Research on efficient methanol production from carbon dioxide driven by thermal catalytic technology

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Abstract. In the context of global carbon neutral strategy, the resource utilization of carbon dioxide (CO_2) has become a key pathway to achieve climate governance goals. In this study, we focus on the thermal catalytic-driven CO_2 methanol production technology and systematically elucidate its reaction mechanism and process characteristics. By comparing the domestic and international methanol preparation technology routes, it is found that coal-based syngas are the mainstream in China (e.g., Ruchi furnace and aerospace furnace technology), which is characterized by low feedstock cost but high energy consumption. Overseas countries mainly rely on natural gas reforming technology (e.g. SMR/ATR), which is eco-friendly but limited by natural gas resources. The industrialization of the current technology faces three core challenges, firstly, copper-based catalysts are easy to deactivate under high temperature and pressure, and multifunctional catalysts (e.g. rare earth doping, nanostructured MOFs derivatives) with both high activity and stability need to be developed. Secondly, the cost of CO_2 capture is high, and breakthroughs in efficient and low-consumption enrichment technologies (e.g., development of new adsorbent materials) are needed. Meanwhile, the harsh reaction conditions (200-300°C/50-100 atm) lead to high investment and energy consumption. Therefore, future research should focus on constructing CO_2/H_2 dual active site catalyst systems, exploring a new paradigm of low-temperature atmospheric pressure reaction, and developing a green process chain for integrated CCUS. This technological breakthrough will strongly promote the recycling of carbon resources and provide key technological support for the low-carbon transformation of the chemical industry.

1 Introduction

As global climate change intensifies, the international community is actively promoting carbon-neutral strategies to address environmental crises such as global warming and sea-level rise. According to the latest statistics, as of May 2024, 148 countries worldwide have formally committed themselves to achieving the goal of carbon neutrality. As one of the main components of greenhouse gases, carbon dioxide (CO_2) emission reduction and resource utilization have become a significant path to achieving the carbon-neutral goal. Studies and

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research have shown that CO_2 is not only an important raw material for the preparation of chemical products such as dimethyl carbonate, vinyl carbonate, propylene carbonate, etc., but also a carbon resource with great circular economic value. Among the many CO_2 conversion pathways, the catalytic conversion to alkanes and other basic chemical materials has attracted much attention, among which alcohol compounds, as multifunctional platform chemicals, have become a research focus due to their wide applications in solvents, plastics, rubber, fibers and other fields.

Thermal catalysis, as a traditional and well-established chemical conversion technology, shows unique advantages in the CO_2 alcohol production process. The reaction mechanism is mainly characterized by the thermodynamic breaking and reorganization of CO_2 molecules, which ultimately converts CO_2 molecules into the ideal alcohol products. In recent years, significant progress has been made in the field of catalytic technology. By means of catalyst composition improvement, structural modification and surface modification, researchers have significantly improved the selective adsorption and activation of alcohols in the catalytic system, and at the same time, effectively inhibited the occurrence of side reactions, thus realizing the preparation of alcohols with high selectivity and high yields. In addition, the systematic optimization of the reaction conditions also significantly enhances the conversion efficiency of the process. However, there are still many scientific problems and technical bottlenecks to be solved in order to successfully expand the technology from laboratory scale to industrialized production.

This paper lies in the systematic elaboration of the reaction mechanism and process characteristics of alcohol production technology under the thermal catalysis of CO_2, as well as the in-depth analysis of the structural properties and application value of alcohol products. This project discusses the main challenges in realizing the industrial application and provides the theoretical basis and practical guidance for promoting the further development of CO_2 thermal catalytic alcohol production technology.

2 Basic properties of methanol

2.1 Physical properties of methanol

Methanol, colorless transparent liquid, its molecular weight is 32.04 g/mol, density 0.791 g/cm^3 under standard conditions, a boiling point of methanol is 64.7℃, melting point is -97.6℃, so it is liquid at room temperature. It is highly volatile and is miscible with polar solvents such as water and ethanol and has good solubility. At the same time, the vapor of methanol is heavier than air and has strong permeability and diffusivity. In addition, its high-octane rating (RON 114) and low pollutant product characteristics make it an important option for clean fuels.

2.2 Chemical properties of methanol

Methanol (CH_3OH) has an abundance of chemical properties, mainly derived from the hydroxyl (-OH) and methyl ($-CH_3$) groups in its molecular structure. Methanol can undergo oxidation reactions, oxidizing to formaldehyde (CH_2O) under combustion conditions in limited oxygen, or further oxidizing to formic acid (HCOOH). And it can be burned under sufficient oxygen conditions to form carbon dioxide and water. Also, with the action of an acidic catalyst, it will generate ester compounds with carboxylic acid and undergo an esterification reaction. In addition, formaldehyde can also be dehydrated to produce dimethyl ether (CH_3OCH_3) or ethylene (C_2H_4) at high temperatures by acidic catalyst conditions. In the field of fuel cells, methanol, as an important hydrogen carrier, can provide hydrogen fuel by releasing hydrogen through reforming reactions. However, methanol is also toxic, as it can be metabolized in the body to produce toxic formic acid, which can lead to poisoning or even blindness or death.

