Synthesis of ethanol, methanol and carboxylic acids using copper-based catalysts

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Abstract: Recently, organic synthesis using carbon dioxide (CO_2) has been actively studied for possible countermeasures against global warming caused by greenhouse gas emissions. The recycling and reuse of CO_2 can reduce the amount of CO_2 in the atmosphere and avoid further damage to the earth's ecological environment. For example, many kinds of methods are advanced to prepare useful chemicals from CO_2, where these useful chemicals include ethanol, methanol and carboxylic acid. The introduction of catalysts in CO_2-based chemical synthesis can speed up the reaction and also tune the product species. The transition metal complexes have become essential in those synthesis reactions. As catalysts, they have a broad prospect because it is cheap in price, vast in reserves and less harmful to the environment. This research summarizes the function of copper-based catalysts in synthesis of different compounds, such as ethanol, methanol and carboxylic acid. The use of these catalysts is expected to provide a new idea for subsequent CO_2-based organic synthesis.

Keywords: Copper-based Catalysts, Ethanol, Methanol, Carboxylic Acid.

1. Introduction

Since the second industrial revolution, there has been an increasing demand for fossil fuels to produce energy and chemicals for everyday use. For example, about 90% of the energy was produced globally in 2011 came from fossil fuels. In addition, oil will continue to be the main source of energy for years to come [1]. The world's growing population and the limited amount of fossil fuels and rapidly diminishing resources are both current problems. Another major problem facing the widespread use of fossil fuels is that during combustion or other oxidation processes they end up converting their carbon content into carbon dioxide (CO_2), thereby resulting in global warming. In addition, the increased levels of CO_2 in the air contribute significantly to global warming, which in turn leads to melting glaciers, rising sea levels, etc. All of these threaten the current state of human existence and development. For this reason, the removal of CO_2 has received increasing attention, and different removal methods or reuse approaches have been developed.

The conversion of CO_2 into useful chemicals or fuels by means of hydrogen plays a key role in environmental protection and new energy development. At present, the resource use of CO_2 has focused on the synthesis of simple small molecule compounds such as methanol, formic acid, methane and carbon monoxide (CO). However, C=O bonds need to be achieved activation and precise regulation of C-C coupling is difficult. The key scientific questions in this area are how to use effective catalysts and reaction processes to minimize CO and CH_4 products and promote the conversion of CO_2 to alcohols at lower temperatures, particularly to ethanol with its thermodynamic advantages, which can play a crucial role in controlling carbon emissions and developing new ways of finding energy. Methanol is an important organic chemical feedstock and a promising fuel for vehicles and fuel cells, so research on synthetic methanol has been of great importance internationally. Although methanol is currently synthesized industrially using synthesis gas ($H_2/CO/CO_2$), recent research has shown that methanol is produced by hydrogenation of CO_2 [2]. CO_2 is not only a major

contributor to the "greenhouse effect", but also a potential source of carbon, so scientists are now constantly researching effective methods of producing methanol from CO_2. For carboxylic acid products, finding the right carboxylation reagent plays a key role in the reaction, as do the most commonly used formatting reagents to meet the conditions required for multiple reactions to be put into use.

This research focuses on the process of research into the conversion of CO_2 into different chemicals, such as ethanol, methanol and carboxylic acids by using copper-based catalysts. Firstly, the efficient use of copper-based catalysts can provide a good basis for the real industrial use of such synthesis. Copper is widely used in low-pressure methanol synthesis because of its excellent properties, but is not widely used today in the production of ethanol and carboxylic acids. Although copper-based catalysts have shown outstanding catalytic performance for methanol synthesis from syngas, the obtained results are not satisfactory. Copper-based catalysts are structurally sensitive catalysts and small changes in preparation conditions, leading to large differences in catalytic activity. Therefore, tuning copper-based catalysts to excellent catalysts is a great challenge. Another important reason for using copper-based catalysts is that copper is relatively inexpensive and will be cheaper to manufacture as compared to other precious metals, so providing a convenience to putting them into use. With regard to the synthesis of methanol, this research focuses on the principles of methanol synthesis in the laboratory and some of its applications in everyday industry. For carboxylic acids synthesis, this research will describe the mechanism of carboxylic acid preparation with copper-based catalysts, the role of copper-catalyzed organometallic reagents in the carboxylation process and the choice of a suitable solvent. All these conditions play an indispensable role for the efficient preparation of carboxylic acids.

