Recent Progress in Using Photocatalytic Carbon Dioxide Reduction Technology to Compound Methane

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Abstract: With the development of modernization process, Massive combustion of fossil fuels not only causes heavy load of carbon dioxide emission in the air, but also causes the worry about the exhausted of future energy resource. By using reduction of carbon dioxide can solve both these problems. Of the various methods used for reducing carbon dioxide, photocatalytic carbon dioxide reduction is more environmentally friendly. In this article, the author begins by outlining the functions and difficulty points of carbon dioxide to methane reduction, then introduce the characteristics introduce how the photocatalytic reduction of CO2 to synthesize CH4 works.Moreover, certain characteristics and more recent developments in the field of photocatalysts of reducing CO2 into CH4, such as TiO2 based photocatalysts, vanadium based photocatalysts and Tungsten based photocatalytic materials and their doping, co-doping, surface modification or nano-structure technology will be presented.The author of this paper additionally concludes with some potential directions for photocatalyst development.

1 INTRODUCTION

With ongoing technological advancements and the accelerating pace of industrialization, the widespread utilization of fossil fuels has become a reality. However, this rapid depletion results in a significant surge of carbon dioxide in the atmosphere. The absence of effective measures to control carbon dioxide emissions will lead to a tripling of these emissions by 2050 compared to 1990. The steady rise in global carbon dioxide emissions will severely impact Earth's temperature over the next few decades, potentially causing the thawing of Arctic permafrost and releasing an unknown quantity of carbon dioxide. Although global carbon emission efficiency has improved, the absolute levels of emissions have not significantly decreased. Current environmental energy sources and technologies have not yet reached a level sufficient to mitigate the intensity of carbon dioxide emissions. Additionally, concerns are mounting regarding the potential depletion of fossil fuels in the future, by their extensive use.

Therefore, to address the greenhouse effect and air pollution stemming from the extensive emissions of greenhouse gases like carbon dioxide, and to seek sustainable and innovative eco-friendly energy sources, researchers have begun exploring the efficient utilization of green energies such as solar, wind, and hydrogen. Carbon dioxide reduction technology offers a novel strategy to tackle the emission issue of greenhouse gases like carbon dioxide, which involves tackling the source of emissions proactively. Additionally, CO2 has been converted into other valuable products by this technology, including methane and other fuels, thereby reclaiming resources. Given that methane yields a significant amount of heat through combustion reactions, the synthesis of methane via carbon dioxide reduction technology represents a more efficacious method for fuel production.

Carbon dioxide is a non-combustible gas with the chemical formula CO2. The optimal solvent for carbon dioxide is organic liquid. Gaseous carbon dioxide has stable chemical properties under conventional conditions, therefore it cannot directly undergo decomposition and redox reactions. Therefore, in most cases, the reaction of carbon dioxide needs to be carried out under high temperature or catalyst conditions. For example, under high temperature conditions, carbon dioxide reacts with carbon to produce carbon monoxide; Under the presence of copper zinc catalysts, carbon

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dioxide reacts with hydrogen to produce products such as methanol and water.

The carbon dioxide reduction reaction is an uphill reaction, which means that additional energy and catalyst are required for reduction. This reaction can be classified based on the source of energy. Common carbon dioxide reduction technologies include thermal catalysis, electrocatalysis, and photocatalysis. Thermal catalytic technology has high efficiency and large output, but high temperature and energy are required, and has poor environmental protection. Electrocatalysis and photocatalytic technology can adapt at room temperature and normal pressure, and have good environmental friendliness. Electrocatalytic technology requires electrical energy support, which may result in energy loss and increased costs. Photocatalytic technology directly utilizes sunlight for catalysis, but is affected by the diurnal periodicity of sunlight. In addition, there are also some hybrid reduction technologies, such as photothermal catalysis, microbial photoelectrochemical catalysis, and photosynthesis.

