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Preview of CO_2 utilization in converting to methanol process

Sizhuo Chen

Department of Chemical Engineering, University College London, London, United Kingdom, WC1E 6B

sizhuo.chen.20@ucl.ac.uk

Abstract. Carbon dioxide, a greenhouse gas, has contributed to environmental issues on the planet in the past few years. Thus, it would be helpful to mitigate the impact that caused by carbon footprint, which is trying to reduce the carbon dioxide emission to the atmosphere and utilize it to generate green products for usage. It has been reported that CO_2 reduction could be converted to a valuable fuel source and thus it could be a potential solution to mitigate the impact of CO_2 . In this paper, it illustrates three underlying approaches which are conventional heterogeneous catalysis, photocatalysis and electrochemical, and flaws existed inCO_2 converted to CH_3OH production. Approach mechanism, principles and barriers are included in the following with detailed product selectivity/yield comparison between different catalysts under various conditions. Studies on different approaches have made substantial information focusing on various aspects and recommending the appropriate catalyst for the technique under the specific scenario. Finally, the overview of the research aims to provide feedback on progress made in CH_3OH production from CO_2 in a large scale along with a summary regarding the future expectations on the research of the methanol conversion approaches developed.

Keywords: methanol, conventional heterogonous catalysis, photocatalysis, electrochemical conversion

1. Introduction

CO_2 emissions to the atmosphere from daily activities could be attributed to the greenhouse gases which caused severe environmental problems such as global warming, air pollution and sea acidic levels to the society. Most activities have CO2 participated or used up; therefore, this gas is over-released to the environment and causes problems [1]. Global warming is one of the most common issues and is caused by the excessive greenhouse gas emissions to the air. In figure 1 it demonstrates the several pathways of carbon dioxide utilization, such as chemicals raw material, combustion, transportation, storage etc. CO_2 plays a vital role in almost every side for humans from household necessary appliance usage to agriculture and industry. In the past fifty years, the average temperature has been raised in a range of 1.1℃ which is due to the emissions of CO_2 and other greenhouse gases [2]. Meanwhile, carbon dioxide is the most emitted gas in all greenhouse gases and based on statistical data, the global atmospheric CO_2 concentration has increased sharply from 356.56 ppm in 1979 to 419.51 ppm in 2023 with a relative change is 25% [2, 3]. These numbers confirmed that carbon dioxide is accumulated now which is the primary reason the global warming by the temperature rising continuously in fifty years. Thus, finding a technical way to regulate the negative sides caused by carbon dioxide is urgently needed.

It is suggested that using carbon dioxide to produce valuable chemical fuels is a win-win situation which may not only reduce the carbon footprint in general but also generate clean source energy to use as recycled. The CO_2 conversion could be facilitated under hydrogenation catalysis to produce methanol as a fuel commercially. The catalysis conversion pathways include conventional thermocatalytic, photocatalysis and electrochemical conversion. Currently, the hydrogeneration approach has been implemented on a big scale but for other aspects like photo and electrochemical, it has not been upgraded to quantity production yet. In the following text, a brief description of different CO_2 conversion pathways will be explained accompanied by catalysts selected based on the availability during conversion.

