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ORIGINAL RESEARCH

A theoretical study on the hydrogen storage properties of planar $(AlN)_n$ clusters (n = 3-5)

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Abstract The structures and hydrogen storage capacities of $(AlN)_n$ (n = 3-5) clusters have been systematically investigated by using density functional theoretical calculations. At ωB97xD/6-311 + G(d, p) level, the planar structures of $(AlN)_n$ (n = 3-5) can adsorb 6-10 H_2 molecules with average adsorption energies in the range 0.16 to 0.11 eV/H_2, which meet the adsorption energy criteria of reversible hydrogen storage. The gravimetric density of H_2 adsorbed on $(AlN)_n$ clusters can reach 8.96 wt%, which exceed the target set by Department of Energy. The hydrogen adsorption energies with Gibbs free energy correction indicate that the adsorption of 6 H_2 in $(AlN)_3$, 8 H_2 in $(AlN)_4$ and 10 H_2 in $(AlN)_5$ is energetically favorable below 96.48, 61.43, and 34.21 K, respectively. These results are expected to motivate further the applications of clusters to be efficient hydrogen storage materials.

Keywords Hydrogen storage · Planar clusters · Theoretical study · Quantum chemistry · DFT

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Introduction

Hydrogen energy has gained much attention and emerged as a promising energy source to replace currently used fossil fuels [1–4] because of its abundance and outstanding performance in terms of environmental protection [5]. However, the hydrogen application is limited due to difficulties in developing safe, dependable and cost-effective hydrogen storage techniques [6–9]. Therefore, much effort has been devoted to seek various hydrogen storage materials. For instance, storage in compressed gas hydrogen tanks [10], liquid hydrogen tanks [11] and solid substrates [12]. Among the various options, solid-state storage in some medium is considered to be the most cost-effective and safest method [13–18].

The solid-state hydrogen storage materials can be classified into two categories: physisorption and chemisorption materials. For instance, Carbon-based nanostructures [19–23], Metal-organic frameworks (MOF) [2, 24–26], covalent organic frameworks (COFs) [27–29] and other microporous solids are good candidates for H_2 storage via physisorption; Metal hydrides [30–34], complex hydrides [35–37], and metal alloys have been proposed as potential H_2 storage materials via chemisorption. Physisorption is difficult to achieve high hydrogen capacity, but hydrogen can be desorbed under ambient conditions. Chemisorption can achieve high hydrogen storage capacity easily, but it is hardly reversible. Therefore, an efficient and reversible hydrogen storage material should meet two requirements: 1.The material can adsorb hydrogen in molecule form with adsorption energy in the range 0.1-0.4 eV/H_2 [38, 39]; 2. The gravimetric density of H_2 should exceed 7.5 wt%, which is proposed by the US Department of Energy (DOS) [40].

In recent years, carbon-based nanostructures decorated with transition metal atoms attract much attention [38, 39, 41–43], because the pure carbon-based materials do not have

