Electrocatalytic Reduction of CO2 Based on Transition Metal Catalysts

Xuan Jiang[1, †], Faguang Liu[2, †], Jiahe Ren[3, *, †]

[1]School of Resources and Environment, Northwest A&F University, Yangling, China

[2]School of Environment and Energy, South China University of Technology, Guangzhou, China

[3]Chimie Pekin, Beijing University of Chemical Technology, Beijing, China

*Corresponding author: 2021100005@buct.edu.cn

†These authors contributed equally

Abstract. As the modern industry develops, the issue of a large amount of fossil fuel emissions is becoming more and more prominent, which leads to a sharp increase of the carbon dioxide (CO_2) in the atmosphere and aggravates the greenhouse effect. Environmental problems like global warming become difficult for human being. How to reduce global warming and ensure energy supply is an urgent problem to cope with. With the deep research on this problem, there are many mature technologies, for instance, thermochemical reduction, photochemical reduction, and electrocatalytic reduction, among which the electrocatalytic reduction technology has the advantages of easy control of the reaction process, high Faraday efficiency, and can be scaled up based on the market needs. In this research, various catalysts ranging from traditional transition metal catalysts to new two-dimensional transition metal MOFs derivatives and new organic ligands will be introduced from the aspects of catalytic efficiency, catalyst stability, product selectivity, etc. This research aims to introduce and promote this series of catalysts and the analytical methods, at the same time, provides ideas for new research in the future.

Keywords: CO_2 Treatment, Functional Materials, Catalysts, Applications.

1. Introduction

Carbon dioxide (CO_2) is the most notorious greenhouse gas, released by natural and man-made processes. Under natural conditions, the production and consumption of CO_2 on Earth should always maintain a stable value. However, as society develops and our dependence on fossil fuels gradually increases, the increased use of fossil fuels leads to an increase in CO_2 emissions. Along with the large amount of CO_2 emissions, the ecological balance of the earth has been disrupted, causing many energy and environmental problems. The CO_2 emissions from fossil fuel combustion and industrial production processes account for 78% of all incremental greenhouse gas emissions. And the increase of CO_2 emissions will lead to the greenhouse effect, which in turn causes global warming. Therefore, to alleviate various environmental problems caused by the greenhouse effect, how to deal with CO_2 has also become a top priority, and governments around the world have expressed great interest in research to solve the problem of CO_2.

With the continuous development of science and technology, different types of CO_2 treatment methods have been developed, including thermochemical reduction conversion, photochemical reduction conversion and catalyst reduction conversion. Among these CO_2 treatment methods, they all have their own drawbacks. For example, thermochemical reduction of CO_2 shows low conversion efficiency, photochemical reduction of CO_2 has low conversion rate to solar energy and complex reaction conditions, and catalyst reduction of CO_2 is difficult to improve the stability of catalyst [1]. The introduction and development of electrochemical reduction of CO2 can compensate for the disadvantages of these conventional methods. This method can easily control the reaction process by the electrode potential difference and reaction temperature, and the electrical energy required for this conversion can be obtained from various clean energy sources such as solar photovoltaic conversion power, wind power, and hydroelectric power, which can be further useful for controlling the CO_2

content in the atmosphere. New electrocatalytic CO_2 materials with high stability and high Faraday efficiency have emerged in recent research, providing the basis for further development of this technology. Due to the simplicity and universal applicability of the reaction device, the application can be scaled up according to market demand.

However, in the electrocatalytic reduction of CO_2 technology, there are still problems such as high reaction energy barrier, insufficient rate, and catalyst selectivity. shortages, etc. Therefore, the selection of suitable catalysts is the focus of electrocatalysis research. Traditional catalyst transition metals have good redox properties due to their d orbitals, which can provide empty orbitals to act as electrophiles in chemical reactions. Transition metals have unique advantages in hydrogenation and dehydrogenation, so they are often used as high-quality catalysts for organic reactions. Transition metal catalysts, especially post-transition metal catalysts (nickel, palladium, iron, cobalt, ruthenium, etc.) have the advantages of high activity, low cost, stable catalytic performance, and easy utilization. They have good development prospects in the field of CO_2 electrocatalytic reduction. This paper will discuss the advantages and development of this direction by discussing the electrocatalytic reduction of CO_2 to formic acid with different transition metal catalysts.

