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Keywords
controlled, separation, nitrogen, natural, charged, gas, fullerene, boron, nitride

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Charged-controlled Separation of Nitrogen from Natural Gas Using Boron Nitride Fullerene

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Abstract: Natural gas (the main component is methane) has been widely used as a fuel and raw material in industry. Removal of nitrogen (N\textsubscript{2}) from methane (CH\textsubscript{4}) can reduce the cost of natural gas transport and improve its efficiency. However, their extremely similar size increases the difficulty of separation N\textsubscript{2} from CH\textsubscript{4}. In this study, we have performed a comprehensive investigation of N\textsubscript{2} and CH\textsubscript{4} adsorption on different charge states of boron nitride (BN) nanocage fullerene, B\textsubscript{36}N\textsubscript{36}, by using a density functional theory approach. The calculational results indicate that B\textsubscript{36}N\textsubscript{36} in the negatively charged state has high selectivity in separating N\textsubscript{2} from CH\textsubscript{4}. Moreover, once the extra electron is removed from the BN nanocage, the N\textsubscript{2} will be released from the material. This study demonstrates that the B\textsubscript{36}N\textsubscript{36} fullerene can be used as a highly selective and reusable material for the separation of N\textsubscript{2} from CH\textsubscript{4}. The study also provides a clue to experimental design and application of BN nanomaterials for natural gas purification.

1. Introduction

Natural gas is a high efficiency fuel and an important raw material in the manufacturing of fertilizer, antifreeze, plastics, pharmaceuticals, fabrics, etc. Moreover, natural gas is the cleanest fossil fuel, because it has less CO\textsubscript{2} emission than either coal or oil and it produces fewer pollutants gases than other hydrocarbon fuels,\textsuperscript{1} so that the demand for natural gas is continuously increasing. Natural gas needs to be transported, either by pipelines or by tankers, from the gas reservoirs to the final market, under the condition that the natural gas must contain at least 75\% methane.\textsuperscript{2} Nitrogen is a common component in natural gas and lowers its value. For natural gas transport by pipeline, typically, the nitrogen content needs to be less than 4\%. In order to remove nitrogen from natural gas, several technologies have been used, including membrane separation, cryogenic removal, and solid adsorbents. Membrane separation isn’t effective because of the very similar sizes of their molecules, as the kinetic diameters of N\textsubscript{2} and CH\textsubscript{4} are 3.64 Å and 3.80 Å, respectively.\textsuperscript{3} Removal of nitrogen through cryogenic technology is an expensive process, which limits large-scale natural gas purification.\textsuperscript{4} Recently, solid materials have been proposed as adsorbents for natural gas purification.\textsuperscript{5} The interactions between most solid adsorbents and N\textsubscript{2} are relatively weak, however, so they cannot effectively separate nitrogen from methane.\textsuperscript{6} Moreover, using a material with high nitrogen selectivity means that nitrogen release is difficult due to the strong interaction between nitrogen and the material, and the adsorbent cannot be reused. Therefore, it is very important to design new materials with high selectivity towards nitrogen removal from natural gas and easy regeneration in order to allow the reuse of these materials.

Fullerene-based materials have attracted considerable attention because of their excellent properties, such as physical and chemical stability. Stoichiometric boron nitrides (BN)\textsubscript{n}, the isoelectronic analogues to the carbon fullerenes, have been the subject of extensive and intensive investigations.\textsuperscript{7-10} The four-fold ring-type B\textsubscript{36}N\textsubscript{36} is considered as a local model for the octahedral-like “family” of BN fullerenes that has been experimentally\textsuperscript{11} observed and theoretically\textsuperscript{8} investigated. Several theoretical studies indicate that B\textsubscript{36}N\textsubscript{36} is energetically\textsuperscript{12,13} and vibrationally\textsuperscript{14} stable. The most stable structure of B\textsubscript{36}N\textsubscript{36} has a T\textsubscript{d} symmetry with 6 four-membered (F\textsubscript{4}) and 32 six-membered (F\textsubscript{6}) rings.\textsuperscript{14} BN fullerenes have properties that could make their use viable in electronic devices or as semiconductors with high chemical and thermal stability. For example, B\textsubscript{36}N\textsubscript{36} has been studied extensively as a material for hydrogen storage,\textsuperscript{9,15} drug delivery,\textsuperscript{16} and natural gas storage\textsuperscript{7}. One potential application of B\textsubscript{36}N\textsubscript{36} is its use as an adsorbent for the selective separation of nitrogen from methane for natural gas purification. The interaction between neutral B\textsubscript{36}N\textsubscript{36} and N\textsubscript{2} is very weak, however, when one electron was introduced onto the system, strong interaction between B\textsubscript{36}N\textsubscript{36} and N\textsubscript{2} could occur. Regardless of whether the B\textsubscript{36}N\textsubscript{36} nanocage is in a charged or neutral state, the CH\textsubscript{4} always takes part in only a weak interaction with it. This study demonstrates that B\textsubscript{36}N\textsubscript{36} in the negative charge state has high selectivity towards the separation of nitrogen from methane. We also investigated the reaction mechanism for the removal of charge from the B\textsubscript{36}N\textsubscript{36}. Once
the negative charge is removed from the BN adsorbent, the N\textsubscript{2} will be released from the BN nanocage. This investigation demonstrates that the BN nanocage can effectively separate nitrogen from a mixture with methane. Furthermore, by switching the charge state off, nitrogen will be released from the material, and the BN nanomaterial can be reused for further separation. Here, we need to point out that the charge state of BN nanomaterial can be modified through electrochemical methods, electron beams, electrospraying, or gate voltage control.\textsuperscript{18-20}