2 THE REACTION MECHANISMS

One way to think of the technology used in photocatalytic carbon dioxide reduction is as a man-made version of photosynthesis. In essence, light energy is transformed into chemical energy via the procedure of photocatalytic reduction of carbon dioxide, which permits carbon dioxide to undertake processes of decomposition or synthesis with other substances. The earliest research on the use of light for carbon dioxide reduction originated from Halmann. Initially, p-GaP photocatalysts were used to reduce carbon dioxide to produce methanol. Later, photocatalysts based on titanium dioxide, zinc oxide, tungsten, vanadium, silicon carbide, etc. gradually emerged, and the mechanism of carbon dioxide photoreduction was gradually determined. The reduction products were also gradually enriched, such as methane, formic acid, formaldehyde, etc.

The mechanism of photocatalytic carbon dioxide reduction originates from the electron hole pairs generated by semiconductor materials under illumination conditions. By successfully transforming light energy into chemical power, this process facilitates the synthesis reaction with other molecules or the breakdown of carbon dioxide. When the illumination energy exceeds the semiconductor bandgap, electrons are excited by light energy and move from valence band to conduction band, leaving holes. Photo-generated charge carriers relocated to the exterior of the catalyst, but recombination also occurs. Photo-generated electrons have strong reducibility and can react with CO2 and H2O to form hydrocarbons. Types of catalyst affects the specific reduction path (Tang et al, 2021).

However, if the transition rate is lower than the pace at which photo-generated carriers recombine, the reaction is difficult to proceed. In addition, the reactions between photo generated holes, photo generated electrons, catalysts, and the influence of surrounding medium can easily lead to photo corrosion of photocatalysts. To prevent occurrence of photo corrosion, as well as decrease the rate at which photo-generated carriers recombine, the number of photo-generated holes and photo-generated electrons needs to be matched as much as possible. In terms of thermodynamics, top potential of valence band and conduction band bottom potential of semiconductor materials need to be between the oxidation reaction potential of water and reduction reaction potential of CO2. In terms of dynamics, it is required that semiconductor materials have good ability to generate electron hole pairs, as well as sufficient sites on surface of photocatalysts to react with CO2 (Tang et al, 2021).

The large Gibbs free energy of carbon dioxide makes it difficult to produce methane and methanol under photoreduction circumstances; however, the reaction can be made easier by using light energy. The oxidation of H2O, which produces oxygen, electrons, and hydrogen ions, is the first step of the reduction reaction of CO2 to make CH4. CO2 then combines with hydrogen ions and electrons to produce methane and water. This process can be thought of as a series of reactions involving carbon dioxide and water, which produce methane and oxygen.

The reaction equation for the oxidation reaction of water is:$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, in which the oxidation-reduction potential is 0.82V vs. NHE. The reaction equation for the reduction reaction of carbon dioxide is: $CO_2 + 4H^+ + 4e^- \rightarrow CH_4 + 2H_2O$, in this reaction, the oxidation-reduction potential is -0.24V vs. NHE. Overall, the equation for the reaction is that the required Gibbs free energy for this reaction is -51.75 Kcal/mol.

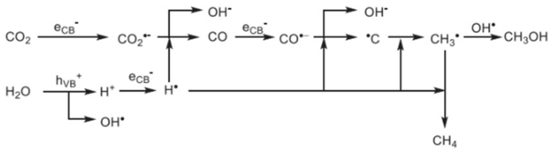

Figure 1. The reaction mechanism of reduction procedures (Copyright 2016, Elsevier)

A reaction pathway for the reduction reaction of CO2 to produce CH3OH or CH4 is depicted in the above image. As we can see from the image, H2O undergoes oxidation at the hole, producing hydroxyl groups and hydrogen ions. Following the reduction of carbon dioxide, the hydrogen ions react to form hydroxyl groups and CO. They eventually react with hydrogen or hydroxyl atoms to generate methane or methanol after going through a number of similar processes.

3 CATALYTIC PATHWAY

Photocatalysts are generally semiconductors that can activate chemical properties through light radiation and promote the occurrence of redox reactions. If photosynthesis is used as an analogy, chlorophyll can be seen as a photocatalyst for photosynthesis. The definition of photocatalyst includes photosensitization, which is the process in which the photochemical quantity changes due to the absorption of radiation by photosensitizer molecules.