This research begins with the introduction of the mechanism of electrocatalytic reduction of CO_2, and analyzes various catalysts such as traditional transition metal catalysts, new two-dimensional transition metal MOFs derivative catalysts and new organic ligands from the aspects of catalytic efficiency, catalyst stability and product selectivity, and makes the prediction of the development direction of new catalysts in the future.

2. Mechanism of electrocatalytic reduction of CO_2

Electrocatalytic reduction occurs at the biphasic interface between the electrode and the electrolyte solution. The reaction can be divided into three steps, including two non-Faraday processes CO_2 adsorption and desorption on the electrode, and one Faraday process as the core step to complete the reduction by breaking the C=O bond through proton coupling of CO_2 and transfer of electrons to form a C-H bond. The electrocatalytic reduction of CO_2 produces numerous C-containing products, which vary according to the electrical potential. And according to the number of C atoms of the products, we can classify the different products, C1 (e.g. HCOOH, CO, CH_3OH), C2 (e.g. C_2H_4), C3 (e.g. C_3H_7OH) [2]. Since the L-layer orbital of the C atom has four electrons giving it many variable valence states, we can also classify the products by their final number of electrons gained, into 2, 4, 6, and 8 electron reductions [3].

Here, we take the electrocatalytic reduction of CO_2 to generate C1-like products as an example to illustrate the reaction mechanism. First, CO_2 can be produced at the first electron transfer, which is the decisive step of the reaction because of its high reaction energy barrier. If a catalyst is introduced, the activation energy of this step can be further reduced, thus enhancing the efficiency of electrocatalytic reduction. Then, CO_2 can generate carboxyl radicals (-COOH) through proton electron transfer to produce CO, or CO_2 can generate HCHO through proton coupling to aldehyde radicals (-CHO), or CH_3OH through proton coupling to methoxy radicals (-CH_3O), while C2 and C3 products can be obtained through the coupling and electron transfer of each product of C1. The reaction mechanism is more complicated. The products of electrocatalytic reduction of CO_2 are generally more complex mixtures. Therefore, the preparation of electrocatalytic reactions with high selectivity for formic acid has also become a priority. In addition, the introduction of catalyst can also control the products after CO_2 catalysis (Figure 1).

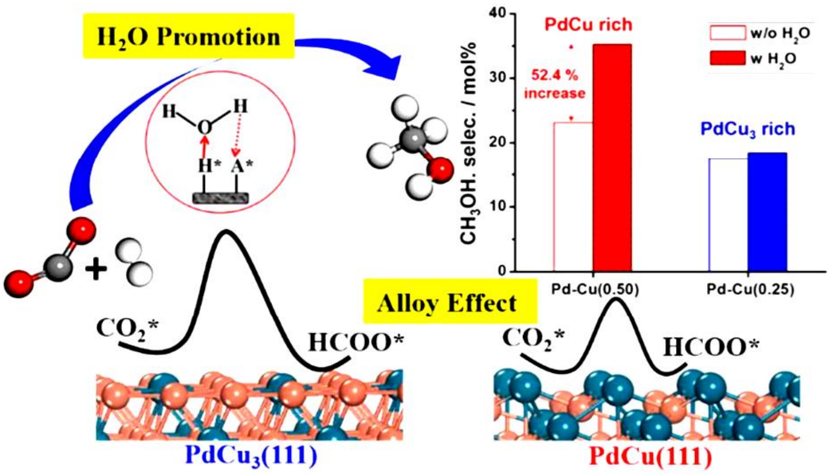

Figure 1. Mechanism of CO_2 to methanol with the prepared catalysts [3]

