reactants and the corresponding structures of the H₂+O@Pt₇ and H+HO@Pt₇ products are optimized for various adsorption sites on the cluster. The frequency analysis has been used to confirm the energy stability of the structures. The geometries of the transition states and the intrinsic reaction coordinates are calculated at the same theoretical level. The energy barrier for each reaction is determined. The results demonstrated that Pt₇ cluster can abstract H or H₂ from H₂O molecule depend on the initial structures of reactant and the active energy. These results are helpful for designing the practical hydrogen generation scheme with these reactions.

Keywords: Hydrogen generation; intrinsic reaction coordinate; water; platinum cluster

1. Introduction

Energy is a necessary material foundation for the survival of human beings, and a good environment is the primary conditions for people to sustainable living. The

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traditional fuel is a non-renewable resource and cause great pollution to the environment ^[1-2]. Therefore, it is urgent to develop economic, efficient, pollution-free and renewable resources. The hydrogen is an ideal energy for its high calorific value and zero pollution ^[3-4]. As a result, the hydrogen generation from water has been paid much attention recently because there is a lot of water on the earth. One H₂O molecule can be dissociated into H⁺ and OH⁻, which subsequently generate H₂ ^[5]. It needs 286kJ/mol energy to generate H₂ from liquid water. In the atmospheric pressure condition and 2200 °C, only 4% of H₂O could dissociate into H₂ and O₂. Although the yield of H₂ could be improve by raising the temperature ^[6-7], the special reactor is difficult to prepare. Without a doubt, the dissociation reaction could be realized with lower energy if a special kind of catalytic materials are used. For the adsorption energy of OH and H on the catalyst are different, they would be respectively collected ^[8-9].

It has been reported that water decomposition on the metal catalyst surface. Feibelman *et al.* ^[10,11] studied the D₂O adsorption and dissociation on the surface of Ru (0001) by using density functional theory (DFT). Zhang *et al.* ^[12] focus on theoretical calculations of water splitting by metal-oxide semiconductors, and investigate the oxygen evolution reaction at 11 hematite (Fe₂O₃) surfaces with DFT ^[13]. The theoretical insights into the photoinduced charge transfer and catalysis at oxide interfaces are presented by Akimov *et al.* ^[14] The electrocatalysis of the hydrogen evolution reaction in acid and alkaline media has been reported by Danilovic *et al.* ^[15] However, the H₂ generation can also be realized through the reactions of metal

clusters with water molecules.^[16] Balbuena *et al.*^[17] studied the O₂, CO and NO decomposition on the Pt surface. Fajinet *al*^[18] performed theoretical investigations of the adsorption and the dissociation process of H₂O on the surface of Pt (111), Pt (100), Pt (110), Pt (211) and Pt (321) and the adsorption energy of H₂O on the Pt_n(*n*=13, 19, 38, 55, 79, 140). Parreira *et al.*^[19] studied the interaction between the Pt₄ cluster and H, OH, and H₂O using the first principles calculations. The dissociation of H₂ on Pt₆ cluster has been theoretical researched by Chen *et. al*^[20]. Zhou *et al.* reported the adsorption of H₂ on Pt_n(*n*=2-5, 7-9) cluster^[21] and on Pt₁₃ and Pd₁₃ cluster^[22]. Li *et al*^[23,24] have reported a three step reactions to generated H₂ from H₂O molecule with Al₆Cu and AlSi₆ clusters. The H₂O dissociated into OH and H on platinum nanoparticles are also studied^[25]. However, we fail to find a report on dissociation of water with Pt₇ cluster, although the platinum clusters as the well-known catalyst for many reactions have been performed. In the present work, the mechanism for water molecule dissociated on Pt₇ cluster is investigated to find more ways to generate hydrogen from H₂O molecule.

2. Computational methods

The calculations are carried out with a gradient-corrected hybrid DFT with exchange-correlation functional in Becke's three-parameter form (B3LYP) with the split basis sets with polarization functions LanL2DZ^[26] implemented in the Gaussian 09 program^[27]. The initial structures of reactants are constructed by placing the H₂O molecule at the top, the bridge, and the face of Pt₇ cluster, while the initial structures of the products are built based on the optimized structures of the complex H₂O and Pt₇

cluster (represented by $\text{H}_2\text{O}@\text{Pt}_7$). The energy stability of all the optimized structures for both the reactants and the products are confirmed by frequency analysis at the same theoretical level as the optimization calculations. After observing the obtained structures of reactants and products, we construct initial structures of the transition states by adjusting the distance of O and H of the H_2O . Both $\text{H}_2+\text{O}@\text{Pt}_7$ and $\text{H}+\text{OH}@\text{Pt}_7$ products are considered. The obtained transition state is confirmed by using optimization with TS keyword and frequency calculation again. The dissociation process is confirmed using the reaction path following intrinsic reaction coordinate (IRC) in order to clarify the connection of the reactants, the transition state, and the products. The adsorption energies of the reactants, the barrier heights of the transition states and the reactive energies of the products are calculated and discussed to identify the preferable reaction to generate hydrogen. All the calculations are carried out using the Gaussian 09 program^[27].

