Chapter 13

CARBON DIOXIDE: CAPTURE AND UTILIZATION

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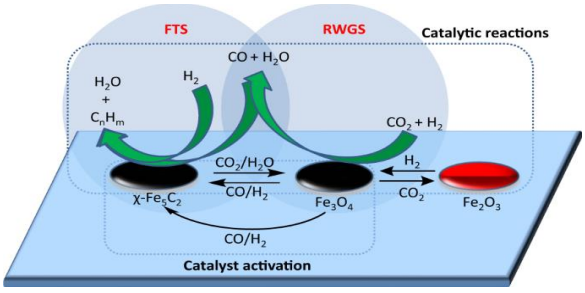
INTRODUCTION

Carbon dioxide is an important atmospheric constituent on the earth and plays an important role in many processes such as photosynthesis and respiration. To attain and maintain environmental stability and sustainability, the amount of carbon dioxide produced and consumed in the atmosphere should be balanced. Unfortunately, human activities such as burning of fossil fuels, transportation, industrial manufacture, deforestation and other human activities become a major cause for the enhancement of the amount of carbon dioxide in atmosphere drastically. Such activities if uncontrolled will significantly disrupt the carbon cycle on earth. Fossil fuels and biomass are the most common feedstock for the production of liquid fuels. Burning of these feedstock results in increase in carbon dioxide emission into atmosphere, hence it is necessary to develop strategies for upgrading this gas into useful products. With the rapid increase the carbon dioxide concentration in atmosphere, growing attention has received on global green house gas effect which causing climate change and rising sea levels. Among strategies for controlling carbon dioxide emission, the conversion of carbon dioxide into valuable chemicals has been recognized as the most long term and economic technology of utilizing carbon dioxide since it enable to produce high energy density carbon fuels.

In this chapter, different strategies for conversion of carbon dioxide in to valuable fuels were summarized and discussed with detailed comments of advantages and disadvantages.

METHODS FOR THE CONVERSION OF CO_2 IN TO FUELS

1. Catalytic Reduction of CO_2



Synthesis of liquid fuel using CO_2 and H_2 is promising for the sustainability of mankind. The reported technologies usually proceed via CO intermediate, which needs high temperature, and tend to cause low selectivity. Direct hydrogenation of CO_2 to liquid fuel, not via CO, is a challenging issue. The reaction could proceed at 200 °C, which is much lower than those reported so far. Hydrogenation of CO_2 to liquid hydrocarbons usually proceeds through tandem catalysis of reverse water gas shift (RWGS) reaction to produce CO, and

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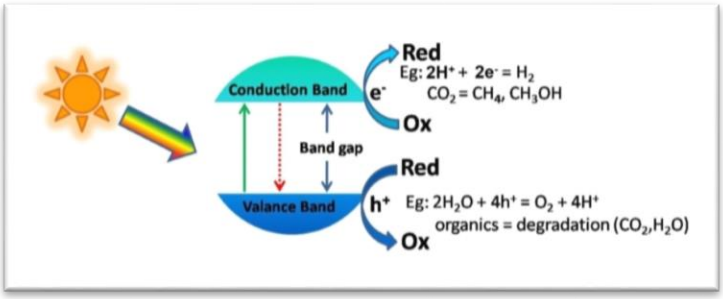
subsequent CO hydrogenation to hydrocarbons via Fischer–Tropsch synthesis (FTS).RWGS reaction is endothermic and needs a higher temperature, whereas FTS reaction is exothermic and is thermodynamically favoured at a lower temperature. There are two ways to convert CO_2 to liquid hydrocarbons; an indirect route, which converts CO_2 to CO or methanol and subsequently into liquid hydrocarbons, or the direct CO_2 hydrogenation route, which is usually described as a combination of the reduction of CO_2 to CO *via* the reverse water gas shift (RWGS) reaction and the subsequent hydrogenation of CO to long-chain hydrocarbons via Fischer-Tropsch synthesis. The key to advancing this process is to search for a highly efficient inexpensive catalyst, which can preferentially synthesise the target hydrocarbon range of interest. Iron-based catalysts, widely used in both the RWGS and FTS reactions, are typically prepared by chemical co-precipitation routes, which unfortunately consume significant amounts of water.