3. Application of different electrocatalysts for electrocatalytic reduction of CO_2

3.1. Two-dimensional transition metal MOFs derivative materials

Since the Geim's team of the University of Manchester successfully made single-layer graphene materials by mechanical stripping method in 2004, two-dimensional (2-D) materials have gradually come into the view of the public [4]. Two dimensional materials refer to the materials in which electrons can move freely in two dimensions and electrons are restricted to move within the nanoscale (1-100 nm) in the third dimension, and they are connected by ionic bonds or covalent bonds and van der Waals force between layers. Due to the superb physical structure, it has many excellent properties. For instance, it has a large specific surface area, which enables it to contact the reactants more fully during the reaction and keeps the atomic utilization rate of the material at a relatively high level. It shows good electrochemical properties because of the small migration distance of electrons in the material, and many coordination unsaturated sites that enables it to have more active centers to catalyze each reaction. And it has also single-layer or multi-layer chemical structural units, which make it easier to conduct chemical modification on its surface. But two-dimensional materials also have weaknesses, such as thermal instability (because of the extremely limited longitudinal height, the structure becomes unstable easily after heating), short life span (because its reaction performance is too great, the reaction intermediates are often left on the surface affecting its activity and service life). In order to cope with the problems of traditional two-dimensional materials, different kinds of new two-dimensional materials have been developed, including metal organic frameworks (MOFs).

MOFs are new materials with intramolecular voids, which are formed by the combination of organic ligands and metal ions or clusters through coordination bonds. In 1995, the Yaghi's team successfully synthesized a compound coordinated by the rigid organic ligand pyromellitic acid (BTC) and the transition metal co, named MOF. Then, MOFs materials came into the view of people [5]. Generally, MOFs have the following advantages. It has synthesis adjustability and can easily change the order in the synthesis path or even the raw materials and make the preparation of MOFs much easier. It has ultra-high porosity. Because of the large number of pores in the material, it is possible for metal ions or clusters to form coordination bonds in it, which can help optimize some properties of Moss greatly. But the conductivity of most MOFs is low, which limits their applications in the electrochemical area. Research shows that MOFs have good conductivity when transition metal ions are embedded in them. For instance, Yaghi's team constructed MOF-5 by using p-benzoic acid (BDC) and transition metal Zn in 1999 [6]. The framework structure of transition metal MOFs can make up for the lack of thermal stability of two-dimensional materials, so the relatively low activity can also make up for the short life span of two-dimensional metals. And two-dimensional metal can make up for the lack of conductivity of transition metal MOFs, the new materials compounded by the complementary advantages of the two materials can be better applied in the electrochemical area. In the following part, we will introduce the performance of this new material in electrocatalytic reduction of CO_2 to formic acid.

The 2-D cobalt-based MOFs were initially prepared by mixing $Zn(Ac)_2$ and $Co(NO_3)_2$, 2-methylimidazole with PVP and then centrifuged and dried, and then annealed at 900 °C for 2 h to become 2D cobalt-based MOFs derivatives at high temperature. Finally, they are ultrasonically exfoliated to obtain 2-D cobalt-based MOFs derivatives for use as electrodes. The unique thin layered hexagonal structure of the 2-D cobalt-based MOFs derivatives provides excellent electrochemical properties and stability. To identify their reduction products, NMR analysis reveals that the main product is formic acid indicating that the 2-D cobalt-based MOFs derivatives have a high selectivity for the product formic acid. The linear scanning voltammetry (LSV) test was carried out, and it is easy to see that the 2-D cobalt-based MOFs derivatives can maintain a high current density at a low overpotential, which proves their high efficiency for the electrocatalytic reduction of CO_2. Similarly, this electrode was electrolyzed in CO_2-saturated 0.5 M $KHCO_3$ at different potentials for 5 h. It is easy to find that the electrocatalytic reduction of CO_2 catalyzed by this material can guarantee a Faraday efficiency of more than 45%, and the highest Faraday efficiency can reach 68% at a suitable potential, as shown in Figure 2. In summary, they have evaluated the two-dimensional cobalt-based MOFs derivatives in terms of catalyst stability, selectivity, low overpotential, and Faraday efficiency, and their excellent electrocatalytic performance can achieve high economic efficiency, which expands their commercial application prospects [7].

