Theoretical Calculation of Different Reaction Mechanisms for CO Oxidation on MnN₃-Doped Graphene

Mingming Luo, Zhao Liang, Chao Liu, Meiling Liu, Xiaopeng Qi, Mingwei Chen, Hui Yang, and Tongxiang Liang*

ABSTRACT: In recent decades, great expectation has always been placed on catalysts that can convert toxic CO into CO₂ under mild conditions. The catalytic mechanism of CO oxidation by Mn-coordinated N-doped graphene with a single vacancy (MnN₃-SV) and a double vacancy (MnN₃-DV) was studied by density functional theory (DFT) calculations. Molecular dynamics simulations showed that CO₂ on MnN₃-SV could not be desorbed from the substrate and MnN₃-SV was not suitable for use as a CO oxidation catalyst. MnN₃-DV was more suitable for CO oxidation (COOR) and from the electronic structure it was found that the Mn atom was the main active site, which was the reaction site for CO oxidation. At temperatures of 0 and 298.15 K, CO oxidation on MnN₃-DV via the Langmuir–Hinshelwood (LH) mechanism was the best reaction pathway. The rate-determining step using MnN₃-DV as the catalyst for CO oxidation through the LH mechanism was O₂ + CO → O₂CO₂, and the energy barrier was 0.861 eV at 298.15 K. MnN₃-DV was suitable as a catalyst for CO oxidation in terms of both thermodynamics and kinetics. This study provides a comprehensive understanding of the various reaction mechanisms of CO oxidation on MnN₃-DV, which is conducive to guiding the development and design of efficient catalysts for CO oxidation.

1. INTRODUCTION

Carbon monoxide (CO) is the most abundant pollutant with the most content and the most widespread gas in the atmosphere, which is mainly the product of incomplete combustion of carbonaceous materials such as coal and petroleum, and CO oxidation has been extensively studied.¹,² The stable combination of CO and hemoglobin can easily cause permanent health damage or even death.³,⁴ Moreover, CO is also closely related to environmental pollution, and the removal of CO is a valuable study and an urgent problem to be solved.³ CO oxidation is one of the most effective methods for conversion or removal of CO and has great industrial application value. For example, pollution control devices for industrial and automotive emissions,⁶ solving the problem of fuel cell poisoning,⁷ CO gas sensors, air purification equipment, etc. have an important role.⁸,⁹ Among them, using low-cost and easily available O₂ to oxidize CO is one of the most effective methods, and various precious metals¹⁰,¹¹ have been frequently used as catalysts for CO oxidation and have shown good catalytic performance. Although noble metal catalysts have higher catalytic activity and selectivity than ordinary metal catalysts, their high price and scarcity limit their large-scale applications. Therefore, considerable attention has been paid to replacing these catalysts with low-cost alternatives.

Single-atom catalysts (SACs) maximize the use of metals and reduce manufacturing costs, which has become a breakthrough in the study of high-efficiency catalysts.¹² In 2011, Zhang et al.¹³ successfully prepared a single-atom catalyst Pt₁/FeOₓ, which showed high catalytic activity and stability in the CO oxidation reaction. Afterward, reports on the catalytic oxidation of CO by single-atom catalysts were endless.¹⁴ However, when the metal atoms are reduced to the atom level, the surface free energy increases sharply, which easily leads to agglomeration of atoms into clusters and catalyst deactivation during preparation and reaction. Therefore, single-atom supports are crucial for catalytic performance.

Graphene is an ideal substrate due to its high stability and excellent electronic performance.¹⁵ The electronegativity difference between dopant atoms and carbon atoms causes charge transfer between atoms, breaking the neutrality and chemical inertness of graphene, which is beneficial to activate O₂ and promote CO oxidation. Graphene doped with single transition metal atoms Fe,¹⁹ Co,²⁰ and Ni¹⁹,²¹ and other¹⁴,²⁴–²⁶ doped graphene show excellent catalytic performance and low activation energy for CO oxidation. CO oxidation on Mn-doped single vacancy graphene (SV-Gra)¹⁵ [double-vacancy graphene (DV-Gra)]¹⁹ was found to have an energy barrier of...
0.55 eV (0.41 eV), and MnN₄ porphyrin-like carbon nanotubes had an energy barrier for the rate-limiting step of merely 0.69 eV for CO oxidation. The synergistic effect of Mn and N can effectively adjust the catalyst activity for the oxygen reduction reaction.38,39 We speculate that Mn and N atoms that are embedded in graphene may have excellent catalytic activity for CO oxidation.40 Although there have been many previous studies on the mechanism of catalytic CO oxidation, few mechanisms have been fully considered; especially, there is lack of research on the reaction routes of termolecular Eley−Rideal (TER) and new Eley−Rideal (NER) mechanisms.

