Materials Research Express

PAPER

Hydrogen adsorption behavior on AXenes Na\textsubscript{2}N and K\textsubscript{2}N: a first-principles study

Shuping Dong, Haona Zhang, Shiqiang Yu, Baibiao Huang, Ying Dai\textsuperscript{*} and Wei Wei\textsuperscript{*}

School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People’s Republic of China

\textsuperscript{*} Authors to whom any correspondence should be addressed.

E-mail: daiy60@sdu.edu.cn and weiwi@sdu.edu.cn

Keywords: hydrogen storage, 2D materials, AXenes, Na\textsubscript{2}N and K\textsubscript{2}N, first-principles

Abstract

It is a consensus that the hydrogen economy has come to a standstill due to the lack of feasible hydrogen storage solutions, especially, the suitable hydrogen storage materials. In this work, the potential of a new kind of two-dimensional (2D) AXenes, Na\textsubscript{2}N and K\textsubscript{2}N, as hydrogen storage materials are evaluated by the first-principles calculations. In particular, we find that Na\textsubscript{2}N in T phase indicates a hydrogen storage capacity as high as 6.25 wt\% with a desirable hydrogen adsorption energy of \(-0.167\) eV per H\textsubscript{2} molecule and a desorption temperature of 216 K, identifying T-phase Na\textsubscript{2}N to be a very promising reversible hydrogen storage material. In accordance to our results, H\textsubscript{2}–Na\textsubscript{2}N interaction causes H\textsubscript{2} charge polarization, which is responsible for the moderate binding strength. In addition, Gibbs adsorption free energy reveals that the system will be more stable as more H\textsubscript{2} molecules are loaded on the surface.

1. Introduction

It is well known that hydrogen is a renewable and environmentally friendly energy source, and as a clean energy source hydrogen is regarded as an alternative to fossil fuels \[1\]. It should be highlighted that the only product of hydrogen combustion is water, which can effectively avoid environmental pollution. In current stage, safe and efficient storage of hydrogen is however a significant challenge, conventional storage methods via liquefaction and pressurization are suffering from low efficiency and low capacity. It is therefore a crucial issue to find or design promising materials for hydrogen storage \[2–4\].

In 2004, graphene was realized, ever since then the study of two-dimensional (2D) material has generated a lot of interest. In the light of the large surface-to-volume ratio and special electronic structures, 2D materials are used to immobilize hydrogen molecules with superiority \[5–8\]. In general, doping and decoration are commonly used to improve the hydrogen storage properties of 2D materials, in terms of modulating the surface properties of the material and adjusting the hydrogen adsorption energy \[9\]. It should be pointed out that carbon-based nanomaterials, which are extensively studied as hydrogen storage systems, indicate weak binding to hydrogen molecule and thus are not suitable for hydrogen storage \[10, 11\]. In addition, an effective way to increase the hydrogen binding energy is doping with transition metals (TM), light alkali metals, alkaline earth metals and nonmetals \[12\]. In a recent work, e.g., Holec \textit{et al} reported theoretically and experimentally the enhancement of H\textsubscript{2} adsorption capacity on metal-doped graphene \[13\]. \textit{In particular}, their experimental measurements demonstrated that although the specific area of the metal-decorated carbon material is smaller than that of the carbon material, the existence of Ru and Pt nanoparticles leads to an improvement in H\textsubscript{2} absorption performance at room temperature. In addition, Zhou \textit{et al} investigated the H\textsubscript{2} adsorption on Ni functionalized defective h-BN substrates on the basis of density functional theory (DFT) simulations \[14\], and their results revealed that the Ni-doped h-BN sheets exhibit an ideal adsorption energy in the range of from 0.40 to 0.51 eV, meeting the H\textsubscript{2} storage requirements. In a recent experiment, Nair \textit{et al} investigated the hydrogen storage capacity on Pd-decorated graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}), and they found that the hydrogen storage capacity at 25 °C and 4 MPa reaches 2.6 wt\% \[15\]. It should be pointed out that, however, the doped or decorated
materials with considerable hydrogen storage properties are often complex and difficult to prepare [16, 17], and the stability under different conditions cannot be assured [18]. It is therefore urgent to design materials with high gravimetric and volumetric density under favorable thermodynamic conditions. In an alternative way, phase transition was considered to improve the performance; for example, MoS2 is one of the most studied. In particular, the potential of monolayer 1T and 1T’ MoS2 as hydrogen storage materials was compared by Chen et al and 1T’ MoS2 was demonstrated to have good hydrogen storage capability with a capacity of 3.9 wt% [19]. In comparison to the 2H counterpart, the hydrogen storage capability was significantly improved through phase transition.

