



Article Catalytic Reduction of N₂O by CO on Single-Atom Catalysts Au/C₂N and Cu/C₂N: A First-Principles Study

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Abstract: The catalytic conversion of greenhouse gases, such as N₂O, is a promising way to mitigate global warming. In this work, density functional theory (DFT) studies were performed to study N₂O reduction by CO over single-atom catalysts (SACs) and compare the performance of noble (Au/C₂N) and non-noble (Cu/C₂N) SACs. The computational results indicated that catalytic N₂O reduction on both catalysts occurs via two mechanisms: (I) the N₂O adsorption mechanism—starting from the adsorption on the catalysts, N₂O decomposes to a N₂ molecule and O-M/C₂N intermediate, and then CO reacts with O atom on the O-M/C₂N intermediate to form CO₂; and (II) the CO adsorption mechanism—CO and N₂O are adsorbed on the catalyst successively, and then a synergistic reaction occurs to produce N₂ and CO₂ directly. The computational results show that mechanism I exhibits an obvious superiority over mechanism II for both catalysts due to the lower activation enthalpy. The activation enthalpies of the rate-determining step in mechanism I are 1.10 and 1.26 eV on Au/C₂N and Cu/C₂N, respectively. These results imply that Cu/C₂N, an abundant-earth SAC, can be as active as expensive Au/C₂N. Herein, our research provides a theoretical foundation for the catalytic reduction of N₂O and broadens the application of non-noble-metal SACs.

Keywords: single-atom catalyst (SAC); C2N monolayer; first principles; N2O reduction

1. Introduction

Nitrous oxide (N₂O) emission comes from microbial nitrification and the denitrification of solids and waters [1], biomass burning, fossil-fuel combustion through industrial processes, and selective catalytic reduction of NO_x [1,2]. Along with carbon dioxide, N₂O is one of the main contributors to the greenhouse effect. The accumulation of N₂O gas in the atmosphere is associated with ozone depletion, global warming, and acid rain [3–5]. Furthermore, N₂O has an atmospheric lifetime that is approximate 300-times longer than CO_2 [6]. Therefore, considerable efforts have been made to regulate N₂O emission and conversion to prevent and alleviate its environmental impact.

It is commonly known that the catalytic reduction of N₂O by carbon monoxide (CO) is one of the most promising methods to mitigate N₂O emissions [7–11]. Not only is CO inexpensive and easily accessible, but the use of CO, a toxic air pollutant, further limits harmful gas emission. Nevertheless, N₂O reduction by CO has a high activation temperature. Indeed, an experimental study carried out by Loirat et al. found that N₂O reduction by CO has an activation energy as high as 193 ± 8 kJ/mol (about 2.0 eV) between 1076 and 1228 K [12]; thus, the reaction needs efficient catalysts to lower the operating temperature. Precious-metal catalysts such as Au, Pt, and Pd have been extensively studied for N₂O reduction [13–17]. However, their high cost, scarcity, and high reaction temperatures limit their application on a larger scale. Consequently, a search for more affordable alternatives, with higher activity, has been the focus in recent years [18–25].



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). In 2011, Zhang et al. created a new class of catalysts called single-atom catalysts (SAC). The synthesized SAC platinum demonstrated excellent catalytic performance for CO oxidation [26]. Due to the excellent stability, high catalytic activity and remarkable atomic efficiency, SCAs have attracted considerable researcher attention in recent years [27–30]. Some SACs proved to be highly active for N₂O reduction [14,18,23,31–34]. Density functional theory (DFT) studies showed that Pt-doped graphene [14], an Fe-embedded graphene SAC [23], the boron nitride nanotube-supported Cr SAC [35] and single-atom Ge-embedded graphene are effective catalyst for N₂O reduction [36]. Furthermore, non-metal SACs, such as Sidoped graphene, also showed comparable catalytic activity to transition-metal-embedded graphene [18].

