How Can the Water Tolerance of the Industrial $Cu/ZnO/Al_2O_3$ Catalyst Used in Methanol Synthesis From CO_2 Be Enhanced?

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Received October 05, 2024
Accepted November 30, 2024
Electronic access December 15, 2024

The industrial $Cu/ZnO/Al_2O_3$ (CZA) catalyst plays a crucial role in the hydrogenation of carbon dioxide (CO_2) to methanol, a process with significant potential for reducing greenhouse gas emissions. However, the CZA catalyst suffers from deactivation primarily due to its limited water tolerance, which poses a significant challenge in maintaining its efficiency and longevity in industrial applications. This review examines methods to enhance the water tolerance of the CZA catalyst, focusing on the mechanisms of water-induced deactivation and summarizing various strategies proposed to mitigate these effects. The paper highlights approaches to improving the durability and performance of CZA in methanol synthesis. The findings provide insights into the development of more robust catalytic systems capable of sustaining high activity in the presence of water, thereby advancing the practical applications of CZA in methanol production from CO_2.

Introduction

Carbon Capture & Utilization/Storage

Carbon dioxide (CO_2) is a colorless, odorless, and non-flammable gas. It is a chemical compound made up of one carbon atom and two oxygen atoms. CO_2 is a component of the atmosphere, although its concentration (0.03% - 0.04%) is significantly lower than nitrogen (78%) or oxygen (21%). CO_2 is also considered the primary greenhouse gas (GHG), along with methane and nitrous oxide. GHGs are the gases that trap heat in the atmosphere by absorbing the wavelengths of radiation that a planet emits. Some of the sunlight absorbed by the Earth's surface increases the planet's temperature. This absorbed energy is then re-emitted as heat. However, it cannot fully escape into space because it is trapped by the greenhouse gases (GHGs) in the atmosphere. In fact, if this heat could freely come back to space, the average temperature on the Earth would be -19 °C, compared to the current average of 15 °C. Overall, gases like CO_2 allow sunlight to enter the atmosphere but prevent heat from leaving. This process is called the greenhouse effect and is the major factor responsible for making the Earth's conditions suitable for life. However, if the concentration of GHGs in the atmosphere increases, the amount of heat trapped will also increase, leading to unpredictable consequences. Unfortunately, humans became the driving force that caused the exponential growth in emissions of CO_2. Since the Industrial Revolution during the late 18th century, the CO_2 concentration increased by more than 50%, from 270 parts per million (ppm) to 425 ppm[1]. If such a rise is not mitigated, the planet will face even more severe consequences, including escalating global warming, increased ocean acidification, and more frequent acid rain. Therefore, urgent measures must be taken to reduce CO_2 emissions and lower its concentration in the atmosphere. CO_2 is produced during chemical procedures used to manufacture certain materials (e.g., cement and steel), or when energy is generated from the combustion of carbon-containing fuels . This is when the process of its capturing was developed, aiming to prevent further CO_2 releases into the atmosphere. This process is currently carried out via an adsorption procedure at the source. In it, flue gases from incineration pass through an absorption unit where CO_2 molecules adhere to a liquid chemical solvent, as described by Veolia. Heat is then applied to separate CO_2 and regenerate the solvent, which can be reused in a closed loop[2]. Alternatively, CO_2 can also be captured directly from the atmosphere. Although capturing CO_2 in this way is the most expensive application of carbon capture, direct air capture (DAC) technologies have the potential to significantly reduce atmospheric CO_2 levels.

CO_2 can also be stored deep underground, better known as Carbon Capture and Storage (CCS) technologies, or used as a raw material in the manufacture of industrial products via Carbon Capture and Utilization (CCU) processes as shown in Figure 1. In the case of CCS, compressed CO_2 is transported to a storage site. Underground reservoirs or saline formations have enough capacity to store large amounts of gas. The CO_2 is then injected into the deep subsurface for permanent storage. For CCS to significantly reduce CO_2 emissions, very large volumes need to be captured and stored, and the risks, such as leakages, high costs, and water contamination, cannot be completely eliminated. In the case of CCU, CO_2 can be used to make certain chemicals and fuels, as well as industrial products such as building materials.

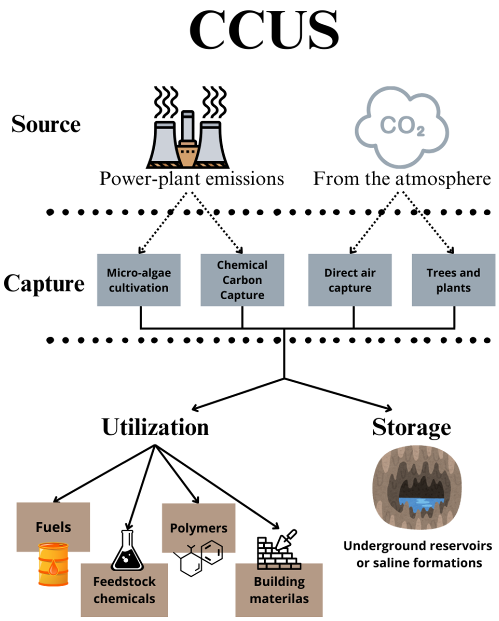

Fig. 1 CARBON CAPTURE, UTILIZATION, AND STORAGE (CCUS) PROCESSES. The figure shows CO_2 sources, capture methods, and CO_2 utilization ways.