In this work, the potential in hydrogen storage of a class of new 2D materials, namely, AXenes [20], is studied by means of the first-principles calculation based on DFT. In particular, 2D Na2N and K2N in different phase (i.e., T, I and H phases) are featured as metal-shrouded monolayers, that is, the exposed light s-orbital metal atoms (Na and K) are the active centers for hydrogen adsorption. It is of interest that the nonstoichiometric Na2N and K2N behave as hole-doped materials, which probably is responsible for the moderate hydrogen binding strength. In light of the 2D nature, large amount active sites and unique electronic structures render AXenes Na2N and K2N appealing candidates of hydrogen storage materials. In accordance to our results, average hydrogen adsorption energy on T-Na2Ni is \(-0.167 \text{ eV/H}_2\), and the hydrogen storage capacity is as high as 6.25 wt%. It therefore can be concluded that T-Na2N could be a very promising material for reversible hydrogen storage without stability problems of doped or decorated materials.

2. Computational methodology

In the present work, the projector augmented wave (PAW) [21] method as implemented in the Vienna \emph{ab initio} simulation package (VASP) [22, 23] was employed for all our calculations. In order to describe the exchange–correlation functional, the generalized gradient approximation (GGA) [24] with Perdew–Burke–Ernzerhof (PBE) formalism was employed [25]. It is necessary to include the van der Waals (vdW) interactions for the adsorption of H2 molecule on AXenes, which were considered by using the DFT–D2 semiempirical correction [26, 27]. In order to prevent the interactions between two periodic layers, a vacuum space of about 20 Å was added in direction perpendicular to the material plane. In the integration of the Brillouin zone, a \(11 \times 11 \times 1\) Monkhorst–Pack \(k\)-point mesh was adopted, and the energy cutoff was set to 500 eV for the plane wave basis [28]. In case of geometry optimization, the calculation will stop when the residual force on each atom was less than \(-0.01 \text{ eV Å}\) and the energy tolerance was \(10^{-6} \text{ eV}\).

3. Results and discussion

3.1. Structure and electronic properties of Na2N and K2N

In figure 1, atomic structures of the new 2D AXenes Na2N and K2N in different phases (T, H and I) are presented, with the unit cells denoted. In particular, the T-phase structure is isomorphic to the experimentally synthesized 2D electrode Ca3N, while the H phase is isomorphic to 2H MoS2. In respect to the structure of I phase, each N atom is bonded to eight Na atoms from both sides, with a different tetragonal symmetry from the H and T phases. In each unit cell of the AXenes considered in this work, it can be seen that two alkali metal atoms and one N atom constitute a three-atomic-layer Na/K–N–Na/K sandwich structure. In other words, the new Na2N and K2N of AXenes can be regarded as metal-shrouded 2D materials. In comparison to carbon-based materials, the exposed metal atoms guarantee the moderate hydrogen adsorption energy, which is the key for reversible...
hydrogen storage. In Table 1, the lattice constants and relevant structural parameters of Na$_2$N and K$_2$N in three
phases are summarized, and it can be found that our results are consistent with previous study [20].