2. Computational Methods

The investigations have been carried out using first-principles density functional theory plus dispersion correction, as implemented in the DMol3 module in Materials Studio,\textsuperscript{21,22} to calculate the structure and energy of the B\textsubscript{36}N\textsubscript{36}-N\textsubscript{2} and B\textsubscript{36}N\textsubscript{36}-CH\textsubscript{4} systems. We used the generalized gradient approximation\textsuperscript{23} treated by the Perdew-Burke-Ernzerhof exchange-correlation potential in density functional theory, with long range dispersion correction via Grimme’s scheme\textsuperscript{24} (PBE-D) for all the calculations. An all electron double numerical atomic orbital augmented by d-polarization functions (DNP) has been chosen as basis set. This calculational level has been used to successfully study adsorptions, desorption and the reaction mechanisms of some gases on boron-containing nanomaterials.\textsuperscript{25-28}

The adsorption energies (\(E\textsubscript{ads}\)) of N\textsubscript{2} and CH\textsubscript{4} on B\textsubscript{36}N\textsubscript{36} are calculated from Eq. (1):

\[
E\textsubscript{ads} = (E\textsubscript{B36N36-gas} + E\textsubscript{gas}) - E\textsubscript{B36N36-gas}
\]  

where \(E\textsubscript{B36N36-gas}\) is the total energy of the B\textsubscript{36}N\textsubscript{36} with the adsorbed gas, \(E\textsubscript{B36N36}\) is the energy of isolated B\textsubscript{36}N\textsubscript{36}, and \(E\textsubscript{gas}\) is the energy of an isolated gas molecule, such as N\textsubscript{2} and CH\textsubscript{4}. All the adsorptions energies are calculated based on their charge states of the adsorbent. The Mulliken method is used to determine the electron distribution and charge transfer of the adsorptions.\textsuperscript{29}

In order to study the nature of the interactions between N\textsubscript{2}, CH\textsubscript{4} and B\textsubscript{36}N\textsubscript{36}, with different charge states, the atoms in molecules (AIM) theory, which has been used to successfully determine the existence and strength of bonds in different gases and nanomaterial systems, has been employed in this system.\textsuperscript{30-32} The topological analysis of B\textsubscript{36}N\textsubscript{36}-gas has been performed by using the AIMALL code.\textsuperscript{32} Please refer to our previous publication\textsuperscript{27} for detailed information on the computational methods used in the system that is the object of the current study.

3. Results and Discussion

In order to evaluate the ability of the B\textsubscript{36}N\textsubscript{36} nanocage to separate nitrogen from methane, we firstly performed PBE-D calculations for the adsorption of the gases, N\textsubscript{2} and CH\textsubscript{4}, on a neutral B\textsubscript{36}N\textsubscript{36} nanocage. We have performed the calculations with all possible configurations of the gases adsorbed on the B\textsubscript{36}N\textsubscript{36}, the computational results show that the interactions between N\textsubscript{2}/CH\textsubscript{4} molecules and the neutral B\textsubscript{36}N\textsubscript{36} are very weak. Then, we analyzed the frontier orbitals of B\textsubscript{36}N\textsubscript{36} and difference in the electron densities between the neutral and 1 e\textsuperscript{-} charge states of B\textsubscript{36}N\textsubscript{36}. The analysis of the frontier orbitals suggests that N\textsubscript{2} may form a strong interaction with 1 e\textsuperscript{-} charged B\textsubscript{36}N\textsubscript{36}. The calculations for N\textsubscript{2} capture on negatively charged B\textsubscript{36}N\textsubscript{36} then followed. Finally, we also have studied the release of N\textsubscript{2} on B\textsubscript{36}N\textsubscript{36} when the charge state is turned off, and compared the adsorption of N\textsubscript{2} and CH\textsubscript{4} on B\textsubscript{36}N\textsubscript{36} in different charge states in order to address the high selectivity and reversibility of the BN adsorbent for nitrogen removal in natural gas purification.

