

Overview of the latest progress and prospects in the catalytic hydrogenation of carbon dioxide (CO₂) to methanol in membrane reactors

Mustapha Grema Mohammed^a, N. Awanis Hashim^{a,b,*}, Wan Mohd Ashri Wan Daud^{a,b,**},
Unalome Wetwatana Hartley^{c,d}, Mohamed Kheireddine Aroua^{e,f}, Sebastian Wohlrab^g

^a Department of Chemical Engineering, Faculty of Engineering, Universiti Malaya, 50603, Kuala Lumpur, Malaysia

^b Sustainable Process Engineering Centre (SPEC), Department of Chemical Engineering, Faculty of Engineering, Universiti Malaya, 50603, Kuala Lumpur, Malaysia

^c Chemical and Process Engineering, The Sirindhorn International Thai-German Graduate School of Engineering (TGGSE), King Mongkut's University of Technology, North Bangkok, Bangkok, 10800, Thailand

^d Joint Graduate School of Energy and Environment (JGSEE), King Mongkut's University of Technology, Thonburi, Bangkok, 10140, Thailand

^e Research Centre for Carbon Dioxide Capture and Utilisation (CCDCU), School of Engineering and Technology, Sunway University, No. 5 Jalan Universiti, Bandar Sunway, 47500, Petaling Jaya, Selangor, Malaysia

^f Department of Engineering, Lancaster University, Lancaster, LA1 4YW, UK

^g Leibniz Institute for Catalysis, Albert-Einstein-Straße 29a, D-18059, Rostock, Germany

ARTICLE INFO

Handling Editor: Dr S Nanda

Keywords:

CO₂ hydrogenation
MOFs
Methanol synthesis
Zeolite membrane
Membrane reactor

ABSTRACT

Rising levels of carbon dioxide (CO₂) emissions due to human activities exert a substantial adverse effect on the environment. The conversion of CO₂ into methanol (CH₃OH) through hydrogenation is a promising way to utilize this greenhouse gas, thus maintaining carbon in the cycle. In terms of sustainability, methanol is of particular interest because of its dual utilization potential as a fuel or base material to produce different chemicals. The versatility of the latter allows it to be used directly as a precursor to produce numerous compounds, including dimethyl ether (DME), olefins, formaldehydes, and hydrocarbon fuels. This paper first reviews the latest developments in catalyst design, focusing on the relationship between catalyst structure and performance. In addition, recent advances in understanding the reaction mechanisms, optimizing catalyst architectures, innovating membrane reactors, and reaction conditions have been discussed. This summarizes the strategies for increasing the efficiency of sustainable methanol production with the help of membranes. This study provides an outlook for future research in this field.

1. Introduction

The burning of fossil fuels remains the world's primary source of energy, accounting for over 85% of global energy output [1,2]. This process releases large amounts of greenhouse gases (GHGs) into the atmosphere, trapping heat and contributing to climate change [1–3]. The significant release of carbon dioxide (CO₂) from various sources contributes to roughly two-thirds of global warming [1,4]. According to a recent report from the National Oceanic and Atmospheric Administration's (NOAA) Global Monitoring Lab, the average global atmospheric CO₂ reached a record-breaking 421 parts per million (ppm) in 2022, despite the ongoing economic impact of the COVID-19 pandemic [5].

The use of CO₂ as feedstock for synthesizing chemicals and fuels is a promising strategy for mitigating gas emissions [6–9]. Global warming resulting from greenhouse gas emissions has recently garnered significant attention [10]. The rise in atmospheric CO₂ levels significantly contributes to climate change, which is characterized by melting ice caps, rising sea levels, and extreme weather events [3]. To address this, the Conference of the Parties (COP) convenes annually to negotiate agreements. In 2015, the COP enacted the Paris Agreement, which seeks to limit global warming to less than 2 °C by 2030 and achieve net-zero greenhouse gas emissions by 2050. COP-27 in 2022 further supported this agreement by promoting clean technology development. Malaysia has pledged to achieve a substantial 45% reduction in its greenhouse gas emissions by 2030 with the intention of achieving carbon neutrality by

* Corresponding author. Department of Chemical Engineering, Universiti Malaya, Kuala Lumpur, 50603, Malaysia.

