DFT Study on the CO\textsubscript{2} Reduction to C\textsubscript{2} Chemicals Catalyzed by Fe and Co Clusters Supported on N-Doped Carbon

Qian Xue\textsuperscript{1}, Xueqiang Qi\textsuperscript{1,2,*}, Tingting Yang\textsuperscript{1}, Jinxia Jiang\textsuperscript{3,*}, Qi Zhou\textsuperscript{1}, Chuang Fu\textsuperscript{1} and Na Yang\textsuperscript{2,*}

\textsuperscript{1} School of Chemistry and Chemical Engineering, Chongqing University of Technology, Chongqing 400054, China; xueq@stu.cqut.edu.cn (Q.X.); tingty@stu.cqut.edu.cn (T.Y.); Qizhou@stu.cqut.edu.cn (Q.Z.); Chuangfu@stu.cqut.edu.cn (C.F.)

\textsuperscript{2} Chongqing Key Laboratory of Chemical Process for Clean Energy and Resource Utilization, School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China

\textsuperscript{3} Chongqing Medical and Pharmaceutical College, Chongqing 400020, China

* Correspondence: xqqi@cqut.edu.cn (X.Q.); jiang106@cqu.edu.cn (J.J.); yna@cqu.edu.cn (N.Y.)

Abstract: The catalytic conversion of CO\textsubscript{2} to C\textsubscript{2} products through the CO\textsubscript{2} reduction reaction (CO\textsubscript{2}RR) offers the possibility of preparing carbon-based fuels and valuable chemicals in a sustainable way. Herein, various Fe\textsubscript{5} and Co\textsubscript{5} clusters are designed to screen out the good catalysts with reasonable stability, as well as high activity and selectivity for either C\textsubscript{2}H\textsubscript{4} or CH\textsubscript{3}CH\textsubscript{2}OH generation through density functional theory (DFT) calculations. The binding energy and cohesive energy calculations show that both Fe\textsubscript{5} and Co\textsubscript{5} clusters can adsorb stably on the N-doped carbon (NC) with one metal atom anchored at the center of the defected hole via a classical MN\textsubscript{n} structure. The proposed reaction pathway demonstrates that the Fe\textsubscript{5}-NC cluster has better activity than Co\textsubscript{5}-NC, since the carbon–carbon coupling reaction is the potential determining step (PDS), and the free energy change is 0.22 eV lower in the Fe\textsubscript{5}-NC cluster than that in Co\textsubscript{5}-NC. However, Co\textsubscript{5}-NC shows a better selectivity towards C\textsubscript{2}H\textsubscript{4} since the hydrogenation of CH\textsubscript{2}CHO to CH\textsubscript{3}CHO becomes the PDS, and the free energy change is 1.08 eV, which is 0.07 eV higher than that in the C-C coupling step. The larger discrepancy of d band center and density of states (DOS) between the topmost Fe and sub-layer Fe may account for the lower free energy change in the C-C coupling reaction. Our theoretical insights propose an explicit indication for designing new catalysts based on the transition metal (TM) clusters supported on N-doped carbon for multi-hydrocarbon synthesis through systematically analyzing the stability of the metal clusters, the electronic structure of the critical intermediates and the energy profiles during the CO\textsubscript{2}RR.

Keywords: DFT; CO\textsubscript{2}RR; clusters; selectivity and activity

1. Introduction

The electrochemical CO\textsubscript{2} reduction reaction (CO\textsubscript{2}RR), as a useful method to convert CO\textsubscript{2} into value-added chemical products, which not only helps to solve the energy and environmental problems caused by fossil fuel combustion but also achieves sustainable development [1–4]. The main products of CO\textsubscript{2}RR are generally divided into C\textsubscript{1} products (e.g., CO, CH\textsubscript{4}, CH\textsubscript{3}OH, HCOOH, etc.) [5] and C\textsubscript{2} products (e.g., C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{5}OH, CH\textsubscript{3}COOH, etc.) [6]. Cu and Cu-derived materials have been considered the most common electrocatalysts for the CO\textsubscript{2}RR in the early stages [7,8]. Furthermore, Ag-based [9,10] and Au-based [11–13] catalysts can selectively reduce CO\textsubscript{2} to CO at low overpotentials. However, they suffer from low utilization of metal atoms and a low C\textsubscript{2}+ selectivity.