3.1 N\textsubscript{2} and CH\textsubscript{4} adsorption on uncharged B\textsubscript{36}N\textsubscript{36} nanocage

We have carried out PBE-D calculations of N\textsubscript{2} and CH\textsubscript{4} adsorption on uncharged B\textsubscript{36}N\textsubscript{36} nanocage with all the possible configurations, and the calculated complexes are shown in Figure 1. For N\textsubscript{2} adsorption on uncharged B\textsubscript{36}N\textsubscript{36} nanocage, the three most stable structures formed between N\textsubscript{2} and the uncharged B\textsubscript{36}N\textsubscript{36}, with one boron atom belonging to the F\textsubscript{3} ring and two boron atoms belonging to F\textsubscript{6} rings, are denoted as type 1 (Figure 1(a)), type 2 (Figure 1(b)), and type 3 (Figure 1(c)), respectively. The important geometry structural parameters and the adsorption energies are summarized in Table 1.
between N$_2$ and B$_{36}$N$_{36}$ are physisorbed configurations. From the data in Table 1 we can see that the three complexes formed by N$_2$ and B$_{36}$N$_{36}$, with contact distances from 2.944 Å to 3.493 Å. The N-N bond distances in the three complexes vary between 1.108 Å and 1.109 Å, which are close to that in the gas phase (where the N-N bond length of the free N$_2$ molecule is calculated to be 1.109 Å). From the configurations in Figure 1 and the data in Table 1 we can see that the three complexes formed between N$_2$ and B$_{36}$N$_{36}$ are physisorbed configurations. Figure S1 in the Supporting Information lists the molecular graphs of those geometries. From Figure S1(a-c) we can see that there are bond critical points (BCP) at the N-B interactions of the three configurations of N$_2$ adsorption on the neutral B$_{36}$N$_{36}$. The relevant topological parameters at the BCP are listed in Table S1 in the Supporting Information. The small electron densities at the BCPs of the N-B contacts of the three structures (Table S1) clearly indicate that the interactions between N$_2$ and B$_{36}$N$_{36}$ are weak. The Mulliken charge distributions of the complexes of N$_2$ adsorption on the B$_{36}$N$_{36}$ nanocage and the charge transfers between N$_2$ and B$_{36}$N$_{36}$ are listed in Table 2. We can see that the charge transfers for the three physisorbed configurations from N$_2$ to B$_{36}$N$_{36}$ are negligible, with the values ranging from 0.005 e to 0.014 e. The adsorption energies of the three configurations for N$_2$ molecule adsorption on neutral B$_{36}$N$_{36}$ are calculated to be 3.32, 3.25, and 2.32 kcal/mol, which are in good agreement with the weak interactions between N$_2$ and the uncharged B$_{36}$N$_{36}$ nanocage. To sum up, the calculations data demonstrates that there are weak interactions between N$_2$ and neutral B$_{36}$N$_{36}$.

We also investigated the adsorption of CH$_4$ on neutral B$_{36}$N$_{36}$. Starting with all possible configurations, the two most stable structures between CH$_4$ and neutral B$_{36}$N$_{36}$ are presented in Figure 1(d) and Figure 1(e). For these two structures, their most important geometrical parameters, adsorption energies, and electron transfer from B$_{36}$N$_{36}$ to CH$_4$ are summarized in Table 1 and 2. From the Figure 1 and the Tables we can see that CH$_4$ is quite far from the B$_{36}$N$_{36}$ for the two configurations of CH$_4$ adsorbed on neutral B$_{36}$N$_{36}$ nanocage, and the N/B…H distances are 2.730 Å and 2.847 Å for the two configurations, respectively. There are small values of electron transfer from methane to B$_{36}$N$_{36}$ of 0.007 e and 0.014 e for the two complexes. The adsorption energies for the two complexes are 4.51 kcal/mol and 4.41 kcal/mol. The above analysis demonstrates that the adsorptions of CH$_4$ on neutral B$_{36}$N$_{36}$ are physical interactions, and the interactions are weak, which is supported by the topological analysis in the AIM calculations. Figure S1 in the Supporting Information shows there are BCP of the H-B contact between CH$_4$ and neutral B$_{36}$N$_{36}$. Similarly to the electron densities at the BCPs of B$_{36}$N$_{36}$-N$_2$ system, the values of H-B between CH$_4$ and the B$_{36}$N$_{36}$ nanocage are small (Table S1). This supports the position that there are only weak interactions between CH$_4$ and neutral B$_{36}$N$_{36}$. In all, the calculational results clearly demonstrate that the interactions between N$_2$/CH$_4$ and neutral B$_{36}$N$_{36}$ are very weak, so that neutral B$_{36}$N$_{36}$ cannot separate N$_2$ from a mixture with CH$_4$.