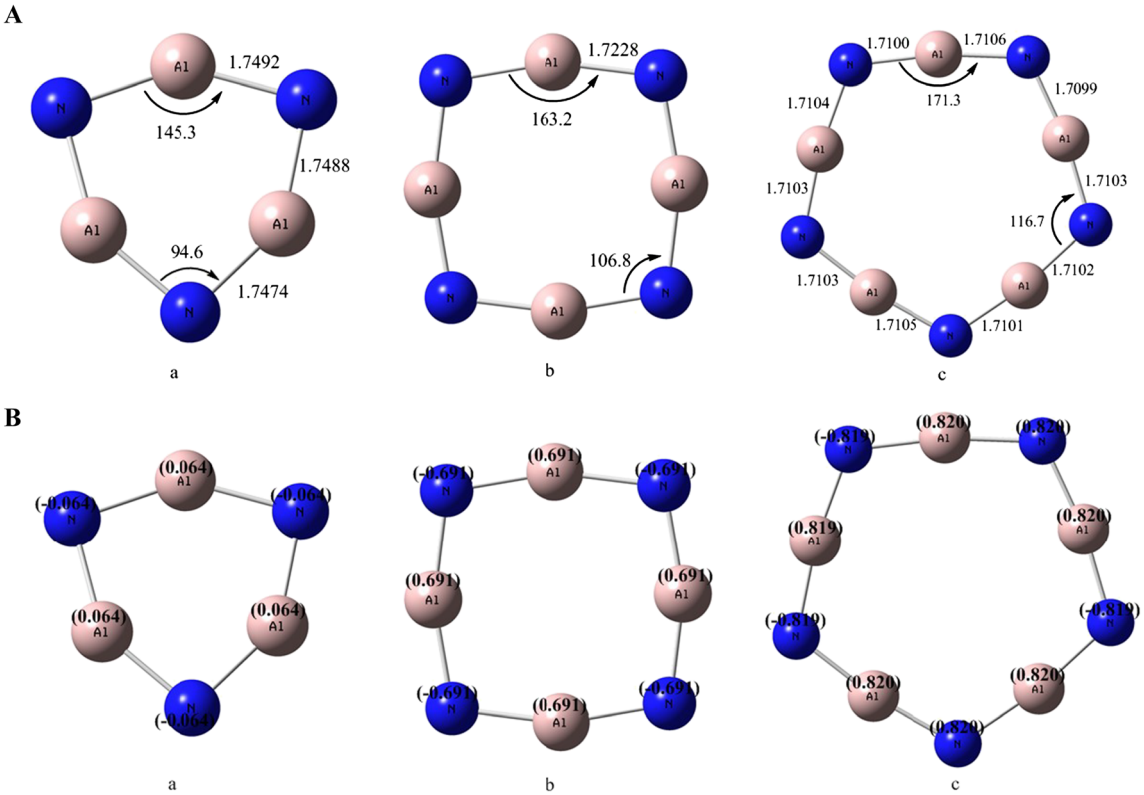

Fig. 1 The structures and electronic structure of $(AlN)_n$ (n = 3-5) at ωB97xD/6-311 + G(d, p) level

high hydrogen storage capacity as predicted previously [19–21]. However, the transition metal atoms tend to form clusters rather than distribute individually because of their large cohesive energies. In order to bypass the problem of clustering, the best method is that hydrogen molecules are adsorbed on the substrate material [44, 45]. In the present work, we choose the $(AlN)_n$ clusters as the researched substrate materials. We systematically study the hydrogen storage materials $(AlN)_n$ (n = 3-5) at ωB97xD/6-311 + G(d, p) level. The gravimetric density and adsorption energies are carried

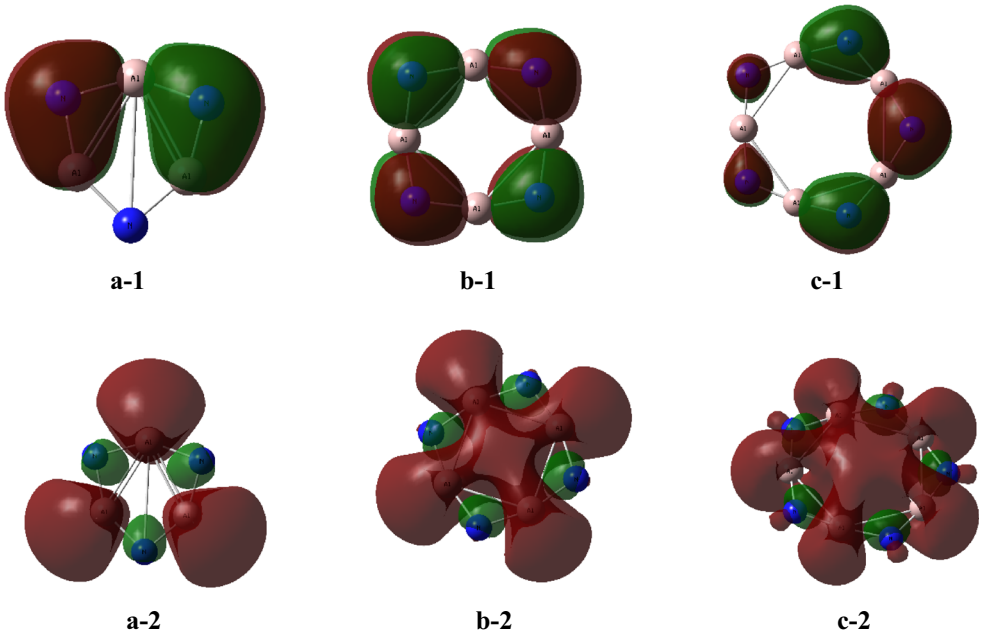

Fig. 2 The frontier molecular orbital (FMO) analyses are performed at ωB97xD/6-311 + G(d, p) level

Table 1 The calculated binding Energy (E_b) of $(AlN)_n$ (n = 3−5) Clusters, successive difference in binding energy ΔE_b, adsorption energies per H_2, number of hydrogen molecules adsorbed (N_{H2}) at the ωB97xD/6-311 + G(d, p) level

Number	E_b(eV)	E_a(eV)	N_{H2}
3	4.99	0.16	6
4	5.66	0.13	8
5	5.90	0.11	10

out to obtain a comprehensive analysis from a theoretical point of view. All the analysis results reveal that $(AlN)_n$ clusters should be considered as a kind of potential hydrogen storage materials.

