

Advances in Carbon Dioxide Catalytic Conversion and Applications

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Abstract. To achieve the global climate goals set out in the Paris Agreement, reducing carbon dioxide (CO₂) emissions and utilizing resources have become key areas of focus within international energy technology research and development. CO₂ can be converted into high-value chemicals, including hydrocarbons, alcohols and hydrocarbons, through the catalytic technology. This process can potentially address environmental issues while generating economic benefits. This paper presents a review of the principal products resulting from the catalytic conversion of CO₂, together with an examination of their practical applications. These include hydrogenation of olefins, light aromatics, methanol, polyols, and synthetic bioconversion technologies. The development of catalysts with high conversion and selectivity represents a key area of current research. In the future, it will be necessary to combine physical, chemical, and biological technologies to establish an engineered heterogeneous carbon sequestration technology system to achieve the efficient conversion and utilization of CO₂.

Keywords: Carbon dioxide conversion, Hydrogenation, Artificial bioconversion, Carbon sequestration, Sustainability.

1. Introduction

To achieve the long-term global climate goals set out in the Paris Agreement, the reduction of greenhouse gas emissions and the utilization of resources have become key areas of research and development in the field of international energy technology. The utilisation of carbon dioxide through chemical technology has the potential to alleviate environmental problems to a certain extent, while simultaneously preparing chemical materials and products. This process can generate economic and ecological benefits and may contribute to the slowing down of human dependence on fossil energy. Carbon dioxide, as an attractive single-carbon building block, can be employed in the synthesis of chemical substances that are of value in both industrial and laboratory contexts. However, given that the CO₂ molecule is resistant to chemical alteration due to its inherent stability and lack of reactivity, the majority of its conversion and utilization necessitates the employment of catalytic technologies. Carbon dioxide capture, storage, and utilization (CCUS) technology will be a pivotal component of this process. After the capture of CO₂, the catalytic conversion process is typically conducted through thermochemical, electrochemical, photochemical, or biological processes to transform CO₂ into high-value products, including formic acid, methanol, and formate (for the synthesis of fuels and polymers), or into thermodynamically stable products (e.g., carbonate minerals) for long-term storage. Furthermore, the synthesis of fuels or the aforementioned high-quality chemicals through this pathway not only reduces the consumption of fossil fuels but these high-value compounds can also be employed in scientific research as reactants for additional chemical reactions. The advancement of CO₂ catalytic conversion technology also signifies a novel opportunity for the growth of the catalytic industry, and the development of catalysts with high conversion and selectivity remains a pivotal objective of contemporary research. This paper provides a comprehensive overview of the principal products of CO₂ conversion, including hydrocarbons, alcohols, and carbohydrates synthesized through artificial pathways. It also offers a detailed examination and assessment of the catalysts employed in the CO₂ conversion process and their practical applications.

2. CO₂ Hydrotransformation

2.1. Hydrogenation of CO₂ for olefin production

Olefins are industrially important chemical raw materials, mainly including low-carbon olefins (C₂-C₄ olefins) and long-chain olefins (C₅ and above), of which low-carbon olefins are the main polymer monomers, while long-chain-terminated olefins (alpha-olefins) are the basic raw materials for the synthesis of advanced lubricating oils, high-carbon alcohols, plasticizers and surfactants.

Catalytic hydrogenation of CO₂ to low-carbon olefins has high economic benefits. Iron-based catalysts are the main catalysts for the Fischer-Tropsch synthesis (FTS) route, where Fe₃O₄ and FeC_x are the main active species for the reverse water gas shift (RWGS) and Fischer-Tropsch synthesis reactions, respectively [2]. Currently, catalyst studies for the production of low-carbon olefins by hydrogenation are mainly focused on loaded iron-based catalysts. The carriers of these iron-based catalysts are usually selected from γ -Al₂O₃, carbon carriers, SiO₂ and molecular sieve carriers. By processing the iron-based catalysts and doping them with metals or metal oxides, efficient modulation of the active phase can be achieved while improving the olefin selectivity. For example, the addition of alkali metal additives K or Na, which enhance the Fe-C bond by utilizing their electron donor properties, can limit the resorption of olefins and prevent them from undergoing secondary hydrogenation reactions [3].

