Al-Decorated C$_2$N Monolayer as a Potential Catalyst for NO Reduction with CO Molecules: A DFT Investigation

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Abstract: Developing efficient and economical catalysts for NO reduction is of great interest. Herein, the catalytic reduction of NO molecules on an Al-decorated C$_2$N monolayer (Al-C$_2$N) is systematically investigated using density functional theory (DFT) calculations. Our results reveal that the Al-C$_2$N catalyst is highly selective for NO, more so than CO, according to the values of the adsorption energy and charge transfer. The NO reduction reaction more preferably undergoes the (NO)$_2$ dimer reduction process instead of the NO direct decomposition process. For the (NO)$_2$ dimer reduction process, two NO molecules initially co-adsorb to form (NO)$_2$ dimers, followed by decomposition into N$_2$O and O$_{ads}$ species. On this basis, five kinds of (NO)$_2$ dimer structures that initiate four reaction paths are explored on the Al-C$_2$N surface. Particularly, the cis-(NO)$_2$ dimer structures (D$_{cis-N}$ and D$_{cis-O}$) are crucial intermediates for NO reduction, where the max energy barrier along the energetically most favorable pathway (path II) is as low as 3.6 kcal/mol. The remaining O$_{ads}$ species on Al-C$_2$N are then easily reduced with CO molecules, being beneficial for a new catalytic cycle. These results, combined with its low-cost nature, render Al-C$_2$N a promising catalyst for NO reduction under mild conditions.

Keywords: NO catalytic reduction; C$_2$N monolayer; Al-C$_2$N catalyst; nitric oxide; DFT calculation

1. Introduction

The increasing emission of nitrogen oxides (NO$_x$) has brought serious harm to the atmospheric environment and human health [1–3]. Nitric oxide (NO), which comprises approximately 95% of NO$_x$ emissions, is considered a major cause of acid rain and photochemical smog formation [4]. Selective catalytic reduction (SCR) is a promising method that typically selects CO [5–9], H$_2$ [8–11], or NH$_3$ [12] as the reducing agent to eliminate emitted NO. Since CO and NO commonly coexist in exhaust gases, the catalytic reduction of NO with CO as a reducing agent can simultaneously convert CO and NO pollutants into harmless N$_2$ and acceptable CO$_2$. Noble metal catalysts such as Pt, Au, or Pd have been extensively studied; however, there are problems, such as high cost, low abundance, and toxicity [13–16]. Thus, it is of utmost importance to design high-efficiency and low-cost alternative catalysts to remove or reduce NO molecules.

Reducing the particle size of active metals to a few atoms is a valuable strategy to improve catalytic activity [17–20]. Compared to traditional catalysts, single-atom catalysts can greatly decrease the amount of metal used, thereby reducing costs. In particular, single-atom catalysts have been proven to efficiently catalyze or adsorb various harmful gas molecules, such as NO [21–25], CO [23,25], H$_2$S [26], and SO$_2$ [27]. Recently, a two-dimensional (2D) graphene porous material, a C$_2$N monolayer, was successfully prepared via a simple wet chemical reaction [28]. This novel material with a uniform pore distribution has attracted much attention due to its large surface area and good structural stability. Given the uniform cavity structure of C$_2$N, it has been demonstrated to be a suitable material for anchoring metal atoms. Previous studies have shown that metal-atom-decorated C$_2$N...
monolayers can efficiently trap small gas molecules. For example, Ma et al. proposed 3D transition-metal-modified C$_2$N as a promising candidate for the low-temperature CO oxidation reaction [29]. Anikina et al. reported that metal-decorated C$_2$N monolayers have high storage capacities for H$_2$ [30]. Furthermore, several studies reported that single metal-atom-anchored C$_2$N monolayers can also act as effective catalysts for N$_2$ reduction, oxygen reduction, and hydrogen evolution reactions [31–35].

The metal aluminum is environmentally friendly, inexpensive, and abundant in storage. Previous work has shown that decoration with Al atoms can significantly improve the adsorption capacity of 2D materials [36–44]. Specifically, Al-doped graphene showed a good adsorption ability for small molecules, such as N$_2$O, NO$_2$, SO$_3$, and CO$_2$ [36–40,43]. The Al-embedded C$_2$N was shown to be a prospective candidate to adsorb and degrade volatile organic compounds, mainly due to a strong electronic transfer between the adsorbed molecules and Al atoms [41,42]. Strong adsorption properties of NO$_2$ and NH$_3$ molecules were also observed in Al-MoS$_2$ [44].

