Adsorption mechanisms of different volatile organic compounds onto pristine C$_2$N and Al-doped C$_2$N monolayer: A DFT investigation

Yuetan Su, Zhimin Ao, Yuemeng Ji, Guiying Li, Taicheng An

Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, Institute of Environmental Health and Pollution Control, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, China

ABSTRACT

Volatile organic compounds (VOCs) are a class of air pollutants which seriously affect the ecological environment and threaten human health. Adsorption of VOCs is considered as a promising technology for VOCs enriching, separation and utilization. In this work, density functional theory (DFT) calculations are employed to investigate the adsorption properties of typical VOCs molecules onto C$_2$N monolayer and Al-doped C$_2$N system due to the huge specific surface and porous structure of newly-reported holey two-dimensional C$_2$N. The results demonstrate that three typical VOCs: formaldehyde, benzene and trichloroethylene, can be absorbed onto pristine C$_2$N monolayer with weak adsorption energy, while the adsorption ability can be improved with the formation of a strong chemical bond. Especially for the formaldehyde molecule, the best adsorption capacity on the Al-doped C$_2$N surface with adsorption energy of $-2.754$ eV, nearly 5 times larger than the pristine C$_2$N system. The PDOS analysis and electronic distribution results also show that doped Al atom can act as a bridge to link VOCs molecules with C$_2$N monolayer and strengthen their interaction, which can significantly enhance the adsorption capacity. Therefore, Al doped C$_2$N monolayer is demonstrated to be a promising adsorbent for VOCs enriching and utilization.

1. Introduction

During the past few decades, rapid modernization and urbanization have gained great success in China. However, environmental pollution problems are emerging during these progresses and trigger public awareness of environmental protection. Volatile organic compounds (VOCs) are those organic compounds with a Reid vapor pressure of over 10.3 Pa at ambient temperature (293.15 K) and pressure (101.325 kPa) [1], which are ubiquitously present in the urban air. Long-term exposure to high concentrations of VOCs can cause serious carcinogenic, mutagenic, and teratogenic effects to human being by irritating the eyes, skin and nasopharyngeal membranes [2–4]. Moreover, they are closely related to the photochemical air pollution due to the formation of photochemical smog and secondary organic aerosol (SOA) [5]. They are classified as a major contributor to atmospheric air pollution. In fact, the removal of VOCs is urgent to mitigate the air pollution and protect human health.

At present, the research on VOCs treatment has become one of the hottest topics in the field of environmental protection. There are various technologies to treat VOCs, such as biodegradation [6], combustion [7], photocatalytic oxidation [8,9] as well as adsorption [10,11]. Among these technologies, adsorption has the advantages of being simple and low-cost with a wide application range and high efficiency. Therefore, it is widely used for the removal and separation of VOCs in industry and internal living areas. Various adsorbents have already been reported, such as zeolites [12], activated carbon [12], graphene [13] and metal organic frameworks (MOF) [14], however, these materials still could not satisfy all the requirements for actual applications due to some internal drawbacks. As for the typical adsorbents, the zeolites are affected by impurities such as sulfur dioxide, hydrogen sulfide, chlorine hydride and ammonia in atmosphere, causing irreversible transformations in the structure, thus reducing the adsorption capacity [15]. For activated carbon, the poor regenerative capacity and the high cost in the post processes limit its wide application in industry [15]. While for the relatively new adsorbents, such as graphene and metal organic frameworks (MOF), the main problems is the stability [16]. The corresponding functional group in graphene or MOF would reunion or collapse at high temperatures, which reduces the adsorption capacities. Therefore, new efficient adsorbents are highly desirable for VOCs treatment.
Recently, a new type of layered material, two-dimensional (2D) holey C$_2$N, has been synthesized using a simple wet-chemical reaction [17]. Recent studies have shown that C$_2$N monolayer is a new promising 2D material, and has wide applications in catalysis [18,19], molecular sieves [20–22], optics devices [23,24], electronics [25–30] as well as photocatalysis [24,25,31–34]. Similar to other 2D carbon nitrides, the atomic structure of the porous C$_2$N monolayer also has periodically distributed uniform pores and high specific surface area, which make it being a promising candidate for absorbing VOCs. Thus, this C$_2$N two-dimensional monolayer is considered for typical VOCs adsorptions. Formaldehyde (H$_2$CO) [35,36], benzene (C$_6$H$_6$) [35,37] and trichloroethylene (C$_2$HCl$_3$) [35] are three typical VOCs, which can be released from building materials, interior decoration, consumer products as well as in industrial applications [33,35–37]. These three VOCs are ubiquitously present in the atmosphere and closely related to our daily life. Therefore, the adsorptions of formaldehyde, benzene and trichloroethylene on C$_2$N monolayer deserves to be investigated in detailed.