CO_2 Utilization

Carbon Dioxide Utilization (CDU) presents a promising approach to combat climate change by converting CO_2 into valuable products. Beyond its environmental benefits, CDU serves as a carbon source by expanding raw material sources and substituting fossil carbon, which is a critical need in the chemical industry. Moreover, CO_2 can be transformed into renewable fuels known as power to X, facilitating grid stabilization through chemical energy storage, thus supporting the transition to sustainable energy. Additionally, utilizing CO_2 for new products promotes waste repurposing, reducing environmental impact, and fostering a circular economy. There are various ways in which CO_2 can be utilized as shown in Figure 2. It can be used in the beverages industry, in food conservation, in urea production, in water treatment, in enhanced oil recovery, in chemical production, and in polymer synthesis with current global usage of 230 Mt per year[3]. However, less than 1% of the CO_2 emitted into the atmosphere is currently utilized as a raw material in the above industries[4]. Thus, human efforts should focus on converting captured CO_2 into valuable products.

One way to utilize CO_2 is enhanced oil and gas recovery, known as EOR or EGR. It is a process where CO_2 is injected into a reservoir to increase pressure and release trapped oil or gas. In CO_2 EOR, the injected CO_2 mixes with the oil, making it lighter and easier to extract. This CO_2 is then separated and reused in a continuous cycle, often yielding more oil per reservoir than traditional methods[4]. While most CO_2 EOR systems use naturally occurring CO_2, recent research focuses on utilizing captured CO_2 from industrial emissions. Despite challenges such as rock formation heterogeneity and various operational parameters, CO_2 EOR is gaining attention and is expected to grow. According to Al-Mamoori et al.[4], EOR currently contributes to only 3% of CO_2 utilization, but its application is expanding due to ongoing advancements and its implementation in more facilities. CO_2 can also be used to produce fuels such as methane, methanol, syngas, alkanes, etc. In the context of fuel production from captured CO_2 there are two main approaches: hydrogenation and dry reforming of methane (DRM)[4]. CO_2 hydrogenation can produce various fuels like methane and methanol, but using fossil fuels as a hydrogen source would defeat the purpose. Renewable energy sources such as solar, wind, and biomass are a better option. While hydrogenation has shown some success, developing efficient catalysts remains a challenge. DRM is another promising route, especially for making syngas (a mixture of hydrogen and carbon monoxide) which can then be used to synthesize fuels. DRM offers advantages like high product purity and low unreacted methane. However, finding catalysts that are active, stable, and resistant to coking at high temperatures is still a major hurdle[5]. Besides fuel production from CO_2, there is an equally important chemical production. Urea, inorganic carbonates,

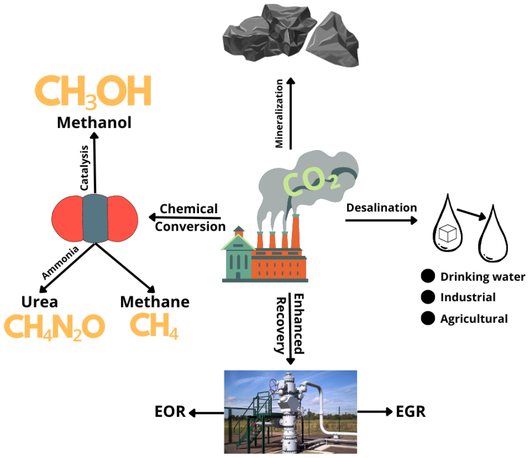

Fig. 2 $C0_2$ UTILIZATION WAYS. The figure presents various technologies for utilizing $C0_2$ such as chemical conversion, mineralization, desalination, and enhanced recovery.

polyurethane, acrylic acid and acrylates, and polycarbonates are some of the most important chemicals synthesized using CO_2 as a feedstock. Formic acid is another valuable chemical that can be synthesized using captured CO_2. Scientists are interested in this process because it happens at moderate temperatures, does not produce unwanted materials, and allows for the safe storage of hydrogen in a liquid form[5]. Additionally, formic acid can be easily broken down back into CO_2 and hydrogen[4]. While there is a strong demand for converting captured CO_2 into useful products like chemicals and fuels, the methods currently being explored in labs are not quite ready for large-scale production. This is because the materials used tend to be expensive and do not last very long. In addition to that, the amount of CO_2 converted and the amount of final product is not high enough to be practical for widespread use[6]. Researchers are still working to fully understand the exact chemical processes involved in transforming CO_2. They also need to consider the practical needs of large-scale production when developing these methods.

Heterogeneous Catalysis

Catalysis is an essential phenomenon in chemistry where a substance, known as a catalyst, provides a new way to a chemical reaction with the lowest activation energy without undergoing any changes in the process[7]. Catalysts bring together reactants that might otherwise may remain almost indifferent to each other under the same conditions. They lower the energy barrier that reactions typically face (Fig. 3), making it easier for molecules to collide, interact, and transform into new substances. However, this definition is limited because actual catalysts undergo structural, activity, and selectivity changes over time while in use and deactivate at varying rates.