In Figure 2, band structures of the 2D AXenes of consideration are shown. It can be seen that Na$_2$N and K$_2$N
in different phases are all characterized to be metallic or half-metallic, indicative of desired electric conductivity.
In particular, for example, T-Na$_2$N shows a 100% spin polarization at the Fermi level. It should be pointed out in
passing that the metallic properties of these materials suggest great potential in applications in electrochemical
catalysis, such as nitrogen reduction reaction (NRR), hydrogen/oxygen evolution reaction (HER/OER), and so
forth.

| structure  | $a$  | $d_{M-N}$ | $d_{M-M}$ | $d_{N-N}$ |
|-----------|------|-----------|-----------|-----------|
| T-Na$_2$N | 3.689| 2.362     | 2.950     | 3.689     |
| H-Na$_2$N | 3.494| 2.378     | 2.517     | 3.494     |
| I-Na$_2$N | 3.018| 2.459     | 2.444     | 3.018     |
| T-K$_2$N  | 4.322| 2.778     | 3.493     | 4.322     |
| H-K$_2$N  | 4.058| 2.815     | 3.133     | 4.058     |
| I-K$_2$N  | 3.527| 2.915     | 3.035     | 3.527     |

Figure 2. Spin-polarized band structure of (a) T-Na$_2$N, (b) H-Na$_2$N, (c) I-Na$_2$N, (d) T-K$_2$N, (e) H-K$_2$N and (f) I-K$_2$N; pink and blue
curves represent spin-down and spin-up channels, respectively, and the Fermi level is set to zero. In (a) and (c), insets are the Brilloin
zones for hexagonal and tetragonal unit cells, respectively, with high-symmetry points denoted.

Figure 3. Gibbs free energy diagram for HER on Na$_2$N and K$_2$N of different phases under standard conditions. In our calculations, one
(−1H) and two H atoms (−2H) adsorption per unit cell are taken into account, see the insets in (a) and (b); for the latter case, $\Delta G_{\text{H*}}$ is
an average value.
3.2. Atomic and molecular hydrogen adsorption on Na$_2$N and K$_2$N

In order to give a complete picture for hydrogen adsorption on Na$_2$N and K$_2$N, atomic H adsorption are evaluated before studying the molecular H$_2$ adsorption. In our study, we consider the hydrogen adsorption and subsequent desorption as an electrochemical HER process, that is,

$$++_2\rightarrow_-^\ast\rightarrow H_2$$

where $^\ast$ denotes the active site. In case of atomic H adsorption, the Gibbs free energy change ($\Delta G_{H^\ast}$) can be obtained by the following expression

$$\Delta G_{H^\ast} = \Delta E_{H^\ast} + \Delta E_{ZPE} - T \Delta S_{H^\ast}$$

where $\Delta E_{H^\ast}$ represents the adsorption energy of hydrogen, $\Delta E_{ZPE}$ and $\Delta S_{H^\ast}$ are the differences in zero-point energy and entropy between the adsorbed hydrogen ($H^\ast$) and hydrogen in gas phase ($H_2$) at 298.15 K, respectively. In figure 3, results are shown for Na$_2$N and K$_2$N in different phases. In most cases, $\Delta G_{H^\ast}$ values are large and positive, approaching 2.0 eV; it is an indication of rather weak adsorption. In these cases, atomic H is adsorbed on top of metal atoms from one or two sides of the material. It can be seen that, however, one H atom adsorption on I-Na$_2$N and two H atoms adsorption on I-K$_2$N reveal strong binding strength, with $\Delta G_{H^\ast}$ being $-1.08$ and $-0.87$ eV, respectively, which suggests difficult hydrogen desorption from the surfaces. In these two situations, the strong adsorption can be attributed to the fact that H species are bound close to the N atoms after full structure relaxation. It therefore can be concluded that Na$_2$N and K$_2$N used for hydrogen storage in an electrochemical manner is not suitable, because of the either too weak or too strong binding strength.