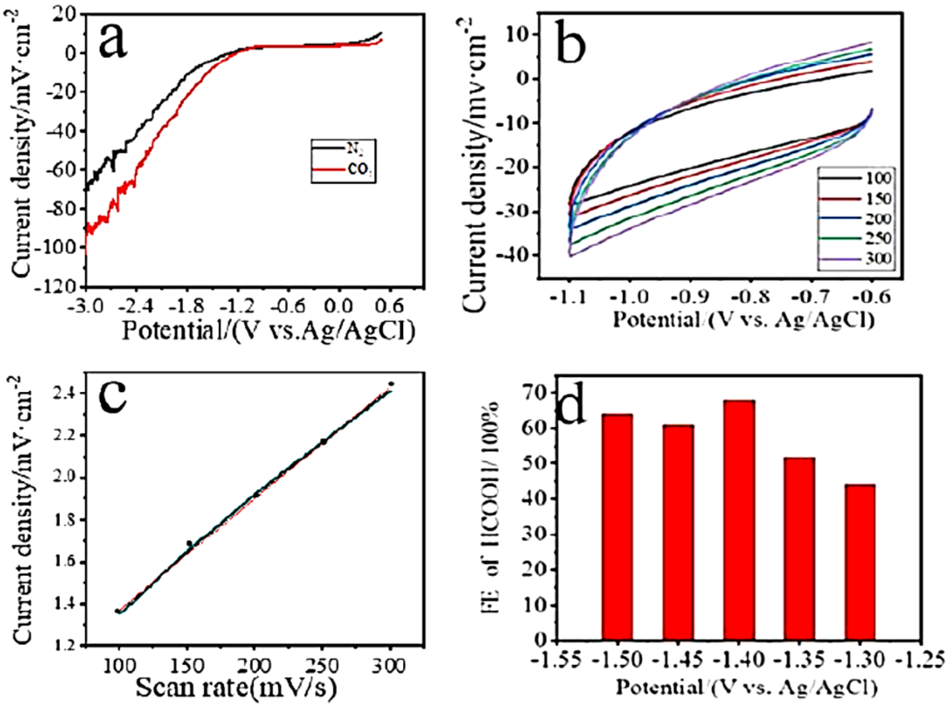

Figure 2. Electrochemical performance of the prepared catalysts [7]

Manganese acetate and dimethylimidazole were used as raw materials, and terephthalic acid was used as surfactant to synthesize manganese-based MOFs derivatives, and then 2-D manganese-based MOFs derivatives were produced as electrodes by ultrasonic stripping. The thin layer-like structure of the 2-D manganese-based MOFs derivatives indicates their high stability, and this structure can reduce the diffusion kinetics and enhance the electron transfer on the electrode. To analyze the reduction products, the products were electrolyzed. The products were found to be dominated by formic acid by NMR analysis, demonstrating the good selectivity of the 2-D manganese-based MOFs derivatives for formic acid. The LSV test was performed, and it is easy to find that the 2-D Mn-based MOFs derivatives with different thinness can maintain high current density at low overpotential indicating that the 2-D Mn-based MOFs derivatives have high catalytic rate and catalytic efficiency.