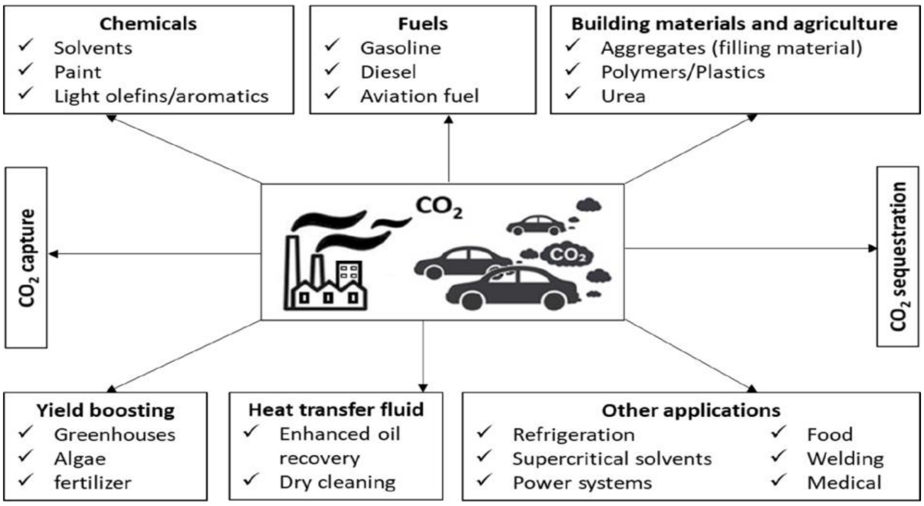

Figure 1. Classification of CO_2 utilisation pathways in life [1].

2. Conventional Heterogeneous Catalysis

In methanol production, carbon dioxide could be consumed and thus mitigate its impact on the environment. Three approaches are introduced in the following aim to transfer the undesired greenhouse gas into a worthy fuel product, by implementing strategies which are hydrogenation with catalysts, photocatalysis and electrochemical conversion.

CO_2 is a thermodynamically stable molecule with a high degree of oxidation and little reactivity. It is necessary to get over a thermodynamic barrier to activate CO_2. Hence, a metal catalyst is beneficial to convert CO_2 and copper-based catalyst is mostly used as the metal catalyst. Hydrogenation using metal catalysts is one of the traditional and major approaches in industry to produce methanol by reacting carbon dioxide. Heterogeneous hydrogenation of CO_2 is already well-established on the industrial scale under certain harsh conditions [4]. The processes involve methane reforming in addition to adding hydrogen, CO and CO_2 into reactions with certain catalysts in order to produce methanol as a clean fuel. The key components and routes under hydrogenation are shown from equations 1 to 5 [5]:

$$CH_4 + H_2O \quad \leftrightarrow \quad CO + 3H_2 \tag{1}$$

$$CH_4 + 2H_2O \quad \leftrightarrow \quad CO_2 + 4H_2 \tag{2}$$

$$CO_2 + 3H_2 \quad \leftrightarrow \quad CH_3OH + 3H_2O \tag{3}$$

$$CO + H_2O \quad \leftrightarrow \quad CO_2 + H_2 \tag{4}$$

$$CO_2 + 2H_2 \quad \leftrightarrow \quad CH_3OH \tag{5}$$

In this methanol synthesis pathway, firstly in equation (1) & (2) methane reacts with water to generate both CO and CO_2. Equation (3) & (4) indicate that after hydrogen takes participation with the CO_2, CO_2 is adsorbed onto the interface of the catalysts and then breaking the highest C-O energy bond (750

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kJ/mol) [6]. Next, hydrogen molecules may participate with CO_2 to form intermediates. Finally, as shown in equation (5), the intermediates turn out to be methanol eventually as the desired product and water produced as the by-product [7]. The reaction conditions could be strict since the optimal operating temperature is around 230 ℃ to 270 ℃ [8] and the ideal pressure range is between 5 Mpa to 10 Mpa [8] to achieve the best yield results.

Scientifically, it has been proven that these meal-based catalysts may do a crucial job on methanol synthesis by improving the stability and activating the overall chemical conversion. Figure 2 is the schematic that illustrates the primary working mechanism of Cu-based catalysts participating with other oxidized additives under hydrogenation reaction to formulate methanol successfully [9]. The interface between the copper-based catalysts and those embedded on an oxidized material surface potentially being the region formate intermediates. After hydrogen comes, the reaction takes place, and the reactor should be used to fully accommodate the entire process to be done. The general order of this thermal catalysis process would be CO_2 activation, hydrogenation, format and methanol generation [10]. The conversion result indicates that the selectivity for Cu- ZrO_2 at three experimental temperatures 433 K, 453 K and 473 K are 0.6-100%, 1.2-85.5% and 2.2%-83.0% which are relatively higher than the Cu-ZnO/ ZrO_2 catalyst [11]. Therefore, the oxide ZrO_2 phase enables a good performance of CO_2 absorption for the intermediate completion than Cu-ZnO interaction with a bad selectivity yield.