Recently, the single-atom catalysts (SACs) of metal loaded on carbon substrates (metal nitrogen-doped carbon-based catalysts) have become a rather hot frontier for the maximized atom utilization efficiency and defined active centers. Rossmeisl et al. [14,15] found that the transition metal nitrogen-doped carbon-based catalysts (M-N-C, M = Mn, Fe, Co, Ni or Cu) performed a high CO selectivity for CO\textsubscript{2}RR. Furthermore, both Mn-N-C and Fe-N-C...
also possessed CO selectivity as well as trace amounts of CH₄, which was assigned to the stronger CO binding of the Fe and Mn porphyrine-like structures. Zu et al. [16] successfully synthesized atomically dispersed Sn sites on nitrogen-doped carbon, which performs excellent activity and stability for formate generation at a kilogram scale with a quick freeze-vacuum drying-calcination method. Many Ni-based, Fe-based and Co-based SACs have exhibited high electrocatalytic activity and Faradaic effectivity (FE) for the CO₂RR with CO as the primary product due to the moderate adsorption energies of *COOH and *CO intermediates, as well as the high activation barrier for the hydrogen evolution reaction (HER) [17,18].

Though the widespread study on the single-atom catalysts enhanced the utilization efficiency of metal atoms, most of the current studies are limited to the reduction of CO₂ to C₁ products. Compared to C₁ products, C₂⁺ products have a higher economic and chemical utilization value [19–21]. Cu-based SACs, up to now, have still performed good electrochemical reduction of CO₂ to C₂⁺ chemicals [22,23]. However, Karapinar [24] revealed that the atomically dispersed CuNₓ sites could reversibly convert into Cu clusters during CO₂RR, which are suggested as the real multiple active sites for CH₃CH₂OH production. Considering the fact that a single metal atom can accommodate only a single CO, it is difficult to activate two CO₂ molecules simultaneously to trigger the C-C coupling reaction based on an isolated metal center. Thus C-C coupling proceeding on the single metal atoms is quite difficult. Therefore, the catalysts with multiple active sites need to be considered to achieve the conversion from CO₂ to C₂ products [25].

Transition metal (TM) clusters with precise atomic numbers can offer multiple active sites, tune the size-dependent catalytic activity [26], and allow them to find the highest reactivity for the activation and dissociation of strong chemical bonds from CO₂. Xu et al. [27] reported a facile underpotential deposition technique to fabricate Cu clusters on carbonaceous substrates via rationally introducing S dopants in graphite foam. The obtained free-standing electrode exhibited high activity and excellent long-term stability toward oxygen reduction reaction. Pei et al. [28] found the trimeric metal clusters anchored on N-doped porous graphitic sheets possess a good selectivity and superiority towards CO₂RR to multi-carbon products due to the multiple active sites.

Considering the loading of metal clusters with a precise number of atoms on the active substrate can not only avoid the problem of low stability of bare metal cluster catalysts at room temperature but also further enhance their stability and catalytic efficiency. Graphite-based materials are currently widely used as substrates for electrocatalysts. To access C₂ products more efficiently, herein, we employed density functional theory (DFT) calculations to explore the CO₂RR catalyzed by Feₙ (n = 1, 3–5) anchoring on N-doped carbon (Feₙ-NC) to C₂H₄ and C₂H₅OH in this work. Furthermore, the Co₅ cluster supported on N-doped carbon (Co₅-NC) was explored comparatively. We found that Fe₅ loaded on NC exhibit significant activity for promoting the reduction of CO₂ to C₂ products, while the Co₅ cluster has higher priority for the selective synthesis of C₂H₄. Our findings provide insights into the design of highly active catalysts for CO₂RR and create a platform for developing metal cluster-NC electrocatalysts.

2. Theoretical Method

First principle calculations were performed using DFT with spin polarization utilizing the Vienna Ab initio Simulation Package (VASP). The projected augmented wave (PAW) [29–31] was used, and the generalized gradient approximation (GGA) realized by the Perdew–Burke–Ernzerhof function (PBE) was adopted to incorporate the exchange-correction functional [32]. A 2 × 2 × 1 Monkhorst-Pack K-point was sampled in the Brillouin zone, and a cut-off energy of 500 eV was set for geometric optimization. The convergence criteria are of 10⁻⁵ eV in energy between two electronic iteration steps and
0.02 eV/Å in force for every atom [33]. Our calculations of catalytic performance are based on the computational hydrogen electrode (CHE) proposed by Nørskov et al. [34]:

\[
H^+_{(aq)} + e^- \rightarrow \frac{1}{2} H_2(g)
\]  

(1)

The change of the free energy for the step \( A^+ + e^- \rightarrow A^* \) can be equal to the reaction: \( A^+ + \frac{1}{2} H_2(g) \rightarrow A^* \) at 0 V versus the reversible hydrogen electrode (RHE) at all pH values.