In this work, we comprehensively study the possible reaction mechanism of CO oxidation on MnN₃-embedded graphene (MnN₃-Gra: MnN₃-SV, MnN₃-DV) through first-principles calculations, which has not been reported previously to our knowledge.

2. RESULTS AND DISCUSSION

2.1. Stability and Active Sites of MnN₃-Gra Theoretical Models. Single-atom Mn has a high surface free energy, which may be agglomerated in graphene and may cause catalyst deactivation. The stability of Mn on graphene is evaluated by the binding energy; the binding energy of Mn on MnN₃-SV and MnN₃-DV was −4.352 and −7.414 eV, respectively, which were significantly smaller than the cohesive energy of bulk Mn (−4.12 eV).41 To study the interaction between Mn and the surrounding atoms, we analyzed the partial density of states (PDOS) of MnN₃-SV and MnN₃-DV (Figure 1). We found that there is an obvious hybridization between the d orbitals of Mn atom and the p orbitals of C or N atoms and significant charge transfer between atoms, which is consistent with the electron density environment shown by the deformation density of MnN₃-SV and MnN₃-DV (Figure 2a1,b1). The consumption and accumulation of electron density are expressed in yellow and blue; the obvious charge transfer of Mn atoms and the surrounding atoms will make Mn atoms stable in the vacancy. The value of the Fermi level of MnN₃-SV is higher than that of MnN₃-DV, which shows that MnN₃-SV may show higher catalytic activity. To ensure the integrity of the graphene structure, the maximum temperature of our dynamics simulation is set to 1000 K.42 We considered the structure and energy changes of MnN₃-SV (Figure S1) and MnN₃-DV (Figure S2) over time at different temperatures (300, 500, 800, and 1000 K) when performing kinetic simulations. During the kinetic simulation process at different temperatures, the energy of MnN₃-Gra fluctuates around a fixed value in a small range, and there is no new bond generation and old bond destruction in MnN₃-Gra, which shows that MnN₃-Gra has high temperature stability.

For subsequent gas adsorption, the active region of MnN₃-Gra needs to be determined first. According to previous studies,43 the catalytic activity of MnN₃-Gra mainly comes from the synergy of doping atoms (Mn and N atoms). Moreover, the highest occupied molecular orbital (HOMO) of MnN₃-Gra indicates that Mn and the surrounding atoms are the main electron-donating regions, which will be the main sites to react with gases (Figure 2a2,b2). The Fukui function of MnN₃-Gra shows that the electrophilic and nucleophilic regions are dominated by Mn atoms and the surrounding three N atoms (Figure 2a3,a4,b3,b4). In summary, Mn and the surrounding coordination atoms will become the adsorption sites of the gas.
2.2. Adsorption Properties of MnN3-SV and MnN3-DV.

We examined many adsorption sites and considered different directions of gas molecules to determine the most favorable gas adsorption structure (Figure S3). Table 1 presents the adsorption energies and key structural parameters of CO and O2 on MnN3-Gra. CO is most stable when adsorbed on MnN3-Gra with an end-on configuration and the C−O bond lengths of the adsorbed CO (1.165 Å on MnN3-SV and 1.169 Å on MnN3-DV) will be slightly elongated compared to those of isolated CO (1.14 Å); electrons are transferred from CO to the substrate MnN3-Gra, and CO is adsorbed on MnN3-SV and MnN3-DV with positive charges of 0.065 and 0.222, respectively. From the total density and deformation density (Figure S4), it is more intuitive to see the overlap of electrons of CO and the substrate, indicating that CO is effectively activated. O2 is adsorbed onto MnN3-Gra in a side-on configuration (O2 is parallel to the MnN3-Gra plane and forms a triangle with the Mn atom) and obtains electrons from the substrate (O2 obtains 0.519 and 0.400 electrons from MnN3-SV and MnN3-DV, respectively) due to increased hybridization of the p orbital of O2 and the d orbital of Mn, which results in a stronger combination of O2 and MnN3-Gra (Figure 3). O2 can occupy the active site in advance, indicating that CO oxidation on MnN3-Gra can react via the Eley−Rideal (ER) mechanism.