In order to illustrate the hydrogen storage capacity of Na$_2$N and K$_2$N, H$_2$ molecules are introduced on the surface step by step (hydrogenation). In order to evaluate the binding strength, the average hydrogen adsorption energy on the surface of AXenes is defined as

$$E_{ads}^{ave} = (E_{H_2-AXenes} - nE_{H_2} - E_{AXenes}) / n$$

where $n$ stands for the number of absorbed hydrogen molecules, and $E_{H_2}$, $E_{AXenes}$ and $E_{nH_2-AXenes}$ represent the total energies of H$_2$ molecule in gas phase, monolayers and H$_2$ adsorbed AXenes system, respectively. In an alternative way, the consecutive hydrogen adsorption energy for H$_2$ molecule on AXenes can be calculated according to

$$E_{ads}^{cons} = E_{nH_2-AXenes} - E_{H_2} - E_{(n-1)H_2-AXenes}$$

In hydrogen storage, an important indicator is the theoretical capacity $C_{the} \%$, which can be calculated according to

$$C_{the} \% = \frac{m_{H_2}}{m_{H_2} + m_{AXenes}} \times 100\%$$

with $m_{H_2}$ and $m_{AXenes}$ being the molar masses of H$_2$ and AXenes (Na$_2$N and K$_2$N), respectively. In our calculations, up to four H$_2$ molecules per unit cell of AXenes are taken into account; for example, one, two, three and four H$_2$ molecules adsorbed on the unit cell of T-Na$_2$N are referred to as T-Na$_2$N + 1H$_2$, T-Na$_2$N + 2H$_2$, T-Na$_2$N + 3H$_2$ and T-Na$_2$N + 4H$_2$, respectively. In respect to T-Na$_2$N + 1H$_2$, it corresponds to a H$_2$ layer on one side of T-Na$_2$N; when introducing the second H$_2$ layer onto the other side gives rise to T-Na$_2$N + 2H$_2$, and T-Na$_2$N + 4H$_2$ implies that there are two H$_2$ layers on each side of the T-Na$_2$N.

Figure 4. Top and side views of the optimized structures of H$_2$ molecule adsorbed T-Na$_2$N and T-K$_2$N. (a) T-Na$_2$N + 1H$_2$, (b) T-Na$_2$N + 2H$_2$, (c) T-Na$_2$N + 3H$_2$, (d) T-Na$_2$N + 4H$_2$, (e) T-K$_2$N + 1H$_2$, (f) T-K$_2$N + 2H$_2$, (g) T-K$_2$N + 3H$_2$ and (h) T-K$_2$N + 4H$_2$. Pink, blue, yellow and violet spheres represent H, N, Na and K atoms, respectively.
In figure 4, as representatives, the optimized structures of T-Na2N loaded with 1, 2, 3 and 4 hydrogen molecules per unit cell are shown. It can be noted that the first H2 layers on both sides of T-Na2N are located above N atoms with the H–H bond perpendicular to the material plane (end-on), while the second two H2 layers are on top of the Na atoms with the H–H bond parallel to the material plane (side-on). In table 2, average adsorption energy, consecutive adsorption energy, hydrogen storage capacity, M–H2 distance and H–H bond length for different systems are summarized.

It can be found that, generally, both the average and consecutive adsorption energies decrease with the increase of H2 molecules on the surface, which is an indication of limited number of H2 molecule to be adsorbed. In case of T-Na2N + 1H2, as an example, the adsorption energy of one H2 is calculated to be −0.169 eV, a desirable value for hydrogen adsorption. In regard to T-Na2N + 2H2, the average and consecutive adsorption energies are −0.167 eV and −0.164 eV, respectively, which are still the acceptable values in hydrogen storage. In the case of a free H2 molecule, its bond length is calculated to be 0.751 Å, which is consistent with previous calculation [29]. In T-Na2N + 1H2 and T-Na2N + 2H2, while the H–H bond lengths are 0.791 and 0.787 Å, respectively. It is an indication that H2 molecules adsorbed on T-Na2N are activated. In the situation of T-Na2N + 3H2, the average adsorption energy reduces to −0.132 eV, and the consecutive adsorption energy turns out to be −0.060 eV, which is too small to firmly adsorb the third layer of H2. In principle, too weak binding strength is not conducive to hydrogen adsorption while too strong binding strength is detrimental to the hydrogen desorption from the surface. In the energy point of view, therefore T-Na2N is identified to a promising candidate for hydrogen storage with a storage capacity as high as 6.25% (T-Na2N + 2H2). In addition, the hydrogen storage capacity of H-Na2N maximizes also at 6.25% (H-Na2N + 3H2) but with slightly reduced hydrogen binding strength.