We employ five types of small iron clusters \( \text{Fe}_n \) (\( n = 1, 3–5 \)) supported on nitrogen-doped carbon sheets as the calculation models. The defects of NC provide ideal anchor sites for the iron cluster. To estimate the stability of supported TM clusters, the binding energy (\( E_b \)) of TM\(_n\) cluster on NC is calculated by Equation (2)

\[
E_b = E_{TM_n-NC} - E_{TM_n} - E_{NC}
\]  

(2)

Here \( E_{TM_n-NC} \) is the total energy of the optimized TM\(_n\) cluster supported on NC. The terms \( E_{TM_n} \) and \( E_{NC} \) refer to the energies of isolated TM\(_n\) cluster and support. We calculated the cohesive energy (\( E_c \)) of each TM\(_n\) cluster to further evaluate the stability of TM\(_n\)-NC catalysts, with \( E_c \) defined as:

\[
E_c = (E_{\text{cluster}} - nE_{TM})/n
\]  

(3)

Here the \( E_{\text{cluster}} \) and \( E_{TM} \) represent the energy of the total energy of the TM\(_n\) cluster and the energy of single TM atom; \( n \) is the number of TM atoms in the cluster. The more negative cohesive energy (\( E_c \)) indicates a more stable structure.

The adsorption energy (\( E_{ads} \)) of every intermediate species is defined by Equation (4)

\[
E_{ads} = E_{C_iH_yO_z-TM_n-NC} - E_{TM_n-NC} - E_{C_iH_yO_z}
\]  

(4)

where \( E_{C_iH_yO_z-TM_n-NC} \) refers to the total energy of the adsorbed species on the supported TM\(_n\) cluster, and \( E_{TM_n-NC} \) is the energy of supported TM\(_n\) cluster. \( E_{C_iH_yO_z} \) refers to the energies of \( C_iH_yO_z \) in gas phase, respectively. The more negative adsorption energy indicates a stronger binding between TM cluster and NC support. Gibbs free energy change (\( \Delta G \)) [35,36] is defined as:

\[
\Delta G = \Delta E + \Delta E_{ZPE} + \Delta \int C_p dT - T \Delta S + \Delta G_{pH} + \Delta G_{Ul}
\]  

(5)

where \( \Delta E \), \( \Delta E_{ZPE} \), \( \Delta \int C_p dT \) and \( \Delta S \) are the total energy difference, the zero-point energy difference, the difference in enthalpic correction and the entropy change between the products and reactants obtained from DFT calculations, respectively. The zero-point energies (ZPE) and total entropies of the gas phase were computed from the vibrational frequencies, and the vibrational frequencies of the adsorbed species were also computed to obtain the ZPE contribution to the free energy expression. Only vibrational modes of the adsorbates were computed explicitly, while the catalyst sheet was fixed (assuming that vibration contribution to the free energy from the substrate is negligible) [37,38]. \( T \) is the temperature (298.15 K). The influence of applied potential is: \( \Delta G_{Ul} = -neU \), where \( U \) is the external potential versus RHE, \( e \) is the electron transfer, and \( n \) is the number of proton–electron pairs. \( \Delta G_{pH} \) is the free energy correction due to the concentration of \( H^+ \). \( \Delta G_{pH} = -k_B T \ln [H^+] = k_B T \ln 10 \times p H \), where \( k_B \) is the Boltzmann constant, and the value of \( pH \) was assumed to be zero for acidic conditions.