### 3.2 Frontier orbitals of B$_{36}$N$_{36}$ and charge distribution of B$_{36}$N$_{36}$ with different charge states

In order to understand the interactions between the neutral B$_{36}$N$_{36}$ nanocage and the gases, the frontier orbitals, the highest occupied molecular orbital (HOMO, Figure 2(a)) and the lowest unoccupied molecular orbital (LUMO, Figure 2(b)), of the B$_{36}$N$_{36}$ are displayed in Figure 2. The Figure 2(b) clearly shows that the LUMO of B$_{36}$N$_{36}$ is distributed on its boron atoms, which suggests that when an extra electron is applied to the B$_{36}$N$_{36}$ nanocage, the electron will migrate to the boron atoms of B$_{36}$N$_{36}$. The above prediction is confirmed by comparing the difference in the electron density distribution for the different charge states.

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**Table 1. Adsorption energy in kcal/mol, bond distance (r) in Å, and bond angle (α) in degrees of N$_2$ and CH$_4$ adsorption on B$_{36}$N$_{36}$ in different charge states.**

<table>
<thead>
<tr>
<th>Gases</th>
<th>Type</th>
<th>Adsorption energy (eV)</th>
<th>r(Na-Nb) (Å)</th>
<th>α(Nb–Na–B) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>Type 1</td>
<td>-3.32</td>
<td>2.944</td>
<td>1.108</td>
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<tr>
<td></td>
<td></td>
<td>-15.73</td>
<td>1.622</td>
<td>1.168</td>
</tr>
<tr>
<td></td>
<td>Type 2</td>
<td>-3.25</td>
<td>3.493</td>
<td>1.109</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-9.00</td>
<td>1.718</td>
<td>1.167</td>
</tr>
<tr>
<td></td>
<td>Type 3</td>
<td>-2.32</td>
<td>2.978</td>
<td>1.108</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-11.30</td>
<td>1.662</td>
<td>1.167</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>Type 1</td>
<td>-4.51</td>
<td>3.475</td>
<td>2.730</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-4.33</td>
<td>3.478</td>
<td>2.723</td>
</tr>
<tr>
<td></td>
<td>Type 2</td>
<td>-4.41</td>
<td>3.385</td>
<td>2.847</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-4.23</td>
<td>3.391</td>
<td>2.841</td>
</tr>
</tbody>
</table>

**Table 2. Mulliken charge distribution (electron) of configurations of N$_2$ and CH$_4$ adsorption on B$_{36}$N$_{36}$ and the net charge (NC) of N$_2$ and CH$_4$ in the adsorbed configurations.**