When a specific substance or a combination of substances experiences two or more simultaneous reactions resulting in different products, the product distribution can be affected by using a catalyst that selectively speeds up one reaction over the others[8]. By selecting the right catalyst, it is possible to favor a particular reaction while minimizing the occurrence of another. Many significant uses of catalysis, including CO_2 conversion to methanol, rely on this key property. The discipline of catalysis is usually divided into three categories: homogeneous (homo = same, generous = phase) catalysis, heterogeneous (hetero = different) catalysis, and biocatalysis[9]. In homogeneous catalysis, the catalyst operates in the same phase as the reactants, typically in a liquid solution. This allows for precise molecular interactions, often resulting in high selectivity and efficiency. An example of a homogeneously catalyzed reaction is the hydrolysis of ethyl acetate to form ethyl alcohol and acetic acid where the catalyst is sulphuric acid. However, homogeneous catalysts can be difficult to separate from the reaction mixture, posing challenges for catalyst recovery and reuse, and sometimes requiring additional purification steps. Conversely, heterogeneous catalysis involves the catalyst and reactants in different phases, such as a solid catalyst in contact with gaseous or liquid reactants. This type of catalysis is widely used in industrial processes due to the ease of separating the solid catalyst from the reaction products, enabling straightforward recovery and reuse of the catalyst[10]. Although heterogeneous catalysis can suffer from lower selectivity compared to homogeneous catalysis, advancements in catalyst design, such as the development of highly porous materials and nanoscale catalysts, continue to improve its efficiency and specificity[8]. The science of heterogeneous catalysis has a long history that began in the early days of modern chemistry. Before the understanding of the molecular nature of matter, foundational work by Lavoisier established the law of conservation of mass

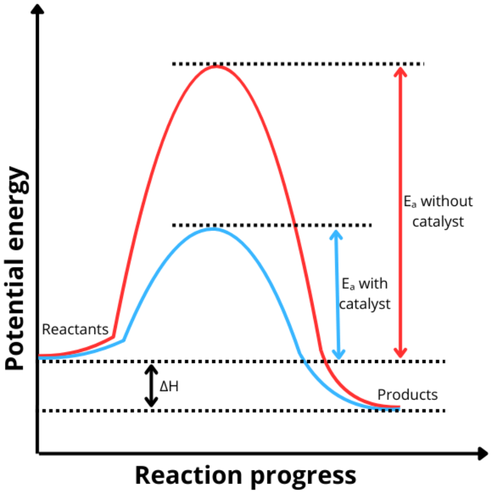

Fig. 3 COMPARISON OF ENERGIES OF CATALYZED AND UNCATALYZED REACTIONS.

and the nature of oxygen. This knowledge led to the development of important heterogeneous catalytic oxidation processes in the 19th century. Key discoveries by Davy and Döbereiner in catalytic oxidation helped establish catalysis as a distinct phenomenon, recognized by Berzelius. These discoveries led to the development of processes such as the oxidation of HCl to produce chlorine and the oxidation of SO2 to yield oleum. In the late 19th century, chemical thermodynamics, defined by Ostwald, provided a physical-chemical foundation for catalysis. Sabatier's discovery of catalytic hydrogenation became a practical technology, and his law of maximum catalytic activity was established. The Haber-Bosch process for ammonia synthesis, developed during this period, revolutionized fertilizer production and demonstrated the potential of continuous heterogeneous catalytic processes operated at high pressures. This historical development highlights the evolution and foundational principles of heterogeneous catalysis that are essential to modern chemical technology. The development of new heterogeneous catalytic processes is primarily driven by the need to provide chemical solutions for an evolving society. This process innovation has often led to the early exploitation of recent scientific discoveries and has given rise to new scientific advances. For example, the discovery of the ammonia synthesis process was influenced by the recent progress in chemical thermodynamics, Sabatier's findings in catalytic hydrogenation, and Bosch's advancements in hydrogen production through coal steam reforming. These important studies gave rise to new understandings of thermochemistry and facilitated the development of modern heterogeneous catalysis, making continuous catalytic process technology feasible. Nowadays, a lot of heterogeneous catalytic reactions are highly important and widely used in industrial processes, where each reaction type has its unique catalysts. Some of the most important processes are hydrogenation reactions using transition metal catalysts such as ammonia and methanol synthesis and olefin hydrogenation, reactions using Brønsted acid catalysts such as catalytic cracking and alkane to aromatics, Fisher-Tropsch catalysis, and polymerization. The ongoing progress in heterogeneous catalysis is crucial for addressing contemporary challenges in energy, environment, and materials science. As research continues to optimize catalyst design, stability, and selectivity, the potential for innovative applications expands. This not only enhances the efficiency of existing industrial processes but also opens avenues for new technologies, such as sustainable chemical production and renewable energy conversion, solidifying the indispensable role of catalysis in modern society.

