Proceedings of the 3rd International Conference on Mechatronics and Smart Systems
DOI: 10.54254/2755-2721/140/2025.21565

The Significance of Studying the Reduction of CO2 to C1 and C2 Products

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Abstract: Exploring the reduction of carbon dioxide to C_1 products and C_2 products has important environmental and economic significance. By effectively converting carbon dioxide into valuable chemicals, we can not only reduce greenhouse gas emissions and alleviate global warming, but also present new ways for the sustainable production of energy - related substances and chemical products. C_1 products are widely used as basic chemicals in industry, while C_2 products can serve as higher value fuels and chemical raw materials. Hence, the advancement of efficient catalysts and the fine - tuning of reaction pathways for carbon dioxide reduction play a crucial role in fostering the growth of green chemistry and renewable energy sources. By doing so, it can effectively lower the dependence on conventional fossil fuels, and its strategic significance is profound. SAC and DAC can reduce CO_2 to C_1(CH_4,COHOH,CH_3OH,C_2H_4) and C_2 products, and reduce water to H_2.

Keywords: Carbon Dioxide Reduction, Single-Atom Catalysts, Double-Atom Catalysts, C_1 Products, C_2 Products

1. Introduction

As the consumption of global fossil fuels keeps increasing without interruption, the atmospheric concentration of carbon dioxide (CO_2) is also on the rise. Correspondingly, the negative impact it has on the environment is growing more and more remarkable. In an effort to cut down on CO_2 emissions and combat climate change, renewable and clean energy forms, namely wind and solar energy, are steadily being regarded as replacements for fossil fuels. Nevertheless, because these energy sources are highly unpredictable, there is an urgent need for us to devise energy storage technologies that are both efficient and can be easily scaled up. In this context, electrochemical CO_2 reduction reaction (CO_2RR) has received widespread attention as a potential solution. CO_2RR not only provides a method for capturing and converting CO_2 into useful chemicals and fuels, but also enables energy storage and conversion, helping to maintain the balance of CO_2 in the atmosphere. In this field, single atom catalysts (SACs) have attracted much attention due to their unique catalytic performance. Single - atom catalysts (SACs) have manifested outstanding performance across diverse catalytic reactions. They have remarkably cut down costs while enhancing catalytic activity. [1] [2] [3] [4] This not only enhances the economic performance of catalysts but also reduces waste generation, in line with the principles of green chemistry. And the active sites of SACs are evenly distributed [5] [6], effectively

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avoiding the problem of uneven active sites in traditional catalysts, thereby improving catalytic efficiency.

However, SACs can only provide isolated active sites, which limits their application in complex reactions and has become an urgent problem in the field of catalysis. In an attempt to break through the limitations of SACs and elevate the performance of catalysts to a greater extent, researchers have introduced a new - fashioned catalyst: Double Atom Catalysts (DACs). Double Atom Catalyst (DAC) is characterized as a catalytic site consisting of two neighboring isolated metal atoms, which can either directly or indirectly modify the activation energy of the reactants within the reaction pathway. It has evolved into a brand - new frontier in the domain of heterogeneous catalysis. Notably, the synergistic interaction between neighboring active sites is capable of remarkably boosting catalytic activity. [7] [8] Compared with SACs, DACs exhibit higher atomic utilization efficiency, selectivity, and stability [9] [10] [11]. The design of this diatomic structure not only provides new ideas for the optimization of catalysts, but also opens up new possibilities for the industrial application of reactions such as CO_2RR. Through in-depth research on the catalytic mechanism and performance of DACs, we are expected to make significant progress in achieving carbon neutrality and the synthesis of sustainable chemicals.