<table>
<thead>
<tr>
<th>Gases</th>
<th>Type</th>
<th>Charge (e)</th>
<th>Na</th>
<th>Nb</th>
<th>NC</th>
<th>H</th>
<th>H</th>
<th>Hc</th>
<th>Hd</th>
<th>NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>Type 1</td>
<td>0e</td>
<td>-0.026</td>
<td>0.040</td>
<td>0.014</td>
<td>0.005</td>
<td>0.009</td>
<td>0.103</td>
<td>0.100</td>
<td>0.102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1e</td>
<td>-0.177</td>
<td>-0.105</td>
<td>-0.282</td>
<td>-0.310</td>
<td>-0.299</td>
<td>0.105</td>
<td>0.100</td>
<td>0.104</td>
</tr>
<tr>
<td></td>
<td>Type 2</td>
<td>0e</td>
<td>-0.006</td>
<td>0.011</td>
<td>0.005</td>
<td>0.026</td>
<td>0.009</td>
<td>0.103</td>
<td>0.100</td>
<td>0.102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1e</td>
<td>-0.122</td>
<td>-0.187</td>
<td>-0.328</td>
<td>-0.299</td>
<td>-0.299</td>
<td>0.105</td>
<td>0.100</td>
<td>0.104</td>
</tr>
<tr>
<td></td>
<td>Type 3</td>
<td>0e</td>
<td>-0.017</td>
<td>-0.026</td>
<td>0.009</td>
<td>0.103</td>
<td>0.009</td>
<td>0.103</td>
<td>0.100</td>
<td>0.102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1e</td>
<td>-0.112</td>
<td>-0.187</td>
<td>-0.328</td>
<td>-0.299</td>
<td>-0.299</td>
<td>0.105</td>
<td>0.100</td>
<td>0.104</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>Type 1</td>
<td>0e</td>
<td>-0.397</td>
<td>0.103</td>
<td>0.100</td>
<td>0.102</td>
<td>0.100</td>
<td>0.102</td>
<td>0.100</td>
<td>0.102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1e</td>
<td>-0.392</td>
<td>0.105</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
</tr>
<tr>
<td></td>
<td>Type 2</td>
<td>0e</td>
<td>-0.396</td>
<td>0.104</td>
<td>0.100</td>
<td>0.102</td>
<td>0.100</td>
<td>0.102</td>
<td>0.100</td>
<td>0.102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1e</td>
<td>-0.391</td>
<td>0.106</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
</tr>
</tbody>
</table>
charge states of B_{36}N_{36}. Figure 1(c) and Table S1 in the Supporting Information show the atom types of the B_{36}N_{36} nanocage and the Mulliken charge distributions of the different atom types, respectively. From Figure 1(c), we can see that there are three types of boron and nitrogen atoms in the B_{36}N_{36} nanocage: the type 1 atoms are denoted as B1 and N1 which are atoms belonging to the four-membered (F4) rings; type 2 atoms are denoted as B2 and N2, which are atoms belonging to six-membered (F6) rings, which are directly connected with the atoms of the F2 rings; type 3 atoms are denoted as B3 and N3, and they are atoms belonging to six-membered (F6) rings and not connected with the atoms of F2 rings. There are six types of bonds in the B_{36}N_{36} fullerene. The distances of the six types of bonds are listed in Table S1 in supporting information.

We can see that the six types of bonds in its negative charge state increase with the values among 0.001~0.004 Å compared with those in its neutral state, which mean that the cluster expands a little bit when it is negatively charged. The Mulliken charges of B1, B2, and B3 of neutral B_{36}N_{36} are 0.297 e, 0.445 e and 0.481 e, and the charge distribution of the three types of atoms in 1 e\(^{-}\) state B_{36}N_{36} are 0.268 e, 0.424 e and 0.459 e, respectively. The boron atoms become negatively charged with the values of -0.029 e, -0.021 e, and -0.022 e, for the atom types B1, B2, and B3, respectively. The changes for the nitrogen atoms in the B_{36}N_{36} are much smaller, however, than those for the boron atoms. For example, the Mulliken charges of N1, N2, and N3 in neutral and 1 e\(^{-}\) B_{36}N_{36} are -0.362 e, -0.420 e, and -0.442 e for neutral B_{36}N_{36}; and -0.376 e, -0.420 e, and -0.440 e for negatively charged B_{36}N_{36}, respectively; the charges for the three types of atom between the two charge states are approximately 0~0.014 e. The difference in electron density distribution between the 0 e\(^{-}\) and 1 e\(^{-}\) B_{36}N_{36} is shown in Figure 2(d). We can see from Figure 2(d) that when an extra electron is applied to the B_{36}N_{36} nanocage, the electron is distributes to the boron atoms of B_{36}N_{36}, and then the negatively charged boron atom of B_{36}N_{36} becomes more likely to donate an electron to N2 than in its neutral state analogue, and N2 is more likely to adsorb strongly on the negative charge state of B_{36}N_{36}. When the extra electron is moved from the B_{36}N_{36} nanocage, the electron density of boron atoms will vanish accordingly, and then the strong adsorption of N2 on B_{36}N_{36} will not exit. The analysis indicates the changes of the charge states of the B_{36}N_{36} nanocage might control its ability to capture/release N2.

It is known that Mulliken charges have some shortcomings, such as they are very sensitive to the basis set. We have performed the Hirshfeld charge analysis because the charge states of B_{36}N_{36} are vital to the performances of separation nitrogen from methane mixture. The Hirshfeld charges of B_{36}N_{36} with neutral and 1 e\(^{-}\) states at the PBE-D are listed in Table S1 in supporting information. From Table S1 we can see that Hirshfeld charges of the three types of boron atoms in 1 e\(^{-}\) state are become negatively charged compared with them in its neutral state with the values of -0.023 e, -0.016 e, and -0.016 e, for the atom types B1, B2, and B3, respectively. The charges for the nitrogen atoms in the B_{36}N_{36} with different charge states are much smaller than those for the boron atoms. The results of Hirshfeld charges are consistent with those of Mulliken charges.