3. Results and Discussion

3.1. The Stability Analysis of Fe\(_n\)-NC

For the Fe\(_n\) clusters supported on the NC substrate (Fe\(_n\)-NC), \( n = 1, 3, 4 \) and 5 were chosen to be studied here since the Fe\(_2\) cluster is unstable [39]. As shown in Figure 1,
for the adsorption of a single Fe atom on the NC substrate (Figure 1a), the mono Fe atom coordinated with the four nitrogen atoms and Fe-NC maintains a perfect monolayer structure, which is in agreement with previous results [40]. For the adsorption of Feₙ clusters with n ranging from 3 to 5 (Figure 1b–d), one Fe atom is anchored at the same position with that in a single Fe atom. Two Fe atoms bound to the doped nitrogen atoms with distances of about 2.1–2.3 Å, respectively, while the other Fe atoms bound together through Fe-Fe metal bonds.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Top-view and side-view of optimized structures of Fe₁ (a), Fe₃ (b), Fe₄ (c) and Fe₅ (d) clusters supported on four nitrogen-doped carbon. The gold, blue and gray spheres represent Fe, N and C atoms, respectively. The different Fe sites are marked with white numbers.

As listed in Table 1, all the binding energies of Feₙ clusters on NC supports are thermodynamically favorable (E₉ < 0). With the increase in Fe atoms, the binding energy decreases except for the magic Fe₅ cluster, which means that the small Fe clusters may tend to aggregate from small clusters to bigger clusters on NC support. The reason for the decreased binding energy of the magic Fe₅ cluster lies in that the Fe₅ site located at the top site, as shown in Figure 1d. Hence there is no interaction with the NC support. What is more, the cohesive energy of various Feₙ clusters was also explored according to Equation (3), as shown in Table 1. It can be found that with the increase in Fe atoms in the cluster, the cohesive energy becomes thermodynamically favorable.

| Catalyst | Fe₁site | Fe₂site | Fe₃site | Fe₄site | Fe₅site | E₀ (eV) | E₉ (eV) |
|----------|---------|---------|---------|---------|---------|--------|--------|
| Fe₁-NC   | −1.07   | −0.32   | −0.31   | −0.19   | −0.01   | −9.01  | 0      |
| Fe₃-NC   | −0.80   | −0.34   | −0.33   | −0.28   | −0.19   | −9.73  | −0.35  |
| Fe₄-NC   | −0.81   | −0.36   | −0.35   | −0.28   | −0.01   | −8.34  | −1.01  |
| Fe₅-NC   | −0.81   | −0.36   | −0.35   | −0.28   | −0.01   | −9.79  | −0.62  |

* negative Bader charge means electron loss.

### 3.2. Electrocatalytic CO₂RR

The charge difference between two active transition atoms plays a key role during CO₂RR, and the mixed oxidation state of the catalytic centers can boost the C-C coupling [41,42]. Thus the Bader charges of various Fe clusters adsorbed on NC were investigated. As listed in Table 1, one can find that the electrons can transfer from the clusters to the support, making the whole Fe cluster positively charged, and each Fe atom in the cluster is positively charged as well. Herein, the Feₙ clusters are favorable to the CO₂RR; thus the electron-accepting properties of the positively charged Fe and Co sites are favorable for stabilizing the CO₂RR intermediates [43]. The largest charge transfer can be determined for
the single Fe atom configuration since the monatomic Fe interacts with four coordinated N atoms. Furthermore, significant discrepancies for each charged Fe atom in the Fe₅, Fe₄ and Fe₃ clusters can be determined, which is beneficial for the C-C coupling reaction.

The conversion of CO₂ to CO catalyzed by various Feₙ clusters was calculated, as shown in Figure 2; the PDS is the *CO to CO for all the Feₙ-NC with a maximum Gibbs free energy (ΔG₃ = ΔG₃CO − ΔG₃CO₂). The ΔG₃ are 0.91, 1.14 and 1.58 eV for the Fe-NC, Fe₃-NC and Fe₄-NC, respectively. This value increases to 1.94 and 2.29 eV at two different sites of Fe₅-NC. Thus it can be deemed that the Fe-NC, Fe₃-NC and Fe₄-NC require a lower overpotential to drive the desorption of CO, indicating that these structures favor the conversion of CO₂ to CO. The *CO → CO(g) step with strong *CO binding leads to a positive ΔG of CO desorption. The relatively strong binding of *CO on Fe-Nₓ is fully supported by the experimentally confirmed exclusive ability of the Fe-Nₓ catalyst to produce the hydrocarbon CH₄ [44].