Computational methodology

In the present work, all the calculations are carried out using the range-separated hybrid density functional theory (ωB97xD) with the valence diffuse and polarization function 6-311 + G(d, p) basis sets. For the lowest energy structures of $(AlN)_n$ clusters, we further study their behavior of hydrogen storage. The procedure of adsorption, i.e., H_2 molecules are successively added on the most stable structures of each $(AlN)_n$ clusters, which is repeated until the H_2 cannot be adsorbed. The adsorption energies are calculated by $\Delta E = \{E_{[mH2-complex]} - E_{[complex]} - m \times E_{[H2]}\}/m$. The $E_{[mH2\text{-}complex]}$, $E_{[complex]}$, and $E_{[H2]}$ are the calculated energies of mH_2 adsorbed on the complex, bare complex, and H_2 molecule, respectively. The bare and hydrogen adsorbed $(AlN)_n$ clusters have no imaginary frequency. All computations are performed using the Gaussian 09 [46] program packages.

Results and discussion

Geometrical structure and Electronic structure

In the previously literatures, BelBruno [47] and Blanco [48] et al. reported the structures of $(AlN)_n$ (n = 3-5). These results showed that the planar geometries are the most stable structures. Therefore, in this paper, we optimize these planar structures of $(AlN)_n$ (n = 3-5) at ωB97xD/6-311 + G(d, p) level. All of the bond lengths and angles are shown in Fig. 1a.

To clarify the electronic structures of $(AlN)_n$, the natural bond orbital (NBO) analysis are performed to reflect AlN clusters' electronic structures. The natural charge of each atom is denoted in Fig. 1b. For instance, Al atom has charge of 0.691 e and N atom has -0.691 e charge in $(AlN)_4$, respectively. It means that the charge transfer from Al atom to N atom, which makes the Al-N bond becomes polar and generates a local electric field.