In 2017, Mahmood et al. synthesized a novel two-dimensional layered C_2N with high thermal and structural stability [37]. This C_2N monolayer proved to be a promising SAC support based on its uniformly distributed N₆ cavity, which is a suitable anchoring site for a single metal atom. Furthermore, many studies have shown that a single metal atom embedded in a C_2N monolayer exhibits excellent catalytic activity in many important reactions, such as CO oxidation, CO₂ reduction, N₂ reduction, oxygen reduction, and hydrogen evolution reactions as well [38–40]. In our previous work, we investigated the reduction of CO₂ to formic acid over Cu/C₂N SAC [41]. Our results suggested that Cu/C₂N can effectively catalyze CO₂ reduction with high selectivity at room temperature.

In the present work, we aim to explore the catalytic performance of Au/C_2N and Cu/C_2N for N_2O reduction using DFT. Additionally, the activity of noble and abundant earth metal SACs was evaluated and compared. Our results showed that both Au/C_2N and Cu/C_2N are highly active and exhibit comparable catalytic efficiency. Therefore, abundantearth-metal SACs proved to be promising catalysts for N_2O reduction. Our study provides theoretical information for the prospects of affordable metal SACs in catalytic reactions and broadens their field of application.

2. Results and Discussion

2.1. Geometric and Electronic Properties of Cu/C₂N and Au/C₂N

Studies have shown that Au and Cu atoms can be embedded in the N₆ cavity of the C₂N monolayer [42,43]. In our previous work, molecular dynamics simulation showed that Cu/C₂N has high thermal stability [41]. Therefore, stable M/C₂N can be formed and used as a catalyst. Due to differences in the atomic radius, the Au and Cu atoms anchor on the C₂N sheet differently, as shown in Figure 1. The Au atom preferably bonds in the center of the N6 cavity, with an average Au-N bond length of 2.752 Å in the case of the Cu atom, which has a smaller atomic radius than Au (1.28 vs. 1.79Å). In contrast, Cu most favorably bonds to two N atoms of the N6 cavity, with a bond length of 2.101 Å. The doping energies for Au/C₂N and Cu/C₂N are -3.88 eV and -4.19 eV, respectively.

To better understand the catalytic potential of both SACs, Mulliken charge analysis was performed. In Au/C₂N, we found that Au carries 0.548 e charge, while each six surrounding N atoms carry a charge of -0.250 e. In the Cu/C₂N case, the charge of Cu is 0.622 e, the Cu two closest N neighbors have a charge of -0.350 e each, while the other four N atoms have a lower charge density of -0.216 e each. The electron transfer between the metal atom and the C₂N sheet indicates metal–N bonding.

The calculated frontier molecular orbitals of Au/C_2N and Cu/C_2N show that the HOMOs are mainly formed by the *d* orbitals of the single metal (Figures S1 and S2). This suggests that the metal atoms can donate electrons to N₂O and, thus, activate the N₂O reduction reaction.



Figure 1. The optimized structures of the two catalysts: (a) Au/C_2N and (b) Cu/C_2N . (Blue, grey, yellow and orange balls represent N, C, Au, and Cu atoms, respectively). Number 1 and 2 in (b) represent the labels of the two N atoms.

2.2. Mechanism of Catalytic N₂O Reduction

Our MEP calculations show that N_2O reduction by CO can proceed via the two following mechanisms on Au/C_2N and Cu/C_2N :

Mechanism I:

 $N_2O + M/C_2N \rightarrow N_2 + O - M/C_2N \tag{1}$

$$CO + O - M/C_2 N \rightarrow CO_2 + M/C_2 N$$
⁽²⁾

Mechanism II:

$$CO + M/C_2N \rightarrow CO-M/C_2N$$
 (3)

$$N_2O + CO-M/C_2N \rightarrow N_2O-CO-M/C_2N \tag{4}$$

$$N_2O-CO-M/C_2N \rightarrow N_2 + CO_2 + M/C_2N$$
(5)

2.2.1. Mechanism I: N₂O Adsorption Mechanism Au/C₂N-Catalyzed N₂O Reduction

In mechanism I: a N₂O molecule is first adsorbed on the catalyst. Then, an O atom is abstracted by catalysts, leading to the release of a N₂ molecule. The O-M/C₂N intermediate then reacts with a CO molecule to produce CO₂ (Equations (1) and (2)). The structure diagram and energy profile of reaction mechanism I on Au/C₂N are shown in Figures 2 and 3. Table 1 lists the relative energies, enthalpies and free energies with zero-point vibrational correction for all the species in the N₂ reduction catalyzed by Au/C₂N and Cu/C₂N. The enthalpy values were used to discuss the energy changes in the reaction systems in the following discussion. The Mulliken charge analysis is shown in Table 2.