The results show that the formic acid Faraday efficiency of 2D Mn-based MOFs derivatives could reach up to about 40% at suitable potentials, which further demonstrates the high efficiency of Mn-MOF electrocatalytic reduction of CO_2 [7]. The researchers have also predicted the potential of new transition metal materials for electrocatalytic reduction of CO_2 to formic acid in the future. Based on density functional theory (DFT), the potential energy diagrams for the conversion of CoPc and ZnN_4 to each radical can be obtained by calculation. It is not difficult to find that both materials require less energy for the conversion to the carboxyl radical -COOH. In other words, the selectivity of these two materials for formic acid is higher. Based on this, the materials containing transition metals Co and Zn-like will have higher selectivity for the electrocatalytic reduction of CO_2 to formic acid. While the monometallic mosaic materials are not conducive to electron migration due to the small number of active sites and the long distance between atoms, so the bimetallic materials can play a synergistic advantage performance will be better than the monometallic materials. The use of Co and Zn to make bimetallic materials becomes a good choice. In electrocatalytic reduction, another problem affects the efficiency of the reaction, which is the competition between the hydrogen precipitation reaction and CO_2 for electrons, and how to effectively reduce the waste of hydrogen precipitation reaction becomes a major problem in the preparation of catalysts. Introducing the concept of hydrogen precipitation overpotential, the larger the hydrogen precipitation overpotential is, the smaller the ability to produce hydrogen, which is much larger than the common electrocatalytic materials such as platinum and gold. Therefore, the competition of hydrogen precipitation reaction of Zn-like materials is also smaller, which further proves that Zn-like materials have higher rate and efficiency in electrocatalytic reduction of CO_2. At the same time, the doping of heteroatoms (N, P, B) can optimize the electron distribution on the carbon lattice surface. In summary, a new type of material with MOF as the main framework, inlaid with Co, Zn bimetals and doped with non-metallic heteroatoms N, P, B may be available.

3.2. Molybdenum-based and nickel-based catalysts

Compared with the traditional copper-based catalyst, the molybdenum-based catalyst is more stable and is not easily inactivated because of absorbing sulfur or other substances in the exhaust gas. Molybdenum disulfide has high current density and low overpotential, leading to high Faraday efficiency of CO generation. The ionic liquid in molybdenum dioxide electrocatalytic CO_2 can stabilize reaction intermediates and inhibit hydrogen evolution reaction [8]. Research show that molybdenum disulfide of different ionic liquids has different catalytic effects on CO_2. Hence, different ionic liquids will also have different results of product and yield. MoS_2 catalyst has obvious high current response and high selectivity. It’s because Mo edge atoms have metal properties, and its high D-level electron density is perfect for CO_2 reduction [9].

In CO dehydrogenase, Ni atoms can promote the selectivity of CO_2 to CO through reducing the energy barrier, and nickel-based materials may affect the selectivity of CO_2 reaction. Su et al. was the first to discover a high-performance Ni-N-Gr catalyst [10], as shown in Figure 3. Through the research of Ni-n bond, the researchers illustrated the possibility of its influence on the reduction selectivity of CO_2. Tan et al. made a research on the effect of nitrogen carbon coated nickel nanoparticles on promoting the efficiency and selectivity of electrocatalytic CO_2, and demonstrated that the nickel-based catalyst in this method can inhibit the generation of hydrogen, and reduce the adverse effect of the side reaction of hydrogen evolution on the reduction of CO_2 [11]. The Ni-Nx structure has obvious HER inhibition ability. The Ni-N_4-C catalyst shows nearly 100% CO selectivity in a wide potential range [12]. Because Ni-N_4-C catalyst has lower *COOH formation energy, it is superior in CO selections. Though nickel-based catalysts show great advantages in CO selectivity, because of the high generation energy of *COOH of Ni single atom the efficiency of activating CO_2 is low. It is necessary to make further study on other better coordination environment.