2. Research progress of SAC for CO_2RR

N-doped graphene can be prepared using nitrogen plasma treatment. N-graphene has much higher oxygen reduction and electrocatalytic performance for hydrogen peroxide than graphene[12][13][14],Its catalytic activity and catalytic activity far exceed the currently widely used platinum based catalysts. The special properties of nitrogen-containing functional groups and graphene materials, which are that N-graphene has excellent electrochemical properties. N-graphene, as a novel electrode material, has significant research value in fields such as fuel cells, metal air batteries, and biosensing. This paper investigates reduction catalysts based on nitrogen doped graphene.

Since Qiao et al. developed the Pt1/FeOx single atom catalyst (SAC) in 2011, SAC has received considerable attention[15].SAC is typically composed of metal centers that coordinate with non-metallic atoms. Due to the fact that most metal sites can be exposed on the catalyst surface and they have unique electronic structures, SAC exhibits high catalytic activity[16].

The strong adsorption energy of CO on bulk Ni (111) makes it easy for CO * to adhere, resulting in a decrease in the catalytic performance of CO2RR at high potentials[17]. Ni single atoms (represented as Ni SAC NA) doped on carbon nanoarrays serve as electrodes without the need for additional catalysts to achieve efficient CO2RR. The unique nano array structure provides a higher specific surface area, more exposed active sites, and enhances electron/mass transfer due to its short diffusion path and ionomer free properties. Su et al. developed Ni Nx doped graphene (Ni-N-G) by rapid heat treatment (900 °C (1 min)) of nickel pentaethyl oxide graphene (GOs) [18], and found that Ni SAC had a high electrocatalytic activity selectivity of over 90% for CO2RR and CO, significantly better than N-doped graphene and Ni metal electrodes. Ni atoms in carbon materials can be stabilized by coordinating with N and/or C on the surface of the carbon material. DFT calculations show that the density of states around the Fermi energy on Ni single atoms is significantly higher than that on Ni (111), leading to a significant decrease in CO binding energy and promoting the conversion of carbon dioxide to CO. And it is proposed that the main active site of CO2RR is Ni atoms anchored within carbon defects in graphene vacancies, while N atoms promote the generation of defects to capture Ni atoms [19].

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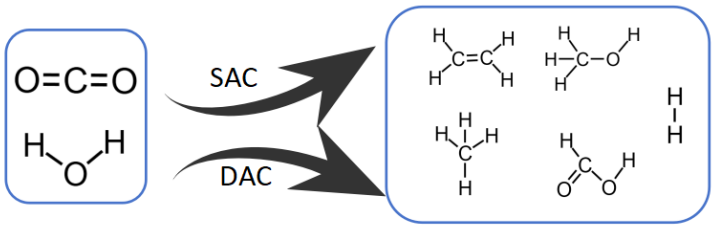

Figure 1: SAC and DAC can reduce CO_2 to C_1 and C_2 products, and reduce water to H_2

We undertook a succession of comparative experiments with the aim of probing into the mechanism through which the Bi - N - C single atom catalyst (SAC) and Bi nanosheets catalyze the transformation of CO_2 to formate. Additionally, another set of experiments focused on the catalytic reaction of the carbon dioxide and water system using a different single - atom catalyst (SAC here refers to a different one from the former) and DAC catalyst. Figure1 shows the product distribution results of this experiment. In the experiment, carbon dioxide and water were used as starting reactants. Under the action of SAC and DAC, substances such as ethylene, methanol, methane, and formic acid were respectively produced. Figure 1 clearly presents the types of products corresponding to different catalysts, providing an intuitive basis for analyzing the differences in the catalytic performance of the two catalysts. Through these experiments, we were able to reveal the different adsorption characteristics of the two catalysts towards the action potential (U). Specifically, Bi-N-C SAC exhibits typical chemical adsorption behavior towards CO2, which is in sharp contrast to the physical adsorption phenomenon on Bi nanosheets [20]. Due to this chemical adsorption characteristic, CO_2 molecules can be activated more effectively on the surface of the catalyst, which in turn decreases the energy barrier for the conversion reaction to CO or formate. This indicates that Bi-N-C SAC has higher selectivity than Bi nanosheets in catalyzing CO2 reduction reactions, and its excellent chemical adsorption capacity makes it an efficient catalyst for CO production. In addition, this study also revealed the unique advantages of single atom catalysts in promoting CO2 conversion, that is, by providing highly dispersed active sites, they can more effectively promote the activation and conversion of CO2[21][22][23].