** Corresponding author. Department of Chemical Engineering, Universiti Malaya, Kuala Lumpur, 50603, Malaysia.

E-mail addresses: awanis@um.edu.my (N.A. Hashim), ashri@um.edu.my (W.M.A.W. Daud).

<https://doi.org/10.1016/j.ijhydene.2024.06.138>

Received 23 January 2024; Received in revised form 5 June 2024; Accepted 10 June 2024

Available online 21 June 2024

0360-3199/© 2024 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

2050 [11].

Carbon capture and utilization (CCU) is becoming an increasingly viable alternative to conventional carbon capture and storage (CCS) methods for reducing CO₂ emissions. CCU involves capturing CO₂ from different sources and utilizing it as a sustainable carbon feedstock to produce valuable chemicals and materials. This approach not only helps reduce CO₂ emissions but also allows for renewable energy storage in chemical bonds by producing valuable fuels and feedstock [12].

Combating atmospheric CO₂ through capture and utilization technologies is essential to curb global warming and preserve the environment. Nonetheless, the primary obstacle to CO₂ conversion is its thermodynamic stability ($\Delta H = -393.5$ kJ/mol). However, many recent reports have confirmed that converting CO₂ into useful products is promising and can help to solve environmental problems [13–16]. Most CO₂ conversion methods are characterized by high energy demand [7], and by utilizing hydrogen for energy production, greenhouse gas emissions can be significantly reduced because its combustion produces only heat and water vapor [17]. Almost all industrial hydrogen comes from fossil fuels (like natural gas and coal), even the "cleanest" methods releasing CO₂. To produce cleaner hydrogen, three options exist: capturing CO₂ emissions (CCS), using non-polluting hydrocarbon conversion, or using renewable energy sources, such as nuclear or solar [18]. The report "Large-scale electricity storage" discovered that by 2050, the UK will require substantial energy storage to achieve its net-zero goal of generating electricity solely from wind and solar sources. The majority of this storage is expected to rely on hydrogen [19]. Hydrogen is the most abundant element in the universe, making up approximately 75% of all matter [20].

The co-utilization of CO₂ and hydrogen gas presents an opportunity to produce diverse chemical products including methanol (CH₃OH), methane (CH₄), carbonate, and formic acid [21,22]. Among these products, CH₃OH is a particularly intriguing candidate because of its wide-ranging utility as an energy source in fuel cells, hydrogen storage applications, and internal combustion engines [5]. It is also regarded as a secure, highly transportable, and swiftly biodegradable liquid fuel with steadily increasing demand [23]. Its compatibility with the existing vehicle technology renders it a viable option for utilization with minimal incremental expenses [24,25].

Additionally, methanol serves as a convenient hydrogen carrier, offering a viable option for hydrogen production in internal reforming methanol fuel cell (IRMFC) applications [26], and demonstrates favorable attributes, such as lower storage costs and enhanced transportability, compared to compressed hydrogen [21]. Compared to other hydrogen carriers, methanol is notable for its high hydrogen-to-carbon ratio, lack of C-C bonds, and relatively low reforming temperature ranging from 250 to 350 °C [27]. Approximately 30% of the globally produced CH₃OH is used to make formaldehyde [28]. Within the broader framework of sustainability, methanol exhibits notable appeal because of its dual functionality as both a fuel source and foundational component for diverse chemicals. Its versatility enables its direct use as a fuel and serves as a precursor to produce various substances, including olefins, dimethyl ether, formaldehyde, and hydrocarbon fuels [9,29,30].

In 2019, global CH₃OH production amounted to 98 million tons (Mt) and annual demand nearly doubled over the last ten years [31]. A prospective analysis indicated an anticipated escalation in worldwide methanol demand, exceeding 120 Mt by 2025 and potentially reaching 500 Mt by 2050. The conversion of CO₂ into CH₃OH represents the inverse process of methanol steam reforming ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 3\text{H}_2$) [27,32]. The conventional method for producing methanol involves a catalytic reaction pathway using syngas primarily composed of CO₂, H₂, and CO. Cu/ZnO/Al₂O₃, also known as CZA catalyst, is commonly used for this process. In this catalyst, copper (Cu) serves as the active component responsible for the catalytic activity and surface area, which is key to the efficiency of the catalyst. Zinc oxide (ZnO) is a secondary component that primarily enhances copper dispersion [33]. Aluminum oxide (Al₂O₃) serves as a support or carrier material,

providing the fundamental structure and morphology of the catalyst.

