The study of Ni₅H(n=1-6) clusters by density functional theory

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Abstract. In this paper, the geometric structures and local relative stability of Ni₅H (n=1-6) have been systematically calculated using the generalized gradient approximation (GGA) under density functional theory. The studied results indicate that adding an H atom to the Ni₅ clusters does not significantly change the basic structures of Ni₅, and the most stable structures can be received by adsorbing an H atom on the side of pure Ni₅ clusters. The binding energy of each atom of Ni₅ and Ni₅H show same variation trend, the values of Ni₅H are larger than that of Ni₅. The fragmentation energy, adsorption energy and HOMO-LUMO gaps don’t show obvious oscillation behavior with cluster size evolution, but the values are larger at Ni₅H, which illustrate that the corresponding cluster has high stability and low chemical activity.

1. Introduction
Metal hydrides is considered as one of the most potential hydrogen storage methods because of its large hydrogen storage capacity and stable performance[1]. Understanding the adsorption structure of hydrogen on the metal surface and the dynamic behavior after adsorption on the atomic scale can provide a critical theoretical basis for the effective control of the catalytic reaction process[2-4]. Nickel is a 3d transition metal with special d-shell structure makes it rich in physical and chemical properties. Many theoretical and experimental studies have been done on the structure of Ni clusters[5-6]. Nickel-based catalyst is considered to have the most promising application prospect in the methanation reaction of syngas[7-9], so it is necessary to investigate its adsorption and activation of gas by means of simulation, which is the key of the catalytic reaction[10]. Study by Zhao et al.[11] about the carbon-monoxide and hydrogen co-adsorbed on Ni(111) surface using density functional theory shown that carbon-monoxide and hydrogen atoms were adsorbed at the HCP and FCC positions of two diagonal p(1×1) cells, respectively. Knicklbein and others[12] studied the effect of CO, N₂ and H₂ on the magnetic properties of Ni₅, and they found the influence of combined gas molecules on the properties of Ni₅ clusters. In order to effectively utilize resources and achieve sustainable development, it has become an important content to research the adsorption characteristics of hydrogen on nickel surface.

2. Computational method
Firstly, we optimized the initial configurations of Ni₅H (n=1-6) by BPW91/LanL2DZ[13], which based on the Density Functional Theory (DFT). All calculations are performed in the Gaussian16 program[14]. In this paper, different spin multiplicities and various possible initial configurations of Ni₅H (n=1-6) clusters are considered in the calculation. In order to verify that the optimized structure is truly globally minimal, the vibration frequency of the corresponding structure is calculated at the same theoretical level. We also compared theoretical values of the binding energy and bond length of Ni₂ cluster with the experimental data. The bond length of Ni₅ is 2.137 Å, the average binding energy is 1.26 eV/atom which are similar with the experimental values of 2.15Å and 1.04 eV/atom[15].

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3. Results and discussion
The lowest energy structures and metastable structures of Niₙ and NiₙH (n=1-6) are displayed in Figure 1, the white ball means H atom and the blue ball means Ni atom, the structures are labelled with (a), (b), (c), which means the steady sequence. The parameters of Niₙ and NiₙH (n=1-6) are displayed in Table 1.

![Diagram of Niₙ and NiₙH clusters](image)

Figure 1. The stable structures of Niₙ and NiₙH (n=1-6) clusters.

3.1. Geometrical structures
The most stable structure of Ni₃ cluster is isosceles triangle structure. The most stable structure of Ni₄ cluster is tetrahedron structure. The Ni₅ cluster is triangle bipyramid, and the Ni₆ cluster is octahedral structure. All above structures are similar to the conclusions of Futschek et al.[16]. The average value of the total bond length (ABL/Å) of NiH is 1.450 Å, and the average binding energy (E_b/eV/atom) is 1.481 eV/atom. For Ni₃H cluster, the lowest energy structure is an isosceles triangle with the E_b of 1.708 eV/atom and the ABL of 1.794 Å. Ni₄H (b) is a linear structure, the E_b and the ABL are 1.470eV/atom and 1.875 Å. The lowest energy structure of Ni₅H is hydrogen atom locating next to the triangle, the 2.0498Å and 1.941eV/atom are the sizes of ABL and E_b. The hydrogen atom of Ni₅H (b) structure is located at the tip of the triangle, the ABL and E_b are 2.096 Å and 1.871 eV/atom, and the energy of Ni₅H (b) is only 0.272 eV larger than that of Ni₅H (a). Putting a hydrogen atom to the tetrahedral side makes the most stable structure of Ni₆H cluster with ABL and E_b of 2.186 Å and 2.161eV/atom, respectively. The hydrogen atoms are located at the surface of the triangle and the tip of the tetrahedron are the other two isomers of Ni₆H cluster, the energy of Ni₆H (b) and Ni₆H (c) are 0.166 eV and 0.354 eV larger than that.
of the lowest energy structure, respectively. Putting a hydrogen atom on the triangle bipyramid side forms the most stable structure of the Ni$_3$H cluster, the $E_b$ and ABL are 2.321 eV/atom and 2.217 Å. Ni$_3$H (b) and Ni$_3$H (c) are the other stable structures of the Ni$_3$H cluster, whose $E_b$ are 2.254 eV/atom and 2.233 eV/atom. The energy of Ni$_3$H (b) and Ni$_3$H (c) are 0.403 eV and 0.525 eV larger than that of Ni$_3$H (a). The addition of a hydrogen atom to the octahedral side constitutes the lowest energy structures of Ni$_6$H, the ABL is 2.236 Å and the $E_b$ is 2.475 eV/atom. The hydrogen atoms of the other two isomers of Ni$_6$H are on the tip and surface of the octahedral vertices, respectively. The energy of Ni$_6$H (b) and Ni$_6$H (c) are 0.203 eV and 0.319 eV larger than that of Ni$_6$H (a).