3. Research progress of DAC for CO_2RR

The inherent linear relationship of adsorption free energy on SAC often limits catalyst activity. For example, in CO_2RR, due to the correlation of adsorption energies of various C_1 reaction intermediates on a single metal site, it is not possible to guarantee the adsorption of all intermediates in the most ideal state at the same time. Double atom catalysts (DACs) have the potential to address, to some extent, the linear correlation between the catalytic activity restricted by single - atom catalysts (SACs) and the adsorption free energy. Moreover, they can engage in a synergistic interaction between two metal atoms to modulate the electronic structure, thereby demonstrating superior catalytic performance. Consequently, they have increasingly captured the attention of researchers. In recent years, the development of double - atom catalysts (DACs) has witnessed remarkable acceleration. In their experiments, Yang and his colleagues fabricated a DAC, which consists of O - coordinated W - Mo heterodimers incorporated into N - doped graphene (W_1Mo_1 - NG). [24] [25] Furthermore, for double - atom catalysts (DACs), attaining high reactivity while preserving high stability under high loads poses a formidable challenge. Leveraging atomic layer deposition (ALD) technology, Lu et al. They resolved this issue by means of synergistic metal - carrier interactions and spatial constraints. This approach enabled the production of high - loaded atomic nickel (3.1 wt%) and dense atomic copper clamps (8.1 wt%) on graphite nitride carbon carriers (Ni_1Cu_2/g - C_3N_4). [26] Besides

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heteronuclear double - atom catalysts (DACs), Yan et al. also managed to successfully prepare homonuclear Pt_2 diatomic catalysts via a two - step atomic layer deposition (ALD) process. Meanwhile, Tian et al. synthesized highly - dispersed Fe_2 bimetallic catalysts supported on mesoporous carbon nitride (mp g - C_3N_4) by adopting the "precursor pre - selection" impregnation method. UN et al. presented a novel design of discrete Zn/Co bimetallic sites that are supported on nitrogen - doped carbon (Zn/CoN - C). This was achieved through a competitive complexation strategy implemented at high temperature. [27] [28] Wang et al. explored the impact of the (Fe, Co)-NC system on oxygen reduction reaction (ORR) performance. Their findings showed that the synergistic action of the two transition metal (TM) atoms is conducive to enhancing catalytic activity. Moreover, they experimentally verified the precise locations of these two TM atoms and the adjacent nitrogen atoms. [29] Theoretical investigations have likewise identified ideal catalysts for the oxygen reduction reaction (ORR) and nitrogen reduction reaction (NRR) centered around paired transition - metal (TM) atoms. Regarding the carbon dioxide reduction reaction (CO_2RR), experimental results indicate that the dual TM atoms at the Ni - Fe sites exhibit high selectivity for carbon monoxide (CO) production. Specifically, the CO Faraday efficiency exceeds 90% across a broad potential range.

The Fe_2N_6 catalyst with the same core has drawn extensive attention on account of its outstanding performance in the electrocatalytic carbon dioxide reduction reaction (CO_2RR). To be more precise, when the potential is - 0.6 V (relative to the standard hydrogen electrode, RHE), this catalyst is capable of attaining a CO Faraday efficiency as high as 96.0%. This implies that at this particular potential, nearly all electron transfer is utilized for the generation of the product, carbon monoxide (CO). This efficiency level far exceeds the level that single atom Fe catalysts can achieve, demonstrating the significant advantages of homonuclear Fe_2 N_6 catalysts in selectivity and catalytic activity. For the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), the Fe - Co - N - C type of double - atom catalyst (DAC) is more active than single - metal N - C single - atom catalysts (SACs). The difference in charge density and Bader charge analysis indicate that Fe and Co double atoms can synergistically promote moderate interactions between active centers and frameworks, balance structural stability and catalytic activity, and thus improve catalytic efficiency. The Fe - Co - N - C type of DAC exhibits particularly remarkable performance in the ORR. This is because the heteronuclear combination of iron (Fe) and cobalt (Co) is able to offer a more intricate electronic structure. As a result, it optimizes the adsorption energy of reaction intermediates, facilitating a smoother reaction pathway. [30]