Several studies have been conducted to enhance catalyst reactivity by augmenting the dispersity, porosity, and surface area of the active ingredient, particularly Cu [34,35]. Recent research has demonstrated that various oxides, such as ZnO, ZrO₂, Al₂O₃, In₂O₃, CeO₂, SiO₂, Ga₂O₃, TiO₂, MgO, Cr₂O₃, and Nb₂O₅, can form support-metal interfacial sites. This leads to enhanced Cu dispersion on the catalyst surface, along with modifications in the acidity, basicity, and oxygen vacancy concentration [36]. ZnO-based catalysts enhance the rate of CH₃OH production by utilizing the synergistic interactions at the interfaces between the Cu and ZnO components [37]. Big data analyses based on the available literature show correlations between the catalyst composition, reaction conditions, and performance [38].

A promising approach to achieving optimal catalyst efficiency is the use of metal-organic frameworks (MOFs), which are characterized by their outstanding crystal structure, large surface area, and considerable porosity. As platforms for Cu-based catalysts, MOF precursors offer a solution to the often inadequate efficacy usually associated with ternary co-precipitated Cu-based catalysts [39].

Owing to the relatively low unidirectional conversion efficiency of the CH₃OH synthesis reactor, a substantial amount of unreacted gas is sent back to the reactor, while a small portion is vented to prevent by-product buildup. Ultimately, the CH₃OH-rich liquid is introduced into the distillation column [40].

By employing a membrane to separate the products within the reactor, the conversion rate within the reactor can be enhanced, according to recent reports. The membrane offers the benefit of extracting reaction products in situ. Such membrane-based processes, also known as membrane reactor (MR) technologies, are based on vapor permeation technology developed to separate vapors (H₂O and CH₃OH) from gases (CO, CO₂, and H₂) in a preferred manner [41].

The development of catalytic membrane reactors (CMR) overcomes the limitations arising from the thermodynamic equilibrium in the conversion of CO₂ to CH₃OH. In this technology, catalytic reactions are integrated with selective membrane separation to facilitate the continuous and in situ elimination of steam byproducts. This approach helps shift the reaction equilibrium, promoting higher conversion rates and improving methanol yields [42,43].

This paper provides a succinct yet comprehensive analysis of recent advancements in membrane and catalyst syntheses. This review places particular emphasis on how factors such as the starting material, chosen support structure, crystallization time, temperature, and reproducibility can significantly impact the final membrane product. Following the analysis of synthesis methods, this review explores the latest advancements in CO₂ hydrogenation to CH₃OH, with a focus on Cu-based catalysts that encompass catalyst formulation (with special attention to the effect of metal-organic frameworks (MOF)), reaction mechanisms, innovative approaches in membrane reactor design, and emphasis on the significance of fine-tuning reaction conditions. Finally, this review summarizes the key findings of analysis methods, catalyst advancements, and reactor design. It also identifies promising avenues for future research and explores the potential environmental implications of these technological advancements.

2. Membranes

2.1. Membrane synthesis

Membrane-based procedures have gained widespread recognition as fundamental steps in numerous industrial separation processes [44,45]. These procedures are prompted by factors such as pressure, concentration gradients, or electrical fields across the membrane and can be categorized based on the driving force, molecular dimensions, or operational nature [44]. Common membrane processes include gas segregation, pervaporation, reverse osmosis, nanofiltration, dialysis, and membrane contactors [44,45]. Although some hydrophobic polymer

membranes exhibit significant separation capabilities for organic and water pervaporation, they also suffer from thermal, mechanical, and chemical limitations. Enhanced properties have been observed in novel membranes, such as polymer blends, polymer membranes infused with zeolite, and dedicated zeolite membranes [46].

The International Zeolite Association (IZA) has documented more than 200 distinct framework structures. However, only 15 of these have been tested for membrane production [47]. Several years ago, the Japanese shipbuilder Mitsui pioneered the industrial application of the zeolite NaA membrane [45,48]. In recent decades, the use of zeolite layers as membranes has gained wide interest for applications such as electrodes, sensors, organized catalysts, and membranes. These materials, which are based on aluminosilicates, have highly ordered and consistent pore arrangements, which make them excellent candidates for membrane production. Among the various zeolite forms, the NaA phase has attracted considerable attention, particularly because of its effectiveness in separating gases and liquids [49].