2. Synthesis of ethanol

Ethanol is a more desirable product than methanol because it is an important chemical with a wide range of uses in different fields, such as acetic acid, beverages, flavors, dyes and fuels. Nowadays, the homogeneous catalytic synthesis of ethanol with CO_2 has grown tremendously. In the following section, we will focus on significant achievements in multiphase catalysis for the hydrogenation of CO_2 to ethanol. In the past, converting CO_2 to ethanol was dominated by homogeneous catalysts for efficient activation of CO_2 molecules and highly selective generation of ethanol. However, homogeneous catalysts are less stable, difficult to separate and require higher synthesis costs in industry. In response to the shortcomings of homogeneous catalysts, scientists have developed multiphase catalysts in recent years [3].

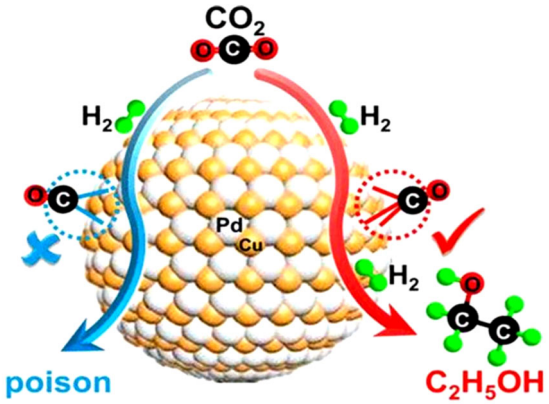


Figure 1. Pd_2Cu NPs/P25 catalyst for CO_2 hydrogenation to ethanol [4]

The thermal and mechanical stability of the prepared catalyst can be improved by using the support. In addition, the used support can be also used to facilitates the chemical stabilization. Scientists have conducted experimental studies on this [4]. At a temperature of 200 °C and a volume fraction of 3:1 (hydrogen:CO_2), the authors studied the prepared Pd_2Cu NPs on different support, including SiO_2,

CeO_2, Al_2O_3 and P25. The mechanism of the catalytic reaction is shown in Figure 1. The ethanol yields of Pd_2Cu NPs were 14.8, 16.2, 19.7 and 41.5 mmol/g/h, respectively. Based on the obtained experimental results, the P25 catalyst has a high ethanol yield depend on the charge transfer between Pd and Cu.

By adjusting the catalytic reaction temperature, the conversion rate and activation of CO_2 can be improved, which allows CO* as an intermediate to further generation of CHxO* that is an important precursor for the formation of ethanol. Since CO_2 is chemically stable and is mainly influenced by kinetics, reaction temperatures in the range of 200-350°C are generally favorable for a higher ethanol selectivity in the product. This was investigated by scientists over the Cs-$C_{0.8}F_{1.0}Z_{1.0}$ catalyst [5]. The ratio of hydrogen to CO_2 is three to one, the pressure is 5 MPa and the temperature varies between 260 °C and 330 °C over a period of three hours. The conversion of CO_2 was found to increase from 16.1% to 36.6% and the yield of ethanol increased. The authors also carried out another set of experiments in which they used Cu@Na-Beta catalysts by keeping the remaining conditions constant [6]. The results show that the increase in temperature increases the CO_2 conversion from 0.85% to 12.2%. In addition, when adjusting the catalytic temperature, the selectivity of ethanol was not the selectivity of ethanol (among the alcohols) remained at 100%. This demonstrates the good catalytic activity for the prepared Cu@Na-Beta catalyst.