In simple terms, one could say that to produce subsequent reaction products from CO during the CO₂RR; the CO molecule must be bound strong and long enough to undergo subsequent dissociation and hydrogenation steps to arrive at CH₄ or other small organic molecules. Herein, our work focuses on the reduction of CO₂ to C₂ products, which requires improved selectivity and activity by inhibiting the unwanted, i.e., C₁ hydrocarbon reaction pathway, which favors both the stabilization of *CO on the catalyst surface and the formation of C-C bonds. The strongest interaction for CO on the two Fe₅-NC sites means that CO does not leave the iron cluster surface easily, which, in turn, favors the subsequent C₂ product conversion. Therefore, the following study focuses on the performance of electrocatalytic CO₂ reduction to C₂H₂ and CH₃CH₂OH over the Fe₅-NC cluster. In order to further extend this result to other systems, the Co₅ cluster supported on NC was chosen to be studied comparatively (Figure S1). As shown in Table 2, the Eₛ value between the Co₅ cluster and the NC is −10.00 eV, and the Eₛ value of the Co atom is −1.39 eV, which means the Co₅ cluster can adsorb stably on the NC.

![Figure 2. Cont.](image-url)
To further study the mechanisms of CO$_2$RR catalyzed by Fe$_5$-NC and Co$_5$-NC, the optimized structures and the energy profiles along the reaction coordinate for CO$_2$RR to both C$_2$H$_4$ and CH$_3$CH$_2$OH on Fe$_5$-NC and Co$_5$-NC are calculated as shown in Figures 3 and 4, respectively. It can be found that two strongly adsorbed CO molecules adsorbed on the two adjacent metal atoms through carbon atoms either on the Fe$_5$ or the Co$_5$ clusters before the C-C bond formation. The two CO molecules will couple with each other via the top Fe or Co atom in the following steps of CO$_2$RR. For the CO$_2$RR on Fe$_5$-NC, the Gibbs free energy for the hydrogenation of the *CO dimer is uphill with an energy value of 0.79 eV, which is the highest energy during the formation of both C$_2$H$_4$ and CH$_3$CH$_2$OH. Thus, it can be deemed that the C-C coupling reaction for the CO$_2$RR from CO$_2$ to C$_2$ chemicals is the PDS. Furthermore, it can be speculated that both C$_2$H$_4$ and CH$_3$CH$_2$OH products can be achieved with Fe$_5$-NC catalyst, and the amount of C$_2$H$_4$ should be much more than the CH$_3$CH$_2$OH. Because the Gibbs free energy for the hydrogenation of *CH$_2$CHO to C$_2$H$_4$ is energy thermodynamically favorable, while the hydrogenation of *CH$_2$CHO to *CH$_3$CHO is an uphill reaction with a free energy of 0.26 eV.
both C$_2$H$_4$ and CH$_3$CH$_2$OH on Fe$_5$-NC and Co$_5$-NC are calculated as shown in Figures 3 and 4, respectively. It can be found that two strongly adsorbed CO molecules adsorbed on the two adjacent metal atoms through carbon atoms either on the Fe$_5$ or the Co$_5$ clusters before the C-C bond formation. The two CO molecules will couple with each other via the top Fe or Co atom in the following steps of CO$_2$RR. For the CO$_2$RR on Fe$_5$-NC, the Gibbs free energy for the hydrogenation of *CO dimer is uphill with an energy value of 0.79 eV, which is the highest energy during the formation of both C$_2$H$_4$ and CH$_3$CH$_2$OH. Thus, it can be deemed that the C-C coupling reaction for the CO$_2$RR from CO$_2$ to C$_2$H$_4$ chemicals is the PDS. Furthermore, it can be speculated that both C$_2$H$_4$ and CH$_3$CH$_2$OH products can be achieved with Fe$_5$-NC catalyst, and the amount of C$_2$H$_4$ should be much more than the CH$_3$CH$_2$OH. Because the Gibbs free energy for the hydrogenation of *CH$_2$CHO to C$_2$H$_4$ is energy thermodynamically favorable, while the hydrogenation of *CH$_2$CHO to *CH$_3$CHO is an uphill reaction with a free energy of 0.26 eV.