Moreover, theoretical computations suggest that the synergistic catalysis occurring at the Co - Cu bimetallic sites leads to a reduction in the activation energy and facilitates the formation of the intermediate *COOH. [31] This research shows that incorporating an additional metal atom into single - atom catalysts (SACs) can notably influence the electronic structure, thus boosting the catalytic activity of SACs. The performance of Ni - Co heteronuclear double - atom catalysts (DACs) in the electrocatalytic carbon dioxide reduction reaction (CO_2RR) is also better than that of Co - Co or Ni - Ni homonuclear DACs. The electrocatalytic activity of Ni_2 - N_3C_4 for reducing carbon dioxide is substantially increased, and it is better than the relevant single - atom nickel catalyst (Ni - N_2C_2). This provides additional evidence that heteronuclear double - atom catalysts (DACs) are capable of furnishing more efficient electron transfer pathways, and consequently, enhancing catalytic activity.

In experimental research, it has been found that nitrogen doped graphene/PtSn composites have high electrocatalytic activity and stability, and these materials exhibit excellent performance in CO_2RR. The advantage of PtSn composite materials is that the heteronuclear combination of platinum (Pt) and tin (Sn) can provide multiple active sites, promote the adsorption and conversion of reaction intermediates, and thus improve catalytic efficiency. Meanwhile, nitrogen doped graphene as a carrier not only provides abundant active sites, but also enhances the overall stability of the catalyst, making PtSn composite materials perform outstandingly in practical applications[32].

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In addition, the research on NiCu bimetallic catalysts also provides valuable insights for the development of low-cost bimetallic electrocatalysts. Nickel (Ni) and copper (Cu), as relatively inexpensive metals, make up DACs that not only approach or surpass precious metal catalysts in catalytic performance, but also have significant advantages in cost control. These research results not only promote the design of catalysts, but also lay the foundation for industrial applications. By optimizing the synthesis process of NiCu DACs, their stability and repeatability can be further improved, paving the way for industrial scale CO_2 conversion[33].

At present, typical literature on CO_2RR on $M_1M_2 - N - C$ indicates that CO is the main product of almost all homonuclear and heteronuclear DACs, while the yield of multi carbon products is relatively low [34][35][36]. In addition, competition in hydrogen evolution reactions is also one of the major challenges faced by carbon dioxide coupling processes [37].There are some electrode catalysts that can promote the generation of C_2 products, but their efficiency is usually low - they require a large overpotential to increase the reaction rate, and the selectivity for the desired products is usually low[38][39][40][41].

4. Summary

Designing bimetallic dimer catalysts (DACs) to generate important C_2 products such as ethanol and acetic acid is a highly challenging task in the fields of catalytic science and green chemistry. Not only does it require us to deeply explore the unique characteristics of bimetallic catalysts, including their synergistic effects, electron transfer mechanisms, and interface effects, but it also requires us to conduct precise and comprehensive analysis of the entire reaction process through theoretical calculations.

Faced with the possibility of a large number of metal combinations, traditional trial and error methods are difficult to comprehensively and systematically study the performance of DACs in terms of time and cost. The first principles calculation method provides us with an efficient approach for exploring the CO_2 reduction reaction (CO_2RR). This method can help us identify and screen catalysts with lower activation energy barriers, thereby effectively improving the yield of C_2 products. In addition, calculating the Gibbs free energy of reaction intermediates is crucial for a deeper understanding and mastery of the CO_2RR process. By constructing an energy change map of the entire reaction pathway, not only can the intrinsic mechanism of the reaction be revealed, but also the key factors affecting catalytic activity can be determined. Through theoretical calculations, the various steps of CO_2RR can be systematically decomposed to comprehensively evaluate the stability and selectivity of DACs in the reaction process, which helps to more efficiently screen and optimize potential efficient bimetallic catalysts.

