

# A review of catalytic reduction of carbon dioxide

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**Abstract.** Carbon dioxide (CO<sub>2</sub>) generated from the consumption of fossil fuels is one of the main factors contributing to the greenhouse effect. How to mitigate the greenhouse effect and reduce the extraction and consumption of fossil fuels has become an issue worthy of study. In recent years, a technology for the catalytic reduction of CO<sub>2</sub> to fossil fuels and chemicals has attracted a great deal of attention by providing a new way to solve this problem. This paper reviews the basic principles of three fundamental catalytic CO<sub>2</sub> reduction, photocatalysis, electrocatalysis and thermocatalysis, and two advanced catalytic modes, thermocatalysis and photoelectrocatalysis, derived from these three modes, as well as their advantages and disadvantages. In addition, the challenges that the catalytic reduction of CO<sub>2</sub> is currently facing are also discussed. Although this technology has made significant progress over the decades, it is still in its preliminary stage with some shortcomings and there is a long way to go before it can be applied in reality.

**Keywords:** Carbon dioxide, Catalysis, Reduction

## 1. Introduction

Fossil fuels are the main fuels currently used in countries around the world. Since the twentieth century, the demand for fossil fuels has been increasing exponentially as a result of large-scale industrial development. As a non-renewable resource, the natural formation of fossil fuels takes hundreds or even tens of millions of years. Therefore, a potential energy crisis has developed. At the same time, the extensive use of fossil fuels has led to massive emissions of carbon dioxide (CO<sub>2</sub>).

CO<sub>2</sub>, one of the major greenhouse gases, has been contributing to global warming at a high rate since the last century. Since CO<sub>2</sub> is a stable gas that normally does not break down easily in nature, reducing CO<sub>2</sub> emissions by using clean energy or absorbing CO<sub>2</sub> by planting trees are considered to be the most effective mitigation measures. However, these methods do not provide a significant solution to the growing shortage of fossil fuels, which currently cannot be completely replaced by clean energy.

In recent years, a way of capturing CO<sub>2</sub> and converting it into hydrocarbons has become a big hit in the scientific field due to its ability to provide hydrocarbon fuels with high-added value while mitigating the greenhouse effect. This process involves catalytic cracking of CO<sub>2</sub>, reducing it to other forms of carbon, and recombining it with other atoms. Although the field is currently being extensively researched due to the huge production value that the method can bring, it is still not currently being put to practical use on a large scale. It is therefore necessary to summarize the technology to better understand the current state of the field.

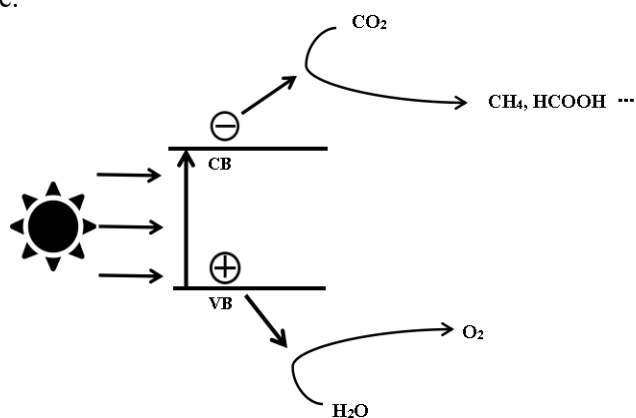
This review begins with a description of the fundamentals of the current catalytic reduction methods commonly used for CO<sub>2</sub>, outlines the reaction energy barriers that are overcome in these catalytic processes, highlights and compares some of the merits and drawbacks of catalytic reduction as well as the bottlenecks that have been overcome currently by science. Also presented are the difficulties encountered in the field and speculates on the potential factors that have prevented the technology from being widely used. This paper can serve as a reference for subsequent research in this area.

## 2. Basic principle of CO<sub>2</sub> reduction

C has a valence of +4 in CO<sub>2</sub> and is in the highest oxidation state, which means that it can be reduced to other lower valence states by gaining electrons and combining with carbon and hydrogen elements to form hydrocarbons. However, CO<sub>2</sub> is a very stable molecule and the dissociation energy required to break the C=O bond is much higher than that of the C-C and C-H bonds, which means that it takes a higher amount of energy to drive the conversion of CO<sub>2</sub> to completion. In addition, for organic reactions, there is a certain amount of uncontrollability in the final product. The intervention of catalysis is necessary in order to reduce the activation energy required for the conversion process in order to reduce the cost and increase the possibility of obtaining specific products. Currently, the catalytic reactions that have received more attention in this field are photocatalysis, thermocatalysis and electrocatalysis.