In addition, K-Fe-Mn-Ce/ γ -Al₂O₃ catalysts were prepared by modifying K-Fe-Mn/ γ -Al₂O₃ catalysts with Ce, and their CO₂ hydrogenation performance was investigated. It was found that the modified catalyst not only increased the CO₂ conversion and C₂-C₅ selectivity, but also decreased the CH₄ selectivity. Under the reaction temperature of 290°C and reaction pressure of 1.37MPa, the addition of CeO₂ increased the conversion of CO₂ from 41.4% to 50.4% and the selectivity of C₂-C₅ to 62.3%. Therefore, the K-Fe-Mn-Ce/ γ -Al₂O₃ catalyst exhibited high CO₂ conversion and good olefin selectivity [4].

2.2. CO₂ hydrogenation to produce light aromatics

Aromatic hydrocarbons are widely used bulk chemicals, which are currently mainly prepared by petrochemical routes, with high energy consumption and accompanied by large amounts of CO₂ emissions. Synthesizing high-value-added aromatics by catalytic hydrogenation using CO₂ as a carbon source is a more environmentally friendly route and one of the measures to solve the energy demand and achieve the goal of carbon neutrality. Currently, there are two main routes for the preparation of aromatics by CO₂ hydrogenation: modified Fischer-Tropsch and methanol intermediates, and a series of advances have been made in these two aspects in recent years [5]. In the route using methanol as an intermediate, methanol is dehydrated to produce dimethyl ether (DME), and the equilibrium mixture of DME and feed methanol is dehydrated to produce aromatics over a ZSM-5 molecular sieve catalyst. However, while low temperatures are thermodynamically favorable for methanol synthesis, high temperatures are required for the conversion of methanol to aromatics, resulting in low aromatics yields. In another route, CO₂ was first generated from CO over iron-based catalysts by a reverse water-gas shift reaction, then CO was converted to olefin intermediates by a Fischer-Tropsch synthesis reaction, and finally aromatics were generated by an olefin aromatization reaction. Studies have shown that CO₂ conversion and aromatics selectivity can be effectively improved by introducing alkali metals, copper and other elements into iron-based catalysts. To effectively regulate the distribution of aromatics in the process of CO₂ hydrogenation to aromatics and to improve the selectivity of target aromatics, the researchers developed a bifunctional catalyst consisting of a copper-based modified iron-based catalyst and chained ZSM-5 molecular sieves. The analytical results showed that the chained ZSM-5 molecular sieves with high acid density and appropriate length-to-diameter ratio could promote the C-C coupling of the products and inhibit the generation of CH₄, thus effectively improving the selectivity of aromatics and the conversion efficiency of benzene, toluene, and xylene.

Regardless of the route, molecular sieves are essential components in the current CO₂ hydrogenation catalysts for the synthesis of aromatics. Among them, ZSM-5 molecular sieve with MFI structure is the preferred catalyst for aromatics synthesis because of its unique three-dimensional ten-membered ring pore structure, which can overcome the diffusion limitation of reactants and products. In addition to the topology of the molecular sieves, the strength, density and nature of the acidic sites of the molecular sieves (Brønsted and Lewis acids) also have a significant effect on aromatic synthesis. The role of molecular sieve Brønsted acid sites in the CO₂ hydrogenation reaction was investigated by combining ZSM-5 molecular sieves with different Brønsted acid properties with NaFe-based catalysts to form a composite catalyst. It was found that the Brønsted acid site was the main active site for arylation, and increasing the Brønsted acid density could significantly improve the selectivity of aromatics, especially light aromatics. Silanization of molecular sieves by chemical liquid deposition can passivate the Brønsted acid sites on the outer surface, which in turn inhibits the alkylation of light aromatic hydrocarbons and the isomerization of xylene. Eventually, the proportion of light aromatic hydrocarbons in aromatics can reach 75%, which is the highest value reported in similar literature, and the proportion of paraxylene (PX) in xylenes can reach 72%. However, excessively high Brønsted acid amounts (>154 μmol g⁻¹) accelerate the formation of highly condensed and difficult-to-oxidize carbon deposits and reduce catalyst lifetime [5].