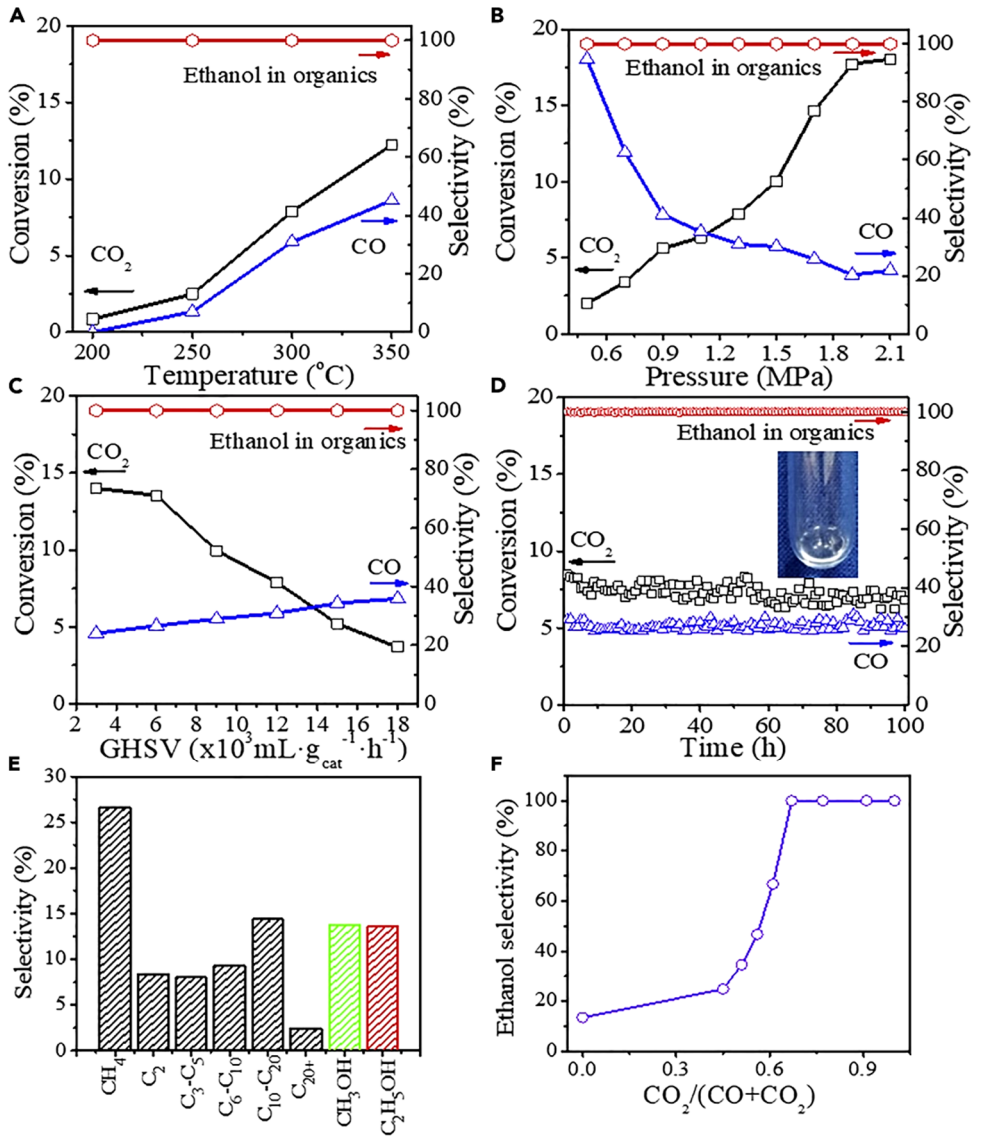


Figure 2. Catalytic performance of the prepared catalysts [6]

It was shown that the equilibrium conversion of CO2 at different temperatures and pressures is based on the thermodynamics of the compound. Figures 2 shows the obtained catalytic performance for the synthesized catalysts. When the catalytic reaction temperature was increased from 200 °C to 350 °C, the conversion of CO also increased gradually, from 0.85% to 12.2%. When the catalytic temperature reaches 250°C, CO is produced as a by-product. When the catalytic reaction temperature was further increased to 350 °C, the selectivity of CO increased to 45.2%. And the catalytic performance of the used catalyst can be affected by the pressure in experiment. When the catalytic temperature was kept constant (300 °C) and the pressure was increased from 0.5 to 2.1 MPa, the CO_2 conversion increased from 2.0% to 18%, while the CO selectivity decreased from 94.6% to 21%.