The catalyst field for photocatalytic carbon dioxide reduction is generally divided into titanium dioxide based series photocatalytic materials, V-based series photocatalytic materials, W-based series photocatalytic materials, carbon nitride based series photocatalytic materials, and other materials. Among them, the catalysts that can efficiently synthesize methane through carbon dioxide reduction are titanium dioxide based series photocatalytic materials, V-based series photocatalytic materials, and W-based series photocatalytic materials (Tang et al, 2021). This article will mainly introduce some research progress on the three catalytic materials mentioned above.

3.1 Titanium Dioxide Based Photocatalysts

The basic principle of titanium dioxide based catalysts is similar to that of photocatalysis mentioned earlier. Titanium dioxide is a semiconductor material that, when exposed to a certain intensity of light, causes the separation of hole and electron carriers. Compared with general conductive materials, titanium dioxide carriers are more difficult to composite. The photo induced holes on the surface of titanium dioxide have strong oxidizing properties, which can oxidize donor molecules, while electrons on the conduction band of titanium dioxide can be used in reduction of receptor molecules.

Titanium dioxide, as a catalyst, has the characteristics of good safety, low cost, and high stability. There are three crystal forms of titanium dioxide in nature: brookite, rutile, and anatase. Of these three crystal forms, anatase or a mixed anatase and rutile crystal structure performs relatively well. In particular, the mixed anatase and rutile crystal form performs exceptionally well in converting carbon dioxide to produce methane and methanol. However, in order to separate holes from electron carriers, a wavelength of light less than 388nm is required, and this range of light is near-ultraviolet light. Therefore, titanium dioxide may face harsh usage conditions during the catalytic process (Tang et al, 2021).

To address the above issues, researchers mainly focus on changing the structure and state of titanium dioxide. By using the above methods, the efficiency of titanium dioxide as a catalyst can be improved, and the applicability of titanium dioxide can be expanded. Now, researchers have attempted various techniques, such as doping, co doping, surface modification, etc., to broaden the photon absorption range of TiO2 and reduce recombination effect of electrons and holes. For example, by doping elements such as iron, cobalt, nickel, manganese, vanadium, and nitrogen into titanium dioxide, the maximum frequency of photons absorbed by TiO2 can be increased to the range of visible light (Abdullah et al, 2017). Akple et al. (2015) conducted N doping and surface fluorination modification on TiO2. On the one hand, nitrogen doping reduced the requirement for light energy absorption, and on the other hand, the fluorine ions generated by surface fluorination modification became an intermediary for surface charge separation. Additionally, surface heterojunctions enhanced electron hole separation. They found that the titanium dioxide catalyst after surface modification and N doping had better activity under visible light conditions. In addition, the efficiency of methane generation can be effectively improved by transforming the structure of titanium dioxide into sponge or titanium dioxide hollow ball structure, while the nanotube structured titanium dioxide formed by solvothermal method, sol gel method, direct oxidation method, deposition and other methods, supplemented by Pt as a cocatalyst, can effectively select methane products (Tang et al, 2021).

3.2 Vanadium Based Photocatalysts

Vanadium, as a transition element, has a lower 3d energy band and is therefore considered a promising synthetic element for visible light catalytic materials. Therefore, vanadium based photocatalytic materials have better application prospects in visible light photocatalytic carbon dioxide reduction. Although vanadium oxide is not an ideal option for reducing carbon dioxide due to its conduction band characteristics, vanadates such as ZnV2O4, InVO4, ZnV2O6, exhibit good activity in carbon dioxide reduction (Tang et al, 2021).

Tahir et al. (2019) synthesized graded 3D microspheres, which not only exhibited good stability and photoactivity under visible light conditions, but also successfully achieved selective reduction of carbon monoxide, methane, and methanol.

Du et al. (2022) prepared vanadates such as copper vanadate, nickel vanadate, chromium vanadate, and zinc vanadate, and tested and compared their catalytic activities. Finally, it was found that nickel vanadate had the best catalytic activity, while copper vanadate was unable to catalyze carbon dioxide reduction technology due to its conduction band properties. This can to some extent verify the Tanabe hypothesis, which suggests that the properties of vanadates as catalysts may mainly come from the properties of their cations.

Tantalum nitride doped with vanadium was developed by Nguyen et al. (2017) in order to the reduction reaction of CO2. Methane, CO, and other products were effectively produced under visible light conditions by reducing carbon dioxide. It was determined by comparison that tantalum nitride doped with vanadium exhibits greater photocatalytic activity.