The adsorption energy of CO oxidation product (CO2) on MnN3-SV and MnN3-DV is −0.992 and −0.256 eV, respectively. The adsorption energy of CO2 on MnN3-SV is less than −0.52 eV, which can prevent the catalyst from being poisoned at room temperature.45 CO2 is physically adsorbed on MnN3-DV, and the distance to the substrate is 2.895 Å, indicating that CO2 can spontaneously detach from the catalyst, and MnN3-DV starts a new COOR. Kinetic simulations of the CO2 adsorption process at room temperature (Figure 4) and other temperatures (Figure S5) showed that the adsorbed CO2 is difficult to detach from the catalyst, resulting in the occupation of active sites and the inability to perform a new COOR cycle. Therefore, MnN3-SV is not suitable as a COOR catalyst.

Table 1. CO and O2 Adsorption Energies ($E_{\text{ads}}$, eV) on MnN3-SV and MnN3-DV, Their Corresponding Bond Lengths [d(C−O/O−O), Å] as well as the Mulliken Charge ($q$, e)

|          | $E_{\text{ads}}$ (eV) | d(C−O/O−O) (Å) | $q$(Mn)  | $q$(3N) | $q$(CO/O2) |
|----------|------------------------|-----------------|----------|---------|------------|
| CO/MnN3-SV | −1.912                 | 1.165           | 0.205    | −1.388  | 0.065      |
| CO/MnN3-DV | −1.460                 | 1.169           | −0.229   | −1.372  | 0.222      |
| O2/MnN3-SV | −3.182                 | 1.431           | 0.554    | −1.319  | −0.519     |
| O2/MnN3-DV | −1.758                 | 1.397           | 0.211    | −1.293  | −0.400     |

Figure 3. PDOS of CO adsorption on MnN3-SV (a) and MnN3-DV (c) and O2 adsorption on MnN3-SV (b) and MnN3-DV (d).
We also considered the situation of bimolecular co-adsorption, including O2 and CO co-adsorption (O2 + CO) and two CO co-adsorption (2CO). The adsorption energies of O2 + CO and 2CO on MnN3-DV are $-2.135$ and $-2.323$ eV, which is more favorable than the adsorption of single O2. Therefore, the LH and TER reaction mechanism corresponding to bimolecular co-adsorption should also be considered.

2.3. Reaction Mechanism of CO Oxidation on MnN3-DV.

We comprehensively considered the four oxidation mechanisms of CO catalyzed by MnN3-DV (Figure 5). There are two ways to combine pre-adsorbed O2 and isolated CO: CO bonds with two O atoms to form a silicate-like structure (CO3) or bonds with one O atom to form CO2, and these two reaction mechanisms are named ER1 and ER2, respectively. Both CO and O2 combine with Mn atoms to form a co-adsorption structure (corresponding to the LH mechanism), and O2 and CO close to each other form the intermediate OOCO, which has been proved to exist by experiments.46 The above two reaction mechanisms are widely studied, and the emerging NER and TER reaction mechanisms are rarely discussed. Lu et al. found that single Ir atom-embedded graphdiyne can catalyze CO oxidation more efficiently through the NER mechanism with the activation energy of 0.317 eV and an exothermic reaction energy of 3.502 eV to form CO3, which is accompanied by bond breakage and bond formation processes (Figure 7). The intermediate CO3 structure is relatively stable and is difficult to decompose into O and CO2, and the decomposition reaction of CO3 requires a high energy barrier (1.162 eV) and a small exothermic reaction energy (0.026 eV). The energy barrier (1.162 eV) of the rate-limiting step for CO oxidation on MnN3-DV through the ER1 mechanism is comparable to the energy barrier (1.129 eV) for O2 direct decomposition, indicating that the reaction of CO and O2 via the ER1 mechanism is not favorable.