Inspired by these findings, we investigated the reaction mechanism of the NO reduction with CO molecules on an Al-C$_2$N monolayer based on density functional theory (DFT) calculations. The geometries of reactants, transition states, and products, as well as reaction energies, were calculated in detail. The key intermediates and preferred reaction pathways for NO reduction on Al-C$_2$N were further identified. The catalytic reactivity of Al-C$_2$N was also compared with other catalytic materials to evaluate the possibility of using Al-C$_2$N as a catalyst for NO reduction.

2. Computational Methods

All DFT calculations were carried out at the level of the B3LYP exchange–correlation functional with Grimme’s DFT-D3 empirical dispersion correction using the Gaussian09 software package [45–48]. Previous literature confirmed that the B3LYP functional with DFT-D3 is a reasonable condition for calculating intermolecular non-covalent interactions [49]. The 6-31G(d, p) basis set was used to describe all atoms [50]. A pristine C$_2$N cluster model in this study contained 37 carbon atoms, 12 nitrogen atoms, and 12 hydrogen atoms. All the energies were corrected with zero-point vibrational energy (ZPE). Vibration frequency calculations were performed to verify the optimized structure, where the minimum structure had no imaginary frequency, and the transition state only had one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were used to verify the transition states [51–53]. Atomic charges were discussed with the natural bond orbital (NBO) analysis [54]. Electron density difference (EDD) plots were obtained with the Multiwfn program [55]. For each adsorption configuration, the EDD plots were calculated as:

$$\Delta \rho = \rho_{A/S} - \rho_A - \rho_S$$  \hspace{1cm} (1)

where $\rho_{A/S}$, $\rho_A$, and $\rho_S$ are the electron density of the total complexes, isolated substrate, and isolated adsorbate, respectively.

The adsorption energy ($E_{\text{ads}}$) of a given adsorbate was defined as:

$$E_{\text{ads}} = E_{\text{total}} - E_A - E_S$$  \hspace{1cm} (2)

where $E_{\text{total}}$, $E_A$, and $E_S$ are the energies of the total adsorbate-substrate systems, isolated adsorbate, and isolated substrate, respectively.

The change in Gibbs free energy ($\Delta G$) was defined as:

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (3)

where $\Delta H$ and $\Delta S$ represent the enthalpy with a zero-point energy correction and the entropy change at 298.15 K, respectively.
3. Results and Discussion

3.1. Geometrical Structures and Stability of Pristine C$_2$N and Al-C$_2$N Monolayer

Firstly, we examined the geometric structure and stability of the designed Al-C$_2$N. The optimized structure of the pristine C$_2$N cluster is shown in Figure 1a. The calculated lattice parameter of 8.286 Å was consistent with the experiment result (8.30 Å) [28]. Then, a single Al atom was attached to the C$_2$N cluster via two adjacent N atoms (shown in Figure 1b), with both bond lengths being 1.939 Å, in which the Al atom was more preferably anchored at the corners of the six-fold cavity of the C$_2$N. The calculated bond length value was in line with the previously periodic system-reported results (1.96 Å) [56]. EDD plots revealed a sizeable interaction area between the Al atom and its two adjacent N atoms. It is worth mentioning that the modification of the Al atoms could effectively change the surface properties of the C$_2$N monolayer. As shown in Figure 1c,d, the uniformly distributed charge on the C$_2$N monolayer changed to a directional concentrated distribution, which was essential for the subsequent adsorption of gas molecules.

![Figure 1. Optimized structures of the (a) pristine C$_2$N cluster and (b) Al-C$_2$N monolayer, respectively. Electron density difference plots (in 0.002 au) for (c) pristine C$_2$N and (d) Al-C$_2$N, respectively. Blue and yellow parts represent charge accumulation and depletion, respectively. All bond lengths are in Å.](image)

To evaluate the thermal stability of the designed Al-C$_2$N systems, we carried out MD simulations at 300 K and 500 K for 8 ps with a time step of 2 fs under the NVT ensemble (see Figure S1 in the Supplementary Materials). According to the MD simulations, the energies of the Al-C$_2$N system fluctuated gently, suggesting its high thermodynamic stability.