2.3. Hydrogenation of CO₂ to produce methanol

Currently, most industrial methanol production is done by gasification of fossil fuels or similar processes to produce syngas, which are then converted to methanol. This process is accompanied by a large amount of carbon emissions, while the production of methanol through CO₂ hydrogenation has a significant carbon reduction effect. The "Liquid Sunshine" program, which utilizes renewable energy sources such as solar and wind power to electrolyze water to produce "Green Hydrogen" and then hydrogenate CO₂ to produce methanol fuel or chemicals, is important for the development of clean energy and carbon reduction. It is of great significance to the development of clean energy and carbon reduction.

The methanol reactor is the core equipment in the methanol synthesis process, and the reactor for direct hydrogenation of CO₂ to methanol evolved from the syngas-to-methanol reactor, and the principles are very similar. Currently, the operating temperature of CO₂ direct hydrogenation is 200-300°C and the pressure is 5-10MPa, while the operating temperature of syngas-to-methanol is 210-350°C and the pressure is 5-8MPa. The C/H ratio in the fresh gas is controlled at 2.0-2.2, and the CO₂ concentration in the incoming gas is controlled at 2-5%.

Currently, the mainstream catalyst systems for CO₂ hydrogenation to methanol mainly include three categories: copper-based catalysts, loaded noble metal catalysts and metal catalysts with semiconductor properties. The Dalian Institute of Chemical Physics of the Chinese Academy of Sciences has developed a CO₂ hydrogenation to methanol catalyst that solves the problem of low activity of catalysts prepared by the co-precipitation method in CO₂ hydrogenation to methanol. Under the test conditions of the pilot skid-block device built in PetroChina Daqing Chemical Research Center, the catalyst has a CO₂ one-way conversion rate of more than 10%, a methanol selectivity of up to 86-91%, and the catalyst has a high thermal stability and resistance to SO₂ and H₂S poisoning, which shows a good prospect for the large-scale industrial application of CO₂ hydrotreating to methanol.

2.4. CO₂ hydrogenation for polyol production

Carbon dioxide-based polyols are oligomers containing two or more terminal hydroxyl groups produced by the copolymerization of CO₂ and epoxides. Compared with methanol, C₂ polyols have a higher application value and can be used either directly as a transportation fuel or as a highly efficient additive to gasoline. The polymer chain segments contain both polycarbonate and polyether units due to the fact that in addition to the copolymerization of CO₂ and the epoxide during the polymerization process, the epoxide itself undergoes self-polymerization.

In addition, cyclic carbonate by-products may be generated during the reaction. The main methods of synthesis of CO₂-based polyols include random copolymerization of CO₂ and epoxide in the presence of catalysts and chain transfer agents, polyfunctional initiation of anionic polymerization, and alcoholysis of high molecular weight polypropylene carbonate (PPC). One of the most commonly used methods is the catalytic copolymerization of CO₂ and epoxides in the presence of a chain transfer agent. The heart of polyol synthesis via CO₂ is the catalyst, which therefore determines the synthetic efficiency of the reaction, product selectivity, and precise control of the molecular weight of the product [6-7].

According to whether the catalyst can be dissolved in the reaction medium, it can be divided into homogeneous and non-homogeneous catalysts; according to whether it contains metal elements, it can be further divided into metal homogeneous catalysts and non-metal homogeneous catalysts. Noble metal Rh-based catalysts have been widely studied for their excellent selectivity in the hydrogenation of CO₂ to polyols. Yang et al. [9] showed that strong metal-carrier interactions between Co and carriers can stabilize the Co-active center and increase the CO₂ hydrogenation activity. The conversion of CO₂ hydrogenation was 13.9% and the ethanol yield was 1.87 mmol/(g·h) by Co₃O₄ nanorods-loaded Cu catalysts at a reaction temperature of 250°C and a reaction pressure of 3 MPa. Despite the high CO₂ conversion of the Cu and Co-based catalysts, the polyol selectivity was low. In contrast, Rh-based catalysts had higher polyol selectivity but lower CO₂ conversion.