In summary, the reduction of CO_2 to multi carbon products still faces many challenges. This project will continue to study the mechanism of CO_2 reduction and coupling, identify bottlenecks, and provide direction for the development of DAC for C-C coupling reactions.

References

[1] *Cheng N , Zhang L , Doyle-Davis K , et al.Single-Atom Catalysts: From Design to Application[J].Electrochemical Energy Reviews, 2019, 2(4):539-573.DOI:10.1007/s41918-019-00050-6.*

[2] *Yang XF, Wang A, Qiao B, Li J, Liu J, Zhang T. Single-atom catalysts: a new frontier in heterogeneous catalysis. Acc Chem Res. 2013;46(8):1740-1748. doi:10.1021/ar300361m*

[3] *Kaiser S K , Chen Z , Akl D F , et al.Single-Atom Catalysts across the Periodic Table[J].[2024-10-11].*

[4] *Li J , Chen S , Yang N , et al.Ultrahigh-Loading Zinc Single-Atom Catalyst for Highly Efficient Oxygen Reduction in Both Acidic and Alkaline Media.[J].Angewandte Chemie, 2019, 58 21:, 7035-7039. DOI:10.1002/anie.201902109.*

[5] *Wang W L , Santos E J G , Jiang B , et al.Direct Observation of a Long-Lived Single-Atom Catalyst Chiseling Atomic Structures in Graphene[J].Nano Letters, 2016, 14(2):450-455.DOI:10.1021/nl403327u.*

[6] Zhang B , Asakura H , Zhang J , et al.Stabilizing a Platinum1 Single-Atom Catalyst on Supported Phosphomolybdic Acid without Compromising Hydrogenation Activity[J].Angewandte Chemie International Edition, 2016.DOI:10.1002/anie.201602801.

[7] Ying Y , Luo X , Qiao J , et al.Double‐Atom Catalysts: "More is Different:" Synergistic Effect and Structural Engineering in Double‐Atom Catalysts (Adv. Funct. Mater. 3/2021)[J].Advanced Functional Materials, 2021, 31.DOI:10.1002/adfm.202170015.

[8] Jiarui W , Donghai W , Dongwei X M .Tailoring the coordination environment of double-atom catalysts to boost electrocatalytic nitrogen reduction: a first-principles study[J].Nanoscale, 2023, 15(39):16056-16067.

[9] Wu D , He B , Wang Y , et al.Double-atom catalysts for energy-related electrocatalysis applications: a theoretical perspective[J].Journal of Physics D: Applied Physics, 2022, 55(20):203001 (40pp).DOI:10.1088/1361-6463/ac4b56.

[10] Zhang L , Guo X , Zhang S , et al.Hybrid Double Atom Catalysts for Hydrogen Evolution Reaction: A Sweet Marriage of Metal and Nonmetal[J].Advanced energy materials, 2024(2):14.

[11] Yang W , Huang H , Ding X , et al.Theoretical study on double-atom catalysts supported with graphene for electroreduction of nitrogen into ammonia[J].Electrochimica Acta, 2020, 335:135667.DOI:10.1016/j.electacta.2020.135667.

[12] Yang X F , Wang A , Qiao B , et al.Single-atom catalysts: a new frontier in heterogeneous catalysis[J].Accounts of Chemical Research, 2013, 46(8):1740.DOI:10.1021/ar300361m.

[13] Guang Xian, Xiao Yan, Yang, 等.Performance of Cu-Alloyed Pd Single-Atom Catalyst for Semihydrogenation of Acetylene under Simulated Front-End Conditions[J].[2024-10-12].