According to Lu et al. (2014), titanium dioxide nanotube arrays doped with vanadium nitrogen perform better at catalyzing the shift between CO2 to CH4 due to the efficient separation of electrons and holes that occurs after doping.

Le Chi et al. (2019) prepared and compared the performance of TaON and vanadium doped TaON in photocatalytic production of methane, hydrogen, oxygen and other products from carbon dioxide. After research, it was found that due to vanadium doping, vanadium doped TaON has a smaller bandgap energy, which increases catalyst activity. Researchers also prepared 1.5V-TaON materials, which have good efficiency in reducing carbon dioxide to produce methane. The above experiments and research cases demonstrate that vanadium doping is beneficial for improve activity of catalysts, and vanadates as catalysts for photocatalytic generation of methane from CO2 also have certain development prospects.

3.3 Tungsten Based Photocatalytic Materials

The first photocatalytic compounds based on tungsten were created in 1979. For the first time, Inoue (Inoue et al, 1979)used elements like tungsten oxide and titanium dioxide in 1979 to successfully reduce carbon dioxide aqueous solutions to fuels like methane and carbon monoxide.

Tungsten based photocatalytic materials mainly include tungstate salts (such as MnWO4) and tungsten oxide materials.

When tungsten oxide is used as a photocatalytic material, the commonly used forms of tungsten oxide include: WO3, W18O49, WO3·0.33H2O, and other forms (Yang et al, 2021). For block WO3 materials, due to their higher conduction band potential compared to the oxidation-reduction reaction of CO2 to produce CH4 (greater than -0.24V vs NHE), block WO3 materials are unable to reduce carbon dioxide to produce methane. However, by preparing WO3 ultra-thin nanosheets, the conduction band potential of WO3 can be reduced, allowing it to be used for catalyzing the reduction of CO2 to compound CH4 (Tang et al, 2021). In contrast to using W18O49 alone as a catalyst to catalyze the generation of methane from carbon dioxide, using W18O49 as a co catalyst has a better effect. For example, catalyzing with Cu2O, carbon nitride, Cu and other catalysts can increase the ability of carbon dioxide reduction to produce methane (Bhavani et al, 2023).

After the study by Jiang et al. (2020), it was found that W18O49 can help increase the selectivity of methane during carbon dioxide reduction catalysis on {1, 1, 1} of Cu2O. WO3·0.33H2O material has been proven to have promising prospects in photocatalytic materials due to its excellent ability to conduct electrons and protons. Doping WO3·0.33H2O can further enhance its catalytic performance (Wang et al, 2019).

For tungstate catalysts, materials such as bismuth tungstate, copper tungstate, and zinc tungstate are used to catalyze reduction reaction. This type of material has the characteristics of low cost and high stability. However, for some tungstate catalysts, the potential of their valence and conduction bands is not a good option for catalyzing the reduction of CO2 to CH4, such as MnWO4. Its conduction band position prevents direct catalysis, and before it can be utilized for carbon dioxide reduction, it frequently needs to undergo a number of additional treatments. Even if some tungstate salts are capable of catalytic processes, doping treatment can greatly enhance their performance.

4 CONCLUSIONS

To summarize, photocatalytic carbon dioxide reduction technology uses light-induced electron hole pairs produced by semiconductors to finish the carbon dioxide reduction process. Methane, carbon monoxide, methanol, and other fuels with high value can all be produced in large quantities using photocatalytic carbon dioxide reduction technology. The mechanism of photocatalytic carbon dioxide reduction to compound methane and various catalysts that can be used for this process are introduced in this article along with the photocatalytic reduction of CO2 to CH4 as well as its catalyst conditions (i.e. meeting the top potential of valence band conduction band bottom potential between oxidation reaction potential of H2O and the reduction reaction potential of CO2). Regarding photocatalytic carbon dioxide reduction catalysts, future research directions will mainly focus on the following points:

(1) By doping, co doping and other means, make the catalyst have a wider range of applications and better activity and efficiency;

(2) By changing the structure of the catalyst, such as constructing nanostructures, improve the performance of the catalyst;

(3)Research and develop new catalysts, such as organic compounds and organic complexes.

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