As with CO₂ hydrogenation of hydrocarbons, the key to CO₂ hydrogenation of polyols is the source and cost of hydrogen. This technology can only be economically and environmentally beneficial if cheap "green hydrogen" is available.

3. CO₂ synthetic bioconversion

In recent years, scientists around the world have been committed to exploring efficient CO₂ synthetic bioconversion technologies. For example, the research team of Jiang Weihong and Gu Yang from the Center of Excellence for Molecular Plant Science of the Chinese Academy of Sciences, through the combined metabolic engineering modification of an autotrophic bacterium, the gas-eating *Clostridium Ljungdahlii* (CL), has realized the simultaneous and highly efficient synthesis of important products such as isopropanol, ethanol and 3-hydroxybutyric acid, demonstrating the good potential of this bacterium to be applied in the industrial bioconversion of carbon-containing gases for the preparation of high-value, long carbon chain compounds. LanzaTec, in collaboration with the Shougang Group, has established the world's first ethanol production plant by CL fermentation using the CL gas fermentation technology, and has achieved the production of acetone and isopropanol using CO₂ on a pilot scale. Although the rate of CO₂ conversion can be increased to the industrial fermentation level by utilizing chemical energy, the energy source of direct chemical energy is not renewable. Autotrophic carbon sequestration of chemical energy and synthesis of specific chemicals through the coupling of photovoltaic and chemical energy conversion with high efficiency is a new option for carbon sequestration of chemical energy. Harvard University reported an inorganic catalyst-biocompatible system coupled photovoltaic system to produce hydrogen through electrolysis of water, and then use hydrogenophilic autotrophic carbon sequestration to bioconvert CO₂ to synthesize biomass and chemicals, with a photovoltaic energy utilization efficiency of 3% to 10% [9]. Peidong Yang's team at Lawrence Berkeley National Laboratory, USA, drove autotrophic carbon-fixing strains to achieve CO₂ to acetic acid conversion through semiconductor nanomaterials mediating the conversion of electrical energy to chemical energy [10].

Although the efficiency of the coupled photovoltaic and chem energy conversion to carbon sequestration system utilizing solar energy has been substantially improved compared to natural photosynthesis, the overall efficiency is still low, limited by process issues such as gas-liquid mass transfer, electrode-biological interface compatibility, and the lack of clarity in the mechanism of bioelectrical energy utilization and metabolic laws of autotrophic organisms. Chemical catalysis can rapidly convert CO₂ into short carbon chain compounds, but it is difficult to realize the selective

synthesis of long-carbon chain compounds. Therefore, giving full play to the advantages of physical, chemical and biological technologies in energy conversion and carbon sequestration conversion, and establishing an engineered heterogeneous carbon sequestration technology system is the best choice to realize the artificial conversion and utilization of CO₂. The Tianjin Institute of Industrial Biotechnology (TIBI) of the Chinese Academy of Sciences (CAS) has made significant progress in the frontier areas of design and construction of artificial carbon sequestration components, pathways and systems [11]. In particular, by combining the advantages of physics, chemistry, biology and other technologies, we have achieved landmark results by utilizing photovoltaic power generation to produce hydrogen and then chemically reducing CO₂ to synthesize carbohydrates through an artificial pathway, which for the first time realizes the total synthesis of CO₂ to starch molecules that does not depend on photosynthesis.