3. Results and Discussion

3.1 The geometrical structures of complex $\text{H}_2\text{O}@\text{Pt}_7$ cluster

The structures of the H_2O molecule adsorbed on Pt_7 cluster are firstly investigated. The initial structures of the Pt_7 cluster are the lowest energy geometry from Lei *et. al.*^[28] The adsorption sites on the top, the bridge, and the face are considered to construct the initial complex structures of H_2O molecule and Pt_7 cluster. From the lot of initial structures, we have obtained 12 stable complex structures after tedious optimization and frequency analysis. The finally obtain structures of $\text{H}_2\text{O}@\text{Pt}_7$ are collect them in Fig. 1. From the figure, one can find that the H_2O molecule inclines to locate at the

top site on Pt₇ cluster. The adsorption energy E_a is used to estimate the strength of the interaction between the H₂O molecule and cluster Pt₇, and can be calculated with the following formula:

$$E_a = E(\text{H}_2\text{O}@\text{Pt}_7) - E(\text{Pt}_7) - E(\text{H}_2\text{O})$$

Where $E(\text{H}_2\text{O}@\text{Pt}_7)$ is the total energy of the stabilized complex structure, $E(\text{Pt}_7)$ is the total energy of the Pt₇ cluster, and $E(\text{H}_2\text{O})$ is the total energy of a free H₂O molecule. As shown in Table1, the values of adsorption energy of H₂O@Pt₇ are from -1.85 to -1.16eV, which indicates that the Pt₇ cluster can capture H₂O molecule and adsorb it at the top site of the Pt atom. The structure of Pt₇ cluster in the H₂O@Pt₇, H₂+O/H and OH@Pt₇ structures is also changed.

3.2 The dissociation of H₂O on Pt₇ cluster

The adsorption structures H₂O@Pt₇ are used as the reactants to investigate the dissociation of the H₂O molecule on Pt₇ cluster. To explore the process of reaction, we determine the geometrical structures of the product of H+OH@Pt₇ or H₂+O@Pt₇ corresponding to all the 12 reactants. The initial geometries are constructed by adjusting the distance of O and H atoms. The bond length of O-H is set to 0.98Å for the case of H+OH@Pt₇, while the H-H is set to 0.75Å for H₂+O@Pt₇. The optimized structures from the initial ones are confirmed by frequency analysis. The final geometries of the products are shown in Fig.2.

Using the obtained stable structures of reactants and products, we optimize the transition state and IRC for each reaction. All the results are collected in Fig. 3. The results show only one of the two products for the dissociated H₂O molecule is

available for a specific reactant, although the transition states for the two products are explored. The final product is $\text{H}_2 + \text{O}@\text{Pt}_7$ for the reaction of R_1 , R_5 , and R_7 reactants, while $\text{H} + \text{OH}@\text{Pt}_7$ for the other reactants. It implies that the efficiency of generation hydrogen for the 12 reactants on the Pt_7 cluster is different. To fully understand the reactions and provide helpful information to generate hydrogen with the Pt_7 cluster, we estimate activation energy E_b (the barrier energy) and heat of reaction E_r by using the following expression.