Zeolite membranes are typically categorized as either zeolite films applied to stable substrates or self-standing crystalline zeolitic membranes. Supporting materials can be broadly categorized into porous supports (porous ceramics, porous Al_2O_3 , and stainless steel) and substrate materials (silicon wafers, quartz plates, glass, and LiTO_3 single-crystal plates) [50]. Zeolite-type materials, including MCM-41, ZIF, SBA-15, and MCM-48, have been explored and promising outcomes have been achieved with MOF fillers. These MOF fillers offer improved interfacial interactions with polymers, making them particularly appealing [51].

The uniform pore structures and strong thermal and chemical stabilities of microporous membranes (zeolites) have attracted considerable attention because of their potential for separating liquid or gas mixtures. Over the last 20 years, significant research has been conducted on the use of hydrophilic membranes (zeolites), such as zeolite LTA (NaA), T, MOR, CHA, MFI (Silicalite-1 and ZSM-5), and FAU (Y and X), for dehydration [52]. Additionally, hydrophilic FAU zeolite membranes, owing to their reduced Si/Al ratio, can be utilized to eliminate water from organic solvents using methods such as pervaporation and steam permeation [53]. Materials with elevated Si/Al ratios in their framework can withstand both high temperatures and water-rich environments, which in turn leads to enhanced hydrophobicity [52].

Numerous approaches have been devised for fabricating supported and self-supported zeolite membranes. These methods include embedding, seeding, in-situ hydrothermal synthesis, and secondary growth [51]. They are broadly classified into two types: indirect pre-seeding/crystallization and direct or in situ synthesis.

In the direct approach, the support material is exposed to a synthesis mixture containing the necessary precursors and templating agents, which can be homogeneous or heterogeneous. These precursors can be introduced as solutions or gels, or pre-applied to porous supports. This process may also involve the use of support materials, such as silica or alumina. Under hydrothermal conditions, nucleation, crystallization, and growth occur on the support surface, resulting in the formation of zeolite films [54].

Zeolite membranes can also be produced using a secondary hydrothermal synthesis method that separates the nucleation and crystal growth processes. This process involves the deposition of zeolite crystals on a support, followed by hydrothermal synthesis. Performing multiple synthesis cycles in succession is suggested to address the limitations of previous syntheses [55].

For example, the secondary growth technique has been effectively employed to synthesize high-quality Si-rich LTA membranes using an organic structure-directing agent (OSDA)-free gel solution with a silica-alumina ratio of 1.5. Notably, one membrane displayed exceptional water selectivity, exceeding 100,000 during vapor permeation at 378 K for the water/isopropanol, water/ethanol, and 90/10 wt% methanol/water mixtures. Si-rich LTA membranes exhibit exceptional stability in environments with water-rich mixtures and high temperatures. They

also demonstrated hydrothermal stability in a 50 wt% aqueous methanol solution at 333 K and maintained thermal stability during the vapor permeation of a water/methanol mixture with equal vapor proportions at 423 K. These findings suggest that Si-rich LTA membranes have significant potential for dehydrating water-rich mixtures and achieving separation under high-temperature conditions [52].

Despite significant advancements in creating LTA membranes through innovative synthesis techniques, such as secondary growth with seeds, multi-stage synthesis, microwave-assisted heating (Fig. 1), and the use of additional organic cations or intergrowth-enhancing substances, the separation factors for hydrogen (H_2) in binary mixtures with H_2/O_2 , H_2/N_2 , H_2/CO_2 , and H_2/CH_4 are closely aligned with Knudsen diffusion values. Consequently, the synthesis of LTA membranes with true molecular sieving capabilities remains challenging. An innovative approach was developed to synthesize dense LTA zeolite membranes without the need for seeding. This method involves the use of 3-aminopropyltriethoxysilane (APTES) as a covalent bridge connecting the zeolite membrane and the porous Al_2O_3 support (Fig. 2) [56].