3.3 N\(_2\) and CH\(_4\) adsorption on B\(_{36}N\(_{36}\) with 1 e\(^{-}\) charge state

In this part, the investigation of N\(_2\) and CH\(_4\) adsorption on B\(_{36}N\(_{36}\) in the 1 e\(^{-}\) charge state has been carried out. From the calculation results, we can see that there are three most stable configurations of N\(_2\) adsorption on 1 e\(^{-}\) charge state B_{36}N_{36} in the three boron positions, where the N\(_2\) molecules interact with the three boron atoms of types B1, B2, and B3 of B_{36}N_{36}. The three configurations are shown in Figure 3(a-c), respectively. Their important geometrical parameters, adsorption energies, and charge transfer from N\(_2\) to B_{36}N_{36} are summarized in Tables 1 and 2. We can see from Figure 3 that N\(_2\) molecules form strong interactions with 1 e\(^{-}\) charged B_{36}N_{36}, and there are chemisorbed configurations formed between them. In the chemisorbed configurations of N\(_2\) adsorption on the negative charge B_{36}N_{36}, the N-N bonds are slightly elongated from 1.109 Å (gas phase) to 1.168 Å, 1.167 Å, and 1.167 Å for the complexes with types 1, 2, and 3, respectively, and the triple-bonds of N\(_2\) molecules in the three configurations are broken. The distances between B atoms and N atoms of the three configurations are 1.622 Å, 1.718 Å, and 1.662 Å for types 1, 2, and 3, respectively, and the triple-bonds of N\(_2\) molecules in the three configurations are broken. The distances between B atoms and N atoms of the three configurations are 1.622 Å, 1.718 Å, and 1.662 Å for types 1, 2, and 3, respectively, and which are shorter than those for N\(_2\) adsorption on the neutral uncharged B_{36}N_{36} (since the distances between N\(_2\) and neutral B_{36}N_{36} for types 1, 2, and 3 are 2.944 Å, 3.493 Å, and 2.978 Å, respectively). This indicates that the stronger interactions between N\(_2\) and 1 e\(^{-}\) B_{36}N_{36} are formed, which is also consistent with the relatively larger electron densities at the BCPs for the N-B bond in the three configurations (Figure S1 and Table S2 in the Supporting Infor-
adsorption energies indicate that there are strong interactions between \( \text{N}_2 \) and \( \text{B}_{36}\text{N}_{36} \) in the \( 1\ e^- \) charge state. The important geometrical parameters for these configurations, adsorption energies, and electron transfer for \( \text{CH}_4 \) adsorption on \( 1\ e^- \text{B}_{36}\text{N}_{36} \) are listed in Tables 1 and 2. From Figure 3 we can see that the configurations of \( \text{CH}_4 \) adsorption on negatively charged \( \text{B}_{36}\text{N}_{36} \) are very similar to those for its neutral state. They are all physisorbed configurations with weak interactions in the range of 3.3 – 3.5 Å, and the weak interactions between \( \text{CH}_4 \) and \( \text{B}_{36}\text{N}_{36} \) are supported by the small values of net charge of \( \text{CH}_4 \) part (in the range of 0.002e – 0.014e) and adsorption energies listed in Table 2, as well as the topological analysis from AIM calculations in the Supporting Information. This means that \( \text{CH}_4 \) can only form weak interactions with the \( \text{B}_{36}\text{N}_{36} \) nanocage, no matter what the charge state of the adsorbed. In order to address the capability of \( \text{B}_{36}\text{N}_{36} \) for \( \text{N}_2/\text{CH}_4 \) separation, the adsorption energies for \( \text{CH}_4 \) and \( \text{N}_2 \) adsorption on \( \text{B}_{36}\text{N}_{36} \) in the different charge states will be compared. In detail, for neutral \( \text{B}_{36}\text{N}_{36} \), the interactions with \( \text{CH}_4 \) and \( \text{N}_2 \) molecules on it are all physical. The adsorption energies of the five configurations of \( \text{CH}_4 \) and \( \text{N}_2 \) on neutral \( \text{B}_{36}\text{N}_{36} \) are in the range of 4.2 – 4.5 kcal/mol. When the \( \text{B}_{36}\text{N}_{36} \) nanocage is introduced with one electron, the interactions of \( \text{CH}_4 \) on \( \text{B}_{36}\text{N}_{36} \) remain weak, and the changes in the adsorption energies are very small in comparison to those on its neutral state. The adsorption energies are ~4.3 kcal/mol for \( \text{CH}_4 \) on \( \text{B}_{36}\text{N}_{36} \) nanocage in the \( 1\ e^- \) charge state. In contrast, the interactions of \( \text{N}_2 \) on \( \text{B}_{36}\text{N}_{36} \) are much stronger (since the complexes formed between them are chemisorbed configurations) than those of \( \text{CH}_4 \) adsorption on the charged \( \text{B}_{36}\text{N}_{36} \) (where the complexes formed between them are physisorbed configurations). The adsorption energy of the most stable configuration (type 1 in Figure 3(a)) of \( \text{N}_2 \) adsorbed on the charged \( \text{B}_{36}\text{N}_{36} \) is 15.73 kcal/mol. The big differences between these configurations and adsorption energies indicate that the negatively charged \( \text{B}_{36}\text{N}_{36} \) has high selectivity towards removal of \( \text{N}_2 \) from \( \text{CH}_4 \), so \( \text{B}_{36}\text{N}_{36} \) can serve as a good candidate for natural gas purification. Previously we have studied \( \text{N}_2 \) capture on solid boron, such as \( \alpha\text{-}\text{B}_{12} \) and \( \gamma\text{-}\text{B}_{28} \) because the \( \alpha\text{-}\text{B}_{12} \) and \( \gamma\text{-}\text{B}_{28} \) are among the most regenerable \( \text{B}_n\text{N}_m \) systems with neutral and \( 1\ e^- \) states at the PBE level without Grimme dispersion correction. The calculational results, such as adsorption energy and bond distance of \( \text{N}_2 \) and \( \text{CH}_4 \) adsorption on \( \text{B}_{36}\text{N}_{36} \) with the two charge states at the PBE level are listed in Table S4 in the Supporting Information. For the chemisorptions, the net charge via Mulliken charges analysis of \( \text{N}_2 \) part increases with the value of 0.282 e\(^-\), 0.310 e\(^-\), and 0.299 e\(^-\) for the three configurations of type 1, type 2, and type 3, respectively. The Hirshfeld charges of the configurations of \( \text{N}_2 \) and \( \text{CH}_4 \) adsorption on \( \text{B}_{36}\text{N}_{36} \) with neutral and \( 1\ e^- \) states and the net charge (NC) of \( \text{N}_2 \) and \( \text{CH}_4 \) in the adsorbed configurations at the PBE-D are listed in Table S3 in supporting information. The NC via Hirshfeld charges distributions of these configurations are consistent with those of Mulliken charges analysis. The absorption energies of the three configurations of types 1, 2, and 3 are 15.73, 9.00, and 11.30 kcal/mol (or 65.75, 37.08, and 47.23 kJ/mol), respectively. The high adsorption energies indicate that there are strong interactions between \( \text{N}_2 \) and \( \text{B}_{36}\text{N}_{36} \) in the \( 1\ e^- \) charge state. Generally speaking, the adsorption energies of a good-performance adsorbent should be in a range of 40 – 80 kJ/mol\(^{}\),\(^3\) which support the negatively charged \( \text{B}_{36}\text{N}_{36} \) could be a good material for \( \text{N}_2 \) separation.