2. Photocatalysis

Solar energy is as an ideal energy source to replace traditional fossil fuels because it is an abundant, cheap, clean, and sustainable energy source. Therefore, the use of photocatalysts for solar-driven fuels from CO_2 is a very attractive approach. Similar to natural photosynthesis, electron–hole pairs are generated when the photocatalysts are exposed to solar light. The photogenerated electrons induce CO_2 to undergo a redox reaction that results in hydrocarbon formation.

There are three crucial procedures during the photocatalytic conversion of CO_2: Absorption of sunlight; Charge separation and transfer; and Catalytic reduction of CO_2 and oxidation of H_2O.



Each procedure during the conversion of CO_2 is closely related with the photocatalysts. Until now, the photocatalysts were mainly from semiconductor materials which are abundant on earth and easy to obtain. The integration of photocatalysts with metal–organic frameworks (MOFs) has been demonstrated to offer more adsorptive sites for CO_2 uptake because of their extreme larger surface area and microporous structure, resulting in remarkable improvement in CO_2 conversion. Integration of photocatalysts with metal–organic frameworks has been are provide more adsorptive sites for CO_2 uptake because of their extreme larger surface area and micro porous structure, resulting in remarkable improvement in CO_2 conversion.

Two dimensional (2D) nanosheets are particularly promising in improving charge separation because the photo generated electrons and holes will move to the interface with shorter distances.

3. Electrocatalysis

The electrocatalytic conversion of CO_2 to valuable chemicals is an attractive solution for reducing atmospheric CO_2 and storing energy. Using an external electric field as an energy source and water as the proton donor, various catalysts are applied to catalyze the reduction of CO_2.The electrocatalytic conversion is a higher cost-effective method because water replacing H_2 is used as the proton donor. Electrocatalytic CO_2 reduction has attracted great attention due to its mild operating conditions (normal temperature and pressure),

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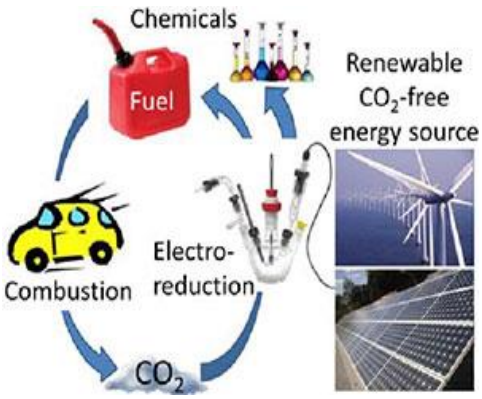
controllable reaction process conditions and reaction rate, recyclable catalyst and electrolyte, high energy utilization, simple equipment, and achievable conversion efficiency. In the past few years, researchers have explored electrocatalytic reduction of CO_2 using different electrode materials, such as metals transition metal oxides , transition metal chalcogenides , metal-free 2D materials ,metal–organic frameworks (MOFs), and various reduction products including CO, methane, formic acid, ethanol, and other compounds were obtained.

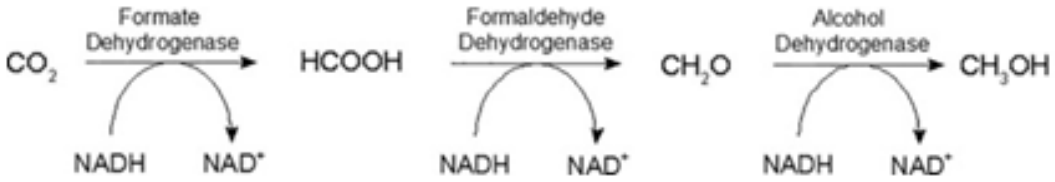
One of the factors that influence electrochemical reduction is the catalyst selection; therefore a catalyst that has a high catalytic activity and has selectivity towards methanol formation is required. Copper-based catalysts have been widely used in the electrochemical reduction of CO_2 to methanol; other metal catalysts have also been widely studied in recent years, including platinum catalysts as noble metals. Generally, electrochemical reduction is mostly carried out on bulk electrodes in electrolyte solutions, but it was found that limitations on mass transport and low solubility of CO_2 in electrolytes.