$$E_b = E(\text{TS}) - E(\text{Reactant}),$$

$$E_r = E(\text{Reactant}) - E(\text{Product})$$

Where $E(\text{Reactant})$ is the total energy of the reactant, $E(\text{TS})$ is the total energy of the transition state, and $E(\text{Product})$ is the total energy of the $\text{H} + \text{OH}@\text{Pt}_7$ or $\text{H}_2 + \text{O}@\text{Pt}_7$. The results are collected in Table 1. The results show that the reactions with R_1 , R_5 , and R_7 reactants can completely abstract the two H atoms in H_2O molecule by undergoing one transition state. These reactions are different from the reactions on $\text{Al}_6\text{Si}^{[23]}$ and $\text{Al}_6\text{Cu}^{[24]}$ clusters where two or three transition states are needed to complete the dissociation processes. Obviously, the reactions with R_1 , R_5 , and R_7 reactants are higher efficient for generating hydrogen. However, the barrier heights (E_b s) of 3.57-3.76 eV are much larger than those of the other reactants of $\text{H}_2\text{O}@\text{Pt}_7$, and also a little larger than those on the Al_6Si and Al_6Cu clusters. Moreover, the present heats of reactions (E_r) with R_1 , R_5 , and R_7 is from -2.79 to -2.32 eV, which means these reactions are an endothermic reaction. For the other reactants, only one H atom in the molecule can be abstracted. However, the E_b s of 0.75-2.17 eV implies that

these reactions can be realized with much smaller energy than the reactions with the R_1 , R_5 , and R_7 reactants. Especially, the E_b s with the reactant R_8 , R_{10} and R_{11} are 0.75 eV, which are the preferable ones among the 12 reactions from the saving energy view. Moreover, the E_r s of the reactions with the three reactants are approximate zero, which implies that they almost don not consume energy finally. Generally, the reactions with the different reactants demonstrate obvious different characteristics. The efficiency of generation hydrogen and the consuming energies are obviously different, which provide us multiple choices of hydrogen generation with the Pt_7 cluster.

4. Conclusion

The present work devotes to find preferable way to hydrogen generation from the dissociated H_2O on Pt_7 cluster based on the first principles calculations. We have identified 12 $H_2O@Pt_7$ complex structures, which can be used as reactants to dissociate H_2O on the Pt_7 cluster to generate H_2 molecule, although the products, transition states, and IRCs for the reactants are obviously different. The R_1 , R_5 , and R_7 reactants can abstract two H atoms, while the other 9 reactants can only abstract one H atom. Therefore, the former is more efficient for hydrogen generation. However, the energy barriers of the former are obviously larger than the latter. The results imply that one can choose a suitable reaction path for the sake of the hydrogen generation efficiency and the consuming energy.

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Figure captions

Fig. 1. The stable structures of an H_2O molecule adsorbed on Pt_7 cluster.

Fig. 2. The products of $\text{H}_2+\text{O}/\text{H}+\text{OH}@ \text{Pt}_7$.

Fig. 3. Reaction paths for splitting H_2O on different adsorption sites of Pt_7 cluster.

Table.1 Adsorption energies of the reactants, barrier energies of the transition states, and reaction energies of the products

Reactants	Products	Adsorption energy	barrier energy	Reaction energy
R ₁	H ₂ +O	-1.25	3.63	-2.39
R ₂	H+OH	-1.17	0.76	-0.62
R ₃	H+OH	-1.67	1.16	-0.37
R ₄	H+OH	-1.41	2.17	-0.39
R ₅	H ₂ +O	-1.41	3.57	-2.32
R ₆	H+OH	-1.47	0.92	-0.17
R ₇	H ₂ +O	-1.85	3.76	-2.76
R ₈	H+OH	-1.16	0.75	-0.03
R ₉	H+OH	-1.28	0.86	-0.23
R ₁₀	H+OH	-1.48	0.75	-0.03
R ₁₁	H+OH	-1.28	0.75	0.04
R ₁₂	H+OH	-1.22	1.37	-0.51

R₁

R₂

R₃

R₄

R₅

R₆

R₇

R₈

R₉

Fig. 1. The stable structures of an H_2O molecule adsorbed on Pt_7 cluster.

Fig. 2. The products of $\text{H}_2 + \text{O} / \text{H} + \text{OH} @ \text{Pt}_7$.

$R_1 \rightarrow P_{1-1}$

$R_2 \rightarrow P_{2-2}$

$R_3 \rightarrow P_{3-2}$

$R_4 \rightarrow P_{4-2}$

$R_5 \rightarrow P_{5-1}$

$R_6 \rightarrow P_{6-2}$

$R_7 \rightarrow P_{7-1}$

$R_8 \rightarrow P_{8-2}$

$R_9 \rightarrow P_{9-2}$

$R_{10} \rightarrow P_{10-2}$

$R_{11} \rightarrow P_{11-2}$

$R_{12} \rightarrow P_{12-2}$

Fig. 3. Intrinsic reaction coordinates for the reactions of hydrogen generation from H_2O on Pt_7 cluster.

H₂ or H can be extracted from a H₂O molecule with different IRC on a small Pt₇ cluster.