4. Other applications of CO₂

4.1. Mineralized curing concrete

The CO₂ mineralization curing technology enhances the mechanical strength and other properties of the product through the carbonation reaction and product deposition process between the early formed concrete materials and CO₂. Researchers have been actively developing alkali metal mineral materials with CO₂ mineralization potential in recent years and exploring the promotion of concrete microstructure and properties after their reaction. During the preparation of conventional Portland cement (OPC), hydration-active calcium silicate clinker components, such as tricalcium silicate (Ca₃SiO₅ or C₃S) and beta-type dicalcium silicate (Ca₂SiO₄ or C₂S), are formed by high-temperature calcination. During the early hydration and molding process, part of the calcium silicate clinker is converted into the hydration products calcium hydroxide and C-S-H gel, which form the material's early strength and alkaline inner environment. By replacing the existing energy-intensive steam curing (1-2 days) or natural curing (28 days) with CO₂ mineralization curing for the production of precast concrete parts, the curing time can be shortened to within a few hours, which reduces the energy consumption for production and improves the mechanical properties and durability [12-16]. Current novel materials used for mineralization curing include hydrated reactive calcium silicate materials, hydrated inert calcium silicate materials, magnesium-based cement materials, and industrial solid waste materials, etc. However, the mineralization conversion rates of these materials have not yet reached or are close to the theoretical maximum value of mineralized CO₂ within a specific curing time. Compared with the existing CO₂ liquid-phase mineralization technology, these materials still have room for improvement in terms of conversion rate and reaction kinetics. In addition, the mineralization maintenance process using different minerals as cementitious materials or aggregates is influenced by a variety of factors, including the mineral properties of the cementitious materials (e.g., the rate and amount of CO₂ mineralization), the concentration and pressure of the CO₂, the temperature of maintenance, the water/cement ratio of the preparation, the pre-conditioning conditions, and the mixing ratios of the cementitious materials and the aggregates, among others. There are also differences in the key influencing factors for different materials. Therefore, future research should focus on the microscopic reaction mechanism and mineral material properties to develop effective methods for mineralization reaction enhancement.

4.2. Curing of sludge

Foamed cement paste is a lightweight slurry material formed by pressurizing and aerating cement paste (in the form of foam). Jones and Jitchaiyaphum et al [17-18] found that by removing a certain volume of sand, the flowability and strength of foamed concrete improved significantly. Kearsley et al. and Goual et al. [19] investigated the interior of the foam specimens pores for permeability properties and found that the increase in the porosity of the specimens helped to improve the permeability properties. Based on the traditional air-foam cement slurry preparation technique and common cement-based carbon sequestration mechanism, we used carbon dioxide instead of air to

prepare carbon dioxide foam cement slurry to solidify silt. It was shown that the unconfined compressive strength of silt increased with the dosage of carbon dioxide foam cement slurry and the age of curing, especially changed significantly between 3 and 14 days. The cohesion and angle of internal friction of the silt also increased with the increase of CO₂ foam slurry dosage and curing age. It was determined that the optimum combination of foam cement blowing and stabilizing agents was A2 4g/L and C1 5g/L. The conversion rate of Ca(OH)₂ to CaCO₃ from CO₂ in the hydration hydrolysis products of the cement increased by about 26.1%, and the optimum dosage of fly ash in the cement slurry was 30%. The unconfined compressive strength, internal friction angle and cohesion of the cured material formed after curing showed an approximate linear increasing relationship with the dosage of foam slurry, while the permeability coefficient showed an approximate linear decreasing relationship with the dosage of foam slurry. These research results provide important guidance for the engineering application of silt curing and the utilization of carbon dioxide "waste to treasure".

5. Summary

The catalytic conversion of CO₂ provides an important way to combat global climate change and realize the goals of the Paris Agreement. This paper reviews the main products of CO₂ catalytic conversion and their practical applications, covering the production of olefins, light aromatics, methanol, polyols and synthetic bioconversion technologies by hydrogenation. Through hydroconversion, CO₂ can be efficiently converted to produce high-value-added chemicals, thereby reducing the environmental burden and bringing economic benefits. Current research focuses on the development of catalysts with high conversion and selectivity to improve the efficiency of CO₂ conversion and the economics of the products. Mineralization applications of CO₂, such as mineralization in concrete and curing of sludge, show its potential in construction and environmental remediation. These applications not only promote the efficient utilization of CO₂, but also contribute to the sustainable use of resources. Future research should integrate physical, chemical and biological technologies to establish an efficient engineered heterogeneous carbon sequestration technology system for efficient conversion and resource utilization of CO₂. Through further technological innovation and engineering optimization, the overall efficiency of CO₂ conversion can be enhanced, and its practical application in various fields can be promoted, providing strong support for the achievement of global sustainable development goals.