2.3 Manufacture of methanol

2.3.1 Industrial processes

The industrial production of methanol relies mainly on the chemical reaction of syngas (a mixture of CO, CO_2 and H_2) in the presence of a catalyst. This process is usually carried out using copper-based catalysts (copper-zinc-aluminum (Cu-Zn-Al), one of the widely studied catalysts, in which copper serves as the main active ingredient, while zinc and aluminum act as co-catalysts, which are able to effectively improve the dispersion and stability of the catalyst [1]. (e.g., $Cu/ZnO/Al_2O_3$), and under high temperature and high-pressure conditions. In modern industry, the main feedstock for methanol production is natural gas or coal, which is steam-reformed (reforming) or partially oxidized to produce syngas. Subsequently, the syngas are compressed and purified and fed into a methanol synthesis reactor to complete the above reaction at 200-300°C and 50-100 atm. The advantage of this process is that it is a mature technology and can meet the high demand for methanol. However, the disadvantages are the high energy consumption and the need for strict temperature and pressure control. In addition, the presence of by-products (e.g., water and other hydrocarbons) may reduce the purity of the product, thus requiring additional separation and purification steps.

2.3.2 Laboratory methods

In the laboratory, methanol is prepared by a variety of methods, including formaldehyde reduction, methyl formate hydrolysis and partial oxidation of methane. Among them, formaldehyde reduction is one of the most commonly used methods. This method uses hydrogen to reduce formaldehyde to methanol, and another common method is methyl formate hydrolysis, which generates methanol by reacting methyl formate with water under alkaline conditions: These methods are simple to operate and suitable for small-scale experimental studies, but the reaction conditions are more demanding and the yield is low. For example, the formaldehyde reduction method requires high temperatures and pressures, while the methyl formate hydrolysis method requires precise control of pH and reaction time. In addition, methanol prepared in the laboratory is usually of low purity and requires further purification before it can be used for analytical or experimental purposes [2].

2.3.3 Domestic production methods

China, as one of the world's largest producers of methanol, has a production process that mainly uses coal as a feedstock and coal gasification technology to generate syngas, which is then catalyzed to synthesize methanol. Typical technologies include Ruchi Furnace Technology and Aerospace Furnace Technology. Ruchi furnace technology is a fixed-bed gasification process, which is suitable for handling low ash melting point coal with high carbon conversion and low operating costs. (The technology was developed by Ruchi in Germany and uses fixed-bed pressurized gasification to generate syngas rich in hydrogen (H_2), carbon monoxide (CO), and a small amount of carbon dioxide (CO_2) by reacting lump coal with oxygen and steam under high temperature and high pressure as the raw material.) Aerospace furnace technology, on the other hand, is a gasification technology developed independently by China, which is able to realize efficient coal conversion at high temperature and high pressure [3].

2.3.4 Foreign methods

Foreign methanol production mainly relies on natural gas reforming technology, through methane steam reforming (SMR) or self-thermal reforming (ATR) to generate syngas , and then synthesize methanol. Steam methane reforming (SMR) is currently the most mature technology for syngas production, in which methanol is produced from CO and H_2 in the presence of a catalyst. This process has the advantages of good economics and environmental friendliness, and is particularly suitable for countries with abundant natural gas resources, but with high energy consumption, while thermal reforming (ATR) is more flexible and has superior energy utilization efficiency, making it more suitable for industrial applications [4].

2.3.5 Advantages and disadvantages of domestic and foreign production methods

The domestic method is mainly based on coal as a feedstock, which is fit for China's energy structure, as coal is abundant and less costly. For example, some large-scale coal chemical projects in China, such as Shenhua Group's coal-to-liquid project, make full use of the abundant coal resources in the country. However, there are some significant problems with this method of production, such as high energy consumption, pollution, and high investment costs for equipment. These problems are also reflected in actual production, such as the large amount of carbon dioxide and other pollutants produced in the coal chemical process, which has a serious impact on the environment.

In contrast, foreign production methods, which are mainly based on natural gas as feedstock, have higher energy efficiency and more eco-friendly advantages. For example, some methanol production plants in the U.S. and Europe, such as Methanex in the U.S., use natural gas as the main feedstock. However, this method is more dependent on natural gas resources and is susceptible to price fluctuations in the international market. In recent years, fluctuations in natural gas prices have had a significant impact on the operating costs of these enterprises.