Figure 3. Optimized structures of intermediate Fe$_5$-NC (a) and Co$_5$-NC catalysts (b) during the CO$_2$RR process.
For the CO$_2$RR on Co$_5$-NC, the Gibbs free energy for the hydrogenation of the *CO dimer is uphill with an energy of 1.01 eV, which is 0.22 eV higher than that of the Fe$_5$-NC. However, the Gibbs free energy for the hydrogenation of *CH$_2$CHO to *CH$_3$CHO is (0.07 eV higher) comparable with that in the C-C coupling reaction, which means that the hydrogenation of *CH$_2$CHO to *CH$_3$CHO becomes the PDS. Thus, most of the final C$_2$ products should be C$_2$H$_4$. In general, the Fe$_5$-NC has good catalytic activity towards the C$_2$ chemicals with relatively lower free energy change (0.53 eV), while the selectivity is not as good as Co$_5$-NC. However, Co$_5$-NC possesses better selectivity while the activity is lower than Fe$_5$-NC.

The d-band center of the TM and its electronic occupancy can affect the bonding strength between the intermediate and the catalytic surface. As shown in Figure 5, the PDOS of Fe d orbit from the top- and sub-layer structures show much more differences than that of the Co d orbit on Co$_5$-NC. Furthermore, the d band center of the top Fe atom in the Fe$_5$ cluster is $-3.48$ eV, while it becomes $-1.59$ eV for the sub-layer atoms. However, the d band center of the top Co atom is $-1.34$ eV, and it only changes to $-1.47$ eV for the sub-layer atoms. A much bigger discrepancy of the d band center between the top Fe atom and sub-layer atoms than that in the Co$_5$ cluster may boost the C-C coupling reaction, which could be called the synergy effect between the top- and sub-layer metal atoms. Our findings are consistent with the synergy effect between Cu$^+$ and Cu$^0$, and the surface can significantly improve the kinetics and thermodynamics of both CO$_2$ activation and CO dimerization. Cu metal embedded in an oxidized matrix catalyst can promote CO$_2$ activation and CO dimerization for electrochemical reduction of CO$_2$ [41].

Our theoretical calculations found that the multiple active sites in both the Fe$_5$ and Co$_5$ cluster-based catalysts facilitate the stabilization of *CO on the catalyst surface and the formation of C-C bonds. Both geometrical effects and electronic effects are the key factors leading to the Fe$_5$ and Co$_5$ clusters exhibiting better activity and/or selectivity over the single metal component. Furthermore, the tunable synthesis of Fe and Co alloys supported on NC may promote both their activity and selectivity toward CO$_2$RR. Therefore, Fe$_5$, Co$_5$ and the related tunable alloy clusters show great potential applications in electrocatalytic CO$_2$RR, and our methods provide a concept for designing the improved CO$_2$RR electrocatalysts.
Figure 5. The PDOS of the d orbitals of the single top Fe atom (red) and average three middle Fe atoms (blue) in Fe$_5$-NC (a), and the PDOS of the d orbitals of the single top Co atom (red) and average three middle Co atoms (blue) in Co$_5$-NC (b).
4. Conclusions

The stability of the Feₙ (n = 1, 3, 4, and 5) clusters was studied first, and it can be found that the Feₙ anchors stably on the nitrogen-doped carbon via a basic Fe-NC structure. With the increasing of Fe atoms in the cluster, both the binding energy and cohesive energy become thermodynamically favorable, which means a small cluster tends to aggregate to be a bigger one. While for the Fe₅ cluster, the binding energy decreases because there is no interaction between the topmost Fe atom with the NC support anymore. In addition, the CO desorption is the most difficult on the Fe₅ cluster, which is beneficial to the subsequent reaction products from CO. Hence, the Fe₅-NC cluster was chosen to be studied as our C₂ catalyst, and Co₅-NC was comparatively studied as well. The results show that Fe₅-NC has better activity towards CO₂RR, and the products should be the mixed C₂H₄ and CH₃CH₂OH, since the PDS is the C-C coupling reaction with a free energy change of only 0.79 eV. The free energy change is only 0.53 eV for the reduction of CH₂CHO to CH₂CHO, and the reduction of CH₂CHO to C₂H₄ is a spontaneous step without any free energy change. Considering the fact that C₂H₄ is a gas, Fe₅-NC should be a good catalyst for CO₂RR to liquid ethanol with a relatively lower yield since part of the C₂H₄ gas will also be produced. Furthermore, Co₅-NC possesses a relatively good selectivity, but bad activity since the reduction of CH₂CHO to CH₂CHO is the PDS, and the free energy change is 1.09 eV. The PDOS and d band center analysis demonstrates that the relative energy favorable C-C coupling reaction on the Fe₅ cluster could be attributed to the larger discrepancy of d electrons of the two CO-adsorbing Fe atoms. This paper predicts a good application prospect of TM clusters supported on nitrogen-doped graphene for CO₂RR, and the new insight into the relationship between selectivity and activity sheds light on a new route for understanding and designing highly efficient non-precious catalysts for CO₂RR.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12132239/s1, Figure S1: The optimized structures of Co₅ supported on four nitrogen doped carbon (NC). Number shown in structures labels the Co atoms.