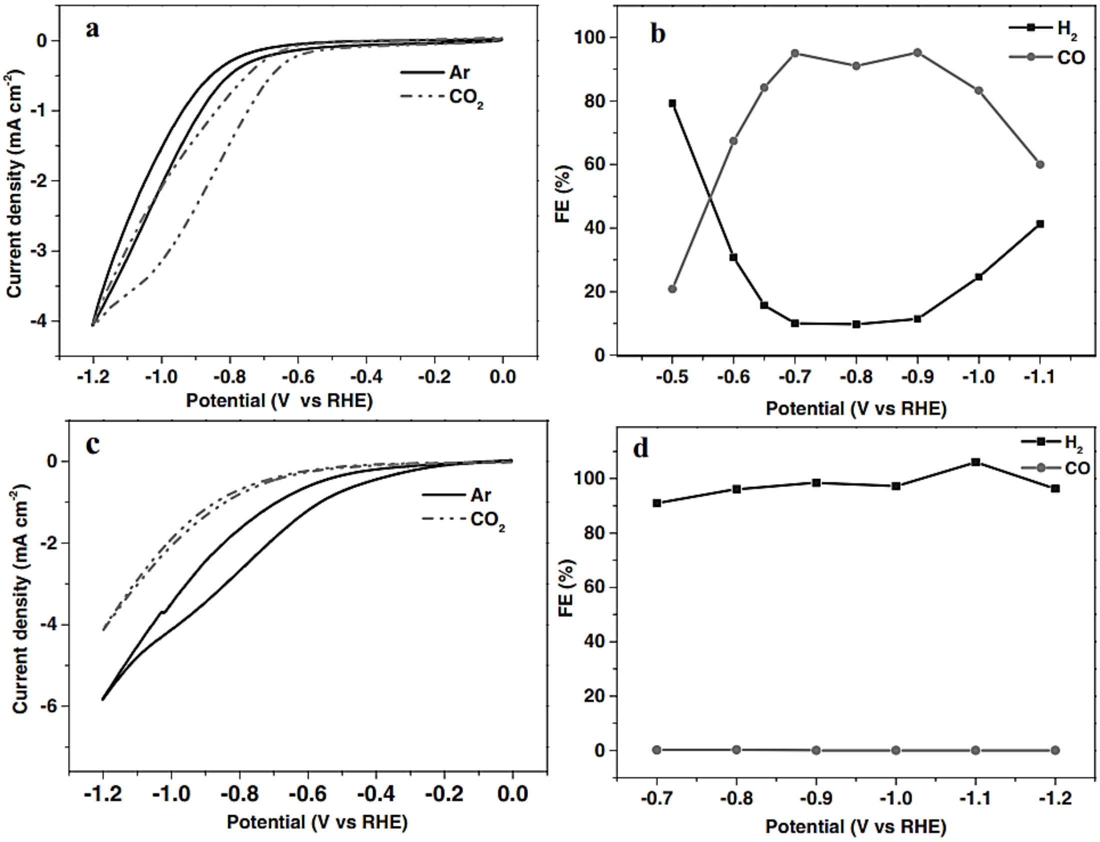

Figure 3. Electrochemical performance of the Ni-N-Gr catalyst [10]

3.3. Organic ligand catalysts

Electrocatalytic reduction of CO_2 is a promising technology for converting waste CO_2 into feedstock or synthetic fuel for chemical industry. It is difficult and important to develop catalysts with high activity and selective electrocatalytic reduction of CO_2. Now transition metal organic ligand catalyst has attracted much attention.

Porphyrin is a kind of macromolecular heterocyclic compound. In the metal nitrocarbon (MNC) molecular catalyst, porphyrin molecular catalyst is one of the better representatives. A porphyrin molecular catalyst (PMC) with metal atom m as active center (M/PMC, M=Fe, Os and Ru) was studied to electrocatalytic CO_2 reduction. It has been shown that the minimum limiting voltage is required to generate C1 product using Fe/PMC catalyst [13]. It has been shown that it is a promising method to hybridize D orbitals of transition metals with P orbitals of non-metallic atoms or to use materials such as metal carbides and nitrides. By exploring the adsorption energy and the corresponding reaction free energy of the intermediate in the electrocatalytic CO_2 reduction process catalyzed by the transition metal embedded porphyrin molecular catalysts (Rh/PMC and Ir/PMC), the correlation between the catalyst and the reaction was obtained, and the best path to form C1 product (Figure 4). By comparing the energy changes of Rh/PMC and Ir/PMC reactions, the limiting steps of C1 products formed by the two catalysts were obtained. The results show that the embedded transition metal affects the structure and catalytic activity of the intermediate of electrocatalytic CO_2 reduction. It was found that Rh/PMC was more effective in electrochemical reduction for CO_2 [13].