However, normally pristine 2D materials sometimes cannot meet the demand of practical application and functionalization is necessary to some extent. It was reported that through doping metal atoms into 2D materials, such as graphene, MoS$_2$ and BN, could significantly increase the adsorption capacity for gas molecules. For example, recent studies show that the adsorption capacity of CO [38] and H$_2$ [39,40] will be enhanced after doping Al atoms into graphene. Furthermore, Al doped MoS$_2$ can increase the adsorption capacity of NO$_2$ and NH$_3$ [41], as well as for the adsorption enhancement of H$_2$CO [42], hydrogen [43], carbon dioxide [44] and cyanogen chloride [45] on Al doped BN monosheet. Therefore, doping Al into the 2D C$_2$N monolayer is also expected to enhance the adsorption capacity of gas molecules.

In this work, density functional theory (DFT) calculations are employed to measure the adsorption configurations and characteristics of three typical VOCs molecules (H$_2$CO, C$_6$H$_6$ and C$_2$HCl$_3$) on pristine and Al-doped C$_2$N monolayers to investigate the potential for VOCs removal. Besides, projected electronic density of states (PDOS) and Mulliken analysis are also adopted to further illuminate the doping effect of Al element on the atomic structures, properties, as well as adsorption performance. This study can provide an alternative for design of new adsorbents for the VOCs enriching and utilization, and further for the photocatalytic degradation afterwards.

2. Calculation methods

Spin-unrestricted density functional theory (DFT) calculations are performed by using the modules DMOL3 [46,47] in Materials Studio software. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) is employed as the exchange-correlation functional [48]. The DFT + D method with the Grimme scheme is adopted to consider the van der Waals forces [49]. The vacuum space is set as 30 Å in order to minimize the interlayer interaction. The Brillouin zone is sampled by using 9 × 9 × 1 or 11 × 11 × 1 k-point grid based on Monkhorst-Pack mesh generation. The former was used for geometry relaxation and the latter for density of states (DOS) analysis as calculation of electronic properties require a dense k-point grid for accurate results. All atoms are allowed to relax. Relativistic effects are accounted for using an all electron relativistic core treatment, which processes all the electrons in the system. A double numerical plus polarization (DNP) basis set is employed as recommended by reference [46]. An energy convergence tolerance of 10$^{-5}$ Ha (1 Ha = 27.2114 eV) is used, and the maximum allowed force and displacement are 0.002 Ha/Å and 0.005 Å, respectively. In the calculation of phonons, GGA-PBE function in CASTEP modules is employed. The calculation method is linear response, with the q-vector grid spacing for interpolation of 0.05 Å and convergence tolerance of 10$^{-3}$ eV/Å$^2$. As for dispersion, the separation value is set as 0.015 Å.