Mechanism I is initiated by the adsorption of N₂O on the Au/C₂N (IS1a). The adsorption enthalpy is -0.06 eV and the distance between the Au and O atoms is 3.010 Å. Compared with isolated systems, Au and O atoms are slightly charged while N₂O is nearly neutral in IS1a, which is consistent with no overlap between the wave functions of the O atom and Au atom near the Fermi level. The small adsorption enthalpy, long interacting distance, and slight charge transfer suggest that N₂O is only physisorbed on Au/C₂N. The FMOs in Figure 4 show no overlap between N₂O and Au/C₂N, further confirming the absence of a chemical bond between the O and Au atoms. As the O atom in N₂O approaches the Au atom, the N–O bond elongates from 1.198 Å to 1.604 Å, and the distance between Au and O shortens to 2.024 Å in TS1a, leading to an activation enthalpy of 1.10 eV. The negative charge of the O atom increases from -0.291 e to -0.466 e, and the positive charge of the Au atom rises from 0.551 e to 0.705 e. Thus, the catalyst donates electrons to

the N₂O molecule, which lengthens the N(a)-O bond (TS1a). The increased charge transfer from the Au to the O atom facilitates the formation of the O–Cu bond and the dissociation of the N–O bond, resulting in the formation of an O–Au/C₂N intermediate (MS1a). The frontier molecular orbitals (FMO) plots and FMO charge density plots in this step are shown in Figures 4 and S5. From the orbital analysis and PDOS in Figure 5b, there is not only an orbital overlap between N₂O and Au/C₂N but also a significant hybridization of the 4d orbital of Au and the 2p orbital of O(a) in TS1a. Both these results confirm the bonding between N₂O and Au in the catalyst. The IS1a \rightarrow TS1a \rightarrow MS1a step has the highest enthalpy barrier, making it the rate-determining step for mechanism I.



Figure 2. The schematic diagram of all species along the MEP for the N_2O reduction on the Au/C_2N monolayer via mechanism I. (Blue, grey, yellow and red balls represent N, C, Au and O atoms, respectively).



Figure 3. The energy profiles along the MEP for N₂O reduction via mechanism I. (R: $M/C_2N + N_2O + CO$, FS: $M/C_2N + N_2 + CO_2$).

		Au/C ₂ N			Cu/C ₂ N	
	ΔE^{corr}	ΔH^{corr}	ΔG^{corr}	ΔE^{corr}	ΔH^{corr}	ΔG^{corr}
R	0.00	0.00	0.00	0.00	0.00	0.00
IS1a	-0.05	-0.06	-0.09	-0.02	-0.01	-0.11
TS1a	0.90	1.04	0.74	1.07	1.25	0.80
MS1a	0.84	0.91	0.40	0.63	0.71	0.20
MS2a	0.98	1.07	0.47	0.81	0.89	0.34
MS3a	0.83	0.93	0.60	0.56	0.63	0.29
TS2a	1.13	1.21	0.95	0.99	1.04	0.83
MS4a	-3.69	-3.62	-3.97	-4.13	-4.15	-3.80
IS1b	-0.32	-0.28	-0.28	-0.90	-0.84	-0.92
MS1b	-0.43	-0.40	-0.14	-1.10	-1.05	-0.96
TS1b	1.87	1.90	2.08	0.72	0.75	0.86
MS2b	-3.48	-3.44	-3.30	-3.58	-3.49	-3.54
FS	-3.40	-3.34	-3.25	-3.40	-3.34	-3.25

Table 1. Relative energy (ΔE^{corr}), enthalpy (ΔH^{corr}) and free energy (ΔG^{corr}) with zero-point vibrational correction for all the species in the both reactions. (unit: eV).

Table 2. The Mulliken charge of species involved in Au/C_2N catalytic N_2O reduction mechanism I. N(a) represents the N atom bonding with O atoms, and N(b) represents the ending N atom in N_2O .