Generally, the composition of the reaction used to represent the precursor mixture for zeolite synthesis is expressed in terms of the molar ratio of the oxide constituents, that is $\text{M}_2\text{O}:\text{R}_2\text{O}:\text{XO}_2:\text{H}_2\text{O}$. The roles of these components in the crystallization process of zeolites can be summarized as follows: (a) X represents framework atoms such as Ti, Ga, B, Al, Si, Fe, and others; (b) M stands for alkali metals like Cs, Rb, K, Na, Li, and others; (c) R denotes the OSDA (also known as the template), which is used to stabilize the zeolite structure and influence its chemical composition (quaternary ammonium compounds are commonly employed), shape, and size; (d) H_2O is the solvent, typically water, although other substances such as ammonia, diols, and alcohols may also be used. Water serves as both a solvent and space filler as well as a catalyst for hydrolyzing chemical reagents and accelerating chemical reactions [57].

Among the methods used to create zeolite membranes, such as secondary growth, vapor-phase transfer, and in situ hydrothermal synthesis, the secondary growth technique utilizing a seed layer has been extensively studied and is considered the most efficient means of producing high-quality membranes with superior separation performance, particularly on the outer surfaces of tubular supports [59]. Regrettably, the mechanical strength of the supportive material can be diminished owing to an excess of pores given its porous nature. An effective technique for enhancing and strengthening ceramics involves incorporation of whiskers. Currently, there are two primary approaches for enhancing the mechanical robustness of ceramics: external incorporation and inherent formation [48].

Despite numerous efforts to enhance zeolite deposition, multiple factors affect the morphology, structure, and physicochemical characteristics of zeolite layers. These factors include elements such as raw materials, composition of the reactant mixture, temperature, and the physical and chemical attributes of the porous support [49]. The secondary growth method with seeding is widely regarded as the most appealing technique for producing a range of zeolites (such as MFI, FAU, SOD, LTA, DDR, and CHA) and zeolite-like (such as MOF and MCM) membranes. It offers enhanced flexibility in managing the crystal growth and film microstructure, providing a higher level of scalability and reproducibility than the direct in situ hydrothermal synthesis method [51].

Zeolite membranes, characterized by a consistent pore structure and excellent thermal stability, are promising options for creating catalytic membrane reactors [43].

2.1.1. Effect of starting material

The performance of a zeolite membrane depends significantly on the chemical composition of the growth gel [45]. In the context of zeolite crystallization, the presence of OH^- ions as mineralizing agents facilitates the translocation of substances between solid and liquid phases, consequently influencing the crystallization process. The impact of the