![Figure 3. Top and side views of three chemisorbed configurations of type 1 (a), type 2 (b), and type 3 (c) of \( \text{N}_2 \) on \( \text{B}_{36}\text{N}_{36} \) in the \( 1\ e^- \) charge carrying state; (d) and (e) are top and side views of the two most stable configurations of \( \text{CH}_4 \) adsorption on \( \text{B}_{36}\text{N}_{36} \) in the \( 1\ e^- \) charge state.](image-url)
Figure 4. Variation of thermodynamic properties with temperatures (K) when an isolated N2 molecule is chemisorbed by 1 e- charged B36N36 in a type 1 configuration. Squares, triangles, and circles correspond to the change in Gibbs free energy (kcal/mol), change in entropy (cal/mol K), and change in enthalpy (kcal/mol), respectively.

In order to study the thermodynamic properties of N2 adsorption on B36N36 in the 1 e- charge state to form chemisorbed configurations under different temperature, the variations in the entropy (ΔS, cal/mol K), enthalpy (ΔH, kcal/mol), and Gibbs free energy (ΔG, kcal/mol) with temperature (K) have been studied. Here, we mainly discuss the thermodynamic properties of the reaction between N2 and B36N36 in the 1 e- charged state to form the most stable configuration, in which N2 is directly connected with an F4 boron atom of the charged B36N36, which is shown in Figure 4. From Figure 4 we can see that ΔS decreases with the temperature increasing from 25 to 300 K, and when the temperature is above 300 K, ΔS is almost constant. Over the whole temperatures range (i.e., from 25 to 1000 K), the value of ΔH is almost constant, which results in a linear increase in ΔG with increasing temperature. In addition, when the temperature is in the range of 25 – 300 K, ΔG is negative, which indicates that when the temperature is below 300 K, the adsorption of N2 on 1 e- charged B36N36 to form a chemisorbed configuration is a spontaneous process. Figure S2(a) and (b) in the Supporting Information lists the thermodynamic properties of N2 adsorption on the 1 e- charged B36N36 in the type 2 and type 3 configurations, in which N2 is directly connected with the boron atoms of F6 rings. Figure S2(a) and (b) shows that ΔG is positive when the temperature is above 200 K, which means that the reactions with the type 2 and type 3 configurations are not spontaneous at room temperature. To sum up, the analysis of the thermodynamic properties of the reaction to form the chemisorbed configuration (type 1) demonstrates that N2 capture on 1 e- charged B36N36 is a spontaneous process when the temperature is below 300 K.