Isolated CO may directly bond with an O atom of O2 to form CO2 (Figure 8). During the reaction between CO and O2, the bond length of CO is stretched from 1.141 to 1.170 Å, and the O atom forms a bond with C of CO, which needs to overcome the reaction energy barrier of 1.164 eV. The resulting CO2 is far away from the O atoms and the catalyst surface, which indicates that CO2 can spontaneously escape the bondage of the catalyst.

The isolated CO overcomes the activation energy of 0.636 eV to form a co-adsorption configuration with pre-adsorbed O2 (Figure 9). The formation of intermediate state OOCO needs an activation energy of 0.925 eV and an endothermic reaction energy of 0.173 eV, and the mutual repulsion of O2 and CO molecules causes difficulty in forming OOCO. The bond of 1.129 eV to decompose the O—O bond, which shows that the O2 structure is stable and the decomposition reaction of O2 is unfavorable (Figure 6). The adsorption energy of the two O is $-7.681$ eV, which causes the Mn atom to protrude upward and break the bond with the surrounding two N atoms.
length of O–O and Mn–C in OOCO is 1.507 and 2.030 Å, respectively, which shows that the decomposition of O–O and the fracture of Mn–C may be easily achieved. OOCO overcomes the activation energy of 0.105 eV to decompose into O and CO₂ with a large exothermic reaction energy (−3.518 eV). The distance between the physically adsorbed CO₂ and the O atom (or the substrate) is 2.935 Å (or 3.097 Å), indicating that CO₂ can spontaneously desorb from the substrate. The remaining O atoms and isolated CO cross a reaction energy barrier of only 0.008 eV to form a second CO₂ with an adsorption energy of −0.256 eV, and the catalyst can be refreshed to prepare for the next COOR cycle.

O₂ may also react with two CO, and the configuration of the two physically adsorbed CO suspended above the pre-adsorbed O₂ molecule was selected as the initial state (Figure 10). As the distance between CO and O₂ gradually decreases, the bond length of oxygen is extended from 1.399 Å to the break distance of 2.506 Å, and two CO and two O atoms form a five-membered ring. The energy barrier and exothermic reaction energy accompanying the bonding process of CO and O₂ are 1.124 and 4.088 eV, respectively. The intermediate product OOCOCO overcomes a reaction energy barrier of 0.779 eV, which breaks the C–C bond and stretches two Mn–O bonds. The final two CO₂ can be directly separated from the substrate, and the catalyst can proceed to the next catalytic process.

The adsorption energy of two CO is −2.323 eV less than the adsorption energy of O₂ (−1.758 eV), indicating that 2CO adsorption on MnN₃-DV is beneficial (Figure 11). The physical adsorption of O₂ gradually close to CO will make its bond length become longer, and O₂ and two CO overcome the reaction energy barrier of 0.962 eV to form an intermediate product (OCOOOCO) containing a five-membered ring. The O–O bond length is 1.485 Å and the Mn–C bond length is greater than 2 Å in OOCOCO, which can be preliminarily judged that OOCOCO is easily decomposed into two CO₂. OCOOCO can easily break down into two free CO₂ only by overcoming the energy barrier of 0.258 eV and release reaction energy of 4.526 eV. Both CO₂ are at a distance of greater than 3 Å from the substrate and the sum of adsorption energies is −0.456 eV, indicating that the catalyst can be refreshed.

In summary, the oxidation mechanism of CO catalyzed on MnN₃-DV was comprehensively considered. The CO oxidation reaction via the LH mechanism is the best reaction path, which has the lowest reaction energy barrier for the rate-determining step (0.925 eV). We considered the influence of temperature on the energy barrier (includes zero-point vibration correction) and calculated the energy barrier of the rate determination step of various reaction mechanisms at room temperature (Table 2). Most energy barriers are lower at room temperature than at 0 K, and CO oxidation on MnN₃-DV via the LH mechanism is the best reaction pathway at room temperature.