3.2. Adsorption Behavior of NO and CO Molecules on Al-C$_2$N Surface

The stable configurations of CO and NO adsorbed on the Al-C$_2$N surface are displayed in Figure 2. Table 1 summarizes the corresponding adsorption parameters for the NO and CO molecules, including the $E_{ads}$, $\Delta G$, and charge transfer values. Note that all the calculated $\Delta G$ values of the CO or NO molecules adsorbed on the Al-C$_2$N surface were negative, suggesting that the adsorption of these species was thermodynamically spontaneous.
Figure 2. Optimized adsorption configurations for the (a) NO (N-end), (b) NO (O-end), (c) CO, (d) ring-(NO)₂ dimers, (e) cis-(NO)₂ dimers (N-end), (f) cis-(NO)₂ dimers (O-end), (g) trans-(NO)₂ dimers (N-end), and (h) trans-(NO)₂ dimers (O-end) on Al-C₂N surface. All bond lengths are in Å.

Table 1. Calculated adsorption energies (E_{ads}, kcal/mol), adsorption free energies (ΔG, kcal/mol), and net charge-transfer values (q, e) for different adsorption species on the Al-C₂N surface, along with the corresponding energy barriers (E_a, kcal/mol) and reaction energies (ΔE_r) for a single NO or (NO)₂ dimer reduction on Al-C₂N surface.

| Adsorbate       | E_{ads}  | ΔG      | q | E_a  | Path  | ΔE_r |
|-----------------|----------|---------|---|------|-------|------|
| CO              | 21.8     | -11.4   | 0.083 |  - | -   | -   |
| NO (O-end)      | 7.4      | -4.1    | -0.337 |  - | -   | -   |
| NO (N-end)      | 29.2     | -17.8   | -0.430 | 68.0 | -41.1 | -   |
| D_{ring}        | -109.7   | -86.3   | -1.377 | 33.5 (43.1) | Ia (Ib) | 23.2 (−67.7) |
| D_{cis-N}       | -53.1    | -31.8   | -0.672 | 3.6 | II  | -8.6 |
| D_{cis-O}       | -61.7    | -39.9   | -0.731 | 2.7 | II  | -24.8 |
| D_{trans-N}     | -73.8    | -52.3   | -1.303 | 16.5 | III | -12.7 |
| D_{trans-O}     | -62.0    | -40.0   | -0.697 | 12.7 | IV  | -24.5 |

1 Positive and negative values of q correspond to the net charge transfer from the adsorbate to the Al-C₂N and the net charge transfer from the Al-C₂N surface to the adsorbate, respectively.

The adsorption geometries of the NO, CO, and (NO)₂ dimers on Al-C₂N are shown in Figure 2. For the NO molecules, two possible adsorption modes (including N-end and O-end) were investigated. From Figure 2a,b, it can be seen that the NO molecules were tilted concerning the Al-C₂N surface, consistent with previous reports [24, 57, 58]. As evident, the calculated N-O bond lengths of the NO molecules were elongated to 1.203 Å and 1.213 Å, respectively, when compared with the free NO molecule (1.160 Å). The E_{ads} values for the N-end and O-end adsorption modes were −29.2 and −7.4 kcal/mol, respectively, which was more negative than the values in Si-doped graphene (−18.4 and −4.4 kcal/mol) [57]. From the viewpoint of adsorption energy, it is clear that the N-end adsorption was energetically more favorable than the O-end. This result was also supported by the NBO charge analysis, in which the N-end mode was accompanied by a larger charge transfer of 0.430 e from the Al-C₂N surface to the 2π* orbital of the NO molecule (Table 1).