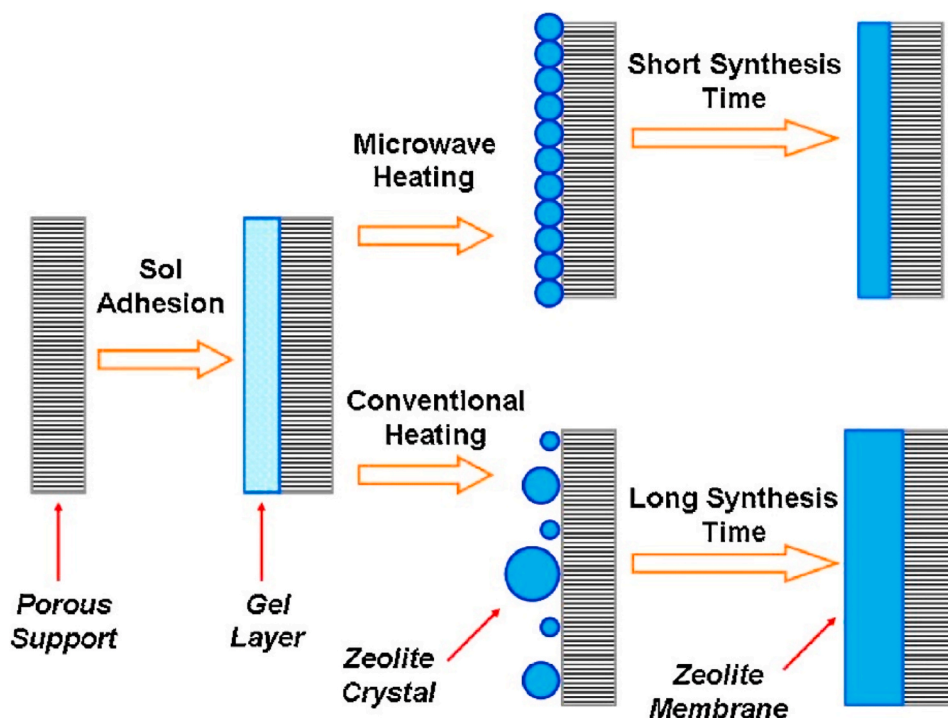


Fig. 1. Zeolite membrane synthesis using traditional/conventional heating and microwave heating. Reprinted from Ref. [58]. Copyright (2008), with permission from Elsevier.

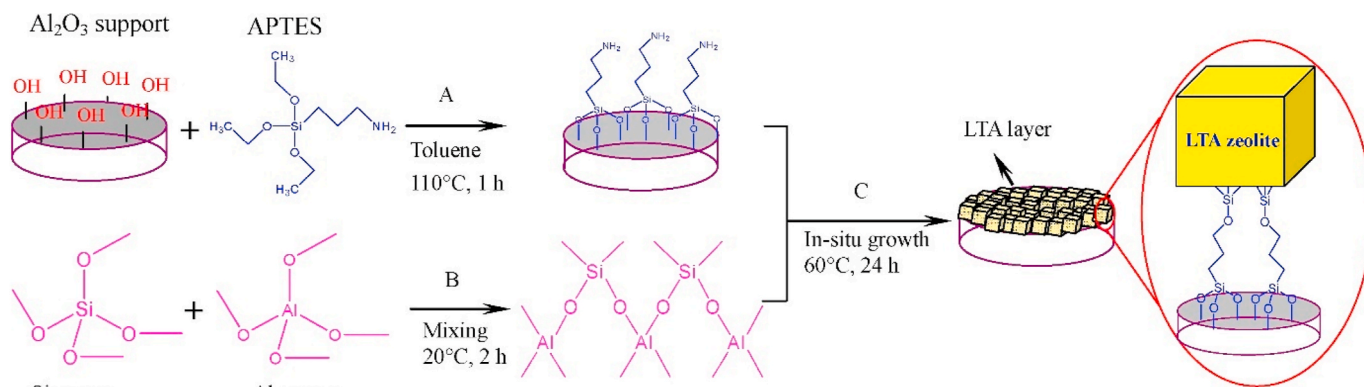


Fig. 2. Illustrative representation of the process for creating an LTA membrane employing 3-aminopropyltriethoxysilane (APTES) as a covalent connector between the alumina support and LTA zeolite membrane. Reprinted from Ref. [56]. Copyright (2010), with permission from Elsevier.

membrane synthesis can be outlined as follows: First, higher concentrations of OH^- ions within the gel matrix promoted the dissolution of the gel substance, concurrently augmenting its saturation capacity. Conversely, a carefully controlled amount of OH^- ions within the gel matrix is imperative; a significant excess of OH^- ions has the potential to induce dissolution of the resultant crystals within the system [60]. In addition, the concentration of Na_2O strongly influences the particle size and distribution of the product but does not alter the chemical composition of the product [61]. Nonetheless, as the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio increases, the separation factors of these zeolite membranes decrease [59].

2.1.2. Effect of crystallization time and temperature

Conventionally, the synthesis of zeolites in powdered form involves conducting syntheses at elevated temperatures ranging from 363 to 473 K, with the duration varying from hours to weeks depending on the specific zeolite configurations and synthesis parameters. The fabrication of zeolite membranes typically occurs under similar conditions, despite some differences compared with the production of zeolite powders [62].

Aging the secondary growth gel is a crucial step in the synthesis of high-quality zeolite membranes [45]. The degree of crystallinity in hydrogels increases as the duration and temperature of pretreatment are extended [59]. This can be explained by the substantial activation energy required for crystal growth in contrast to the lower energy required for nucleation. Consequently, as the temperature increased, the crystal growth rate surpassed the nucleation rate [63]. Synthesis at lower temperatures promotes nucleation over crystallization, resulting in the production of much smaller zeolite crystals, ultimately leading to the formation of thin zeolite membranes (Fig. 3), albeit with a considerable reduction in the overall product yield.