Catalytic Conversion of CO_2 to Methanol

Methanol is one of the world's largest-volume commodity chemicals, with an annual production exceeding 100 million metric tons[11]. As an essential platform chemical, methanol is integral in the production of various downstream products, including formaldehyde, acetic acid, and olefins. These chemicals are foundational for manufacturing a wide array of consumer goods, such as resins, plastics, paints, and polyester. Additionally, methanol is increasingly utilized in fuel applications, where methanol itself or one of its derivatives is used as a power and heat source. This broad range of applications highlights methanol's versatility and underscores its critical role in both the chemical industry and the energy sector. The concept of the "methanol economy"has emerged as a viable solution to the limitations of traditional fossil fuels. Methanol, traditionally derived from fossil-fuel-based syngas, can also be produced by the direct oxidative conversion of natural gas or the reductive conversion of atmospheric CO_2 with hydrogen. This allows hydrogen to be stored in the form of methanol, providing a convenient liquid fuel and raw material for synthetic hydrocarbons. This process not only opens up alternative energy sources but also offers a method to store renewable energy[12]. In recent years, driven by the need to reduce greenhouse gas emissions, the focus on sustainable production methods for methanol has intensified, and the demand for methanol continues to grow, with global production capacity expected to exceed 190 million metric tons by 2025[13]. One of the most promising methods for both producing methanol and fighting global warming is the hydrogenation of CO_2 to methanol. By using hydrogen derived from renewable sources such as wind, solar, or biomass, the synthesis of methanol aligns with the vision of creating "liquid sunshine”[5]. This strategy aims to combine renewable energy with CO_2 and water to produce green liquid fuel, thereby offering a sustainable alternative to fossil fuels and contributing to the reduction of carbon emissions. According to thermodynamics, the most stable reaction pathway for CO_2 hydrogenation yields methane as the product. The pathway to a particular reaction can be selectively controlled by selecting appropriate catalysts and reaction conditions. Low temperatures favor methanol synthesis, but it is kinetically unfavorable for breaking the O–C–O bonds in CO_2 molecules[13]. It is a challenge to obtain both a high single-pass CO_2 conversion and a high methanol selectivity with the current industrial catalyst via direct CO_2 hydrogenation. Thus, a selective catalyst is required to optimize methanol synthesis. Understanding the detailed mechanisms of CO_2 hydrogenation is crucial for designing effective catalysts. Research has identified two main pathways for converting CO_2 to methanol: one involving CO intermediates via the Reverse Water Gas Shift (RWGS) reaction and another through formate intermediates derived directly from CO_2 hydrogenation. According to the density functional theory (DFT) calculations, CO_2 hydrogenation prefers the formate pathway[13]. Different strategies can be employed to enhance methanol yield by suppressing CO formation, although challenges arise when pathways share intermediates with CO production. Optimizing these processes requires understanding and manipulating the specific pathways and intermediates involved in CO_2 hydrogenation. The history of Cu-based catalysts for methanol synthesis from CO_2 spans over a century of development and refinement. Initially patented in 1921 by Patart, these catalysts faced challenges, such as susceptibility to sulfur poisoning, which hindered commercial viability until the late 1960s. Imperial Chemical Industries’ introduction of the Cu/ZnO catalyst marked a significant advancement, allowing operation at pressures of 50-100 bar and temperatures of 200-300 °C using syngas[14]. Further innovations in the 1970s and 1980s, including the ternary Cu-based catalyst incorporating zinc oxide and alumina, enhanced catalyst stability, activity, and resistance to poisoning, such as by dimethyl ether (DME) by-products[13]. Efforts to utilize CO_2 as a sole feedstock for methanol synthesis were recognized as early as the 1930s, with significant milestones achieved by the 1940s, demonstrating the feasibility of producing methanol from CO_2 over copper-alumina catalysts under high pressures and temperatures[15]. Research expanded in the 1980s, focusing intensively on optimizing Cu-based catalysts for CO_2 hydrogenation[16]. Today, the ternary copper-based catalyst ($Cu/ZnO/Al_2O_3$) remains pivotal in industrial methanol synthesis from CO_2 and syngas mixtures, operating at temperatures of 220-300 °C and pressures of 50-100 bar[14]. This advancement responds to the global imperative for clean fuel sources and environmental stewardship, despite ongoing challenges in developing highly efficient catalysts for direct CO_2 conversion.

The present industrial catalyst ($Cu/ZnO/Al_2O_3$)

$Cu/ZnO/Al_2O_3$ (CZA) catalysts have attracted significant interest in methanol synthesis due to their distinct properties and effectiveness. The exceptional catalytic performance of CZA systems stems from their high surface area, superior thermal stability, and the synergistic interaction between Cu and ZnO that enhances the adsorption and activation of CO_2 and H2, making them highly efficient and durable for methanol synthesis[17]. CZA catalysts comprise 50–70% CuO, 20–50% ZnO, and 5–20% Al_2O_3[13]. The reaction mechanisms occurring within the CZA formulation and the potential roles of its different components in driving activity have been extensively researched and debated for over 100 years, with this debate continuing to the present day. As new characterization techniques have emerged, our comprehension of these mechanisms has advanced, but the debate is likely to endure. The methanol synthesis over CZA systems involves several stages. Initially, hydrogen and carbon dioxide adsorb onto the catalyst’s surface. Copper sites are primarily responsible for hydrogen adsorption and activation, while ZnO aids in CO_2 adsorption. The activated H2 and CO_2 then undergo a series of reactions to form methanol. The overall mechanism can be described by the following steps: hydrogen adsorption and activation, CO_2 adsorption, formation of intermediates, and hydrogenation of intermediates. During the first step, H2 molecules dissociate on the copper surface. Next, CO_2 molecules are adsorbed on the ZnO sites. Adsorbed H2 and CO_2 react to form formate (HCOO-) and other intermediates on the catalyst surface, which are further hydrogenated, primarily on the Cu sites, leading to the formation of methanol[18]. Each compound in the CZA catalyst plays a specific role. Copper acts as the primary active site for hydrogen adsorption and activation. It is also involved in the hydrogenation of CO_2 and reaction intermediates to methanol. Zinc oxide facilitates the adsorption of CO_2 and stabilizes the Cu nanoparticles, enhancing the overall catalytic activity. ZnO also plays a role in the dispersion of copper, preventing sintering and maintaining high surface area. Alumina enhances the structural integrity of the catalyst and increases its thermal stability. Al_2O_3 also affects the distribution of copper and zinc species, contributing to the overall efficiency and longevity of the catalyst[13]. The preparation of CZA catalysts typically involves co-precipitation, a process that ensures intimate mixing of the precursor salts of Cu, Zn, and Al. The common steps in the preparation include precipitation, aging, filtration and washing, drying and calcination, and reduction. In the precipitation step, a solution of metal nitrates (Cu, Zn, and Al) is mixed with a carbonate solution under controlled pH and temperature conditions to precipitate the metal hydroxides or carbonates. The precipitate is aged to ensure complete precipitation and maturation of the solid phase, which influences the final catalyst's microstructure. The precipitate is then filtered and washed to remove any residual ions such as carbonate or hydroxide that could affect the catalyst's performance. Following this, the filtered precipitate is dried and then calcined at high temperatures to decompose the hydroxides or carbonates into oxides, forming the active CZA phases. Finally, the calcined catalyst is reduced in a hydrogen atmosphere to convert CuO into metallic copper (Cu), the active phase for methanol synthesis[18]. CZA catalysts have been a cornerstone in industrial methanol synthesis for decades, constantly serving as the primary catalyst in this process. Over the years, extensive studies and numerous improvements have been made to enhance its performance. Despite significant advancements, there remain unanswered questions regarding how to further improve its selectivity and effectiveness. The ongoing investigation and enhancement of the CZA catalyst underscore its further potential in methanol synthesis, though scientists are in a continuous search of alternatives.