As for the CO molecules, our results demonstrated that CO preferred to adsorb on the Al-C₂N surface via its C-end. Figure 2c demonstrates that the C-O bond length of CO was nearly unchanged compared to that of the free CO molecule (1.14 Å), indicating that CO was not activated after being adsorbed on the Al-C₂N surface. Based on the E_{ads} value, the adsorption of CO (−21.8 kcal/mol) on Al-C₂N was weaker than that of NO (−29.2 kcal/mol). In this case, it was expected that the tendency of the NO molecule to adsorb onto the Al-C₂N surface was greater than that of CO. Unlike the NO molecules, CO acted as the electron donor, where the charge value transferred from the CO molecule to the Al-C₂N surface was 0.083 e (Table 1).
Next, we considered the \((\text{NO})_2\) dimer configuration formed by two NO molecules co-adsorbed on the Al-C\(_2\)N surface. The \((\text{NO})_2\) dimer was characterized for the first time by Dinerman and Ewing using infrared spectroscopy \cite{59}. The stable \((\text{NO})_2\) dimer adsorption configurations are illustrated in Figure 2d–h. The IR spectra plots of five \((\text{NO})_2\) dimers on the Al-C\(_2\)N surface are displayed in Figure S2. As can be seen, five different \((\text{NO})_2\) dimers were obtained on the Al-C\(_2\)N surface.

Figure 2d shows a five-membered ring \((\text{NO})_2\) dimer structure (labeled as D\(_{\text{ring}}\)), in which both NO molecules were bound to the Al site through their O-end. The bond lengths of the two formed Al-O bonds and the N\(_1\)-N\(_2\) bond were 1.788, 1.770, and 1.248 Å, respectively. This structure was similar to that of Si-doped graphene (1.783, 1.762, and 1.240 Å for two Si-O bonds and the N\(_1\)-N\(_2\) bond) \cite{60}. Figure 2e,g display the cis- and trans-\((\text{NO})_2\) dimer structures at the N-end (labeled as D\(_{\text{cis-N}}\) and D\(_{\text{trans-N}}\)), respectively, in which one NO molecule was adsorbed into the Al site via its N-end and two NO molecules were bound through N-N bonds. The calculated bond lengths of the N\(_1\)-N\(_2\) bond were 1.469 and 1.286 Å, respectively. It is noteworthy that two novel \((\text{NO})_2\) dimer structures were explored in this work, which have not been reported in current catalysts \cite{57,59,61–64}. Figure 2f,h correspond to two novel cis- and trans-\((\text{NO})_2\) dimer structures at the O-end (labeled as D\(_{\text{cis-O}}\) and D\(_{\text{trans-O}}\)) with N\(_1\)-N\(_2\) bond lengths of 1.240 and 1.254 Å, respectively. Among the above \((\text{NO})_2\) dimers, the calculated N\(_1\)-N\(_2\) bond lengths ranged from 1.505 to 1.233 Å, which were much shorter than the value in the gas phase \((\text{NO})_2\) dimer (1.970 Å).

As shown in Table 1, the calculated adsorption energies of the five \((\text{NO})_2\) dimers on the Al-C\(_2\)N surface were significantly enhanced, with values of −109.7, −53.1, −61.7, −73.8, and −62.0 kcal/mol, respectively, which were larger than twice that of a NO molecule (−29.2 kcal/mol). This indicated that the addition of the second NO molecule was beneficial for strengthening the interaction between the catalyst and NO molecule. Similar results were further verified with the NBO charge analysis, where the considerable charge-transfer values from the Al-C\(_2\)N surface to \((\text{NO})_2\) dimers were −1.377, −0.672, −0.731, −1.303, and −0.697, respectively (Table 1).

3.3. NO Reduction Mechanism on Al-C\(_2\)N Surface

Here, the NO reduction mechanism mainly included the direct decomposition process and the \((\text{NO})_2\) dimer reduction process. For the former, a NO molecule was directly decomposed into O and N atoms. For the latter, two NO molecules were co-adsorbed forming \((\text{NO})_2\) dimers, followed by their decomposition into N\(_2\)O molecules and O atoms. Subsequently, the N\(_2\)O molecules were desorbed, and the remaining O atoms could be removed with the NO or CO molecules.