To understand the doping possibility of Al atom into C$_2$N, binding energy of an Al atom with C$_2$N $E_{\text{B-Al}}$ is calculated and defined as:

\[ E_{\text{B-Al}} = E_{\text{Al}+\text{C}_2\text{N}} - E_{\text{Al}} - E_{\text{C}_2\text{N}} \]

where $E_{\text{Al+C}_2\text{N}}$, $E_{\text{Al}}$ and $E_{\text{C}_2\text{N}}$ denote the energies of the systems of Al-doped C$_2$N, a free Al atom in the same vacuum slab and a pristine C$_2$N layer with a vacancy defect, respectively. To understand the adsorption properties of VOCs on C$_2$N monolayer, the adsorption energy of three typical VOCs molecules (H$_2$CO, C$_6$H$_6$ and C$_2$HCl$_3$) adsorbed onto C$_2$N $E_{\text{Al-VOC}}$ is also calculated and defined as:

\[ E_{\text{Al-VOC}} = E_{\text{C}_2\text{N-VOC}} - E_{\text{C}_2\text{N}} - E_{\text{VOC}} \]

where $E_{\text{C}_2\text{N-VOC}}$, $E_{\text{C}_2\text{N}}$ and $E_{\text{VOC}}$ denote the energies of the system with a VOC molecule adsorbed onto C$_2$N with or without Al dopant, the energy of the C$_2$N layer with or without dopant and a VOC molecule in the same vacuum slab, respectively.

3. Result and discussion

3.1. The structure optimization of pristine/Al-doped C$_2$N monolayer

The structure of 2D porous C$_2$N monolayer is initially studied, and the optimized structure is shown in Fig. 1a. Previous work already reported that a C$_2$N unit cell can be considered as a 2D honeycomb lattice of benzene rings connected through nitrogen atoms with distributed pores in a fused aromatic network structure.
including 12C atoms and 6N atoms [18,21,27]. The optimized lattice parameters are \(a = b = 8.325\, \text{Å}\), and the bond lengths are obtained as 1.337, 1.426 and 1.473 Å for the C–N, C–C(1) and C–C(2) bonds as shown in Fig. 1a, respectively, which are in good agreement with early reported results (1.34, 1.43 and 1.47 Å for the C–N, C–C(1) and C–C(2) bonds) [18]. Furthermore, the electronic structure of the pristine monolayer C\(_2\)N is also considered. The results showed that this monolayer material exhibited semiconducting behavior with a band gap of 1.67 eV at \(\Gamma\) point (Fig. 1b), which is consistent with the previously theoretical result (1.66 eV) and the experimental result (1.96 eV) [26].

Therefore, the calculation method for pristine C\(_2\)N monolayer has been confirmed, and the adsorption of VOCs on C\(_2\)N monolayer is investigated. To avoid high work load, the \(2 \times 2 \times 1\) supercell of C\(_2\)N monolayer consisted of 48C atoms and 24N atoms is selected to study the adsorption behaviors of \(\text{H}_2\text{CO}, \text{C}_6\text{H}_6\) and \(\text{C}_2\text{HCl}_3\) molecules. The optimized structure for the \(2 \times 2 \times 1\) C\(_2\)N supercell is shown in Fig. 2.