Polybipyridine ligands are defined as organic ligands with at least two pyridine units. They have extremely rich and diverse molecular structures and can also form a variety of coordination structures with transition metal ions. There are mainly o-phenanthroline, bipyridine, tripyridine and tetrabipyridine. Polybipyridine ligands can generally form stable complexes with transition metals through multiple coordination bonds. In this way, in addition to the metal center of the complex can receive and transfer electrons, the polybipyridine ligand can also accept electrons through ligand based redox reactions. Polybipyridine metal complexes have the following structural characteristics:

(1) Polybipyridine ligands can disperse the negative charge of metal complexes to a certain extent, and can form low valence active intermediates at relatively small overpotential. (2) The space structure and electronic structure of the catalyst can be adjusted by adding different substituents to the polypyridine ligand. (3) It can exist stably in acidic or alkaline water or organic solution for a long time. (4) A stable coordination structure is formed with the metal center through its own rigid structure and multiple coordination bonds. A complete identification and characterization of the catalysts for the electrocatalytic reduction of CO_2 with tetradentate polypyridine ruthenium complexes were carried out. As a result, polybipyridine metal complexes have been widely used to prepare different types of catalysts for electrocatalytic reduction of CO_2. For example, the activity and mechanism of the CO_2 electrocatalytic reduction reaction in CH_3CN were studied by electrochemical testing technology and model [14]. Under the optimal conditions, the catalytic effect of the complex is extremely excellent. The TOF max of the reduction of CO_2 to CO is 1084.1 s^{-1}, and the Faraday efficiency is 66%.

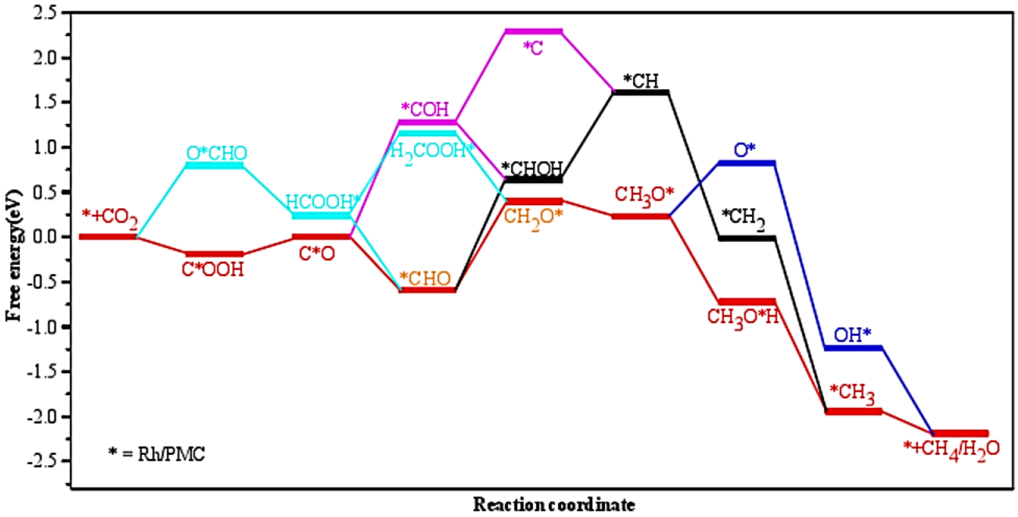

Figure 4. Potential energy diagrams of all possible pathways for electrocatalysis of CO_2 to CH_4 on the catalyst [13]