3.3.1. NO Direct Decomposition Process

Figure 3 shows the energy profile of the NO direct decomposition process on Al-C\(_2\)N, where the energy sum of Al-C\(_2\)N and free NO molecules was set as the reference energy. As seen, the reaction began with the NO molecule adsorbed on Al-C\(_2\)N via its N-end. In the TS structure, the calculated O-N bond length of the NO molecule was elongated from 1.215 Å to 2.420 Å. In the FS structure, the O-N bond was broken and the distance between the O and N atoms was 3.292 Å. Our results showed that the NO direct decomposition process was unfavorable both in kinetics and thermodynamics due to the high reaction energy barrier (68.0 kcal/mol) and endothermic nature (41.1 kcal/mol), which agreed with previous reports, such as Si-doped graphene (39.2 kcal/mol) \cite{24}, Si-doped BN nanosheets (57.9 kcal/mol) \cite{60}, and Fe-doped graphene (124.1 kcal/mol) \cite{25}.
were 43.1 and 1.6 kcal/mol, respectively, which could be provided by the larger exothermic (the MS1 structure). In the TS1 structure, two N-O bonds broke with the bond lengths

\[ \text{CO} + \text{O} \rightarrow \text{N} + \text{NO} \]

The energy profile and corresponding minima state and transition state are displayed

1.240 Å for two Si-O bonds and the N1-N2 bond) [60]. Figure 2e,g display the cis- and trans-
respectively. This structure was similar to that of Si-doped graphene (1.783, 1.762, and
1.286 Å, respectively. It is noteworthy that two novel (NO) 2 dimer structures were ex-
plored in this work, which have not been reported in current catalysts [57,59,61–64]. Fig-
ure 2f,h correspond to two novel cis- and trans-(NO) 2 dimer structures at the O-end (la-
plored as path I, path II, path III, and path IV , respectively. For simplicity, the remaining oxygen atoms on the Al-C2N surface were labeled as Oads.

In path Ia, the five-membered ring (NO)2 dimer structure (D_{ring}) was the initial state. The energy profile and corresponding minima state and transition state are displayed in Figure 4a. As can be seen, the D_{ring} structure could be decomposed into the product (N2O + Oads) through the transition state with a high-energy barrier of 33.5 kcal/mol. In the TS structure, the N2-O2 bond broke with the bond length increasing from 1.398 to 2.364 Å, while the N1-N2 bond length decreased from 1.248 to 1.141 Å. The entire process from D_{ring} to the FS structure was endothermic by 23.2 kcal/mol. Given the high reaction barrier and endothermicity, it was expected that the D_{ring} dimer reduction on Al-C2N was unfavorable both kinetically and thermodynamically.

In path Ib, a two-step reaction was identified: (i) (NO)2 \rightarrow N2 + 2Oads, followed by (ii) CO + Oads \rightarrow CO2. As shown in Figure 4b, the D_{ring} structure was taken as the initial state and, subsequently, CO was physisorbed over Al-C2N to form an intermediate state (the MS1 structure). In the TS1 structure, two N-O bonds broke with the bond lengths increasing to 1.880 and 1.978 Å, respectively, while the N1-N2 bond length was shortened to 1.144 Å. Next, N2 was completely formed in the MS2 structure. In the next step, CO approached the O1 atom. The O1···C bond’s length reduced from 2.859 to 2.152 Å and, finally, formed the CO2 molecule. Note that the energy barriers of the first and second steps were 43.1 and 1.6 kcal/mol, respectively, which could be provided by the larger exothermic reaction energy (−67.7 kcal/mol, from D_{ring} to FS).

In path II, the reaction started with the co-adsorption of two NO molecules to generate a cis-(NO)2 dimer (N-end, D_{cis-N}) structure, as shown in Figure 5. As seen, this step had a negligible energy barrier and was exothermic by 17.3 kcal/mol. Then, the D_{cis-N} structure could be converted to the more stable cis-(NO)2 dimer (O-end, D_{cis-O}) structure by overcoming a small energy barrier of 3.6 kcal/mol, being exothermic by 8.6 kcal/mol. Finally, the D_{cis-O} structure decomposed into the product (N2O and Oads species) through TS2 by breaking the N1-O1 bond. In the TS2 structure, the N1-O1 distance significantly elongated from 1.469 to 1.659 Å, while the N1-N2 distance decreased from 1.240 to 1.207 Å. We note that there was a negligible energy barrier for this step (2.7 kcal/mol), which was exothermic by 24.8 kcal/mol. Since the entire reaction was a highly exothermic process (−50.7 kcal/mol, from IS to FS), it was thermodynamically feasible under mild conditions.