![Thermodynamic function](image-url)

Figure 5. Energy change for reactions involving N2 adsorption on B36N36 of type 1 (a) involves the change from physisorbed to chemisorbed configurations with the 1 e- charged B36N36, respectively; (b) is the change from physisorbed to chemisorbed configurations with the neutral B36N36.

We have also investigated the reaction mechanism of N2 capture/release on/from B36N36 in different charge states, the energy changes for the reactions involving turning on/off the charge states of B36N36 of the three types of adsorptions are plotted in Figure 5 (type 1) and Figure S3 (type 2 and 3) in the Supporting Information. Figure 5(a) and (b) lists the energy changes in the type 1 configuration, in which N2 molecules are connected with boron atoms of the F4 ring of B36N36. Figure S3(a-d) shows the energy changes in the type 2 and type 3 configurations, in which the N2 molecules are connected to the boron atoms of the F6 ring of B36N36. The changes in energy with relaxation from physisorbed to chemisorbed states have been plotted in Figure 5 (a), Figure S3(a) and Figure S3 (c), when the electrons are added into the B36N36–N2 systems. In Figure 5 (b), Figure S3(b) and Figure S3(d), starting with the minimum energy configurations of 1 e- charged B36N36 with chemisorbed N2. When the electrons are removed, so that the systems are allowed to relax, the systems change from their chemisorbed to physisorbed N2 adsorption configurations on B36N36. In detail, when the electrons are introduced onto the B36N36–N2 systems, the interactions between N2 and B36N36 dramatically increase compared with those with the neutral states, and the N2 molecules are chemisorbed onto the B36N36. The calculation results (Figure 5 (a), Figure S3(a) and Figure S3 (c)) indicate that the processes are exothermic with the values of -9.51, 2.52 and 6.03 kcal/mol for the three types, respectively. On the other hand, after the negative charges are released from the systems, the adsorptions of N2 on B36N36 spontaneously change from chemisorbed to physisorbed configurations (Figure 5(b), Figure S3(b) and
and variation of thermodynamic properties with temperature of the systems at the PBE-D level as well as the important charging/discharging of the B$_{36}$N$_{36}$. Once the charge states are turned on/off, both adsorption and release processes of N$_2$ on B$_{36}$N$_{36}$ are spontaneous. To sum up, our calculations demonstrate that the B$_{36}$N$_{36}$ could be a reusable nanomaterial for the removal of N$_2$ from CH$_4$ for neutral gas purification.

4. Conclusions

To the best of our knowledge, this is the first investigation of the reversible removal of N$_2$ from CH$_4$ by using boron nitride nanomaterial. The study demonstrates that N$_2$ adsorption on B$_{36}$N$_{36}$ can be dramatically enhanced by adding electrons to the adsorbent, which indicates that the negatively charged B$_{36}$N$_{36}$ is an excellent sorbent for the selective separation of N$_2$ from CH$_4$ for neutral gas purification. Moreover, the absorbed N$_2$ can be spontaneously released from the BN nanocage with no reaction barrier once the electron is released, so that the adsorbent can be reused. In summary, this study provides information on experimental research that BN nanomaterial and the approach of switching the charge state of the nanomaterial on/off can remove N$_2$ from CH$_4$ for natural gas purification, and the addition/removal of the negative charge to/from the sorbent can be easily realized experimentally.

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Supporting Information

 Mulliken and Hirshfeld charges of B$_{36}$N$_{36}$ with different charge states, molecular graphs of the absorbed configurations and variation of thermodynamic properties with temperature of the systems at the PBE-D level as well as the important properties of B$_{36}$N$_{36}$-N$_2$ and B$_{36}$N$_{36}$-CH$_4$ systems calculated at the PBE level are listed in supporting information. This information is available free of charge via the Internet at http://pubs.acs.org.

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