Author Contributions: Conceptualization, X.Q. and N.Y.; Methodology, N.Y., Q.X. and X.Q.; Software, Q.X., T.Y., Q.Z. and C.F.; Visualization, Q.X. and J.J.; Formal analysis, X.Q., N.Y., and Q.X.; Writing—Original Draft, X.Q. and Q.X.; Writing—Review and Editing, X.Q. and N.Y.; Supervision, Q.X. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the China Postdoctoral Science Foundation (2021M700621), and the 2021 Talent Introduction Project of Chongqing Medical and Pharmaceutical College: ygz20211104.

Data Availability Statement: The data presented in this study are available in this article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Birdja, Y.Y.; Pérez-Gallent, E.; Figueiredo, M.C.; Göttle, A.J.; Calle-Vallejo, F.; Koper, M.T.M. Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels. Nat. Energy 2019, 4, 732–745. [CrossRef]
2. Wei, X.; Xiao, S.; Wu, R.; Zhu, Z.; Zhao, L.; Li, Z.; Wang, J.; Chen, J.S.; Wei, Z. Activating COOH* intermediate by Ni/Ni₆ heterostructure in porous N-doped carbon nanofibers for boosting CO₂RR. J. Energy Storage 2022, 43, 128882. [CrossRef]
3. Li, Z.; Wu, R.; Xiao, S.; Yang, Y.; Lai, L.; Chen, J.S.; Chen, Y. Axial chlorine coordinated iron-nitrogen-carbon single-atom catalysts for efficient electrochemical CO₂ reduction. Chem. Eng. J. 2022, 430, 132882. [CrossRef]
4. Lu, S.; Wang, Y.; Xiang, H.; Lei, H.; Xu, B.B.; Xing, L.; Yu, E.H.; Liu, T.X. Mass transfer effect to electrochemical reduction of CO₂: Electrode, electrocatalyst and electrolyte. J. Energy Storage 2022, 52, 104764. [CrossRef]
5. Wu, Y.; Jiang, Z.; Lu, X.; Liang, Y.; Wang, H. Domino electroreduction of CO₂ to methanol on a molecular catalyst. Nature 2019, 575, 639–642. [CrossRef] [PubMed]
6. Wang, Y.; Ngoc Pham, T.; Tian, Y.; Morikawa, Y.; Yan, L. Density functional theory study on a nitrogen-rich carbon nitride material C₃N₅ as photocatalyst for CO₂ reduction to C1 and C2 products. J. Colloid Interface Sci. 2021, 585, 740–749. [CrossRef] [PubMed]
7. Xiao, C.; Zhang, J. Architectural Design for Enhanced C₂ Product Selectivity in Electrochemical CO₂ Reduction Using Cu-Based Catalysts: A Review. ACS Nano 2021, 15, 7975–8000. [CrossRef]
8. Wang, Y.; Lei, H.; Lu, S.; Yang, Z.; Xu, B.B.; Xing, L.; Liu, T.X. Cu2O nano-flowers/graphene enabled scaffolding structure catalyst layer for enhanced CO2 electrochemical reduction. *Appl. Catal. B Environ.* 2022, 365, 121022. [CrossRef]

9. Lu, Q.; Rosen, J.; Jiao, F. Nanostructured Metallic Electro catalysts for Carbon Dioxide Reduction. *ChemCatChem* 2015, 7, 38–47. [CrossRef]

10. Mistry, H.; Choi, Y.W.; Bagger, A.; Scholten, F.; Bonifacio, C.S.; Sinev, I.; Divins, N.J.; Zegkinoglou, I.; Jeon, H.S.; Kisslinger, K.; et al. Enhanced Carbon Dioxide Electroreduction to Carbon Monooxide over Defect-Rich Plasma-Activated Silver Catalysts. *Angew. Chem. Int. Ed. Engl.* 2017, 56, 11394–11398. [CrossRef]