Figure 3. The energy profile and corresponding structure for the NO direct decomposition process on Al-C2N. All bond lengths are in Å.

3.3.2. (NO)2 Dimer Reduction Process

In this section, we examined the possible reaction pathways of the (NO)2 dimer reduction process on Al-C2N. There were four reaction pathways starting with different (NO)2 dimer structures described as path I, path II, path III, and path IV , respectively. For simplicity, the remaining oxygen atoms on the Al-C2N surface were labeled as Oads.

In path Ia, the five-membered ring (NO)2 dimer structure (D_{ring}) was the initial state. The energy profile and corresponding minima state and transition state are displayed in Figure 4a. As can be seen, the D_{ring} structure could be decomposed into the product (N2O + Oads) through the transition state with a high-energy barrier of 33.5 kcal/mol. In the TS structure, the N2-O2 bond broke with the bond length increasing from 1.398 to 2.364 Å, while the N1-N2 bond length decreased from 1.248 to 1.141 Å. The entire process from D_{ring} to the FS structure was endothermic by 23.2 kcal/mol. Given the high reaction barrier and endothermicity, it was expected that the D_{ring} dimer reduction on Al-C2N was unfavorable both kinetically and thermodynamically.

In path Ib, a two-step reaction was identified: (i) (NO)2 \rightarrow N2 + 2Oads, followed by (ii) CO + Oads \rightarrow CO2. As shown in Figure 4b, the D_{ring} structure was taken as the initial state and, subsequently, CO was physisorbed over Al-C2N to form an intermediate state (the MS1 structure). In the TS1 structure, two N-O bonds broke with the bond lengths increasing to 1.880 and 1.978 Å, respectively, while the N1-N2 bond length was shortened to 1.144 Å. Next, N2 was completely formed in the MS2 structure. In the next step, CO approached the O1 atom. The O1···C bond’s length reduced from 2.859 to 2.152 Å and, finally, formed the CO2 molecule. Note that the energy barriers of the first and second steps were 43.1 and 1.6 kcal/mol, respectively, which could be provided by the larger exothermic reaction energy (−67.7 kcal/mol, from D_{ring} to FS).

In path II, the reaction started with the co-adsorption of two NO molecules to generate a cis-(NO)2 dimer (N-end, D_{cis-N}) structure, as shown in Figure 5. As seen, this step had a negligible energy barrier and was exothermic by 17.3 kcal/mol. Then, the D_{cis-N} structure could be converted to the more stable cis-(NO)2 dimer (O-end, D_{cis-O}) structure by overcoming a small energy barrier of 3.6 kcal/mol, being exothermic by 8.6 kcal/mol. Finally, the D_{cis-O} structure decomposed into the product (N2O and Oads species) through TS2 by breaking the N1-O1 bond. In the TS2 structure, the N1-O1 distance significantly elongated from 1.469 to 1.659 Å, while the N1-N2 distance decreased from 1.240 to 1.207 Å. We note that there was a negligible energy barrier for this step (2.7 kcal/mol), which was exothermic by 24.8 kcal/mol. Since the entire reaction was a highly exothermic process (−50.7 kcal/mol, from IS to FS), it was thermodynamically feasible under mild conditions.
1.6 kcal/mol, respectively, which could be provided by the larger exothermic reaction energy (\( \Delta H \)).

### 3.3.2. (NO)\(_2\) Dimer Reduction Process

In this section, we examined the possible reaction pathways of the (NO)\(_2\) dimer reduction on the Al-C\(_2\)N surface. There were four reaction pathways starting with different (NO)\(_2\) dimer structures described as path I, path II, path III, and path IV, respectively. For simplicity, the remaining oxygen atoms on the Al-C\(_2\)N surface were labeled as O\(_{\text{ads}}\).