### 2.1. Photocatalysts

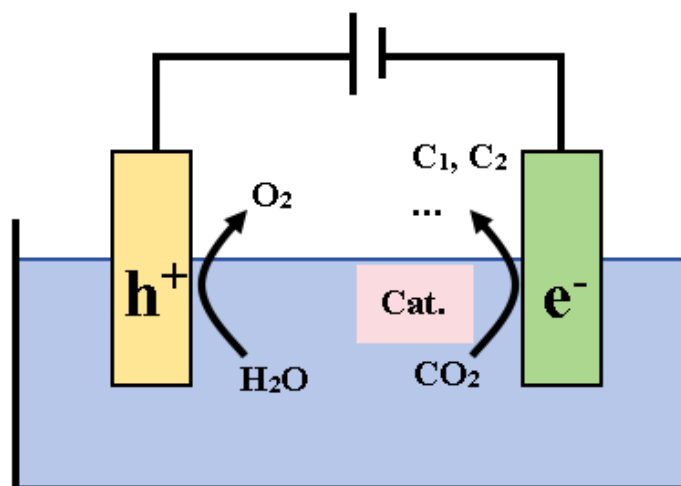
In photocatalysis, the entire redox is only driven by solar energy. Semiconductor materials in which the band gap of electron transition can be satisfied by the energy of light, are therefore used as photocatalysts throughout the reaction [1]. When they absorb light energy not less than the band gap, the valence electrons in the covalent bond break free from the covalent bond and jump from the valence band (VB) to the conduction band (CB) to become free electrons, and at the same time leave holes in the covalent bond. These photogenerated electron-hole pairs are able to migrate to the catalyst surface and participate in the ensuing reaction [2]. Photoelectrons are able to reduce the C<sup>+4</sup> of CO<sub>2</sub> molecules adsorbed on the surface of the catalyst to a lower valence state, resulting in C<sub>1</sub> products such as CH<sub>4</sub>, HCOOH, or CH<sub>4</sub>OH, which are more value-added and able to be used as precursors for other organics. H<sub>2</sub>O, on the other hand, is oxidised by holes, which serves the purpose of maintaining the reduction properties of the catalyst (Fig. 1). In its initial use, photocatalysis was carried out by exposing the photocatalyst particles to a solvent and the energy was exclusively derived from light energy, which led to the low efficiency and a certain degree of uncontrollability of this catalysis [3]. Since the photogenerated electron-hole pairs are all present in the same catalyst, the electrons in the excited state may return to the position of the holes, resulting in energy loss. In addition, both the reduction and oxidation reactions take place on the surface of the same catalyst, which can lead to the mixing of compounds and failure to obtain an efficient end product, and the reduction product of CO<sub>2</sub> is likely to be reoxidized by the hole.



**Figure 1.** Basic principle of photocatalytic reduction of CO<sub>2</sub>

## 2.2. Electrocatalysis

Electrochemistry reduces  $\text{CO}_2$  by means of an electrolytic cell, where  $\text{CO}_2$  is reduced to a lower valence state by electrons released from an electrode. However, since the reduction process takes place in an electrolyte solution, the solubility of  $\text{CO}_2$  in water is low and may ionise substances other than  $\text{CO}_2$ . Therefore, specific catalysts, transition metal complexes, are usually added to the solution to adsorb  $\text{CO}_2$  and reduce the activation energy [4] (Fig. 2). Compared to Photocatalysts, electrocatalytic reduction provides electrons by applying an electric field, which has the advantages of high efficiency and controllability. In addition, the reduced  $\text{CO}_2$  product may still be adsorbed on the catalyst surface, allowing the reaction to continue to produce  $\text{C}_2$  products such as  $\text{CH}_3\text{COOH}$  [5]. However, this poses another problem, as during the ionisation process, the electrons are concentrated near the anode and are not uniformly diffused in the solution or dispersed on the surface of the catalyst, which can result in some of the  $\text{CO}_2$  products having been formed into  $\text{C}_2$  products by coupling through the  $\text{C}_1$  intermediates, while some remain  $\text{C}_1$  products. Furthermore, as the reaction proceeds, some of the properties of the electrolyte solution such as the pH, also change. Even if these changes are small in magnitude, they still affect the reaction pathway and the final product [6]. This means that the final product in the cell may be a mixture of dozens of compounds.



**Figure 2.** Basic principle of electrocatalytic reduction of  $\text{CO}_2$

## 2.3. Thermocatalysis

The thermocatalytic reduction of  $\text{CO}_2$  is usually a hydrogenation process. Unlike Photocatalysts and Electrocatalysis, thermal catalysis is usually carried out in a fluidised bed and does not require a solution as a medium. Throughout the process  $\text{CO}_2$  and  $\text{H}_2$  flow through the catalyst bed, which is subject to temperature and pressure, overcoming the activation energy, accelerating the reaction rate and generating products. Since the process of reduction takes place more in the catalyst pores than on the surface, the diameter of the catalyst pores can be adjusted to regulate the product selectivity, obtaining specific products and prompting specific reactions by varying the temperature and air pressure [7]. However, some of the reactions are limited by thermodynamic equilibrium, e.g., the enthalpy change for the reaction of  $\text{CO}_2$  and  $\text{H}_2$  to form  $\text{HCOOH}$  is greater than 0 [8]. These exothermic reactions are difficult to carry out under heated conditions, thus limiting the products that can be obtained. In addition, thermal catalysis usually needs to be carried out between about  $250\text{ }^\circ\text{C}$  and  $500\text{ }^\circ\text{C}$ , which may consume a lot of energy and deactivate the catalyst at high temperatures [8].