[14] Cheng Y , Yang S , Jiang S P , et al.Supported Single Atoms as New Class of Catalysts for Electrochemical Reduction of Carbon Dioxide[J].Small Methods, 2019.DOI:10.1002/smtd.201800440

[15] Muci A R , Buchwald S L .Practical Palladium Catalysts for C-N and C-O Bond Formation[J].Springer Berlin Heidelberg, 2002.DOI:10.1007/3-540-45313-X_5.

[16] Agúndez, M, Cernicharo J , Guélin, M, et al.Astronomical identification of CN-, the smallest observed molecular anion[J].Astronomy & Astrophysics, 2010, 517(3):L2.DOI:10.1051/0004-6361/201015186.

[17] Ehara M , Kanazawa Y , Sommerfeld T .Low-lying π resonances associated with cyano groups: A CAP/SAC-CI study[J].Chemical Physics, 2017:S0301010416306012.DOI:10.1016/j.chemphys.2016.09.033.

[18] Zhu Y , Dai J , Zhou W , et al.Synergistically enhanced hydrogen evolution electrocatalysis by in situ exsolution of metallic nanoparticles on perovskites[J].Journal of Materials Chemistry A, 2018:10.1039.C8TA02347F.DOI:10.1039/C8TA02347F.

[19] Fan Y , Zhang L Y , Dai F R , et al.Preparation, characterization, and photophysical properties of Pt-M (M = Ru, Re) heteronuclear complexes with 1, 10-phenanthrolineethynyl ligands.[J].Inorganic Chemistry, 2008, 47(7):2811-2819.DOI:10.1021/ic702055n.

[20] He Y , Li Y , Zhang J , et al.Low-temperature strategy toward Ni-NC@Ni core-shell nanostructure with Single-Ni sites for efficient CO2 electroreduction[J].Nano Energy, 2020, 77:105010.DOI:10.1016/j.nanoen.2020.105010.

[21] Yu Zhou, Wenjun Zhou, Chunhua Ni, 等."Tree blossom" Ni/NC/C composites as high-efficiency microwave absorbents[J].Chemical Engineering Journal, 2022, 430:132621-.DOI:10.1016/j.cej.2021.132621.

[22] Yang, H. B. et al. Atomically dispersed Ni(i) as the active site for electrochemical CO2 reduction. Nat. Energy 3, 1–8 (2018).

[23] Yaotang, Zhong, Bin, et al.Bi Nanoparticles Anchored in N-Doped Porous Carbon as Anode of High Energy Density Lithium Ion Battery[J].Nano Micro Letters, 2018.DOI:CNKI:SUN:NANO.0.2018-04-002.1

[24] Yang Y , Qian Y , Li H , et al.O-coordinated W-Mo dual-atom catalyst for pH-universal electrocatalytic hydrogen evolution[J].Science Advances, 2020, 6(23):eaba6586.DOI:10.1126/sciadv.aba6586.

[25] Deshmukh M A , Bakandritsos A , Zboil R .Bimetallic Single-Atom Catalysts for Water Splitting[J].Nano-Micro Letters, 2025, 17(1).DOI:10.1007/s40820-024-01505-2.

[26] Jian G , Minzhen J , Li H , et al.Synergizing metal–support interactions and spatial confinement boosts dynamics of atomic nickel for hydrogenations[J].[2024-10-12].

[27] Zhang Y , Li J , Cai J , et al.Construction of Spatial Effect from Atomically Dispersed Co Anchoring on Subnanometer Ru Cluster for Enhanced N 2 -to-NH 3 Conversion[J].ACS Catalysis, 2021:4430-4440.DOI:10.1021/acscatal.0c05544.