#### Path I

Path Ia: (NO)\(_2\) → N\(_2\)O + O\(_{\text{ads}}\)

Path Ib: (NO)\(_2\) + CO → N\(_2\) + CO\(_2\) + O\(_{\text{ads}}\)

#### Path II

Path II was energetically the most favorable pathway with the max energy barrier for the (NO)\(_2\) dimer reduction process on Al-C\(_2\)N. There were four reaction pathways starting with different (NO)\(_2\) dimer structures (Table 1). Path II was taken as the initial state (IS) and, subsequently, CO was physisorbed over Al-C\(_2\)N to form an intermediate state (the MS1 structure). In the TS1 structure, two N-O bonds broke with the bond lengths increasing from 1.398 to 1.451 Å, while the N1-N2 bond length decreased from 1.248 to 1.141 Å. The entire process from Dring (NO)\(_2\) to FS (N\(_2\)O + O\(_{\text{ads}}\)) was thermodynamically feasible under mild conditions.

#### Path III

For path III, the reaction started with the co-adsorption of two NO molecules to generate N\(_2\)O and O\(_{\text{ads}}\) moieties. This path revealed a high reaction energy (\( \Delta H \)) of 24.5 kcal/mol. Since the entire reaction was a highly exothermic process (\( \Delta H > 0 \)), it was thermodynamically feasible under mild conditions.

#### Path IV

In path Ib, a two-step reaction was identified: (i) (NO)\(_2\) → N\(_2\) + 2O\(_{\text{ads}}\), followed by (ii) (NO)\(_2\) + CO → N\(_2\) + CO\(_2\) + O\(_{\text{ads}}\). The energy profile and corresponding structures of the D\(_{\text{ring}}\) dimer reduction process on Al-C\(_2\)N are shown in Figure 4. As can be seen, the Dring structure could be decomposed into the product (N\(_2\)O + O\(_{\text{ads}}\)) through an extremely low-energy barrier (1.6 kcal/mol). Then, the N\(_2\)-O\(_2\) bond was significantly extended from 1.451 to 2.604 Å. Finally, the N\(_2\)-O\(_2\) bond was completely broken, forming N\(_2\)O and O\(_{\text{ads}}\) moieties. This path revealed a high reaction energy (\( \Delta H \)) of 34.6 kcal/mol, being exothermic by 8.6 kcal/mol.

#### Path V

In path V, the reaction started with the co-adsorption of two NO molecules to generate N\(_2\)O and O\(_{\text{ads}}\) moieties. This path revealed a high reaction energy (\( \Delta H \)) of 24.5 kcal/mol. Since the entire reaction was a highly exothermic process (\( \Delta H > 0 \)), it was thermodynamically feasible under mild conditions.

### Figure 4

The energy profile and corresponding structure of the D\(_{\text{ring}}\) dimer reduction process on Al-C\(_2\)N: (a) (NO)\(_2\) → N\(_2\)O + O\(_{\text{ads}}\) (path Ia), (b) (NO)\(_2\) + CO → N\(_2\) + CO\(_2\) + O\(_{\text{ads}}\) (path Ib). All bond lengths are in Å.

### Figure 5

The energy profiles and corresponding structures of the D\(_{\text{cis-N}}\) and D\(_{\text{cis-O}}\) dimer reduction process on Al-C\(_2\)N. All bond lengths are in Å.
In path III, the trans-(NO)$_2$ dimer structure (N-end, D$_{trans-N}$) was considered the starting point for the NO reduction on Al-C$_2$N. From Figure 6a, one could see that the NO molecule bonded with the Al site through the N-end, whereas another NO molecule was weakly physisorbed on the surface, with the distance between the N$_1$ and N$_2$ atoms being 2.445 Å. The co-adsorption energy of 2NO was $-35.6$ kcal/mol. Next, the D$_{trans-N}$ structure was formed through a barrierless process. In this structure, the calculated N$_1$-N$_2$ bond was shortened to 1.286 Å, while the N$_2$-O$_2$ bond was extended to 1.451 Å. In the TS structure, the N$_2$-O$_2$ bond was significantly extended from 1.451 to 2.604 Å. Finally, the N$_2$-O$_2$ bond was completely broken, forming N$_2$O and O$_{ads}$ moieties. This path revealed a high reaction barrier of 16.5 kcal/mol and was exothermic by 12.7 kcal/mol. Figure 6b exhibits path IV, starting from the trans-(NO)$_2$ dimer structure (O-end, D$_{trans-O}$). In this path, 2NO molecules formed the D$_{trans-O}$ structure through an extremely low-energy barrier (1.6 kcal/mol). Then, the N$_1$-O$_1$ bond length was significantly extended from 1.374 Å in the D$_{trans-O}$ structure to 1.696 Å in the TS2 structure. The energy barrier for this step was 12.7 kcal/mol, which could be provided by the exothermic reaction energy ($-24.5$ kcal/mol).