Table 1. The average binding energy ($E_b$/eV/atom), total energy ($E_t$/a.u.), the average value of the total bond length (ABL/Å), vibrational frequency (LVF/cm$^{-1}$) and the energy of HOMO-LUMO for the most stable structure of Ni$_n$ and Ni$_n$H(n=1–6) clusters.

| Clusters | $E_b$/eV/atom | $E_t$/(a.u.) | ABL/Å | HOMO/eV | LUMO/eV | LVF/cm$^{-1}$ |
|----------|---------------|--------------|--------|---------|---------|---------------|
| NiH      | 1.481         | -169.929     | 1.450  | -5.224  | -2.558  | 1863.1        |
| Ni$_2$   | 1.264         | -338.738     | 2.137  | -4.354  | -2.667  | 325.6         |
| Ni$_5$H  | 1.708         | -339.328     | 1.794  | -3.673  | -2.503  | 299.9         |
| Ni$_4$   | 1.613         | -508.149     | 2.248  | -3.701  | -2.667  | 204.2         |
| Ni$_5$H  | 1.941         | -508.745     | 2.049  | -4.109  | -3.075  | 157.6         |
| Ni$_4$   | 1.908         | -677.576     | 2.336  | -3.456  | -3.129  | 132.7         |
| Ni$_6$H  | 2.161         | -678.177     | 2.186  | -4.136  | -3.075  | 77.3          |
| Ni$_5$   | 2.129         | -847.011     | 2.336  | -4.218  | -3.401  | 68.6          |
| Ni$_6$H  | 2.321         | -847.612     | 2.217  | -4.027  | -3.401  | 101.9         |
| Ni$_6$   | 2.252         | -1016.440    | 2.375  | -3.619  | -3.347  | 91.7          |
| Ni$_7$H  | 2.475         | -1017.057    | 2.236  | -4.435  | -2.639  | 56.9          |

3.2. Stability analysis

The average binding energy ($E_b$) and the fragmentation energy ($\Delta E$) have been calculated by equation (1) and equation (2):

$$E_b(Ni_nH)=[nE(Ni)+E(H)-E(Ni_nH)]/(n+1)$$  \hspace{1cm} (1)

$$\Delta E(Ni_nH)=E(Ni_{n-1}H)+E(Ni)-E(Ni_nH)$$  \hspace{1cm} (2)

$E$ represents the energy of a clusters or a single atom. The relationship between $E_b$ of Ni$_n$ and Ni$_n$H (n=1–6) clusters and the number of Ni atoms are shown in Figure 2, where the $E_b$ of Ni$_n$ and Ni$_n$H clusters show a monotonous increasing trend with the increase of cluster size. The same change of $E_b$ between Ni and Ni$_n$H indicate that the adsorption of H atom has little effect on the stability of Ni$_n$ clusters. The values of Ni$_n$H are obviously larger than those of Ni$_n$ in $E_b$ indicate that the stability of Ni$_n$H clusters is further enhanced after adsorption of H atom.

The $\Delta E$ can better reflect the relative stability of the system than $E_b$. Therefore, the $\Delta E$ of Ni$_n$ and Ni$_n$H clusters under BPW91/LanL2DZ are displayed in Figure 3. Ni$_2$ and Ni$_3$ are the local peaks of Ni$_n$, which indicate that the Ni$_2$ and Ni$_3$ clusters have higher local relative stability than adjacent clusters. For Ni$_n$H (n=1–6) clusters, As the size of the cluster increases, the $\Delta E$ increases monotonically, and the growth rate decreases gradually at the $n=5$, and end with larger value at Ni$_6$H. The results show that the Ni$_6$H cluster has the strongest thermodynamic stability in the study range.
The adsorption energy ($E_{ads}$) of hydrogen has been calculated by equation (3).

$$E_{ads} = E(Ni_n) + E(H) - E(Ni_nH)$$

The adsorption energy is negative, indicating that the adsorption process is exothermic. When the $E_{ads}$ is lower, it indicates that the binding force is enhanced, and the final adsorption configuration is more stable. The $E_{ads}$ of $Ni_nH$ is displayed in Figure 4. It can be concluded from the figure that $Ni_3H$ has high stability in the study range.

The electronic properties of $Ni_nH$ have been studied by calculating the energy gaps ($E_{gap}$) between HOMO and LUMO molecular orbital. The $E_{gap}$ reflects the ability of electrons to transition from occupying orbital to unoccupied orbital. The cluster size and the $E_{gap}$ are shown for $Ni_n$ and $Ni_nH$ clusters in Figure 5. As seen from Figure 5, the $E_{gap}$ of $Ni_n$ shows obvious odd-even oscillations in the study range, and has local peaks at $n=2,5$. The $E_{gap}$ of $Ni_1H$ and $Ni_6H$ is larger than that of other clusters indicating that the corresponding structure has low chemical activity and is more stable than other clusters.

4. Conclusions
In summary, using density functional theory, we have systematically studied the geometries and local relative stability of $Ni_nH$ ($n=1-6$) clusters. The results show that the lowest energy structures of $Ni_nH$ ($n=1-6$) clusters can be received by adsorbing an H atom on the side of pure $Ni_n$ clusters. It is also found...
that doping an H atom to the Ni₇₅ clusters does not significantly influence the basic structure of Ni₇₅. Local relative stability analysis results show that the Ni₇₅H cluster is more stable than neighbouring clusters.

**Acknowledgments**

This research was financially supported by the Youth Innovation Fund of Xi'an Shiyou University under No. 2013QN004 and the National Natural Science Foundation of China under No. 11247229 and 11304246.

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