3. CONCLUSIONS

In summary, we explored single-layer graphene-immobilized MnN₃ as a catalyst for CO oxidation by DFT calculations.
Both MnN₃-SV and MnN₃-DV exhibited good thermodynamic stability by molecular dynamics simulations and binding energy calculations. Electronic performance analysis shows that the Mn atom in MnN₃-Gra is the main activator and the site for the CO oxidation reaction. CO₂ can be stably adsorbed on MnN₃-SV, and desorption does not occur under molecular dynamics simulations at different temperatures (300, 500, 800, and 1000 K) molecular dynamics simulation, indicating that MnN₃-SV can only be used as a one-time CO oxidation catalyst but not as a recycling catalyst. Physically adsorbed CO₂ can spontaneously desorb on MnN₃-DV, which is more suitable as a catalyst for CO oxidation. The four possible oxidation mechanisms of CO catalyzed by MnN₃-DV are discussed, which shows that CO oxidation on MnN₃-DV prefers the traditional LH mechanism rather than other catalytic mechanisms and the energy barrier of this reaction mechanism was as low as 0.861 eV at room temperature. This article comprehensively considers the four reaction mechanisms of CO oxidation on MnN₃-DV, which will provide theoretical guidance for future CO oxidation mechanism research. The calculated results may provide valuable guidance for the development or design of low-cost and high-efficiency catalysts for low-temperature CO oxidation.

### 4. COMPUTATIONAL METHODOLOGIES

All spin-polarized calculation results were obtained through the Dmol³ code. The exchange-correlation functional employed was the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional. The Grimme custom method was used for DFT-D, which was suitable for describing the van der Waals interaction between the reactant and the substrate. We selected the DFT semi-core pseudopotential that was useful for calculating materials containing transition metal atoms. Sampling was done with a k-point grid (5 × 5 × 1) using the Monkhorst–Pack method. For the geometric optimization process, the convergence tolerances for energy, maximum force, and displacement were set to 1 × 10⁻⁵ Ha, 0.002 Ha/Å, and 0.005 Å, respectively. All transition-state structures were determined by the unique virtual frequency and the vibration direction of the virtual frequency. The ensemble of constant-temperature molecular dynamics simulations was set to NVT, where N, V, and T represent the number of particles, volume, and temperature, respectively.

A single layer of periodic 4 × 4 graphene with lattice parameters a = 8.522 and b = 9.840 Å was constructed. The vertical vacuum layer was of 20 Å, which made the interaction between layers negligible. We deleted atoms in the pure graphene model with periodic boundary conditions to create vacancies, where three undercoordinated carbons were replaced by N atoms (SV/DV-Gra), and the Mn atom bound by the undercoordinated atoms protruded from the surface after structural optimization. The final target structure of MnN₃-Gra is shown in Figure 1.

The binding energy (E_b) can be used to characterize the stability of doped atoms in vacancies. The larger the binding energy, the stronger the bond between the doped atoms and surrounding atoms. Adsorption energy (E_ads) can be used to evaluate the binding strength of the substrate to the gas, and proper adsorption is essential for subsequent reactions. E_b and E_ads are defined as follows:

\[
E_b = E_{\text{MnN}₃-\text{Gra}} - E_{\text{SV/DV-\text{Gra}}} - E_{\text{Mn}}
\]

\[
E_{\text{ads}} = E_{\text{adsorbate/MnN}₃-\text{Gra}} - (E_{\text{MnN}₃-\text{Gra}} + E_{\text{adsorbate}})
\]

where \(E_{\text{MnN}₃-\text{Gra}}\), \(E_{\text{SV/DV-\text{Gra}}}\), and \(E_{\text{Mn}}\) are the total energy of MnN₃-Gra, defective graphene with vacancies, and an isolated doped Mn atom. \(E_{\text{adsorbate/MnN}₃-\text{Gra}}\) and \(E_{\text{adsorbate}}\) are the total energy of MnN₃-Gra with adsorbed species and the free adsorbate.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acsomega.0c02930](https://pubs.acs.org/doi/10.1021/acsomega.0c02930).

Kinetic simulations at different temperatures, the most stable gas adsorption configuration, and electronic structure (PDF)

### AUTHOR INFORMATION

#### Corresponding Authors

Chao Liu — Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China; orcid.org/0000-0002-0025-3636; Email: liuchao198967@126.com

Tongxiang Liang — Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China; Email: liang_tx@126.com

#### Authors

Mingming Luo — Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China

Zhao Liang — Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China; orcid.org/0000-0003-4377-8034

Meling Liu — Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China

Xiaopeng Qi — Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China

Mingwei Chen — Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China

Hui Yang — Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China

Complete contact information is available at: [https://pubs.acs.org/10.1021/acsomega.0c02930](https://pubs.acs.org/10.1021/acsomega.0c02930)

#### Notes

The authors declare no competing financial interest.
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