4. Conclusions

In this research, the application of different types of catalysts in electrocatalytic reduction of CO_2 was discussed, including MOFs, molybdenum-based catalysts, nickel-based catalysts and transition metal organic ligands. It is not difficult for us to find that transition metal materials have excellent electrochemical catalytic properties, which makes us have certain expectations in the field of CO_2 treatment. Electrocatalytic conversion of CO_2 also has unique advantages that other CO_2 resources do not have, such as mild reaction conditions, no secondary pollution to the environment, simple and easy equipment preparation and small volume occupied by the equipment. However, at present, the research in the field of electrocatalytic reduction of CO_2 is still at the theoretical stage, and various factors also restrict the commercialization of electrocatalytic technology. For example, there is no good solution to the large amount of electric energy required for electrocatalysis. If one day, the excess power in industrial power, such as the computer wasted in the high-voltage power transmission process, the power wasted in the transformer, and the power wasted in the unstable power supply voltage can be saved and transported to the electrocatalytic device with good media, then the electrocatalytic reduction of CO_2 will have the conditions for large-scale commercialization, and the electrocatalytic reduction of CO_2 also has a good market application prospect.

References

[1] GUO Zhen-liang, BIAN Xiao-lü, DU Yu-bo, ZHANG Wen-chao, YAO Ding-ding, YANG Hai-ping. Recent advances in integrated carbon dioxide capture and methanation technology [J]. Journal of Fuel Chemistry and Technology, 2022, 51: 1-2.

[2] Gottle, A. J., Koper, M. T. M. Proton-coupled electron transfer in the electrocatalysis of CO2 reduction: prediction of sequential vs. concerted pathways using DFT [J]. Chemical Science, 2017, 8(1): 458-465.

[3] Liu, A. et al. Current progress in electrocatalytic carbon dioxide reduction to fuels on heterogeneous catalysts [J]. J. Mater. Chem. A, 2020, 8: 3541-3562.

[4] Geim A K, Novoselov K S. The rise of graphene [J]. Nature Materials, 2007, 6(3): 183-191.

[5] Yaghi O M, Li G, Li H. Selective binding and removal of guests in a microporons metal-organic framework [J]. Nature, 1995, 378: 703-706.

[6] Li H L, Eddaoudi M M, O’Keeffe M, et al. Design and Synthesis of an exceptionally stable and highly porous metal organic framework [J]. Nature, 1999, 402: 276-279.

[7] Taiguo Chen. Synthesis and Studies of Two Dimensional Transition Metal-based Materials for Electrocatalytic Carbon Dioxide Reduction [D]. Northwest Normal University, 2021.

[8] Rehman Adeela, Nazir Ghazanfar, Rhee Kyong Yop, Park Soo-Jin. Electrocatalytic and photocatalytic sustainable conversion of carbon dioxide to value-added chemicals: State-of-the-art progress, challenges, and future directions [J]. Journal of Environmental Chemical Engineering, 2022, 10(5): 108219.

[9] Jinhui Hao, Weidong Shi. Transition metal (Mo, Fe, Co, and Ni)-based catalysts for electrochemical CO2 reduction [J]. Chinese Journal of Catalysis. 2018, 7: 1157-1166.

[10] Su P, Iwase K, Nakanishi S, Hashimoto K, Kamiya K. Nickel-Nitrogen-Modified Graphene: An Efficient Electrocatalyst for the Reduction of Carbon Dioxide to Carbon Monoxide. Small. 2016, 12(44): 6083-6089.

[11] Dongxing Tan, et al. Nitrogen-carbon layer coated nickel nanoparticles for efficient electrocatalytic reduction of carbon dioxide [J]. Nano Research, 2019, 12(5): 1167-1172.

[12] Shujin Shen, Cheng Han, Bing Wang, et al. Transition Metal Single-Atom Electrocatalysts for CO2 Reduction to CO [J]. Progress in Chemistry. 2022, 3: 533-546.

[13] Han Yu. Theoretical Study on Electrocatalytic CO2 Reduction with Transition Metal Atoms Embedded in Porphyrin Molecular Catalyst [D]. Shanxi Normal University, 2021.

[14] Huang Yan. Research on the catalytic reduction of polybipyridine transition metal complexes (CO2RR and HER) [D]. Guangzhou University, 2022.