Atom/	Charges/e							
Molecule	Isolated Systems	IS1a	TS1a	MS1a	MS2a	MS3a	TS2a	MS4a
Au	0.548	0.551	0.705	0.734	0.739	0.736	0.708	0.561
$O(N_2O)$	-0.278	-0.291	-0.466	-0.478	-0.474	-0.474	-0.475	-0.275
N(a)	0.420	0.435	0.141	0.013				
N(b)	-0.143	-0.140	-0.112	-0.016				
N_2O	0	0.004	-0.437					
С	0.08					0.080	0.102	0.543
O(CO)	-0.08					-0.088	-0.164	-0.261
CO	0					-0.008		

IS1a

MS1a



TS1a

Figure 4. The frontier molecular orbitals (FMOs) for the rate-determining step IS1a \rightarrow TS1a \rightarrow MS1a in the N₂O reduction mechanism I on Au/C₂N. (The isovalue is setting is default, 0.03 a.u.).



Figure 5. The PDOS of relevant species in N_2O reduction mechanism I on Au/C_2N . (N(a) represents the N atom bonding with O atoms, and N(b) represents the ending N atom in N_2O . O(a) and O(b) are from N_2O and CO, respectively). (a) IS1a, (b) TS1a, (c) MS1a, (d) MS3a, (e) TS2a, (f) MS4a.

From TS1a to MS1a, the negative charge on the O atom changes from -0.466 e to -0.478 e, while the positive charge on the Au atom increases from 0.705 e to 0.734 e. The decrease in charge transfer between the N and O atoms leads to the dissociation of the N(a)–O bond and the release of N₂. It can also be proved by the disappearance of hybridizations between the N(a) 2p and O 2p orbitals in Figure 5c. Figure 4 shows that the orbital overlap between the O atom and Au in HOMO rises from IS1a to MS1a, indicating that there is an increase in electron transfer between the O and Au atom, resulting in a stronger interaction between N₂O and the catalyst. From the PDOS in Figure 5c, Au 4d orbital peaks change in position, and the O 2p orbital becomes sharper near the Fermi energy level. Such changes stem from hybridization between Au 4d and O 2p, demonstrating the strong Au–O interaction. This is also consistent with the above charge and orbital analysis. In MS1a, the Au–O bond length is 2.046 Å and the N–O bond length is 3.157 Å, indicating that a normal chemical bond is formed between the O atom and Au atom, while the N–O bond is broken. This results in the formation of the O-Au/C₂N (MS2a) intermediate and the release of a N₂ molecule from MS1a with a low desorption enthalpy of 0.14 eV.

In MS2a, the catalyst donates -0.478 e to an O atom, and the Au-O bond is 2.144 Å. Based on MS2a, CO is adsorbed to form intermediate MS3a with an adsorption enthalpy of -0.18 eV. Due to the high negative charge of adsorbed O in MS2a, it can easily react with CO. In MS3a, the charge of the CO molecule then changes from electroneutrality to -0.008 e, and the positive charge of the Au atom decreases slightly from 0.739 e to 0.736 e. Small adsorption enthalpy and slight charge transfer are consistent with the weak overlap between O(a) 2p and C 2p orbitals in Figure 5d. Next, the O atom bonded to Au is abstracted by the CO molecule, and adsorbed CO₂ is produced via the transition state TS2a, by overcoming a low enthalpy barrier of 0.28 eV. Finally, CO₂ gas is released with a small desorption enthalpy of 0.28 eV. The dissociation of the Au–O bond and formation of C–O(a) bond from TS2a to MS4a can be found by the PDOS plots in Figure 5e, f. The highest activation enthalpy (TS1a) is 1.10 eV and the overall reaction in mechanism I is exothermic, releasing 3.34 eV of heat.