Reasons for the CZA deactivation

Even though CZA catalysts are currently the most widely used industrial catalysts for methanol synthesis from CO_2, they still have their own disadvantages. One of the significant challenges faced by CZA catalysts is deactivation over time[5]. Deactivation of catalysts is a common issue in heterogeneous catalysis, leading to a decline in catalytic activity and efficiency. For CZA catalysts, several mechanisms contribute to their deactivation. A major cause of deactivation in CZA catalysts is sintering, a process where catalyst particles agglomerate, leading to a decrease in active surface area. Sintering can occur in two stages: coalescence, which is the initial and rapid agglomeration of particles, and Ostwald ripening, a slower process driven by surface diffusion and thermodynamic stability[19]. During the early stages, finely dispersed copper particles merge, reducing the catalyst's surface area and activity. Over time, the catalyst particles continue to grow, further diminishing the catalyst's effectiveness[20]. The sintering of both Al_2O_3 and Cu particles is exacerbated by the presence of water, which promotes particle migration and agglomeration[21]. Another contributing factor to CZA deactivation is the formation of surface deposits from reaction intermediates and by-products. These deposits, particularly carbonates and water-derived species, can block active sites on the catalyst surface, hindering the adsorption and activation of reactants. Additionally, the structural integrity of the catalyst can be compromised over time. The alumina support, which provides thermal stability and structural support, can undergo phase changes or degradation under reaction conditions, further reducing the catalyst's performance[22]. Thermal and hydrothermal conditions during methanol synthesis also play a significant role in catalyst deactivation. High temperatures can induce structural changes in the catalyst, leading to the loss of active sites. Moreover, the continuous exposure to steam, a by-product of the reverse water-gas shift (RWGS) reaction, can accelerate the sintering process and alter the catalyst's physical and chemical properties[23]. While efforts have been made to improve the stability and longevity of CZA catalysts through various methods, including the incorporation of stabilizing agents and the development of advanced preparation techniques, the fundamental issue of deactivation remains a critical area of research.

Effect of Water on the CZA

Water, produced as a by-product in the RWGS reaction during CO_2 reduction to methanol, significantly influences the deactivation of CZA catalysts. The presence of water affects both the physical structure and the chemical properties of the catalyst. One of the primary ways water deactivates the catalyst is through sintering. Water molecules facilitate the migration and coalescence of copper particles, leading to the growth of larger particles and a consequent reduction in active surface area[21]. This sintering process diminishes the catalyst's ability to adsorb and activate reactants effectively. Additionally, water can interact with the catalyst components, leading to the formation of hydroxyl groups on the catalyst surface. These hydroxyl groups can block active sites necessary for CO_2 hydrogenation, reducing the overall catalytic activity[21]. Water also promotes the oxidation of metallic copper into less active or inactive copper oxides, further impairing the catalyst's performance. Studies have shown that water can lead to the crystallization of ZnO and Cu particles, accelerating the deactivation process. The adsorption of water on the catalyst surface can also lead to the formation of carbonate species when reacting with CO_2. These carbonates can block active sites, preventing the efficient conversion of CO_2 to methanol[24] . The combined effects of particle sintering, site blockage, and oxidation underscore the detrimental impact of water on CZA catalysts, highlighting the need for strategies to mitigate these effects to enhance catalyst durability and performance in methanol synthesis.