## 3. Advanced catalytic reduction

Photocatalysis, electrocatalysis and thermocatalysis, as three fundamental  $\text{CO}_2$  reduction methods, have attracted extensive interest from the scientific community. Based on some of the advantages and

disadvantages of these three single catalytic reduction methods, the combination of multiple catalytic methods to achieve complementary advantages and disadvantages has been developed. In this section, photothermal catalysis and photoelectrocatalysis, two popular new catalytic methods, are introduced.

### 3.1. Photothermal catalysis

Photothermal catalysis, as a way to combine photocatalysis and thermal catalysis, does not a simple superposition of effects, but makes the two catalytic modes promote and coordinate each other. The provision of thermal energy significantly improves the efficiency of the catalyst in absorbing light energy and accelerates the photogenerated electron-hole pairs production. At the same time, due to the thermal effect, the electrons in the excited state are less likely to return to the ground state, which promotes the separation of photogenerated electron-holes, and solves the problem of low photocatalytic efficiency and the phenomenon of energy waste [9]. On the other hand, the intervention of light can significantly lower the high temperature and high pressure conditions required for thermocatalytic reduction as a way to alleviate the problem of high energy consumption. In addition, light energy can cause changes in the structure of the active sites of catalysis, thus promoting different reactions and adjusting product selectivity [10].

Currently, there exist four main modes in photothermal catalysis. Thermal-assisted photocatalysis driven by photogenerated electron-hole drive with thermal energy assistance and photo-assisted thermocatalysis driven by thermal energy with light assistance are simpler in terms of the mechanism. Photo-driven thermocatalysis converts collected light energy into thermal energy for catalysis [11]. Photothermal co-catalysis is more complex, usually using nanocomposites with both thermal and photocatalytic activity as catalysts, driven by two kinds of energy at the same time to obtain higher catalytic activity than the above three.

Although these four photothermal catalytic modes have shown a qualitative leap in efficiency and energy saving compared to single photocatalysis or thermocatalysis. It is worth noting, however, that the problem of the catalysts easily collapsing at high temperatures and being clogged by carbon leading to deactivation of the active sites, which occurs in thermocatalysis, has not yet been solved.

### 3.2. Photoelectrocatalysis

Compared to photothermal catalysis, photoelectrocatalysis does not have as many different modes. Photoelectrocatalysis is the combination of photogenerated electron-hole pairs in a photocatalytic system with an applied electric field in an electrocatalytic system, which is often referred to as a photoelectrochemical (PEC) cell system. In photoelectrocatalysis, the photocatalyst acts as an electrode to absorb light energy and generate electrons, and the photogenerated electrons and holes separate and the electrons move towards the surface of the electrode by the external electric field migration, which substantially improves the reduction efficiency and effectively alleviates some of the problems arising in single photocatalysis [12]. And the risk of the reduction products being re-oxidised can be avoided by using a proton exchange membrane. Compared with electrocatalysis, the intervention of solar energy can significantly decrease the required energy input.

However, photoelectrocatalysis also suffers from some of the problems inherited from electrocatalysis. Firstly, the problem of low product selectivity is still unresolved and the reduction products are still affected by the variation of the parameters of the electrolyte solution. Although it has been investigated that the external electric field on the surface can affect the electron density on the surface of the photoelectrode, thus dynamically affecting the active sites of the catalysts and controlling the products, the investigation of this mechanism is not yet mature, and more research is needed to see how to arrive at the control of the product selectivity through the regulation of the electric field [13].

## 4. Conclusion

In recent years, the need for energy sources such as fossil fuels has risen steeply in recent years as the population has continued to rise, contributing to an increase in the concentration of CO<sub>2</sub> in the atmosphere, leading to the greenhouse effect. In this context, catalytic reduction of CO<sub>2</sub> is undoubtedly

an attractive technology that can provide hydrocarbons and other chemicals with high-added value while mitigating the greenhouse effect.

Photocatalysis, electrocatalysis and thermocatalysis have been widely studied as three typical methods for catalytic reduction of CO<sub>2</sub>. Based on these three approaches, various catalytic modes have been combined to form new catalytic modes to take advantage of their respective advantages. Photothermal catalysis and photoelectrocatalysis as two new catalytic modes have made great progress. In addition to the reaction mode, the catalysts have also experienced dramatic changes, which are not discussed in this paper.

However, at present, the exploration of this technology is still at an early stage and the catalytic reduction process is still subject to some uncertainties. Some typical challenges are as follows: (1) firstly, although the efficiency of the new catalytic technology for CO<sub>2</sub> reduction has been greatly improved, the benefits it can bring are not proportional to the cost, which is still unable to satisfy the practical applications; (2) secondly, whether it is photothermal catalysis or photoelectrocatalysis, the catalyst's active point position is easy to be changed or even deactivated during the catalytic process, which results in the catalytic efficiency becoming lower; (3) lastly, the poor product selectivity, which is related to the dynamic changes of the catalyst and the environment during the reaction process, cannot meet the market demand. For the future development of CO<sub>2</sub> catalytic reduction, more efforts need to be invested to overcome these challenges.

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