In terms of technology, the country has accumulated rich experience in the field of coal chemical industry, but there is still room for improvement in environmental protection and energy conservation. For example, some domestic coal chemical enterprises are actively developing new environmental protection technologies to reduce pollutant emissions. On the other hand, foreign production methods pay more attention to sustainable development, especially leading in green methanol production technology. What’s more, some European companies have developed highly efficient green methanol production processes, which not only reduce energy consumption, but also substantially reduce environmental pollution. This difference reflects the different strategies and priorities of different countries in terms of energy utilization and environmental protection.

3 Challenges and development

The technology of converting carbon dioxide to methanol under thermal catalysis still faces many challenges in industrial applications.

The design and development of catalysts is the core issue. At present, copper-based catalysts are widely studied for their high activity, but because of poor stability, sintering or poisoning is easy to occur under high temperature and high-pressure conditions, which produces safety hazards as well as a decrease in the catalytic performance, so development or improvement of multifunctional catalysts is a valuable research topic, such as doped with rare-earth elements or nano-structured materials, to improve catalytic activity and stability, and also to reduce energy consumption as well as high costs and improve safety[5]. In terms of rare earth elements, their unique electronic structure and redox properties can promote CO_2 adsorption and activation e.g. Ce^{4+}/Ce^{3+} etc. [6]. Nanostructured materials are also good choices for catalyst applications , with their high specific surface area and abundant active sites, they show great potential development value in catalysts, for example, after pyrolysis of MOFs, porous carbon-loaded metal nanoparticles can be formed, and these nanoparticles have excellent dispersion and stability, and they can effectively activate CO_2 and H_2 [7].

In addition to this, reducing the source and capture cost of carbon dioxide is also an important study. Although China has made some progress in carbon capture and storage technology, the cost of efficiently capturing carbon dioxide from industrial emission sources or the atmosphere is still high, and the energy consumption is large, which greatly enhances the cost of this technology [8]. Therefore, the development of carbon dioxide capture technology is also a path of concern, the capture of carbon dioxide can reduce greenhouse gas emissions to mitigate global warming, but at this stage, most of the capture of carbon dioxide is captured by combustion, which not only consumes a large amount of energy, but also incidentally produces a number of toxic gases to pollute the atmosphere, therefore, the vigorous development of stronger adsorbents such as porous materials to obtain carbon dioxide directly from the air, to reduce energy consumption and to achieve the goal of reducing the cost of the technology [9].However, the small percentage of carbon dioxide in the atmosphere, coupled with the slow capture rate , makes it difficult to promote the industrialization of air capture, and there is still a lack of a more efficient experimental method or a catalyst that can help promote capture.

Of course, how to promote the industrialization has also become a challenge. The thermal catalytic hydrogenation of carbon dioxide to methanol over copper-based catalysts requires extremely harsh reaction conditions, and the reaction can be completed at 200-300°C and 50-100 atm. Although the technology is mature, to achieve such conditions, the investment in the equipment as well as the operating cost is also very large, which has created resistance to the promotion. Therefore, the optimization of the reaction conditions, by exploring the way to promote the reaction at low temperature or even at room temperature, can greatly reduce the energy consumption as well as the cost, and reduce the technical difficulty in order to achieve a better industrialization [10]. In combination with rare earth elements and nanomaterials, catalysts that are less affected by temperature are explored.

4 Conclusion

As a carbon resource with abundant reserves, the utilization of carbon dioxide (CO2) is of great significance for achieving the goal of carbon neutrality. The thermal catalytic-driven CO2-to-methanol technology shows good prospects for development, not only because methanol is widely used in the fields of chemical raw materials and clean fuels, which has high application value, but also because it can effectively realize the carbon cycle and alleviate the global warming effect. However, by comparing and analyzing the industrial syngas technology (such as domestic aerospace furnace and Ruchi furnace technology) and foreign natural gas reforming process (SMR/ATR), as well as the laboratory formaldehyde reduction method, methyl formate hydrolysis and other technology paths, it is found that the current CO_2 conversion technology generally suffers from the problems of high energy consumption, harsh reaction conditions and insufficient product purity. Therefore, the future technology will show three major trends, the first is the development of new multifunctional catalyst systems, such as through the doping of rare earth elements, nano-structure modulation and other means, to improve its stability and selectivity at high temperatures and pressures, while reducing the reaction energy consumption. The second is to break through the technical difficulties of CO_2 capture with high efficiency and low consumption, and to develop new porous materials with high adsorption characteristics, which can significantly improve the energy efficiency. Finally, we will optimize the reaction conditions, explore low-temperature and normal-pressure reaction catalysts, reduce equipment investment and operating costs, provide technical support for large-scale industrial applications, and lower the threshold of industrialization conditions.

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