11. Chen, Y.; Li, C.W.; Kanan, M.W. Aqueous CO2 reduction at very low overpotential on oxide-derived Au nanoparticles. *J. Am. Chem. Soc.* 2012, 134, 19969–19972. [CrossRef] [PubMed]

12. Zhu, W.; Michalsky, R.; Metin, O.; Lv, H.; Guo, S.; Wright, C.J.; Sun, X.; Peterson, A.A.; Sun, S. Monodisperse Au nanoparticles for CO2 electroreduction. *Chem. Soc. Rev.* 2017, 56, 11394–11398. [CrossRef]

13. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868. [CrossRef] [PubMed]

14. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. *Phys. Rev. B* 1976, 13, 5188–5192. [CrossRef]

15. Nørskov, J.K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J.R.; Bilggaard, T.; Jónsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B* 2004, 108, 17886–17892. [CrossRef]

16. Rossmeisl, J.; Logadottir, A.; Nørskov, J.K. Electrolysis of water on (oxidized) metal surfaces. *Chem. Phys.* 2005, 319, 178–184. [CrossRef]
36. Peterson, A.A.; Abild-Pedersen, F.; Felix Studt, F.; Rossmeisl, J.; Nørskov, J.K. How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels. *Energy Environ. Sci.* **2010**, *3*, 1311–1315. [CrossRef]
37. Wang, Y.; Yuan, H.; Li, Y.; Chen, Z. Two-dimensional iron-phthalocyanine (Fe-Pc) monolayer as a promising single-atom-catalyst for oxygen reduction reaction: A computational study. *Nanoscale* **2015**, *7*, 11633–11641. [CrossRef]
38. Lim, D.H.; Wilcoxon, J. Mechanisms of the Oxygen Reduction Reaction on Defective Graphene-Supported Pt Nanoparticles from First-Principles. *J. Phys. Chem. C* **2012**, *116*, 3653–3660. [CrossRef]
39. Cui, C.; Zhang, H.; Luo, Z. Nitrogen reduction reaction on small iron clusters supported by N-doped graphene: A theoretical study of the atomically precise active-site mechanism. *Nano Res.* **2020**, *13*, 2280–2288. [CrossRef]
40. Li, X.F.; Li, Q.K.; Cheng, J.; Liu, L.; Yan, Q.; Wu, Y.; Zhang, X.H.; Wang, Z.Y.; Qiu, Q.; Luo, Y. Conversion of Dinitrogen to Ammonia by FeN$_3$-Embedded Graphene. *J. Am. Chem. Soc.* **2012**, *138*, 8706–8709. [CrossRef]
41. Xiao, H.; Goddard, W.A., 3rd; Cheng, T.; Liu, Y. Cu metal embedded in oxidized matrix catalyst to promote CO$_2$ activation and CO dimerization for electrochemical reduction of CO$_2$. *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 6685–6688. [CrossRef] [PubMed]
42. Zhou, Y.; Che, F.; Liu, M.; Zou, C.; Liang, Z.; De Luna, P.; Yuan, H.; Li, J.; Wang, Z.; Xie, H.; et al. Dopant-induced electron localization drives CO$_2$ reduction to C$_2$ hydrocarbons. *Nat. Chem.* **2018**, *10*, 974–980. [CrossRef] [PubMed]
43. Chen, S.; Wang, B.; Zhu, J.; Wang, L.; Ou, H.; Zhang, Z.; Liang, X.; Zheng, L.; Zhou, L.; Su, Y.Q.; et al. Lewis Acid Site-Promoted Single-Atomic Cu Catalyzes Electrochemical CO$_2$ Methanation. *Nano Lett.* **2021**, *21*, 7325–7331. [CrossRef] [PubMed]
44. Varela, A.S.; Ranjbar Sahraie, N.; Steinberg, J.; Ju, W.; Oh, H.S.; Strasser, P. Metal-Doped Nitrogenated Carbon as an Efficient Catalyst for Direct CO$_2$ Electroreduction to CO and Hydrocarbons. *Angew. Chem. Int. Ed. Engl.* **2015**, *54*, 10758–10762. [CrossRef] [PubMed]