References

- [1] Wang Rui, Xu Yirong, Meng Kexin, et al. Progress of carbon dioxide conversion to fuels and high-value chemicals. *Journal of Environmental Engineering Technology*, 2020, 10 (04): 639-646.
- [2] Guo L, Sun J, Ge Q, et al. Recent advances in direct catalytic hydrogenation of carbon dioxide to valuable C₂ hydrocarbons. *Journal of Materials Chemistry A*, 2018, 6 (46): 23244-23262.
- [3] Dorner R W, Hardy D R, Williams F W, et al. Effects of ceria-doping on a CO₂ hydrogenation iron-manganese catalyst. *Catalysis communications*, 2010, 11 (9): 816- 819.
- [4] Zheng Xuezhong, Zhang Yuewen, Zhang Xiujuan, et al. Advances in technologies related to the catalytic conversion of carbon dioxide for the production of chemicals. *Petroleum Refinery Engineering*, 2024, 54 (7).
- [5] Jian Wei, Ruwei Yao, Qingjie Ge, et al. Precisely regulating Brønsted acid sites to promote the synthesis of light aromatics via CO₂ hydrogenation. *Applied Catalysis B: Environmental*, 2021, 283: 0926-3373.
- [6] Kember M R, Buchard A, Williams C K. Catalysts for CO, epoxide copolymerisation. *Chem Commun*, 2011, 47: 141-163.
- [7] Kuran W, Listos T. Initiation and propagation reactions in the copolymerization of epoxide with carbon dioxide by catalysts based on diethylzinc and polyhydric phenol. *Macro Chem Phys*, 1994, 195: 977-984.
- [8] Yang C, Mu R, Wang G, et al. Hydroxylmediated ethanol selectivity of CO₂ hydrogenation. *Chem Sci*, 2019, 10: 3161 - 3167.

- [9] Liu C, Colón BC, Ziesack M, et al. Water splitting-biosynthetic system with CO₂ reduction efficiencies exceeding photosynthesis. *Science*, 2016, 352 (6290): 1210-1213.
- [10] Su Y, Cestellos-Blanco S, Kim JM, et al. Close-packed nanowire-bacteria hybrids for efficient solar-driven CO₂ fixation. *Joule*, 2020, 4 (4): 800-811.
- [11] Cai T, Sun H, Qiao J, et al. Cell-free chemoenzymatic starch synthesis from carbon dioxide. *Science*, 2021, 373 (6562): 1523-1527.
- [12] Hewlitt PC. *Lea's chemistry of cement and concrete*. Oxford: Butterworth-Heinemann, 2019.
- [13] Wang Tao, Huang Hao, Hu Xutao, et al. Accelerated mineral carbonation curing of cement paste for CO₂ sequestration and enhanced properties of blended calcium silicate. *Chemical Engineering Journal*, 2017, 323: 320-329.
- [14] Rostami V, Shao Yixin, Boyd A J. Carbonation curing versus steam curing for precast concrete production. *Journal of Materials in Civil Engineering*, 2012, 24 (9): 1221-1229.
- [15] Huang Hao, Guo Ruonan, Wang Tao, et al. Carbonation curing for wollastonite-Portland cementitious materials: CO₂ sequestration potential and feasibility assessment. *Journal of Cleaner Production*, 2019, 211: 830-841.
- [16] Huang Hao, Wang Tao, Fang Mengxiang. Research progress of carbon dioxide mineralization curing concrete technology and new materials. *Chemical Progress*, 2019, 38 (10): 4363-4373.
- [17] Jones M R, McCarthy A. Utilising unprocessed low-limecoal fly ash in foamed concrete. *Fuel*, 2005, 84 (11): 1398-1409.
- [18] JMitchaiyaphum K, Sinsiri T, Chindaprasirt P. Cellular Lightweight Concrete Containing Pozzolan Material. *Procedia Engineering*, 2011, 14: 1157-1164.
- [19] Kearsley E P, Wainwright P J. Porosity and permeability of foamed concrete. *Cement & Concrete Research*, 2001, 31 (1): 805-812.