This dual-stage synthesis approach is a promising alternative to the single-step method. Specifically, initiating the first step at a lower temperature promotes rapid nucleation and allows the nuclei to migrate into the pores of the seed layer. Subsequently, during the second step, conducted at higher temperatures, these nuclei continued to expand in all directions, effectively bridging the gaps. Conversely, the single-stage heating technique accelerates crystal growth, resulting in a thicker and

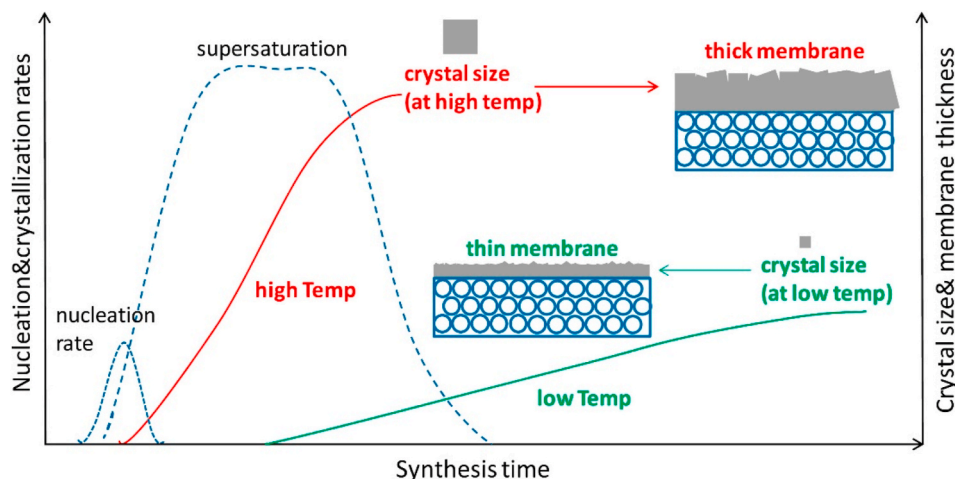


Fig. 3. Demonstration of the approach used to synthesize thin zeolite membranes. Reprinted from Ref. [62]. Copyright (2020), with permission from Elsevier.

less defect-free membrane layer [64].

2.1.3. Effect of support on membrane formation and separation performance

The composition and arrangement of the support materials are crucial factors in the creation of zeolite films, and significantly affect the separation characteristics of the membrane. The surface texture and pore size dictate the optimal dimensions of the zeolite crystals and the membrane thickness (Fig. 3). The chemical properties of the support surface influence the initiation of the zeolite formation, crystal growth, and film adhesion. It has been shown that chemical modifications to the support surface can markedly transform the formation of zeolite films. Porous stainless steel supports coated with extremely thin layers (20 nm) of metals and metal oxides offer exceptional reproducibility in film microstructures and hold promising potential for widespread utilization in the large-scale production of zeolite membranes [54]. The growth of the membrane layer relies heavily on the condition of the supporting surface [48,60].

Embedding is commonly employed in the fabrication of composite membranes and is referred to as a mixed-matrix membrane. These membranes incorporate zeolite particles that are evenly distributed within the bulk matrix and are typically composed of polymers. Typically, zeolite membranes are affixed, secured, or developed on porous supports with tailored mechanical, thermal, and chemical resilience using metals or ceramics [51]. The consistency of zeolite membranes improves when they are applied to coated supports [54].

Li et al. introduced a simple method to create a highly effective membrane designed for selective water vapor removal in challenging environments. CAU-10-H and [BMIM][BF₄] were selected owing to their strong hydrophilicity, exceptional stability, and compatibility. Functionalizing the MOF membrane with a hydrophilic ionic liquid (IL) not only increases its water capture capability but also closes off inter-crystal voids within the polycrystalline layer. The initial IL layer separated CO₂ and H₂O from H₂, whereas the subsequent MOF layer further impeded CO₂ permeation, resulting in impressive separation factors for H₂O/H₂ and H₂O/CO₂. At 473 K and 2.0 MPa with 10 mol% water content, the separation factors reached 446 and 273, respectively, with water permeance improving from $2.1 \times 10^{-8} \text{ molm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ to $7.7 \times 10^{-8} \text{ molm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ after IL treatment. Notably, IL treatment enabled water removal even at a low water content (5 mol%), where the original membrane failed. This selective water permeation suggests promising applications for IL-treated MOF membranes for in situ water removal under severe conditions, although membrane stability remains an area of improvement [65].