Figure 6. The energy profiles and corresponding structures of the (a) D$_{trans-N}$ and (b) D$_{trans-O}$ dimer reduction process on Al-C$_2$N. All bond lengths are in Å.

According to our results, it was found that the NO reduction preferred to proceed via the (NO)$_2$ dimer reduction process. First, the E$_{ads}$ values of the (NO)$_2$ dimers were much larger than that of the single NO molecule. Second, the (NO)$_2$ dimer reduction process
was thermodynamically and kinetically more favorable than the NO direct decomposition process. Based on the energy barriers ($E_r$) and reaction energies ($\Delta E_r$), the NO dimer reduction on the Al-C$_2$N surface could occur via path II and path IV (Table 1). Path II was energetically the most favorable pathway with the max energy barrier for the $(\text{NO})_2 \rightarrow \text{N}_2\text{O} + \text{O}_{\text{ads}}$ reaction of only 3.6 kcal/mol, which was even smaller than the values in noble metal catalysts, such as Pd-BNNS (14.9 kcal/mol) [58], Au (8.1 kcal/mol) [65], and Ag (6.2 kcal/mol) [66]. These results implied that the Al-C$_2$N catalyst exhibited good catalytic activity towards the NO reduction.

After the N$_2$O desorption, the remaining O$_{\text{ads}}$ atom could be removed with the NO or CO molecules. In our previous work, we revealed that Al-C$_2$N could serve as a promising catalyst for N$_2$O reduction to environmentally friendly N$_2$ molecules [67]. Figure 7 shows the reaction pathways of O$_{\text{ads}}$ + NO → NO$_2$ and O$_{\text{ads}}$ + CO → CO$_2$ on Al-C$_2$N, respectively. Our results showed that O$_{\text{ads}}$ + NO → NO$_2$ was an endothermic process (7.5 kcal/mol), and quite a high-energy barrier (15.5 kcal/mol) required to be surmounted. As seen in Figure 7b, the O$_{\text{ads}}$ + CO → CO$_2$ reaction was an exothermic process, and an energy barrier of only 6.6 kcal/mol was needed for Al-C$_2$N, which was smaller than the value for Pt-graphene (13.4 kcal/mol) [68]. This meant that CO$_2$ molecules were more likely to form on the Al-C$_2$N catalyst in the existence of NO molecules.

Figure 7. The energy profiles and corresponding structures for the step of (a) O$_{\text{ads}}$ + NO → NO$_2$ and (b) O$_{\text{ads}}$ + CO → CO$_2$ on Al-C$_2$N, respectively. All bond lengths are in Å.

4. Conclusions

In this work, we investigated the NO reduction over low-cost Al-C$_2$N catalysts using DFT calculations in detail. According to the adsorption energy and charge transfer values, the adsorption of NO on the catalyst was significantly stronger than that of CO, which suggested that the Al-C$_2$N catalyst was more selective to NO than CO. For the NO reduction mechanism, our results showed that the NO direct decomposition process was barely possible due to the extremely high-energy barrier and endothermicity. In contrast, the catalysis of the NO reduction via the $(\text{NO})_2$ dimer reduction process was both thermodynamically and kinetically favorable. It was found that cis-$(\text{NO})_2$ dimer structures were key intermediates for the NO reduction, where the calculated max barriers along the most energetically favorable pathway (path II) was only 3.6 kcal/mol. The remaining O$_{\text{ads}}$ species on Al-C$_2$N could be eliminated with CO molecules, which required overcoming the energy barriers of only 6.6 kcal/mol. Overall, Al-C$_2$N is expected to be a promising catalyst for NO reduction with CO.
**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27185790/s1. Figure S1: molecular dynamics simulation for Al-C$_2$N catalyst at (a) 300 K and (b) 500 K, respectively; Figure S2: IR spectra plots for five kinds of (NO)$_2$ dimers on the Al-C$_2$N surface.

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