Overall, conventional catalytic hydrogenation seems to be a well-implemented choice to synthesize methanol. However, the stability of this process is limited, and selectivity is also a constraint. Thus, the following two approaches would be better replacements under certain situations.

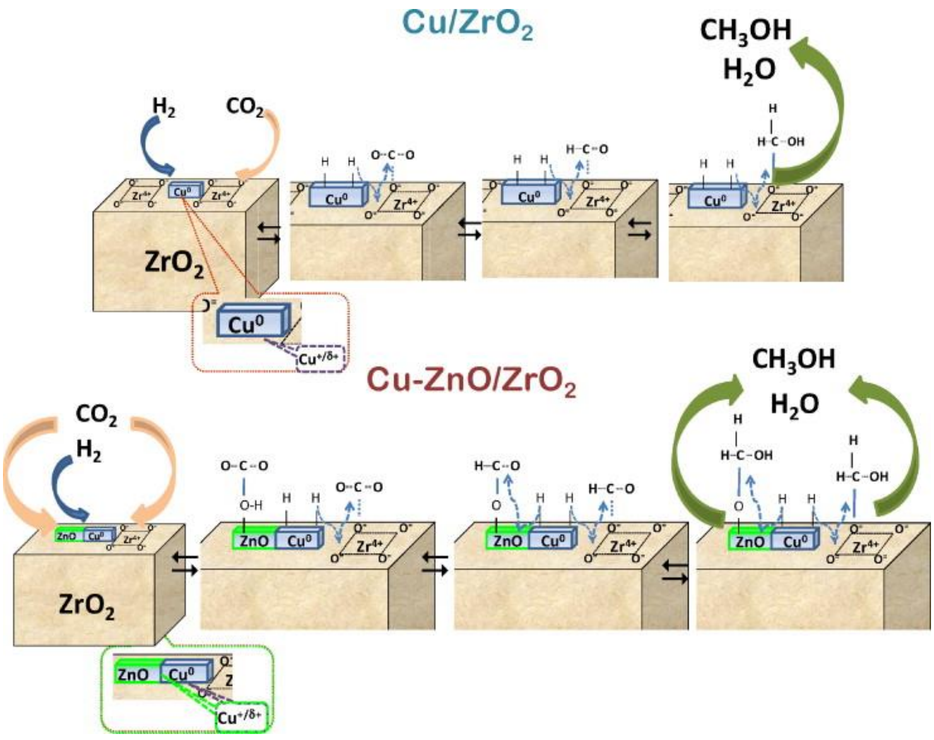

Figure 2. Reaction mechanism for CO2 hydrogenation to methanol catalyzed by $Cu - ZnO/ ZrO_2$ [11]

3. Photocatalysis Conversion

Although the conventional approaches may be effective and practical in transferring carbon dioxide to methanol, they still have several drawbacks such as unsustainability, environmental issues in terms of pollution and over-weight energy consumption [12]. Regarding the quest for sustainable solutions to mitigate the effects of climate change and focusing on the green chemistry aspect, a promising shift to advanced methods of converting CO_2 is underway.

The emergence of novel and innovative approaches not only offers a path to reducing greenhouse gas emissions but also creates the potential to revolutionise the way to produce methanol sustainably on an industrial scale, instead of the traditional way of hydrogenation. The new frontier conversions developed as photocatalytic catalytic conversion and electrochemical methodology.

Photocatalysis is a groundbreaking technique that transfers carbon dioxide into methanol by providing an alternative way of CO_2 utilisation apart from hydrogenation. The primary principle of photocatalysis is capturing solar energy and applying different photocatalysts which may convert CO_2 to methanol [13]. At its core, photocatalysis utilizes various materials to speed up in terms of photocatalysts implemented for the conversion from solar to chemical [14]. A typical photocatalyst is Titanium Oxide (TiO_2) particles which are used in photocatalysis from CO_2 reduction to methanol synthesis which yields 2330 $\mu mol g^{-1} h^{-1}$ methanol [15]. It is commonly used due to its property with high stability and activation to convert, good operating performance and low cost [16]. Even though TiO_2 provides the basic potential to achieve photoreduction to produce methanol, the efficiency is still limited [17]. Experimental results shown that pure TiO_2 has a lower efficiency compared with incorporating Ag with TiO_2, which the 1.5 wt% Ag/TiO_2 catalyst is the most effective. The amount of CH_3OH produced using pure TiO_2 and 1.5 wt% Ag/TiO_2 after 6 hrs photocatalysis of is 14.9 $\mu mol/g$ and 25.2 $\mu mol/g$ respectively, which proves the 1.5wt% Ag/TiO_2 has a better performance on photoreduction of carbon dioxide [18]. Hence, doping is a technique that enhances efficiency rather than a pure metal photocatalyst.