Ways to mitigate CZA deactivation

The deactivation of CZA catalysts, particularly due to the presence of water during methanol synthesis from CO_2, poses a significant challenge to their long-term effectiveness. Numerous studies have explored various strategies to mitigate this deactivation and enhance the water tolerance of CZA catalysts. These strategies focus on improving the stability of the catalyst's structure, preventing the sintering of active components, and enhancing the overall catalytic activity. The use of promoters and modifiers is one of the most promising strategies to enhance the water tolerance and overall qualities of CZA catalysts. Various elements such as K, Ba, Zr, Ce, Mn, La, Si, Pd, Ga, Mg, and Y have been utilized as promoters[25 26 27]. These elements are expected to increase the Cu surface area, improve Cu dispersion, and ease the reducibility of CuO to metallic Cu, thereby enhancing the catalytic performance[25]. According to Etim et. al.[13], the specific surface area, Cu surface area, Cu dispersion, and the number of basic sites increase in the order: Cu/Zn/Al < Cu/Zn/Al/Mn < Cu/Zn/Al/La < Cu/Zn/Al/Ce < Cu/Zn/Al/Zr < Cu/Zn/Al/Y, while the CH3OH selectivity increases in the order of Cu/Zn/Al < Cu/Zn/Al/Mn < Cu/Zn/Al/La < Cu/Zn/Al/Ce < Cu/Zn/Al/Y < Cu/Zn/Al/Zr. This suggests that Y and Zr showed the best results as promoters for the CZA catalyst, both in methanol selectivity and Cu improvement. Lee et al.[28] investigated incorporating Zr, Ga, and Mg additives into the traditional CZA catalyst. Ga and Mg didn't enhance CZA performance; indeed, they lowered both methanol yield and conversion ratio. This was attributed to difficulties in reducibility and the increased crystalline size of copper particles. Whereas the Zr promoter improved the methanol selectivity. However, CZA-Zr catalyst displayed significantly reduced CO_2 conversion, possibly due to intensified water-gas shift reaction activity. The use of glucose pretreatment has emerged as a novel method to improve the structural properties of CZA catalysts[29]. This pretreatment results in better dispersion of Cu particles and increases the specific surface area of the catalyst, leading to enhanced performance and stability. Glucose pretreatment generates a carbonaceous layer during catalyst synthesis, which acts as a protective barrier against water-induced sintering. At the molecular level, this treatment enhances Cu dispersion and increases the specific surface area, ensuring that more active sites remain accessible. Additionally, the carbon layer stabilizes Cu nanoparticles, preventing their agglomeration and maintaining high catalytic activity over extended periods. Studies have demonstrated that glucose-treated catalysts exhibit higher resistance to water-induced deactivation, as the treatment helps in maintaining the structural integrity and preventing the formation of inactive copper oxides. The improved dispersion and stability of Cu particles achieved through glucose pretreatment contribute to the overall durability and effectiveness of the catalyst in methanol synthesis[29] . To overcome water-caused deactivation Barrow et al.[11] incorporated silicon (Si) into the conventional CZA catalyst and evaluated its performance over a range of conditions and different timescales. Silicon doping introduces Si-O bonds into the catalyst's framework, creating a more robust support structure that resists hydrothermal degradation. At the molecular level, these bonds reduce the mobility of copper particles, mitigating sintering—a major cause of deactivation. Additionally, the incorporation of Si improves the distribution of Cu nanoparticles, maintaining a higher active surface area in water-rich environments. However, excessive Si loading can block active sites, necessitating precise optimization to balance stability and accessibility. The silicon-doped catalyst was tested against CZA in the production of methanol from CO_2 for about 50 days. The results showed that the modified catalyst demonstrated a substantial stability benefit with an activity benefit of 1.4 in less than 600 hours. The study concluded that the addition of silicon resulted in a significant enhancement and was associated with improved retention of copper surface area. However, a substantial proportion of Si component caused active sites' blocking. Thus, an optimal amount has to be determined for the catalyst to allow maximum incorporation of Si while maintaining a free copper surface[11].

ZrO_2 is another effective promoter for the CZA due to its hydrophobicity and surface basicity[30]. Moreover, its high thermal stability and catalytic activity is superior to that of Al_2O_3 or SiO_2. The hydrophobicity and basicity of ZrO_2 play crucial roles in enhancing water tolerance. Molecularly, ZrO_2 prevents water adsorption on active sites, reducing the risk of hydroxyl group formation that blocks catalytic activity. Its oxygen vacancies facilitate the activation of CO_2 molecules by forming stable intermediates, such as formates, which are critical for methanol synthesis. Furthermore, the strong interaction between Cu and ZrO_2 enhances hydrogen spillover, wherein activated H atoms migrate from Cu to ZrO_2, enabling efficient hydrogenation reactions. The addition of ZrO_2 increases the surface area of Cu species and modifies the Cu+/Cu0 ratio, thus providing an interface conducive to methanol synthesis[30]. The hydrophobic nature of ZrO_2 also contributes to its resistance to water deactivation, promoting the desorption of formed water and benefiting methanol formation. The strong interaction between Cu and ZrO_2 enhances the catalytic conversion of CO_2 to methanol, with $Cu/ZnO/ZrO_2$ catalysts showing higher activity and selectivity due to structural and surface modifications[30]. The addition of a small amount of silica to a $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst significantly improved its long-term stability in methanol synthesis from CO_2, suppressing the crystallization of Cu and ZnO[31]. Xu et al. modified Cu/ZnO catalyst by adding silica (SiO_2) with hydrophobic organic groups[23]. The new catalysts can remove water from the catalyst's surface, mitigating Cu and ZnO sintering, and improving the catalyst's stability ($CuZn/SiO_2$-Methyl < $CuZn/SiO_2$-Ethyl < $CuZn/SiO_2$-Propyl). Hydrophobic coatings involve functionalizing the catalyst surface with organic groups like methyl, ethyl, or propyl chains. These groups form a physical barrier, repelling water molecules and preventing their interaction with active Cu sites. The hydrophobic nature of these coatings minimizes sintering and oxidation processes, preserving catalytic activity. However, overly long organic chains may obstruct the adsorption of CO_2 and H2, reducing catalytic efficiency. The research found that the length of the organic group chain was significant as a physical barrier, hindering the migration and growth of the Cu particle, and ultimately delaying the deactivation of the catalyst[23] .