It has been reported that aggregation of doped metal atoms on 2D materials surface would reduce the gas molecule adsorption capacity [39]. To avoid the aggregation, strong binding between metal atoms and 2D materials is required, and the binding energy should be larger than the cohesive energy of the metal [39]. Therefore, the doping position of Al atoms into C\(_2\)N monolayer is investigated. As shown in Fig. 2, there are five possible sites (d1–d5, d1–d4 are substitution position and d5 is vacancy position) of an Al atom doping based on the highly symmetrical structure. After geometry optimization, it is found that the Al atom prefers to be doped at d1 site, which replaces a N atom near the hole. The relaxed atomic structure is shown in Fig. 3. In order to calculate the binding energy of the Al atom on the C\(_2\)N monolayer based on Eq. (1), the total energies of C\(_2\)N monolayer with a vacancy at d1 and an isolated Al atom in the same slab are also calculated. In this way, the binding energy of an Al atom on the C\(_2\)N monolayer \(E_{\text{b-Al}}\) is obtained as \(-4.57\, \text{eV}\) which is stronger than the cohesive energy of Al \(-3.39\, \text{eV}\) in experiment, and \(-3.64\, \text{eV}\) [51] by using LDA (Local Density Approximation) and \(-3.23\, \text{eV}\) [50] by using VMC (Variational Monte Carlo) in DFT study. Therefore, the aggression of Al atoms can be prevented, and Al atoms have good dispersion into the C\(_2\)N monolayer surface. As shown in Fig. 3, Al-doped C\(_2\)N causes slight distortion of the atomic structure, and the bond lengths of C–C(1) bonds, C–C(2) bonds and C–N bonds are obtained as 1.411, 1.382 and 1.346 Å, respectively, which are slightly different from those before Al doping (they are respectively 1.426, 1.473 and 1.337 Å). However, the Al–C bonds are 1.873 Å, which are much larger than the C–C bonds and C–N bonds. This indicates that the Al–C bonds prefer to be disrupted in the chemical reactions due to their weak bonding.

In considering the Al doping, the corresponding binding energy Al at the most stable position N site is \(-4.57\, \text{eV}\), indicating that this is a process of energy reduction, which indicates that the doping reaction is an exothermic reaction and is thermodynamically favourable. In experiment, Morozova et al. reported that the spark plasma sintering technique and heat processing technology was used to prepare Al-doped Mg\(_2\)Si, and the doping concentration can be controlled by adjusting the experimental parameters, such as the number of Al chips (0, 1, 2...) [52]. We believe this technology can be adopted in the C\(_2\)N system due to the similar resistance to effect of heat of this carbonitride material. Regarding to the stability of C\(_2\)N with one vacancy, the density of phonon states (DOPS) of the system with N site vacancy is calculated and shown as Fig. 4.

To understand the strong binding between the Al atom and C\(_2\)N layer, electron transfer between them is also discussed through Mulliken analysis. Since the doping mainly affects the charge

![Fig. 2. Top view of the geometric structure of C\(_2\)N (2 × 2 × 1 supercell) monolayer. d1–d4 are four possible doping sites for the Al atom. For VOCs molecule adsorption on pristine C\(_2\)N monolayer, five different high symmetry adsorption sites are considered: hollow-I (H1), hollow-II (H2), hollow-III (H3), corner-I (C1), corner-II (C2) and vacancy (V). Atoms 0–9 are the selected atoms for Mulliken analysis.](image)

![Fig. 4. The density of phonon states (DOPS) of the C\(_2\)N with N site vacancy.](image)
distribution near the doping site, the atomic charges of the doped Al atom and 9 atoms near the doped Al atom (sites 1–9 in Fig. 3) are also analyzed. For comparison, the atomic charges of the 9 atoms before doping are also calculated. Table 1 lists the atomic charges of these 9 atoms in the pristine C2N and Al doped C2N systems. From the table, it is shown that doping Al changes the electronic distribution significantly. The Al atom loses electrons and has +1.198 e charge, and the nearby atoms obtain electrons, especially the C atoms at sites 3 and 7 which bind with the doped Al atom, changing the electron charge from 0.071 and 0.071 eV to -0.547 and -0.548 eV, respectively. Therefore, a large charge transfer occurs from the Al atom to the C2N monolayer, inducing a strong interaction between Al atoms and C2N monolayer and confirms the result of binding energy calculation. Similar situations are also reported in the cases of lithium [53] and boron atom [54,55] doped C2N systems. In addition, the projected electronic density of states (PDOS) of the Al atom and C2N sheet is also calculated as shown in Fig. 5. From the figure, the main peaks of the Al atom are found located at 0.983, 0.414 and 2.99 eV, as guided by the dash lines. As indicated, the main peaks of the Al atom overlap with the bands of the C2N sheet greatly, suggesting the strong interaction between the Al atom and the C2N monolayer.