3. Synthesis of methanol

Methanol, as an industrial chemical, is very important. Their main use is in the preparation of formaldehyde or acetic acid chemicals, as a production feedstock. What's more, it can be used to make organic solvents. Currently, the global demand for methanol is about 32 million tons/year, according to the methanol research institute [7]. The world's first plant to use syngas to make methanol was built in 1923 by BASF. The plant uses zinc oxide/chromium oxide catalysts operating at 300 °C and 200 ATM which are temperature and pressure. This process is high pressure methanol synthesis. In modern times, the early methanol process has been improved. And in this era, the main use is the low-pressure process. At present, this process has been well developed, however, there are still many disputes about the reaction mechanism. The big question is whether methanol will be produced from CO or CO_2. Of course, the process still leaves much to be desired. First, the source of the mixed hydrogen is a difficult problem, but it can be solved by dry reforming (using CH_4) to produce hydrogen. This reaction is also going to consume CO_2. However, the syngas obtained by this method contains a large amount of CO, so it cannot be used for the synthesis of methanol. If you can find a way to leverage CO, then this solution makes sense. And in terms of environmental friendliness, especially cost, the technology is far from being commercialized. The preparation of methanol by adding hydrogen element to CO_2 through copper-based catalyst is mature in theory and can be commercialized in recent practice. After generations of efforts, this technology has been gradually perfected and applied. As its shortcomings are gradually improved, the technology will undoubtedly be better at tackling the environmental problems caused by CO_2.

In recent years, as human activities produce more and more CO_2, and this has led to a greater change in the human living environment. Data suggest that atmospheric CO_2 concentrations will continue to increase, with levels of CO_2 concentrations likely to increase twofold from 2018 to 2100, and with this, there will be an average temperature increase of 0.15 to 0.3 °C per decade [8]. These data, and the potential changes from the increased number of extreme events, many uncertainties may affect the biology of productive pests and will lead to biological losses in plant systems in the future. Increases in atmospheric CO_2 concentrations have the potential to alter pest biology in two aspects. The first is that an increase in CO_2 will raise surface temperatures, cause the occurrence of rain weather change, and change the temperature difference between day and night, as well as leading to more unpredictable extreme weather events. The second is that increased CO_2 concentrations will fertilize plants through photosynthesis. Certain higher plants rely on the C3 pathway for photosynthesis, which account for about 95% of plant species, will grow and reproduce faster, and these plants include a variety of weeds. From a pest biology perspective, changes in various environmental indices on a global scale may establish more pest species, increase dispersal, and exacerbate impacts. Therefore, the use of CO_2 to prepare methanol is an attractive way to solve the CO_2 problem.

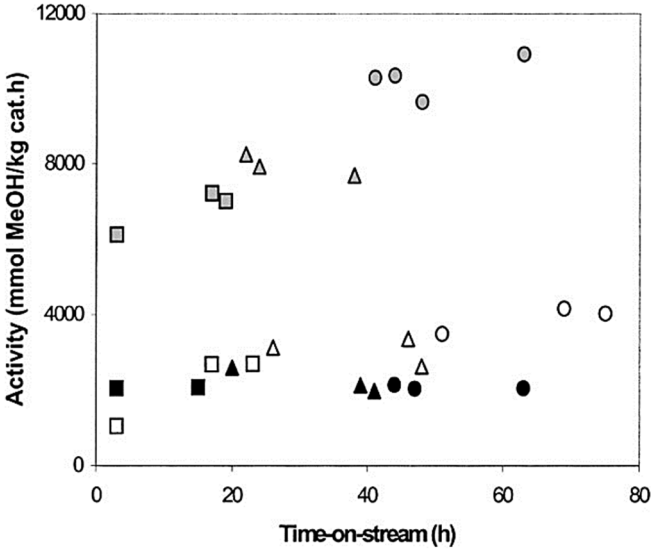


Figure 3. Methanol synthesis activity [9]

For example, methanol was prepared using CO_2 through a copper-based catalyst [9]. The experiment was carried out in a specific type of reactor called a fixed-bed continuous flow reactor where the temperature in the catalytic bed could be monitored at any time. The samples were reduced with H_2/He (10/90) mixture catalyst for 2 hours at 573 K and 2 MPa total pressure. The next step was to reduce the temperature to 523 K in pure H_2. Meanwhile, the prepared catalyst catalyzes the mixture of CO_2 and H_2 in a ratio of one to three. As can be seen from Figure 3, in the production of methanol, the catalyst Cu-Zn-Ga/SiO_2(HD) has the best effect. And it has good performance in activity, selectivity and stability. The relationship between the Ga/Cu ratio in the catalyst and the catalyst activity was further evaluated. When Ga/Cu>2.0, the catalyst activity revealed almost no difference. Nevertheless, when the Ga/Cu ratio was higher, the methanol yield increased. It can be found that gallium oxide is very important for the activity of the catalyst.

