Density Functional Theory Study of Hydrogen Adsorption on Pt Pd/γ-Al₂O₃ Surface

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Abstract. At present passive hydrogen recombiners (PAR) are used to prevent hydrogen explosion. Hydrogen removal catalyst is the core component of PAR. The adsorption of hydrogen on the solid catalyst surface is the premise of catalytic hydrogen removal and is of great significance for deeper understanding of hydrogen removal mechanism. The adsorption behavior of H₂-Pt Pd/γ-Al₂O₃ system has been studied by using density functional theory and periodic slab model. The results of different adsorption sites indicate the adsorption energy of top site is highest, which is -1.2584eV. Higher adsorption energy means stronger interaction between H₂ and catalyst substrate, which elongates H-H bond and increases the negative charge on H₂. With increasing doping content of Pd, the adsorption energy of substrate decreases gradually. The adsorption energy absolute value of Pt₄/γ-Al₂O₃ is highest and its H-H bond is longest, arriving at 0.0967nm. After adsorbed on substrate, the energy gap of H₂ decreases drastically with the lowest energy gap of H₂-Pt₄/γ-Al₂O₃ that is 0.5197eV, and the peaks of density of state pattern move to lower energy level. This is because that the d orbital of Pt/Pd atoms interacts with the σ* anti-bond orbital of H₂ strongly, transferring electrons to the σ* anti-bond orbital of H₂. Doping Pd increases the energy gap of molecule orbital.

Keywords. Passive H₂ recombiner, catalyst carrier, adsorption, density functional theory, γ-Al₂O₃

1. Introduction

Nuclear safety is an important goal of nuclear power development. Nuclear reactors will produce hydrogen in accident conditions (due to the zirconium-water reaction, core melt-concrete reaction) and normal conditions (due to irradiation decomposition and adding hydrogen to suppress water oxidation). So there is a danger of hydrogen explosion [1, 2]. At present, nuclear power plants use igniters and passive autocatalytic hydrogen recombiners (PAR) to prevent hydrogen explosions. The hydrogen removal catalyst is the core part of the passive hydrogen recombiner, which is mainly composed of three parts: carrier, coating and catalytically active components. The adsorption of hydrogen on the surface of the solid catalyst is the prerequisite for catalytic hydrogen removal. Therefore, studying the adsorption of hydrogen on the solid surface is of great significance for understanding the mechanism...
of catalytic hydrogen removal. With the continuous development of computer technology and theoretical calculation methods, theoretical calculations have become more and more sophisticated, and density functional theory have been widely used to explore the adsorption laws of gas elements on the surface of crystals. Watson et al. [3] calculated the adsorption energies of H atoms at different adsorption sites on Pt(111) and Ni(111) surfaces and the surface mobility of H atoms. Okamoto et al. [4] used density functional theory to calculate and compare the adsorption energy of H₂ molecules on the surface of Pt(111) and Pt13, Pt38, Pt55, and Pt147 clusters of FCC structure.

Ishimota et al. [5] studied the adsorption behavior of NO on Pt clusters and found that the adsorption energy of NO at the vertex is the largest, and the charge is transferred from metal to NO, which elongate N-O bond and increase activity. Meanwhile, other scholars utilized density functional theory to calculate the effect of the geometry parameters of H₂ molecular orbital [6], the adsorption behavior of O₂ and SO₂ on catalyst substrate [7, 8], effect of doping element on vacancy forming and adsorption energy [9-11], and charge distribution [12, 13], revealing the doped elements can increase the vacancy formation energy and adsorption energy, and alter the charge distribution of the adsorption system. However, there are few reports on the research of the γAl₂O₃ supported Pt and Pd multi-element catalytic system. The hydrogen removal catalyst is used in the harsh working environment of the reactor containment, which puts forward higher requirements on the performance of the catalyst carrier. It is necessary to study the mechanism of multi-element catalytic material removing hydrogen.