3.2. Adsorption of VOCs molecules on pristine C2N monolayer

The adsorption properties of three typical VOCs molecules (H2CO, C6H6, and C2HCl3) onto pristine C2N monolayer are first investigated. To determine the most stable adsorption configuration, six different representative adsorption sites are all considered as indicated as H1, H2, H3, C1, C2 and V in Fig. 2 for the case of VOCs adsorption onto the pristine C2N monolayer. After geometry optimization, the most favorable adsorption configurations of H2CO, C6H6 and C2HCl3 on the pristine C2N monolayer are shown in Fig. 6. The corresponding adsorption energy and structure parameters of these three typical VOCs adsorption configurations are listed in Table 2. As shown in Fig. 6(a), the H2CO molecule is located at the vacancy site V of the C2N monolayer and the oxygen atom goes up while the hydrogen atom goes down. The C-O bond and C-H bonds show slight change from 1.216 and 1.117 Å to 1.223 and 1.114 Å after the adsorption, respectively. It is clearly shown that the C2HCl3 molecule prefers to be adsorbed onto the hollow site H1 with an inclined angle, and the bond lengths are essentially invariant in the process of adsorption. As for C2HCl3 molecule, the most stable configuration is that the C2HCl3 molecule vertically locates at the vacancy site V of the C2N monolayer with the hydrogen atoms downwards. All the bond lengths show the negligible changes before and after adsorption. In addition, the C2HCl3 molecule adsorbed onto the C2N monolayer induces slight deformation of the C2N monolayer where slight curve below the monolayer as shown in Fig. 6(b), while both the H2CO and C2HCl3 prefer to be adsorbed normally onto the C2N monolayer surface. The adsorption of these three VOC molecules onto the pristine C2N monolayer can be define weak chemisorption based on the adsorption energy $E_{ad}$ of -0.556 to -0.775 eV (Generally the energy of 0.5 eV is a standard to distinguish the physical adsorption from chemical adsorption [56], and 1 eV = 96.154 kJ/mol). Note that short distances of 1.264 and 1.442 Å between VOCs molecules and the pristine C2N monolayer in the cases of H2CO and C2HCl3 are found. However, as shown in the top view of the Fig. 6(a) and (c), the two molecules are adsorbed onto the vacancy of the C2N monolayer, which are embedded into the C2N monolayer without the chemical bonds.

### Table 1

<table>
<thead>
<tr>
<th>Atom (species)</th>
<th>Pristine C2N</th>
<th>Al doped C2N</th>
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<tr>
<td>0 (N/Al)</td>
<td>-0.141</td>
<td>1.198</td>
</tr>
<tr>
<td>1 (N)</td>
<td>-0.140</td>
<td>-0.280</td>
</tr>
<tr>
<td>2 (C)</td>
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<td>0.251</td>
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<tr>
<td>3 (C)</td>
<td>0.071</td>
<td>-0.547</td>
</tr>
<tr>
<td>4 (C)</td>
<td>0.071</td>
<td>0.103</td>
</tr>
<tr>
<td>5 (N)</td>
<td>-0.141</td>
<td>-0.155</td>
</tr>
<tr>
<td>6 (C)</td>
<td>0.071</td>
<td>0.104</td>
</tr>
<tr>
<td>7 (C)</td>
<td>0.071</td>
<td>-0.548</td>
</tr>
<tr>
<td>8 (C)</td>
<td>0.071</td>
<td>0.255</td>
</tr>
<tr>
<td>9 (N)</td>
<td>-0.141</td>
<td>-0.283</td>
</tr>
</tbody>
</table>