4. Carboxylation reactions

Direct carboxylation of grignard reagents and other organometallic reagents with CO_2 has been developed and widely used to prepare different organic chemicals. Researches on converting CO_2 into high value-added complex chemicals have attracted scientists' attention recent years. Among all the products, carboxylic acid is the most significant class and has a wide range of applications. Although there are many mature carboxylic acid synthesis techniques, using CO_2 as a carboxylation reagent is the most appropriate method to meet overall needs, due to its diversity, multifunctionality and accessibility, also the potential of forming new C-C bonds. For example, reactions of organometallic reagents such as organolithium with CO_2 are advanced, but the bad compatibility of functional groups restricts the application. Therefore, to improve the efficiency of converting CO_2 into carboxylic acids, it is more applicable to focus on carboxylation reactions that catalyzed by transition metals with milder organometallic reagents and simpler reaction conditions. This will made it possible to obtain lots of carboxylic acids and derivatives more easily.

From the perspective of structure, CO_2 can be considered as an electrophile. Carboxylic acid and its derivatives are obtained by attacking the center carbon with a nucleophile. Because of its thermodynamic and kinetic stability, only nucleophiles with large energy such as grignard reagents can easily react with CO_2 without applying a catalyst. However, these reagents are very reactive, which makes the reactions difficult to carry out. As result, transition metal-based catalysts are significant in carboxylation reactions that involving CO_2, which gives higher efficiency, wider range of substrates and better applicability. Reaction of magnesium metal with alkyl or alkenyl halides gives out grignard reagents, which are strongly nucleophilic and can react with different kinds of electrophiles, such as

CO_2 and some epoxides. When grignard reagents are added to CO_2 (mostly in the form of dry ice), carboxylate salts will be formed in the reaction. This is similar to that with aldehydes and ketones.

By studying the plasma diagnostics experiment that carried out by Wang and his co-workers, the synthesis of acid in plasma-driven CO_2 conversion over copper-based catalyst was showed [10]. They set the slit width to 20 μm and the grating of spectrometer to 300 g/mm, then the CO_2 plasma emission spectra were recorded under different conditions within the range of 200 to 1200 nm. The main product, acetic acid, was produced directly under mild conditions and noted as R-COOH. The effect of Cu-based catalyst and support on R-COOH formation were shown in Figure 4. Obviously, when the pure substrate is placed into the reactor, the effect of the substrate on the selectivity of acid compounds is not specified. However, it changes regularly after adding copper to the corresponding substrate, where the R-COOH selectivity increases.

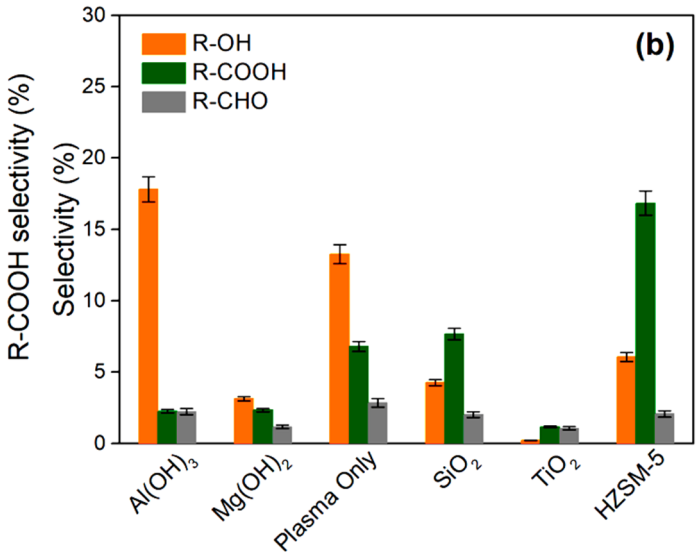


Figure 4. Analysis of plasma-catalytic conversion of CO_2 [10]