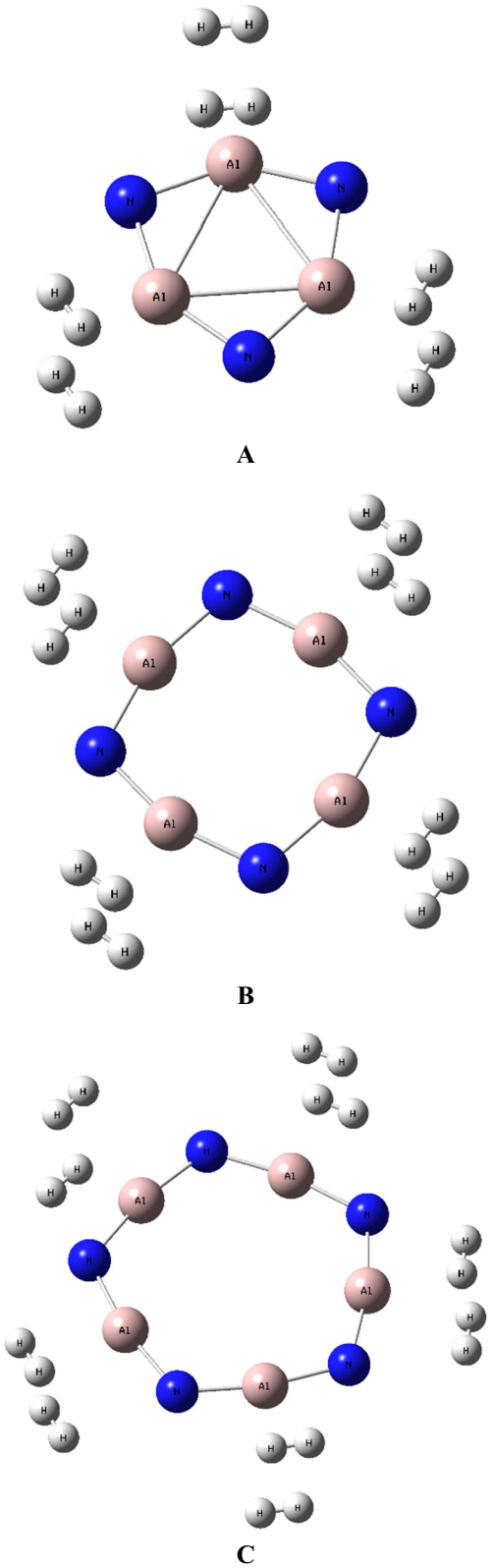

Fig. 3 The planar structures of $(AlN)_n$ (n = 3-5) adsorb hydrogen molecules at ωB97xD/6-311 + G(d, p) level (The hydrogen molecules are adsorbed on the Al atoms)

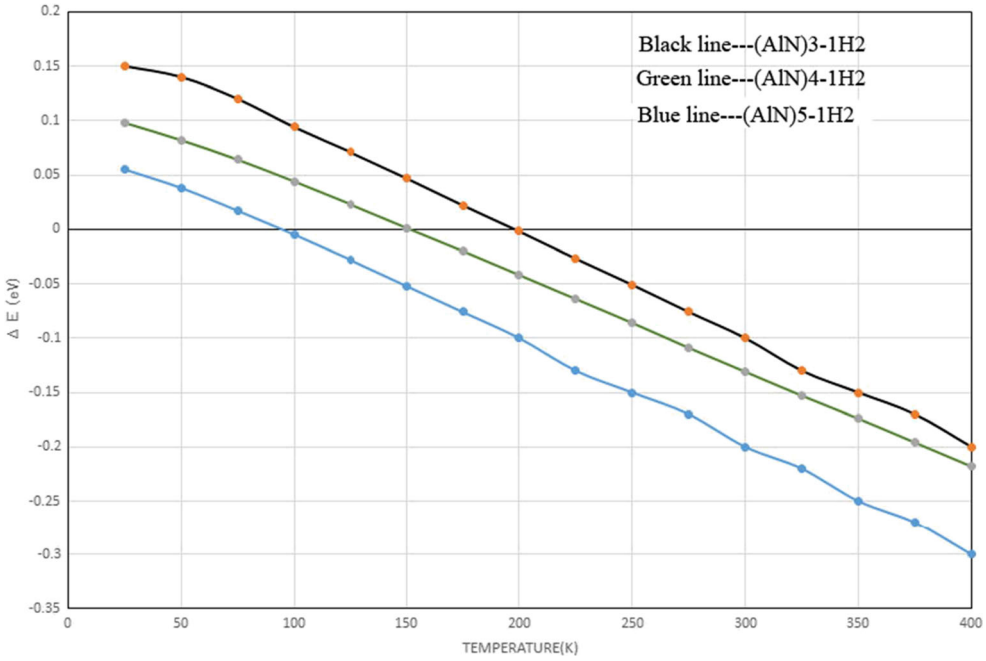

Fig. 4 Temperature dependence of Gibbs free energy corrected adsorption energies (ΔE_G) for $(AlN)_n$-1H2 at ωB97xD/6-311 + G(d, p) level

Therefore, the hydrogen storage behavior of $(AlN)_4$ is attributed to its polarize ability for hydrogen molecules. Moreover, the frontier molecular orbitals (FMO) are analyzed at the same level. The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of stable ground state geometries of $(AlN)_n$ (n = 3-5) clusters are shown in Fig. 2. We can see that HOMOs are mostly contributed from N atoms, and the LUMOs are mostly contributed from Al atoms. These results indicate that the hydrogen molecules should be preferentially adsorbed on Al atoms.

Binding energies of $(AlN)_n$ (n = 3-5)

Since binding energy is an important analysis method for researching the stability of clusters, we list the binding energies of $(AlN)_n$ (n = 3-5) at ωB97xD/6-311 + G(d, p) level in