This paper intends to use density functional theory combined with the periodic slab model to simulate the adsorption behavior of H₂ on the surface of the γAl₂O₃/Pt Pd catalyst, and calculate the adsorption energy, bond length and charge distribution of the different adsorption sites of the Pt/γAl₂O₃ model, as well as the effect of doping Pd on adsorption performance, molecular orbital energy gap and density of state. It provides a theoretical basis for further research on the interaction between hydrogen and solid catalyst surface and the improvement of catalyst performance.

2. Model and Calculation Method

The Inorganic Crystal Structure Database (ICSD) number of γAl₂O₃ is 173014, the spatial point group is P1, and the unit cell parameters are a=3.4009, b=2.7895, c=7.0762, α=β=γ=90°. On this basis, a supercell of 16 Al atoms and 24 O atoms was established, and the γAl₂O₃ (001) crystal plane was cut, and a vacuum layer was established along the c-axis for research.

Density functional theory combined with periodic slab model was used to simulate the adsorption behavior of H₂ on the surface of γAl₂O₃/Pt and Pd catalysts. The model was established by Material Studio, and the numerical simulation calculation was completed by the CASTEP software package. In the calculation, generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) is selected for the exchange-related functional, the cutoff energy is 300 eV, and spin polarization is used. K-point and convergence accuracy are set to mediate. The thickness between two adjacent slabs is 1 nm to ensure that the interaction between the plates is small enough.

The adsorption energy is defined as the change in the energy of each substance before and after adsorption, and its magnitude can indicate the stability of the adsorption system. The calculation formula is: \( E_{\text{ads}} = E_{\text{H₂-Pt γ-Al₂O₃}} - E_{\text{H₂}} - E_{\text{Pt γ-Al₂O₃}} \). In the formula, \( E_{\text{ads}} \) is the adsorption energy, \( E_{\text{H₂}} \) and \( E_{\text{Pt γ-Al₂O₃}} \) are the energy of the H₂ molecule and the substrate before adsorption, respectively, and \( E_{\text{H₂-Pt γ-Al₂O₃}} \) is the total energy of the system after adsorption.
3. Results and Discussion

3.1. The Activity of Different Adsorption Sites of Pt4/γ-Al2O3 Model

The adsorption of H2 molecules at three different positions of the Pt4/γ-Al2O3 model was observed. The three adsorption positions were lateral position, bridge position and vertex position, as shown in figure 1. The adsorption energy, H-H bond length and charge distribution of H2 adsorbed at three different positions are calculated, as shown in table 1. The results show that the absolute value of the adsorption energy at the vertex site is the largest, followed by the adsorption energy at the bridge and the smallest at the lateral site. The greater the adsorption energy, the stronger the interaction of H2 with the catalyst matrix and the more stable the combination.

![Figure 1](image)

**Figure 1.** Three different adsorption sites of Pt4/γ-Al2O3 model (a) is lateral site, (b) is bridge site and (c) is vertex site.

| Adsorption site | Adsorption energy eV | H-H bond length I-nm | q(H2) |
|-----------------|----------------------|-----------------------|-------|
| Vertex          | -1.2584              | 0.0967                | -0.19 |
| Bridge          | -0.0644              | 0.0768                | -0.18 |
| Lateral         | -0.0318              | 0.0758                | -0.09 |

The calculation results of the bond length show that the H-H bond length of each adsorption site has different degrees of elongation comparing with the bond length free H2 molecule(0.074nm) [6], and the vertex site has the largest elongation of the H-H bond. This is consistent with the analysis result of adsorption energy. The greater the adsorption energy, the stronger the interaction between H2 and the matrix, which will extend and weaken the H-H bond, then being conducive to the further dissociation of H2 molecules. This is consistent with the calculation results in literature [12]. Liu studied the adsorption of SO2 by different adsorbents and showed that the S-O bond length was elongated with the increase of adsorption energy.

The results of Mulliken charge distribution analysis show that the charge transferred from the matrix to H2 at the vertex is at most -0.19, and the charge transferred at the side is at least -0.09. The more charge transfer, the stronger the interaction between H2 and the matrix. Later, the vertex position with the largest adsorption energy is selected for the research and analysis of Pd doping. This
corresponds with the results of references [7] and [13]. When the adsorption energy increases, the charge transferred from the substrate to the adsorbed gas molecules increases accordingly.