With the help of transition metal catalysts, CO_2 can be used in the reactions of C-C bond formation. Copper metal, which is abundant, environmentally friendly and inexpensive as catalysts for carboxylation using CO_2 has been investigated. The reactivities of organoborate, organoaluminium and organozirconium with CO_2 are not so high in the absence of transition metal catalysts, whereas copper metal is active enough to achieve those carboxylations. Generally, there are three key steps for copper-catalyzed carboxylation reaction: generating C-Cu species from substrate, inserting CO_2 into C-Cu bond and forming copper carboxylates and releasing the carboxylate and copper catalyst. According to density-functional theory calculation, C-Cu bond has the least barrier of insertion compared to other C-M bonds, this property hugely favors the insertion in the second step. With copper-based catalysts, carboxylations between C-H bonds and aryl iodides, aryl sodium sulfonates have been managed.

Due to the poor functional group tolerance of grignard reagents and other reagents, organoboron has been explored. As a milder organometallic reagent, ogranoboron shows better tolerance and moderate reactivity. Organoboron compounds are compounds containing B-C bonds, they are easy to prepare and have better stability, lower poisonousness and excellent ability of undergoing a variety of chemical transformations. Iwasawa and co-workers firstly presented one example of catalytic carboxylation of organoboron reagents with copper-based catalysts [11]. The combination of CuI, bisoxazoline and CsF enabled the carboxylation of aryl- and alkenyl-boronic esters with CO_2 in the atmosphere and gave the corresponding quantitative yields of the carboxylic acids produced. The results clearly show that copper catalyst has wide applicability and generality than other transition metals.

Alkanes will be produced if organometallic reagents react with water or any protic solvents, so everything must be dry during the whole reaction. The resulting reaction mixture will be used directly

in the next step, with no separation or isolation procedures in between. At present, ether (Et_2O) and tetrahydrofuran (THF) are two frequently used organic solvents. However, these typical solvents often have problems when applied to large-scale industrial processes. The main disadvantages of Et_2O are that it is flammable and narcotic, while THF forms explosive peroxides gradually and has difficulty with recovery due to its miscibility in water. According to recent reports, an alternative "green" solvent has emerged, which is the biomass-derived 2-methyltetrahydrofuran (2-methF). The 2-methF has a wider range of applications in organic chemistry that involving grignard reagents and other organometallic reagents. Changing solvents into more environmentally friendly alternatives also catches great attention, as it can make existing industrial processes more "sustainable" and less harmful to the earth.

5. Conclusions

In recent years, people have clearly felt from the body temperature that the annual temperature is very high. That said, the impact of CO_2 on the world's climate is already huge and making good use of it is an urgent topic. This research mainly introduces the synthesis of three common chemical substances, including ethanol, methanol and carboxylic acids, by using CO_2 and copper-based catalysts. For ethanol synthesis, having identified CHO* intermediates as the key to ethanol synthesis, further environmental design should reduce energy consumption and prevent the production of CH_4 and CO in the production process, where these two gases are harmful to the environment. In terms of research, more efficient conversion of ethanol to increase its yield is expected. On the industrial side, the catalyst is expected to have better activity, selectivity and stability, which can be used for subsequent recyclability analysis. For methanol synthesis, the research on the hydrogenation of CO_2 to methanol over copper-based catalysts has matured in theory and can be commercialized in recent practice. After several generations of efforts, this technology has been gradually perfected and applied. With the gradual improvement of their disadvantages, these technologies will no doubt better solve the environmental problems caused by CO_2. For the synthesis of carboxylic acids, there are also many areas where the technique can be improved. The use of carboxylation in industrial or synthetic chemistry is still not practical and limited to high-energy substrates. However, the carboxylic acids synthesis is limited by the development of organometallic chemistry and the lack of effective methods. The penultimate point is that the application of expensive reducing agents, such as hydro silanes and organometallic reagents, makes the cost prohibitive for widespread use. Finally, the synthesis of carboxylic acid technology needs more experiments and research to find more suitable energy sources.

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