In figure 4, hydrogen adsorption structures are also shown for T-K2N. It is different from H2 adsorption on T-Na2N, the first two layers of H2 are adsorbed above the K atoms with the H–H bond parallel to the surface, while the second two layers of H2 will be located on top of the opposite K atoms with the H–H bond perpendicular to the surface. In case of T-K2N + 1H2, the adsorption energy is −0.237 eV, corresponding to a storage capacity of 2.13%. In respect to T-K2N + 2H2, the average adsorption energy turns out to be −0.142 eV and the consecutive adsorption energy is only −0.046 eV (−0.017 eV for H-K2N and −0.084 eV for I-K2N with the same H2 loading). In consideration of the unstable adsorption, therefore, hydrogen adsorption behavior on K2N will not be discussed.

| System | \(E_{\text{ads}}\) (eV) | \(E_{\text{ads,cons}}\) (eV) | \(C_{\text{wt}}\) | \(d_{\text{M–H}}\) | \(d_{\text{H–H}}\) |
|--------|----------------|----------------|-------------|----------------|----------------|
| T-Na2N + 1H2 | −0.169 | −0.169 | 3.23 | 2.386 | 0.791 |
| T-Na2N + 2H2 | −0.167 | −0.164 | 6.25 | 2.412 | 0.787 |
| T-Na2N + 3H2 | −0.132 | −0.060 | 9.10 | 3.522 | 0.752 |
| T-Na2N + 4H2 | −0.113 | −0.058 | 11.76 | 3.523 | 0.752 |
| H-Na2N + 1H2 | −0.134 | −0.134 | 3.23 | 2.275 | 0.788 |
| H-Na2N + 2H2 | −0.147 | −0.159 | 6.25 | 2.284 | 0.787 |
| H-Na2N + 3H2 | −0.118 | −0.062 | 9.10 | 3.567 | 0.753 |
| H-Na2N + 4H2 | −0.104 | −0.061 | 11.76 | 3.491 | 0.752 |
| I-Na2N + 1H2 | −0.067 | −0.067 | 3.23 | 2.417 | 0.757 |
| I-Na2N + 2H2 | −0.072 | −0.077 | 6.25 | 2.387 | 0.764 |
| I-Na2N + 3H2 | −0.064 | −0.048 | 9.10 | 5.210 | 0.751 |
| I-Na2N + 4H2 | −0.060 | −0.048 | 11.76 | 5.201 | 0.751 |
| T-K2N + 1H2 | −0.237 | −0.237 | 2.13 | 3.051 | 0.751 |
| T-K2N + 2H2 | −0.142 | −0.046 | 4.17 | 3.015 | 0.751 |
| T-K2N + 3H2 | −0.124 | −0.089 | 6.12 | 3.224 | 0.753 |
| T-K2N + 4H2 | −0.113 | −0.078 | 8.00 | 3.321 | 0.753 |
| H-K2N + 1H2 | −0.214 | −0.214 | 2.13 | 3.354 | 0.752 |
| H-K2N + 2H2 | −0.115 | −0.017 | 4.17 | 3.514 | 0.752 |
| I-K2N + 1H2 | −0.257 | −0.257 | 2.13 | 2.954 | 0.761 |
| I-K2N + 2H2 | −0.172 | −0.084 | 4.17 | 2.842 | 0.762 |
| I-K2N + 3H2 | −0.129 | −0.045 | 6.12 | 2.846 | 0.763 |
| I-K2N + 4H2 | −0.108 | −0.044 | 8.00 | 2.847 | 0.762 |
3.3. Mechanism of hydrogen adsorption on Na$_2$N