Cu/C₂N-Catalyzed N₂O Reduction

Although the two metal atoms are doped on different sites, mechanism I is the most favorable path for N_2O reduction on both catalysts. The structure diagram of reaction mechanism I on the Cu/C_2N catalyst is shown in Figure S3. The FMO, FMO charge density and PDOS of relevant species in the reaction are shown in Figures 6, S6 and 7. Firstly, N_2O molecule is weakly physisorbed on Cu/C_2N (IS1a) with an adsorption enthalpy of -0.01 eV. From Table 3, the positive charge of the Cu atom increases from 0.622 e to 0.639 e, and the negative charge of the O atom increases from -0.278 e to -0.306 e. This means that the charge of N_2O increases by 0.023 e, indicating more charge transfer between N_2O and Cu/C_2N than that between N₂O and Au/C₂N (0.004 e). Different from Figure 5a, Figure 7a shows observable overlaps of the O 2p and Cu 4d orbitals. The difference in interaction strength between N₂O and the two catalysts can be found from the adsorption enthalpy, charge transfer and PDOS. As N₂O gradually approaches the Cu atom, the N-O bond stretches from 1.205 A to 1.678 A, while the Cu–O atom bond distance shortens to 1.792 Å. The process has an activation enthalpy of 1.26 eV (TS1a) which is slightly higher than TS1a over Au/C₂N. The negative charge of the O atom increases from -0.306 e to -0.515 e, and the positive charge of the Cu atom increases from 0.508 e to 0.585 e. The charge transfer from the Cu atom to the O atom leads to Cu–O bond formation and N–O bond cleavage. The PDOS analysis in Figure 7b also shows the overlaps of O 2p and Cu 3d at a lower energy and weaker hybridization peak between O and N(a) than that in Figure 5b, which implies the formation of Au–O chemical binding and the dissociation of the N–O bond and TS1a on the Cu/C_2N catalyst is more like a product and may need a higher activation enthalpy.



Figure 6. The frontier molecular orbitals (FMOs) for rate-determining step IS1a \rightarrow TS1a \rightarrow MS1a in N₂O reduction mechanism I on Cu/C₂N. (The isovalue was set as default value, 0.03 a.u.).



Figure 7. The PDOS of relevant species in N₂O reduction mechanism I on Cu/C₂N. (N(a) represents the N atom bonding with O atoms, and N(b) represents the ending N atom in N₂O. O(a) and O(b) are from N₂O and CO, respectively). (a) IS1a, (b) TS1a, (c) MS1a, (d) MS3a, (e) TS2a, (f) MS4a.

This oxygen abstraction leads to the intermediate MS1a where the charges on the O atom and Cu atom are slightly increased compared with TS1a. The Cu–O bond length is 1.749 Å, and there is an evident orbital overlap between the O atom and Cu, and disappearance of the overlap of O and N orbitals (Figure 7c), showing O–Cu bond formation and C–O bond dissociation. The weak N–O bond results in facile N₂ desorption (0.26 eV), and the formation of intermediate O-Cu/N2C (MS2a).

In MS3a, CO is adsorbed on the catalyst along with MS2a. CO adsorption has a weak adsorption enthalpy of -0.26 eV. The adsorption is evidenced by a new C–O bond formation and Cu–O bond cleavage. This step results in the formation of adsorbed CO₂ on

 Cu/C_2N (MS4a) with an enthalpy barrier of 0.41 eV (TS2a). Finally, CO_2 gas is released with a desorption enthalpy of 0.61 eV.

Table 3. The Mulliken charge of species involved in Cu/C_2N catalytic reduction of N_2O reaction mechanism I. (Note that N(a) represents the N atom bonding with N and O atoms, and N(b) represents the ending N atom).

Atom/ Molecule	Charges of the Systems/e							
	Isolated Systems	IS1a	TS1a	MS1a	MS2a	MS3a	TS2a	MS4a
Cu	0.622	0.639	0.785	0.809	0.807	0.806	0.725	0.685
$O(N_2O)$	-0.278	-0.306	-0.515	-0.530	-0.526	-0.527	-0.504	-0.265
N(a)	0.420	0.449	0.148	0.006				
N(b)	-0.143	-0.120	-0.095	-0.006				
N ₂ O	0	0.023	-0.462					
С	0.08					0.080	0.156	0.538
O(CO)	-0.08					-0.086	-0.123	-0.237
CO	0					0.006		

2.2.2. Mechanism II: CO Adsorption Mechanism

In mechanism II, CO and N_2O molecules are adsorbed on the catalysts, and react through a synergistic step as shown in Equations (3)–(5).