### 3.2. Influence of Pd Doping on Adsorption Performance

The adsorption energy, chemical bond and charge distribution of the catalyst substrate under different Pd doping ratios were calculated. The results are shown in table 2. The ratio of Pt/Pd is Pt4, Pt3Pd, Pt2Pd2, Pt1Pd3, Pd4, respectively. The results show that the absolute value of the adsorption energy of Pt4/γ-Al2O3 is the largest. With the increase of Pd doping, the adsorption energy gradually decreases. The greater the adsorption energy, the stronger the adsorption bond between H2 and the catalyst matrix, and the more stable the system.

| Pt/Pd ratio       | Adsorption energy eV | H-H bond length nm | H-Pt bond length nm | q(H2)  | q(Pt) |
|-------------------|----------------------|--------------------|---------------------|--------|-------|
| Pt4/γ-Al2O3       | -1.2584              | 0.0967             | 0.167               | -0.21  | 0.18  |
| Pt3Pd/γ-Al2O3     | -1.2173              | 0.0931             | 0.1701              | -0.17  | 0.17  |
| Pt2Pd2/γ-Al2O3    | -0.9400              | 0.0954             | 0.1677              | -0.2   | 0.21  |
| Pt1Pd3/γ-Al2O3    | -1.0187              | 0.0913             | 0.1719              | -0.2   | 0.23  |
| Pd4/γ-Al2O3       | -0.7148              | 0.0847             | 0.1835              | -0.19  | 0.26  |

The calculation results of the bond length show that the H-H bond length is extended at different degree, after H2 molecules are adsorbed on catalyst substrate with different Pt/Pd ratios. Among them, the maximum extension of the H-H bond at the vertex is 0.0967nm, and the H-H bond length decreases with the increase of doping Pd. At the same time, the H-Pt bond length increases with the increase of Pd doping, that is, the interaction between the matrix and the hydrogen molecules is weakened. This is consistent with the analysis results of adsorption energy. The greater the adsorption energy, the stronger the interaction between H2 and the matrix, which will extend the H-H bond and weaken its binding strength, which is conducive to the further dissociation of H2 molecules. This is consistent with the research results of Zhang [10], and the experiment of Lee [11] shows that Pt has higher catalytic performance than Pd and can dissociate oil fume more effectively.

The Mulliken charge distribution results show that the H2 molecule gets electrons, and its charge is negative, between -0.17 and -0.21. It is not sensitive to the amount of Pd doping; while the Pt atoms in contact with H2 molecules lose electrons and are positively charged, and their charge decreases with the increase of Pd doping. This may be due to the fact that the electronegativity of Pd is less than that of Pt, which transfers electrons to Pt to reduce its positive charge. This corresponds with the calculation results in references [10] and [13]. Zhang and Xie studied the adsorption properties of black phosphorene and iron oxide respectively, and both showed that with the increase of adsorption energy, more charge was transferred from the substrate to the adsorbed molecules.

### 3.3. Effect of Doping Pd on Energy Gap and Density of States of Molecular Orbital

The energy gap Eg between the highest occupied molecular orbital and the lowest unoccupied molecular orbital with different doping Pd content was calculated, and the results are shown in table 3.
The energy range of free hydrogen molecules is 12.56 eV, and the molecular orbital form is \( \sigma_1^2 \sigma_1^{*0} \), whose energy gap sharply decreases to between 0.52 and 0.70 eV after being adsorbed on the catalyst substrate. This is because the d orbital of the Pt/Pd atom interacts strongly with the \( \sigma^* \) antibonding orbital of the \( \text{H}_2 \) molecule, which transfers electrons to the \( \sigma^* \) antibonding orbital of \( \text{H}_2 \), causing it to move to a lower energy range, thereby reducing the energy gap. Through further analysis of the energy gap of the molecular orbital with different doping Pd content, it is found that the minimum molecular orbital energy gap of \( \text{H}_2\text{-Pt}4/\gamma\text{-Al}_2\text{O}_3 \) is 0.52. With the increase of doping Pd content, the molecular orbital energy gap increases, and the energy gap of the \( \text{H}_2\text{-Pt}1\text{Pd}3/\gamma\text{-Al}_2\text{O}_3 \) molecular orbital is largest, reaching 0.70 eV. The reduction of the energy gap makes it easier for the adsorbed molecule to form a bond with the matrix, and the bond is more stable, and it is helpful to weaken the H-H bond and further dissociate the \( \text{H}_2 \) molecule. This is consistent with the previous analysis results of adsorption energy and chemical bonds.