In order to obtain the charge redistribution behavior upon hydrogen adsorption on T-Na$_2$N, charge density difference was calculated according to

$$\Delta \rho = \rho_{H_2-Na_2N} - \rho_{H_2} - \rho_{Na_2N}$$

where $\rho_{H_2-Na_2N}$, $\rho_{H_2}$, and $\rho_{Na_2N}$ are the charge densities of H$_2$ adsorbed T-Na$_2$N, H$_2$ molecule and T-Na$_2$N, respectively. In figure 5, charge redistribution upon H$_2$ molecule adsorption is shown for T-Na$_2$N + 2H$_2$. It can be found that the first two H$_2$ layers show apparent charge polarization and some charge are transferred to the N $p_z$ orbitals, which is responsible for the moderate binding strength (~0.167 eV per H$_2$ molecule). In respect to the T-Na$_2$N + 4H$_2$, while deposition of the second two H$_2$ layers does not cause charge redistribution, corresponding to the weak binding strength.

In figure 6, the projected density of states (PDOS) plots are shown for T-Na$_2$N before and after H$_2$ molecule adsorption. It can be found that T-Na$_2$N is spin-polarized, with a 100% polarization at the Fermi level; the states near the Fermi level are predominantly contributed by N 2$p$ orbitals and slightly by Na 2$p$ / 3$s$ states. In line with the band structure, T-Na$_2$N is featured as half-metallic materials. In case for hydrogen adsorption, H 1$s$ states mainly appear ~7.50 eV below the Fermi level, with weak interactions with N 2$s$ / 2$p$ states. In respect to the first two layers of H$_2$, H 1$s$ states are polarized, consistent with the charge density difference; while the electronic structure of the second layer of H$_2$ is undisturbed due to the quite weak interaction with the substrate. In a previous study for hydrogen adsorption on Li-decorated 2D C$_4$N monolayer, H 1$s$ states appear in a similar energy range from ~10 to ~8 eV and hybridize with Li 1$s$ states [30].

It has already been known that structure stability is closely related to the temperature and pressure, therefore, ab initio atomistic thermodynamics approach in combination to the DFT results is employed to qualitatively evaluate the effects of temperature and pressure on the stability of hydrogen storage systems. In respect to hydrogen adsorption on T-Na$_2$N, H$_2$ adsorption free energy can be defined as
\[ \Delta G_{\text{ads}} = \Delta G_{\text{ads}}(T, p, n\text{H}_2) = G^{(i)}_{\text{H}_2\text{-Na}_2\text{N}} - [G^{(i)}_{\text{Na}_2\text{N}} + \mu^{(i)}_{\text{H}_2}(T, p)] \]

where \(G^{(i)}_{\text{H}_2\text{-Na}_2\text{N}}\) and \(G^{(i)}_{\text{Na}_2\text{N}}\) are the Gibbs free energies of hydrogen adsorbed \(\text{Na}_2\text{N}\) and clean \(\text{Na}_2\text{N}\), respectively; \(\mu^{(i)}_{\text{H}_2}(T, p)\) is the chemical potential of isolated \(\text{H}_2\) molecule in the gas phase \([31, 32]\). In regard to the Gibbs free energy of solid phase, it reads

\[ G^{(s)} = E_{\text{tot}} + E_{\text{conf}} + E_{\text{vib}} + PV \]