The adsorption of H2CO, C6H6 and C2HCl3 molecules adsorbed onto the Al-doped C2N monolayer in the cases of H2CO and C2HCl3 are obtained as 2.754 eV and 1.595 eV, respectively, which are much stronger than those in the cases of adsorption onto pristine C2N monolayer, and all the adsorption energies of these three VOCs molecules are in the range of chemical adsorption, which is also confirmed by the short bond lengths in Table 2 and the formation of chemical bonds between VOCs molecules and the Al-doped C2N monolayer as shown in Fig. 7. From the figure, it is shown that the Al-doped C2N monolayer has slight distortion after the adsorption of H2CO, C6H6 and C2HCl3. For the adsorption of H2CO, the O atom forms chemical bond with the doped Al atom, the Al–O bond length is 1.703 Å as shown in Table 2. Besides, the C atom in the H2CO molecule also forms C–C bond with the C atom in the C2N sheet, and the bond length is 1.525 Å. These two chemical bonds induce large adsorption energy of -2.754 eV in the case of H2CO absorbed onto Al-doped C2N monolayer, while $E_{ad}$ of C6H6 and C2HCl3 are obtained as -1.595 and -1.247 eV, respectively. As shown in Fig. 7(b) and (c), chemical bonds are also formed between the Al-doped C2N monolayer with C6H6 or C2HCl3 molecule, and the corresponding Al–C bond lengths are obtained as 2.243 and 2.344 Å, respectively. The Al–C bond in the case of C6H6 adsorption and Al–Cl bond in the case of C2HCl3 adsorption are much longer than the C–C and Al–O bonds in the case of H2CO adsorption. This
also confirms that the adsorption of H$_2$CO onto the Al-doped C$_2$N is much stronger than that in the cases of C$_6$H$_6$ and C$_2$HCl$_3$ adsorption. Therefore, after Al doping, the adsorption of the three typical VOCs molecules onto C$_2$N monolayer can be greatly enhanced, i.e. the Al-doped C$_2$N monolayer would be a promising material for VOCs adsorption, especially for H$_2$CO removal. Compared with the early reports, the Al-doped C$_2$N system has been shown to have a much better adsorption performance than that of the iron-doped graphene system for H$_2$CO adsorption (\(E_{\text{ad}} = -1.45 \text{ eV}\)) [57] and Ag surface [58] for C$_6$H$_6$ adsorption (\(E_{\text{ad}} = -0.85 \text{ eV}\)).

3.4. The adsorption enhancement mechanism of VOCs molecules onto Al-doped C$_2$N monolayer

To understand the adsorption enhancement mechanism of three VOCs molecules onto the Al-doped C$_2$N system, projected electronic density of states (PDOS) of the three different adsorbed molecules (H$_2$CO, C$_6$H$_6$, and C$_2$HCl$_3$), the doped Al atom, and the C$_2$N monolayer in the pristine or Al-doped C$_2$N layer are calculated as shown in Fig. 8. As mentioned above, the adsorption strength can be indicated by the overlap of the bands. In Fig. 8, the red dash
areas indicate the overlap parts of the adsorbed molecules and the C\textsubscript{2}N monolayer, while the blue dash areas indicate the overlap parts of the adsorbed molecules, the doped Al atom and C\textsubscript{2}N sheet. It is shown above that the adsorption energies of the three VOCs molecules are calculated as \(-1.247\) to \(-2.754\) eV for the Al-doped C\textsubscript{2}N system. The strong interactions can be explained by the interaction of the electrons among the adsorbed molecules, Al atom and the C\textsubscript{2}N sheet as shown in Fig. 8(b), (d) and (f). For comparison purpose, PDOS of the VOCs molecule adsorption onto pristine C\textsubscript{2}N monolayer is also calculated and shown in Fig. 8(a), (c), and (e). It is clearly shown that the overlap of the bands increases significantly after Al doping, and the VOCs molecules can interact with both the C\textsubscript{2}N monolayer as well as the doped Al atom. In other words, the doped Al atom can act as a bridge to link VOCs molecules with the C\textsubscript{2}N monolayer. In contrast, for the case of the pristine C\textsubscript{2}N monolayer, the overlap of the main bands is just between the adsorbed molecules and the C\textsubscript{2}N monolayer, which confirms the relatively weak interactions in the undoped system. In addition, the doped Al atom has changed the electronic structure of the absorbed molecules, where PDOS are shifting to a lower energy, indicating more stable VOCs molecules adsorption.