The findings from various studies underscore the critical role of modifying the CZA catalyst to enhance its water tolerance during methanol synthesis from CO_2. The strategies presented have demonstrated varying degrees of success in mitigating the deactivation of the catalyst. While these modifications offer promising improvements in catalyst stability and performance, each approach also comes with certain limitations, such as the potential for active site blocking or the increased cost associated with certain treatments. These findings lay the groundwork for a deeper exploration into the mechanisms by which these modifications influence the CZA catalyst, as well as the potential trade-offs involved, which will be thoroughly discussed in the following section.

Discussion

The discussion on enhancing the water tolerance of the CZA catalyst used in methanol synthesis from CO_2 revolves around a complex interplay of strategies designed to mitigate the detrimental effects of water on catalyst performance. Water, an inevitable byproduct in methanol synthesis, has been shown to promote the sintering of copper particles, facilitate the crystallization of zinc, and cause structural degradation of the active sites, ultimately leading to catalyst deactivation. The studies shown in the previous section present various strategies to counter these challenges, each offering distinct advantages and potential limitations. One of the primary strategies is the incorporation of promoters and modifiers such as K, Ba, Zr, Ce, La, and Y. These additives were expected to improve the Cu surface area, increase Cu dispersion, and facilitate the reduction of CuO to metallic Cu. However, not all provided a great modification to the CZA: among these promoters, only Y and Zr have been particularly effective, demonstrating significant improvements in both methanol selectivity and Cu surface enhancement. Thus, the effectiveness of these promoters can vary. For example, while Y and Zr enhance Cu dispersion and methanol selectivity, they may also introduce complexities related to optimal promoter loading. Excessive amounts of these promoters can lead to reduced catalytic efficiency or even increased formation of inactive copper oxides, thus necessitating careful optimization. Another approach explored is the application of hydrophobic coatings to the catalyst surface. These coatings aim to repel water molecules, thereby preventing their interaction with the active sites of the catalyst. Studies have shown that hydrophobic modifiers such as silica and hydrophobic organic groups can effectively shield the copper nanoparticles from water, thus preserving their dispersion and preventing agglomeration. However, while this approach appears promising, it introduces new complexities in the preparation and application of the catalyst. The implementation of hydrophobic coatings may require additional steps in the synthesis process, potentially leading to increased production costs. Furthermore, even though longer organic groups demonstrate higher hydrophobic properties, they also block the catalyst's active sites, decreasing its performance. The use of metal oxides as supports for the CZA catalyst is another method investigated to enhance its water tolerance. Among these, ZrO_2 stands out as a particularly promising modifier. ZrO_2 offers several significant advantages: it provides a more robust support structure that resists degradation by water, thereby preserving the dispersion of copper particles and preventing sintering. This enhances the catalyst's long-term stability and performance. ZrO_2 also positively influences the catalyst's properties by improving CO_2 adsorption and activation, which are critical for efficient methanol synthesis. Additionally, ZrO_2 promotes the dissociation of H2 and facilitates the spillover of atomic hydrogen, which further contributes to the catalytic activity. The high thermal stability of ZrO_2 ensures that the catalyst maintains its structural integrity under harsh reaction conditions, leading to sustained catalytic performance. Still, the multiple roles of ZrO_2 in the catalytic process are currently under debate, and there is not enough experience and optimization data for ZrO_2. Moreover, ZrO_2 is generally more expensive than other support materials like Al_2O_3 or SiO_2. Recent innovations have also introduced novel improvements, such as glucose pretreatment. This method has shown considerable promise in enhancing the structural properties of CZA catalysts. Glucose pretreatment improves the dispersion of copper particles and increases the specific surface area, leading to enhanced performance and stability. However, achieving widespread application in methanol production remains challenging due to factors such as complex synthesis processes, higher costs, and the need for precise optimization. These novel methods hold promise but require further development and refinement to address practical challenges and ensure their effective integration into industrial processes. When comparing the various modifiers for CZA, it becomes evident that certain modifications hold more promise than others. Y and Zr emerge as particularly effective promoters, significantly enhancing

Table 1 COMPARATIVE SUMMARY OF CATALYST MODIFICATION STRATEGIES FOR CZA

Study/Source	**Method**	**Strengths**	**Limitations**	**Key Results**
Barrow et al., 2024[11]	Silicon doping	Enhanced stability; extended lifespan; mitigates sintering	Potential active site blocking at high Si levels; added cost	1.4× activity increase; stable over 50 days
Jiang et al., 2023[29]	Glucose pretreatment	Improved Cu dispersion; better structural integrity; increased surface area	Complex synthesis; scalability issues; higher cost	Higher resistance to water-induced deactivation; 10% increased methanol yield
Xu et al., 2021[23]	Hydrophobic organic coatings	Protects active sites from water; mitigates sintering	Blocks active sites if coating is too thick	Stabilized activity for over 1000 hours
Lee et al., 2020[28]	Zr promoter	Improves Cu dispersion; enhances methanol selectivity	Reduced CO_2 conversion due to intensified water-gas shift reaction	Increased stability and methanol yield
Li & Chen, 2019[30]	ZrO_2 support modification	High thermal stability; improves CO_2 adsorption and H2 activation	Higher cost compared to Al_2O_3; limited optimization data	Enhanced methanol selectivity and water resistance
Wu et al., 2001[31]	SiO_2 addition to $Cu/ZnO/ZrO_2$	Suppresses Cu and ZnO crystallization; long-term stability	Needs precise optimization to prevent overloading	Prolonged catalyst lifespan