[28] Ying Y , Luo X , Qiao J , et al.Double‐Atom Catalysts: "More is Different:" Synergistic Effect and Structural Engineering in Double‐Atom Catalysts (Adv. Funct. Mater. 3/2021)[J].Advanced Functional Materials, 2021, 31.DOI:10.1002/adfm.202170015.1

[29] Wang J , Huang Z , Liu W , et al.Design of N-Coordinated Dual-Metal Sites: A Stable and Active Pt-Free Catalyst for Acidic Oxygen Reduction Reaction[J].Journal of the American Chemical Society, 2017, 139(48):17281-17284.DOI:10.1021/jacs.7b10385.

[30] Guo X , Gu J , Lin S , et al.Tackling the Activity and Selectivity Challenges of Electrocatalysts towards Nitrogen Reduction Reaction via Atomically Dispersed Bi-Atom Catalysts[J].Journal of the American Chemical Society, 2020, XXXX(XXX).DOI:10.1021/jacs.9b13349.

[31] Facile synthesis of a highly efficient Co/Cu@NC catalyst for base-free oxidation of alcohols to esters[J].New Journal of Chemistry, 2020, 44.DOI:10.1039/D0NJ00172D.

[32] Liu X , Xiao J , Peng H , et al.Understanding trends in electrochemical carbon dioxide reduction rates[J].Nature Communications, 2017, 8:15438.DOI:10.1038/ncomms15438.

[33] Back S , Lim J , Kim N Y , et al.Single-atom catalysts for CO2 electroreduction with significant activity and selectivity improvements[J].Chemical Science, 2017, 8.DOI:10.1039/C6SC03911A

[34] Synergistic Effect of Atomically Dispersed Ni–Zn Pair Sites for Enhanced CO2 Electroreduction[J].Advanced Materials, 2021.DOI:10.1002/adma.202102212.

[35] Cui T , Liu Q , Chen S .Dual-Atom Catalysts for Electrochemical Energy Technologies[J].Energy Technology: Generation, Conversion, Storage, Distribution, 2023.

[36] Feng M , Wu X , Cheng H , et al.Well-defined Fe–Cu diatomic sites for efficient catalysis of CO 2 electroreduction[J]. Journal of Materials Chemistry A, 2021.DOI:10.1039/D1TA02833B.

[37] . Kuhl K P , Hatsukade T , Cave E R , et al.Electrocatalytic Conversion of Carbon Dioxide to Methane and Methanol on Transition Metal Surfaces[J].Journal of the American Chemical Society, 2014, 136(40):14107-14113.DOI:10.1021/ja505791r.

[38] Appel, A.M.Bercaw, J. E.Bocarsly, A.B.Dobbek, H.Dubois, D.L.Dupuis, M.Ferry, J.G.Fujita, E.Hille, R.Kenis, P.J. A.Kerfeld, C.A.Morris, R.H.Peden, C.H.F.Portis, A.R.Ragsdale, S.W.Rauchfuss, T.B.Reek, J.N.H.Seefeldt, L.C. Thauer, R.K.Waldrop, G.L.Frontiers, opportunities, and challenges in biochemical and chemical catalysis of CO_ 2 fixation[J].Chemical Reviews, 2013, 113(8).

[39] Torelli D A , Francis S A , Crompton J C , et al.Nickel-Gallium-Catalyzed Electrochemical Reduction of CO2 to Highly Reduced Products at Low Overpotentials[J].ACS Catalysis, 2016, 6(3).DOI:10.1021/acscatal.5b02888.

[40] Fu L , Wang R , Zhao C , et al.Construction of Cr-embedded graphyne electrocatalyst for highly selective reduction of CO2 to CH4: A DFT study[J].Chemical Engineering Journal, 2021, 414(18):128857.DOI:10.1016/j.cej.2021.128857.

[41] He B , Cui Y , Lei Y B , et al.Design and application of g-C3N4-based materials for fuels photosynthesis from CO2 or H2O based on reaction pathway insights.[J].Journal of colloid and interface science, 2022, 629 Pt B:, 825-846. DOI:10.1016/j.jcis.2022.09.114.