The electronic density distribution of the H\textsubscript{2}CO, C\textsubscript{6}H\textsubscript{6} and C\textsubscript{2}HCl\textsubscript{3} molecules adsorbed on the Al doped C\textsubscript{2}N system are also calculated and shown in Fig. 9. It is clearly shown that high density of electrons appears in the area among the adsorbed molecules, the Al atom and the C\textsubscript{2}N sheet. This further confirms that the doped Al atom is a bridge to link the electron clouds of the adsorbed molecules and the C\textsubscript{2}N sheet, thus the interactions of electrons among

Fig. 8. The PDOS of adsorbed VOCs molecule, doped Al atom and C\textsubscript{2}N sheet before and after Al doping. The red dash areas demonstrate the overlap parts of the adsorbed molecules and the C\textsubscript{2}N monolayer, while the blue dash areas indicate the overlap parts of the adsorbed molecules, the doped Al atom and C\textsubscript{2}N sheet. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
them are much stronger, inducing much stronger adsorption energy of VOCs molecules onto Al-doped C2N monolayer, which agrees well with above results.

The Mulliken analysis is also adopted to calculate the atomic charges for the adsorption of VOCs molecules onto the pristine and Al-doped C2N monolayer. The charges of the adsorbed molecules and the Al or N atom are listed in Table 3. It is shown that the electronic transfer between the VOCs molecules and C2N monolayer is much stronger after Al doping (around 10 times amount of the electrons transferred), which also indicates the stronger interactions between the adsorbed molecules and the C2N monolayer. It is interesting to note that the H2CO molecule has negative charge when adsorbing onto the Al-doped C2N monolayer, while the other two cases of C6H6 and C2HCl3 have positive charges. It is shown from above discussion that the doped Al atom loses 1.198 e, and has strong positive charge, indicating the strong capacity to attract electrons from other places. This explains why the C6H6 and C2HCl3 are relatively positively charged. For the case of H2CO adsorption onto Al-doped C2N monolayer, there are two chemical bonds (Al–O and C–C bonds) formed between H2CO and Al-doped C2N monolayer, and the strong electronegativity O atom can further attract 0.264 e electrons from the Al atom (the charge is 1.462 e), then the remaining electrons are obtained from the C–C bond.

4. Conclusions

In summary, the adsorption of three typical VOCs molecules (H2CO, C6H6, and C2HCl3) onto the pristine C2N and Al-doped C2N monolayer were investigated by using first principles calculations. It is found that the VOCs molecules are relatively weakly adsorbed onto the pristine C2N monolayer. After Al doping, the adsorptions of all the three VOCs molecules are enhanced significantly and strong chemical adsorption is found. Therefore, Al-doped C2N monolayer is a promising candidate for VOCs molecules adsorption. In addition, the adsorption enhancement mechanism is also investigated through analyzing PDOS, electronic distribution, and atomic charges. It is found that the doped Al atom can act as a bridge to link the VOCs molecules with C2N monolayer together. Therefore, Al doped C2N is shown to be a promising adsorbent for VOCs enriching and utilization.

Conflicts of interest

There are no conflicts to declare.

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Table 3

<table>
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<tr>
<th>Type</th>
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<th>Absorbed molecule</th>
<th>Al doped C2N</th>
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<td>N atom</td>
<td></td>
<td>Al atom</td>
</tr>
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<td>H2CO</td>
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<td>C6H6</td>
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<td>C2HCl3</td>
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References