methanol selectivity and improving the Cu surface area and dispersion. Zr, in particular, not only enhances the catalyst's methanol synthesis efficiency but also contributes to its long-term stability by resisting water-induced deactivation. In contrast, modifiers such as Ga and Mg were found to decrease catalytic performance, highlighting the importance of carefully selecting and optimizing promoters. Hydrophobic coatings, such as those involving silica or hydrophobic organic groups, also show promise by protecting the catalyst from water-related deactivation; however, their effectiveness depends heavily on the balance between hydrophobicity and the accessibility of active sites. Similarly, glucose pretreatment has shown potential in improving Cu dispersion and stability but requires further development to overcome practical application challenges. Each modification strategy for enhancing CZA water tolerance carries distinct implications for scalability and long-term stability. Promoters such as Zr and Y offer promising enhancements in catalyst performance but pose challenges related to large-scale implementation due to the precise optimization required for promoter loading. Excessive addition can lead to active site blocking, reducing efficacy. Strategies like glucose pretreatment and hydrophobic coatings, though effective in lab-scale settings, may encounter difficulties in industrial scalability. The complexity and cost of synthesis processes for hydrophobic coatings or glucose pretreatment might hinder widespread adoption. Conversely, silicon doping and ZrO_2 support modifications demonstrate scalable potential due to relatively simpler synthesis methods and long-term stability benefits, as evidenced by performance over extended reaction times. Modified CZA catalysts show competitive advantages compared to emerging alternatives like Cu/ZrO_2 and novel bimetallic systems. ZrO_2-based catalysts exhibit superior hydrophobicity and thermal stability, enhancing water resistance, while bimetallic systems offer tailored catalytic properties by combining two active metals. However, Cu/ZrO_2 systems often surpass CZA in CO_2 adsorption efficiency and methanol selectivity, albeit at a higher cost. Bimetallic catalysts, such as Cu-Fe and Cu-Ni systems, introduce unique synergies that can enhance reaction pathways but may lack the established industrial viability and optimization data available for CZA. Environmental sustainability is a critical factor in evaluating catalyst modifications. Additives like Zr and Y can increase environmental footprints due to mining and production requirements, while glucose pretreatment represents a greener alternative due to its use of renewable materials. However, life cycle assessments of these modifications are essential to quantify their overall impact. Strategies that improve water tolerance also indirectly enhance sustainability by extending catalyst lifespan and reducing waste. Hydrophobic coatings using organic groups may offer sustainable advantages by minimizing water-related degradation without relying heavily on rare materials.

Economic considerations are paramount for industrial implementation. Strategies like silicon doping and ZrO_2 incorporation appear more cost-effective due to their dual benefits of long-term stability and performance enhancement.

Table 2. SYSTEMATIC COMPARISON OF CATALYST MODIFICATION STRATEGIES FOR CZA

Study	Modification	Operating Conditions	Water Tolerance	Economic Considerations
Barrow et al., 2024[11]	CZA + Si	220–300 °C, 50–100 bar	Improved	Moderate cost; risk of site blocking at high Si loading
Jiang et al., 2023[29]	CZA + Glucose pretreatment	220 °C, 50 bar	Improved	High cost; complex synthesis
Xu et al., 2021[23]	CZA + Hydrophobic organic coatings	220–250 °C, 50 bar	Excellent	High cost; potential site blocking
Lee et al., 2020[28]	CZA + Zr promoter	230 °C, 55 bar	Improved	Moderate; requires optimization
Li & Chen, 2019[30]	CZA + ZrO_2 support	220–260 °C, 50–100 bar	Excellent	High cost; limited industrial trials
Wu et al., 2001[31]	Cu/ZnO/ZrO_2 + SiO2	240 °C, 60 bar	Excellent	Moderate; precise loading required

On the other hand, glucose pretreatment and complex hydrophobic modifications, though innovative, may involve higher production costs that could limit adoption. An optimal strategy would balance cost and performance, ensuring modifications do not disproportionately increase methanol production expenses.

The discussion on enhancing the water tolerance of the CZA catalyst highlights the delicate balance between improving catalyst performance and managing the practical challenges associated with each modification. While the strategies explored offer promising solutions to water-induced deactivation, they also introduce new variables that must be carefully considered to ensure the long-term viability of the catalyst in industrial applications. The research underscores the importance of continued exploration and optimization of these methods to develop a catalyst that not only withstands the challenges posed by water but also maintains high activity and selectivity for methanol synthesis from CO_2. The ultimate goal is to achieve a catalyst that is both technically and economically feasible and capable of operating under the harsh conditions of industrial methanol production while minimizing the impact of water on its performance.

Conclusion

The investigation into the water tolerance of the industrial CZA catalyst for methanol synthesis from CO_2 reveals significant potential for enhancement through various strategies. Successful methods, such as incorporating Y or Zr and modification of CZA with hydrophobic organic groups, aim to mitigate the detrimental effects of water on the catalytic performance, ensuring better stability and activity under industrial conditions. The study also highlights the importance of optimizing the synthesis process and the choice of support materials to further improve the catalyst's resistance to water-induced deactivation. Future research should focus on the experimental validation of these proposed strategies, particularly the development and testing of novel hydrophobic coatings and surface modifications in real industrial environments. Additionally, investigating the long-term stability of these enhanced catalysts under varying operational conditions will be crucial for their practical application. By advancing the understanding and application of these techniques, the field can move closer to achieving more efficient and durable catalysts for sustainable methanol production from CO_2, ultimately contributing to the broader goal of carbon capture and utilization.

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