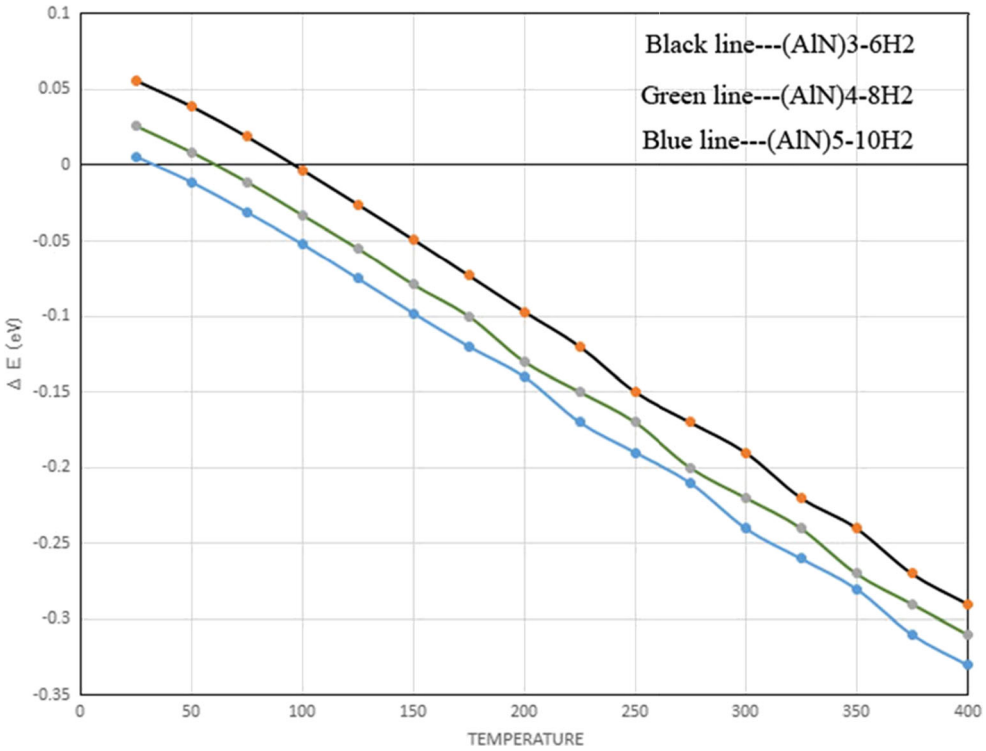

Fig. 5 Temperature dependence of Gibbs free energy corrected adsorption energies (ΔE_G) for $(AlN)_n$-mH2 at ωB97xD/6-311 + G(d, p) level

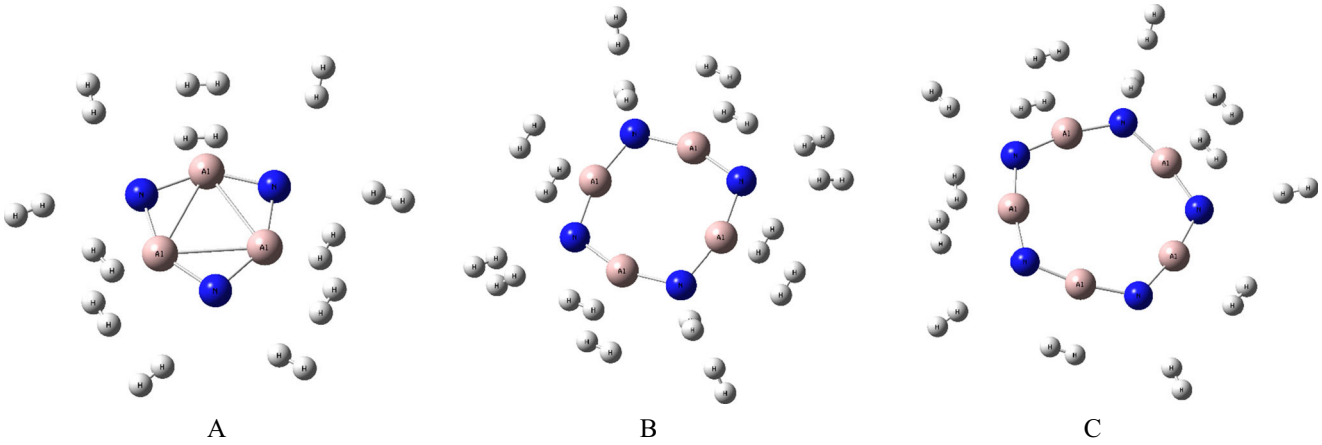

Fig. 6 The planer structures of $(AlN)_n$ (n = 3-5) adsorb hydrogen molecules at ωB97xD/6-311 + G(d, p) level. The hydrogen molecules are adsorbed on the Al and N atoms

Table 1. The binding energy is calculated by the formula of $E_b = -\frac{E_{(AlN)n} - n \times E_{(AlN)}}{n}$. The $E_{(AlN)n}$ is the total energy of the $(AlN)_n$ clusters, and $E_{(AlN)}$ is the energy of single AlN molecule. When the value of E_b is positive, it indicates that the formation of cluster is exothermic and the cluster is stable. As listed in Table 1, the binding energy values of clusters are 4.99-5.90 eV. We can find that the binding energies of the clusters increase monotonically, which indicate the stability of clusters is increasing. These results indicate that large clusters are relatively more stable.