Au/C₂N-Catalyzed N₂O Reduction

The schematic diagram and energy profile of mechanism II are shown in Figures 8 and 9. Here, CO first adsorbs onto Au/C₂N with an adsorption enthalpy of -0.28 eV (IS1b). The C-Au atom distance is as long as 2.426 Å and is accompanied by a small charge transfer of 0.046 e from CO to the catalyst. Then, the N₂O molecule also adsorbs on the catalyst, resulting in a co-adsorption state (MS1b), with an adsorption enthalpy of -0.40 eV. In MS1b, the Au–C bond length is 2.419 Å, and the distance between C and O atoms in N₂O is 3.335 Å. A negligible charge transfer is also found between the reactants and the catalyst. On the geometry analysis, adsorption enthalpy, and charge transfer, the interaction between reactants and catalyst is weak in both IS1b and MS1b.



path II

Figure 8. The schematic diagram of all species along the MEP for the N_2O reduction on the Au/C_2N monolayer via mechanism II. (Blue, grey, yellow and red balls represent N, C, Au and O atoms, respectively.)



Figure 9. Energy profiles along the MEP for the N₂O reduction via mechanism II. (R: $M/C_2N + N_2O + CO$, FS: $M/C_2N + N_2 + CO_2$.)

As both N₂O and CO are in proximity to each other, they can react. The N–O bond in N₂O extends from 1.198 Å to 2.113 Å and the distance between the C in the CO and O atom in N₂O is 2.023 Å in TS1b. This is considered a loose transition state, initiating the oxygen abstraction of N₂O by CO. This step has an activation enthalpy of 2.30 eV, leading to the formation of N₂ and CO₂, which are subsequently released with a small desorption enthalpy of 0.10 eV.

Cu/C₂N-Catalyzed N₂O Reduction

Similar to the initial step on Au/C₂N (Figures S4 and 8), the CO molecule is adsorbed first on Cu/C₂N (IS1b). The adsorption enthalpy (-0.84 eV) is, in contrast, more exothermic than on Au/C₂N (-0.28 eV). In IS1b, the length of the Cu–C bond is 1.834 Å and the charge transfer from CO to the catalyst is much higher (0.053 e). Then, as the N₂O molecule is physisorbed, a co-adsorption state (MS1b) is formed, and the total adsorption enthalpy is -1.05 eV. The adsorption energy mainly originates from the interaction between CO and the catalyst, since the charge transfer between N₂O and Cu/C₂N is negligible. Subsequently, the N–O bond extends from 1.199 Å to 1.592 Å in TS1b. As the O atom in N₂O approaches the C atom of CO, a stable state is reached with a N₂O–CO distance of 2.042 Å. For both reactants to react, an enthalpy barrier of 1.80 eV has to be overcome to form TS1b, a more reactant-like TS. Although significant, this activation enthalpy is lower than on Au/C₂N (2.30 eV), where the TS is more product-like. Then, the N–O bond in N₂O is broken and the O atom is abstracted by C in CO to form adsorbed CO₂ in MS2b with a newly formed C–O bond length of 1.205 Å. Finally, N₂ and CO₂ are released with a desorption enthalpy of 0.15 eV, and the catalyst is regenerated and available for a new reaction cycle.

In summary, the homology of Au and Cu elements results in a similar N₂O + CO reaction mechanism. By comparing the highest activation enthalpy of the two reaction mechanisms, we found that mechanism I is the most favorable route on both Au/C₂N and Cu/C₂N for N₂ reduction. In mechanism I, N₂O activation is the rate-determining step, i.e., IS1a \rightarrow TS1a \rightarrow MS1a. The calculated activation enthalpy are 1.10 eV and 1.26 eV on Au/C₂N and Cu/C₂N, respectively, which demonstrates that non-precious-metal SAC can exhibit a high catalytic activity comparable to a noble-metal SAC. It is worth noting that the calculated activation enthalpies are much lower than experimental values without any catalyst (about 2.0 eV) [12].