Table 3. Energy gap of molecule orbit by doping different content of Pd.

| Pt/Pd ratio       | HOMO eV | LUMO eV | Eg eV  |
|-------------------|---------|---------|--------|
| \( \text{H}_2 \)  | -10.1684| 2.3890  | 12.5574|
| \( \text{H}_2\text{-Pt}4/\gamma\text{-Al}_2\text{O}_3 \) | -4.2339 | -3.7142 | 0.5197 |
| \( \text{H}_2\text{-Pt}3\text{Pd}/\gamma\text{-Al}_2\text{O}_3 \) | -4.2312 | -3.5700 | 0.6612 |
| \( \text{H}_2\text{-Pt}2\text{Pd}_2/\gamma\text{-Al}_2\text{O}_3 \) | -4.1958 | -3.6380 | 0.5578 |
| \( \text{H}_2\text{-Pt}1\text{Pd}3/\gamma\text{-Al}_2\text{O}_3 \) | -4.2856 | -3.5836 | 0.7020 |
| \( \text{H}_2\text{-Pd}4/\gamma\text{-Al}_2\text{O}_3 \) | -4.2393 | -3.5618 | 0.6775 |

The analysis results of the density of states are shown in figure 2. The results show that the density of states of free \( \text{H}_2 \) has a peak at the Fermi level, which corresponds to the low-level orbital of the \( \text{H}_2 \) molecule, and the electron density of the high-level orbital is dispersed between 9–12 eV. When \( \text{H}_2 \) is adsorbed on the catalyst matrix, the peak of the density of states diagram shifts to a lower energy level, and the energy range of the high-level orbital is further widened. This is mainly due to the interaction between the d orbital of the Pt/Pd atom and the orbital of the \( \text{H}_2 \) molecule to transfer electrons to the \( \sigma^* \) antibonding orbital of \( \text{H}_2 \), causing it to move to a lower energy range. Among them, the peak density of states of \( \text{H}_2\text{-Pt}4/\gamma\text{-Al}_2\text{O}_3 \) shifts the most, and the peak shift of \( \text{H}_2\text{-Pd}4/\gamma\text{-Al}_2\text{O}_3 \) is the smallest. This is consistent with the analysis results of energy gap and bond length.
Figure 2. DOS of H₂ adsorbed on substrate with different content of Pd: (a) H₂, (b) H₂-Pt₄/γ-Al₂O₃, (c) H₂-Pt₃Pd/γ-Al₂O₃, (d) H₂-Pt₂Pd₂/γ-Al₂O₃, (e) H₂-Pt₁Pd₃/γ-Al₂O₃, (f) H₂-Pd₄/γ-Al₂O₃.

4. Conclusions
The adsorption behavior of the H₂-PtPd/γ-Al₂O₃ system is calculated by density functional theory combined with the periodic slab model. The results show that the absolute value of the adsorption energy at the vertex site is the largest. The greater the adsorption energy is, the stronger the interaction between H₂ and the catalyst substrate. Thus the H-H bond is elongated and the negative charge of H₂ increases, which is conducive to the further dissociation of the H₂ molecule. With the increase of doping Pd, the adsorption energy of the catalyst substrate gradually decreases, and the absolute value of the adsorption energy of Pt₄/γ-Al₂O₃ is the largest. After H₂ is adsorbed on the catalyst substrate, the energy gap of system decreases sharply, and the peak of the density of states shifts to a lower energy level. This is because the Pt and Pd atom’s d orbital interacts strongly with the σ* anti-bonding orbital of H₂ molecule, transferring electrons to the σ* anti-bonding orbital of H₂. The increase of doping Pd makes the orbital energy gap increase.
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