4. Enzyme Coupled to Photocatalysis

The reduction of CO_2 via biocatalytic processes received particular attention because of their special substrate and product selectivity as well as high conversion efficiency. Enzymes are biocatalysts renowned for their high efficiency and selectivity. In living cells, different enzymes often work together or in a specific order to catalyze multi-step biochemical reactions, playing crucial roles in the synthesis of natural products and metabolism. It is obvious that the research has presented an increasing tendency, especially in the recent 10 years, suggesting more and more attention was paid to the biocatalytic conversion of CO_2.

In general, to reduce CO_2 to methanol three enzymes, formate dehydrogenase (FateDH), formaldehyde dehydrogenase (FaldDH) and alcohol dehydrogenase (ADH), are required. In addition NADH is used as sacrificial coenzyme for the hydrogen and electron transfer. This means that for each reduction step one NADH molecule is irreversibly oxidized to NAD+ as depicted in the figure.



The photosynthesis that occurs in green plants and certain bacteria converts solar energy into chemical energy that can be well utilized by organisms and, at the same time, absorbs carbon dioxide and produces oxygen to maintain the carbon–oxygen cycle on the earth. This inspired people to explore the intrinsic mechanism of the photosynthesis process and to construct artificial analogues via bio mimetic mythologies for alternative sustainable energy carriers instead of traditional fossil fuels. In particular, photoreaction coupled with enzymes provides a highly efficient, specific, and energy saving strategy for CO2 conversion and has attracted special attention in recent years.

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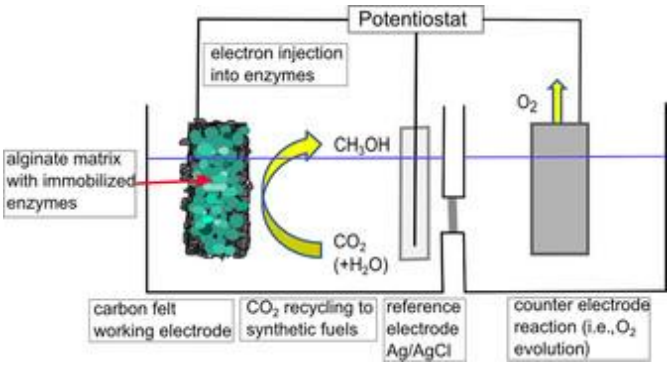
Generally, enzymes are easily affected by the reaction environment, making the enzyme electrode unstable. For example, the enzyme cannot perform its maximum activity at a non-optimal pH solution. For the stability and reusability of the enzyme, appropriate fixation methods can be adopted.



CONCLUSIONS

This chapter summarizes the different methods for the conversion of carbon dioxide in to fuels and valuable feed stocks. Catalytic hydrogenations, electromicrobial, electrochemical, photo electrochemical are various methods used for the conversion. Catalyst is a major component in all these methods. There are several routes for CO_2 reduction by H_2. CO production by RWGS can be used in downstream FT and MeOH synthesis, direct MeOH synthesis offers a liquid product with many application and finally CO_2. FT produces olefins and alkanes that can be used directly as fuels. Currently there is no preferred route for CO_2 hydrogenation by H_2 because the specific application ultimately dictates which route is the most attractive. Electrochemical methods are mainly attractive and effective because of superior in high efficiency, easy operation and various reaction pathways. Recent studies have reported the benefits of catalyst for CO_2 reduction and more researches will be carried out to improve its efficiency, develop new catalyst and reduce overpotential problem. The major obstacles are finding stable and low cost catalyst. Photoelectrochemical methods are preferred as it uses the easily available solar energy. There is a bright future in the reduction of carbon dioxide into valuable fuels. Cheap catalysts are developing and various researches are still going on in this field.

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