3. Computational Methods

All calculations, from the geometric optimizations to electronic properties, were performed in DMol³ package [44] using the spin-polarized Perdew-Burke-Ernzerhof (PBE)

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functional [45]. The double numerical basis set with polarization function (DNP) and the DFT semi-core pseudopotentials (DSPPs) were employed [46]. As the generalized gradient approximation (GGA) method is insufficient in describing weak interaction, dispersion correction was added to the system [47]. Transition state (TS) correction was also employed to evaluate dispersion interactions [48]. The global orbital cutoff was set to fine quality: 4.5 Å and 4.4 Å for Au and Cu, respectively. The sampling of the Brillouin zone integration was carried out with $3 \times 3 \times 1$ k-points for the C₂N monolayer [49]. To avoid C₂N monolayer interaction with its periodic image, the cell length along the z-direction was set to 15Å. For all optimization calculations, the cutoff energy and force were set to 1.0×10^{-5} Ha and 2.0×10^{-3} Ha/Å, respectively, and the SCF convergence was set to 1.0×10^{-6} . Au-and Cu- embedded C₂N monolayers were modeled with a C₂N (2 × 2) supercell. To study the minimum-energy pathway (MEP) for N₂O reduction, the linear synchronous transit (LST), and quadratic synchronous transit (QST) methods were used for transition state (TS) search [50,51]. The vibrational frequencies for each obtained structure along the MEP were calculated to ensure that every TS had a single imaginary frequency.

The adsorption enthalpy (H_{ads}) was defined as follows:

$$H_{ads} = H_{total} - (H_{M/C2N} + H_{adsorbate})$$

where H_{total} , $H_{M/C2N}$, and $H_{adsorbate}$ represent the enthalpies of the gas molecules adsorbed on the catalyst, M/C_2N , and gas molecules, respectively. The more negative the E_{ads} value, the higher the stability of the gas molecules on the catalyst.

The activation enthalpy (H_a), i.e., enthalpy barrier, which is one of the most important factors to evaluate the catalytic activity, was defined as follows:

$$H_a = H_{TS} - H_{IM1}$$

where H_{TS} and H_{IM1} represent the enthalpies of the transition state and intermediate IM1 in the reaction step of IM1 \rightarrow TS \rightarrow IM2.

4. Conclusions

Herein, the catalytic reduction of N₂O by CO on the SACs Au/C₂N and Cu/C₂N was investigated using DFT. The reaction can proceed through two mechanisms: Mechanism I starts with the N₂O adsorption on the catalyst, followed by its decomposition into N₂ gas and O-M/C₂N intermediate. The adsorbed oxygen species then reacts with CO to produce CO₂. The highest activation enthalpy on Au/C₂N and Cu/C₂N are 1.10 eV and 1.26 eV, respectively. In mechanism II, both CO and N₂O are co-adsorbed on the catalyst, and in a one-step synergistic reaction, they react to produce N₂ and CO₂ gas. The activation enthalpies on Au/C₂N and Cu/C₂N and Cu/C₂N are 1.80 eV and 2.30 eV, respectively. Our results show that mechanism I is noticeably more favorable on both catalysts, rendering it the dominant path. Based on these results, abundant-earth-metal SACs can demonstrate catalytic efficiency comparable to that of a noble-metal SAC for N₂O reduction. Our work provides a theoretical basis for the catalytic reduction of N₂O and broadens the application of non-noble-metal single-atom catalysts.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/catal13030578/s1, Figure S1: The schematic diagram of frontier molecular orbitals for catalyst Au/C₂N; Figure S2: The schematic diagram of frontier molecular orbitals for catalyst Cu/C₂N; Figure S3: The schematic diagram of all species along the MEP for the N₂O reduction on the Cu/C₂N monolayer via mechanism I; Figure S4: The frontier molecular orbitals (FMOs) for rate-determining step IS1a \rightarrow TS1a \rightarrow MS1a in N₂O reduction mechanism I on Cu/C₂N; Figure S5: The HOMO and LUMO charge-density plots for IS1a, TS1a and MS1a on Au/C₂N; Figure S6: The HOMO and LUMO charge-density plots for IS1a, TS1a and MS1a on Cu/C₂N; Table S1: The Mulliken charge of species involved in N₂O reduction mechanism II. Author Contributions: Conceptualization, H.S.; methodology, S.S.; formal analysis, S.S., J.M., Z.L. and H.S.; investigation, S.S. and J.M.; writing—original draft preparation, J.M. and S.S.; writing—review and editing, D.H., Z.L. and H.S.; supervision, H.S. All authors have read and agreed to the published version of the manuscript.

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