Hydrogen Storage Behavior of $(AlN)_n$ Clusters

The hydrogen adsorption properties of $(AlN)_n$ are investigated at ωB97xD/6-311 + G(d, p) level. The hydrogen average adsorption energy can be derived from the following formula as follows: $\Delta E = \{E_{[mH2-complex]} - E_{[complex]} - m \times E_{[H2]}\}/m$. The optimized structures of $(AlN)_n$ clusters with adsorbed H_2 are depicted in Fig. 3. The numbers of hydrogen adsorbed and hydrogen adsorption energies of all clusters studied here are listed in Table 1. As shown in Fig. 3, we can find that $(AlN)_n$ (n = 3-5) adsorb 6-10 H_2 molecules on Al sites with the average adsorption energy of 0.16-0.11 eV/H_2(the detailed structural information is displayed in Fig. S1 of the Supporting Information). They are all in the range of reversible H_2 adsorption, and their gravimetric density reach 8.96 wt%. These results have met the criteria for hydrogen storage requirements of average adsorption energy and gravimetric density.

The Gibbs corrected adsorption energy is positive for the complex indicate that the formation of the complex is energetically favorable. In Figs. 4 and 5, we calculate the Gibbs free energy corrected adsorption energies at different temperatures and 1 atm.

From these two pictures, we can find that the clusters $(AlN)_n$ adsorb one hydrogen molecule in a wider temperature range than that of multiple hydrogen molecules. For instance, $(AlN)_3(1H_2)$ with positive Gibbs corrected adsorption energy below 200 K, however, $(AlN)_3(6H_2)$ with positive Gibbs corrected adsorption energy below 96.48 K.

Therefore, the hydrogen adsorption energies with Gibbs free energy correction indicate that the adsorption of 6 H_2 in $(AlN)_3$, 8 H_2 in $(AlN)_4$ and 10 H_2 in $(AlN)_5$ is energetically favorable below 96.48, 61.43, and 34.21 K, respectively.

Further, when the Al and N atoms are all considered as the reaction sites, more hydrogen molecules can be adsorbed (Fig. 6) (the detailed structural information and energies are displayed in Fig. S2 and Table S1 of the Supporting Information). $(AlN)_3$ can adsorb 12 H2 with 0.13 eV/H2, which corresponds to 16.44 wt% of hydrogen adsorption. For $(AlN)_4$, this cluster can adsorbs 16 H2 with 0.10 eV/H2, and its gravimetric density is 16.44 wt%. For $(AlN)_5$, when it adsorbs 14 H2, its average adsorption energy has dropped to 0.10 eV/H2. Its gravimetric density is 12.10 wt%. The average adsorption energy indicates that the H_2 adsorbed on the clusters are actual significance [49]. However, it can be readily inferred from the analysis of Figs. 4 and 5 that this adsorption processes are energetically favorable at much lower temperatures and higher pressures.

Conclusion

Theoretical calculations are performed using the density functional theory to research planar clusters of $(AlN)_n$ (n = 3-5). The hydrogen storage capacities of the complexes are investigated. According to our calculations, the hydrogen storage capacity can reach 8.96 wt% for $(AlN)_n$, which meet the target specified by U.S. Department of Energy. Moreover, $(AlN)_n$ clusters can avoid the problem in metal clustering of metal-decorated materials, because the metal atom Al is the part of the substrate itself. Most importantly, the adsorption energies of H_2 are within 0.16−0.11 eV/H_2, which is a recommended

range for reversible hydrogen physisorption under standard test conditions. Therefore, $(AlN)_n$ clusters are considered to be a promising materials for hydrogen storage. These results may be useful for extending the species of efficiency hydrogen storage materials, and appeal much more research on the experiment.

Compliance with ethical standards

Funding The authors declare no competing financial interest.

Ethical Statement The paper entitled "**A theoretical study on the hydrogen storage properties of planar $(AlN)_n$ clusters (n = 3–5)**" by **Chen Guo*, and Chong Wang** to the famous journal *Structural Chemistry*. We declare that all the co-authors are aware of and approve of the submission.

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