where \(E_{\text{tot}}\) is the total energy that can be obtained from the DFT results, \(E_{\text{conf}}, E_{\text{vib}}\) and \(PV\) are the configurational, vibrational free energies and pressure volume work \([33, 34]\), separately. In particular, the chemical potential of \(\text{H}_2\) in gas phase as a function of pressure \(p\) and temperature \(T\) can be written as
\[
\mu_{\text{H}_2}^{(e)}(T, P_{\text{H}_2}) = \mu_{\text{H}_2}^{(e)}(T, P_0) + k_B T \ln \left( \frac{P}{P_0} \right)
\]

with \(\mu_{\text{H}_2}^{(e)}(T, P_0)\) being the chemical potential of hydrogen molecule, and \(k_B\) is the Boltzmann constant. In standard conditions with pressure \(P_0\), the chemical potential is then given by

\[
\mu_{\text{H}_2}^{(e)}(T, P_0) = \mu_{\text{H}_2}^{(e)}(0K) + [H(T, P_{\text{H}_2}) - H(0K, P_0)] - TS(T, P_0)
\]

which can be expressed at 0 K as

\[
\mu_{\text{H}_2}^{(e)}(0K) = E_{\text{el}}^{\text{H}_2} + E_{\text{ZPV}}^{\text{H}_2}
\]

In our calculations, we obtained that \(\text{H}_2\) has a total energy \(E_{\text{el}}^{\text{H}_2}\) of -6.726 eV, and the zero-point vibrational energy \(E_{\text{ZPV}}^{\text{H}_2}\) is 0.296 eV, in accordance with previous results [31]. In addition, entropic contributions to the standard chemical potential are available in the JANAF thermochemical table.

In figure 7, the corresponding thermodynamic stability diagrams for \(T-\text{Na}_2\text{N} + \text{H}_2\) (hydrogen storage capacity: 3.23 wt%) and \(T-\text{Na}_2\text{N} + 2\text{H}_2\) (hydrogen storage capacity: 6.25 wt%) are shown. It should be pointed out that the lower the Gibbs free energy, the more stable the structures. In comparison to low hydrogen coverage, T-Na2N prefers hydrogen adsorption on both sides, and the adsorbed system tends to be more stable. In particular, the hydrogen storage capacity of T-Na2N reaches 6.25 wt% with a desirable hydrogen adsorption energy of 0.167 eV per \(\text{H}_2\) molecule. It can be concluded that interactions between \(\text{H}_2\) molecules and \(\text{N}\) atoms cause \(\text{H}_2\) charge polarization, which is responsible for the moderate binding strength. It is of interest that \(T-\text{Na}_2\text{N}\) prefers hydrogen adsorption on both sides, and the adsorbed system tends to be more stable. In accordance to the van’t Hoff model, the desorption temperature is calculated to be 216 K.

4. Conclusion

In summary, we have systemically investigated the hydrogen adsorption behavior on a new class of 2D AXenes, \(\text{Na}_2\text{N}\) and \(\text{K}_2\text{N}\) in different phases (referred to as T, H and I), by first-principles calculations on the basis of DFT. In particular, the hydrogen storage capacity of \(T-\text{Na}_2\text{N}\) reaches 6.25 wt% with a desirable hydrogen adsorption energy of -0.167 eV per \(\text{H}_2\) molecule. It can be concluded that interactions between \(\text{H}_2\) molecules and \(\text{N}\) atoms cause \(\text{H}_2\) charge polarization, which is responsible for the moderate binding strength. It is of interest that \(T-\text{Na}_2\text{N}\) prefers hydrogen adsorption on both sides, and the adsorbed system tends to be more stable. In accordance to the van’t Hoff model, the desorption temperature is calculated to be 216 K.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (51872170 and 12074217), Shandong Provincial Key Research and Development Program (Major Scientific and Technological Innovation Project) (2019JZZY01302), Natural Science Foundation of Shandong Province (ZR2019MEM013). WW acknowledges the Young Scholars Program of Shandong University (YSPSDU).
Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Ying Dai  https://orcid.org/0000-0002-8587-6874
Wei Wei  https://orcid.org/0000-0002-1034-1867

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