Indeed, several limitations could be cons caused by less effective production in photocatalysis conversion, it still possibly handles carbon dioxide under the natural condition. Apart from photocatalysis, electrochemical approach alternatively offers another pathway to convert methanol, in a flexible and handy manner.

4. Electrochemical Conversion

The electrochemical aspect of converting CO_2 into methanol is an innovative and environmentally friendly solution that aims to address the current problem of GHG (Green House Gases). Electrochemical CO_2 conversion has not been applied on a big scale in the industry but has proven successful in labs. This approach transfers CO_2 using electricity as the source of energy [19] and allows hydrogenation to methanol. It follows as an electrochemical cell is employed, at the anode side of the cell water is oxidized for electrochemical reduction and at the cathode side, carbon dioxide is reduced as an intermediate product for further conversion. The electrochemical reaction routine for CO_2 transferring to methanol is shown from equations (6) to (8) [20]:

$$\text{Cathode: } CO_2 + 6H^+ + 6e^- \rightleftharpoons CH_3OH + H_2O \tag{6}$$

$$\text{Anode: } 3H_2O \rightleftharpoons 1.5O_2 + 6H^+ + 6e^- \tag{7}$$

$$\text{Overall: } CO_2 + 2H_2O \rightleftharpoons CH_3OH + 1.5O_2 \tag{8}$$

Additionally, the intermediate product could be converted with methanol under an electrochemical catalytic hydrogenation process [21]. Solid metal electrocatalysts and other alloys are beneficial under ambient conditions since their high selectivity and energy efficiency when formulating methanol. It is reported that the faradaic efficiencies for methanol (CH_3OH) production between electrodes in acidic solution are 1.1% for bulk Cu, 4.9% for nanostructures and 16% for Cu-Au alloys [20, 22]. As a result, alloying copper with other metals could improve the performance of CO_2 conversion to CH_3OH.

This process offers the advantage of utilizing renewable source electricity for the reduction of CO_2 and subsequent methanol production. The electrocatalysts selected may enhance the overall efficiency and yield higher methanol products. In terms of the long run, this methodology could be deployed to a large scale in industry and other disciplines.

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5. Conclusion

In conclusion, carbon dioxide (CO_2) conversion to methanol (CH_3OH) could be an environmentally viable approach which brings a sustainable prospect. Even though this conversion process still faces several challenges and limitations yet, its potential could be fully achieved and progressed to the next stage later. Three methodologies discussed each reflects own characteristics on carbon dioxide reduction, including conventional heterogenous catalysis, photocatalysis and electrochemical conversion. Catalysts are required in the conversion process to sort out the selectivity problem to produce the amount of methanol expected. Nevertheless, the main challenges in the different catalysis are the high operating conditions in temperature, pressure and the catalysts selected. Ideal catalysts with high efficiency could be classified as metal alloyed type, doped metal catalyst in electrochemical and photocatalysis conversion. For the electrochemical approach, it is recommended since its flexibility and a high selectivity in CO_2 reduction. The material type of electrocatalysts should be compared and selected well to avoid the loss of faradaic efficiency. Similarly, photocatalysis is also innovative and attractive by using renewable sources of energy like solar power. In future's perspective, the conversions needed to scale up in both photocatalysis and electrochemical in order to be implemented massively in industry. The efficiency and product yield results are still limited so far, as the incompleteness in technologies and lack of cost. Lastly, research efforts and attention should be put in this specific area to possibly increase the CO_2 reduction efficiency in the upcoming years.

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