2.1.4. Reproducibility of membrane synthesis

Replicability of the synthesis is crucial for industrial advancement [60,66], and immature seeding techniques can hinder the reproducibility of membrane synthesis. Seeding is a critical step in the membrane fabrication process to produce high-quality zeolite membranes [66]. A study investigated the consistency of the membrane production process by synthesizing six membranes using mullite and porous stainless-steel supports. The membranes produced on mullite and stainless steel supports exhibited variations of 9% and 6% in flux and 22% and 19% in the separation factor (gases ...), respectively [67]. The partial spontaneous transformation of the inorganic support to MOF membranes can enhance heterogeneous nucleation and increase the adhesion between the MOF grains and the support. This, in turn, enhances the reproducibility of the as-synthesized membranes [68]. Finally, the reproducibility of the zeolite membrane synthesis is a key challenge that requires attention to make these membranes more commercially viable [69].

3. Catalysts

3.1. Catalysts for CO₂ hydrogenation to methanol

The conversion of CO₂ into CH₃OH by the reaction ($\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$) is seen as a promising approach, as it contributes both to mitigating the greenhouse effect and reducing dependence on fossil fuels [70]. At present, CH₃OH is synthesized from syngas using a copper-zinc catalyst at 473–573 K and 5–10 MPa [29,71–73]. Industrially, these Cu-ZnO-Al₂O₃ (CZA) catalysts are commonly used because of their remarkable catalytic activity, prolonged operational longevity, exceptional resistance to poisoning, and favorable reaction parameters concerning temperature and pressure [74]. While these CZA catalysts exhibit activity in the hydrogenation of CO₂ to CH₃OH, their practical implementation faces several issues. A significant concern is their pronounced activity in the rWGS reaction, where CO₂ and H₂ combine to yield CO and H₂O. This poses a major drawback for the CZA catalysts. The $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ (WGS) reaction is crucial for the synthesis of CH₃OH from syngas over these catalysts because the primary reaction mechanism involves direct hydrogenation of CO₂ [29,75].

Over the years, scientists have developed a diverse range of catalysts to facilitate CO₂ hydrogenation into CH₃OH. Notably, significant attention has been paid to Cu-based systems, which are often employed in conjunction with various metal oxides. These metal oxides act as carriers and promoters to optimize the catalytic processes [76]. In many countries, both companies and scientific research institutions are enthusiastically engaged in developing and executing projects focused on CH₃OH synthesis via CO₂ hydrogenation. Key participants in this area include Imperial Chemical Industries, Haldor Topsøe, Carbon

Recycling International in Iceland, Mitsui Chemicals Inc. from Japan, the Korea Institute of Science and Technology, and Lurgi [77]. Diverse catalyst materials have also been utilized for CO₂ conversion to CH₃OH through hydrogenation. These materials include Cu, noble metals (Ru, Pd, Pt, etc.), MaZrO_x (Ma = Zn, Ga, etc.) solid solution, and indium oxide (In₂O₃). However, their susceptibility to Ostwald ripening and particle migration in high-temperature aqueous environments leads to catalyst deactivation [78]. Table 1 presents a concise survey of the diverse catalysts employed in the contemporary methanol synthesis industrial sector.

3.1.1. Effect of catalyst preparation method

In addition to the constituent elements of the catalyst system, the preparation method has a significant impact on the solid-state surface and textural, structural, and catalytic characteristics of the intended materials. The most common synthesis method involves precipitation reactions. In this method, solutions containing precipitating agents such as oxalates and sodium carbonates are introduced into a solution with a targeted salt concentration to create catalyst precursors. An alternative method is impregnation; however, catalysts prepared through this method typically exhibit inferior performance compared to those prepared through coprecipitation [81].

Zain et al. investigated the influence of the preparation technique on the catalytic efficiency. They found that In₂O₃/ZrO₂ catalysts synthesized via the citric acid-based sol-gel method exhibited the best performance, followed by deposition-precipitation assisted by wetness impregnation and urea hydrolysis. These catalysts achieved 16.23% CO₂ conversion, 94.39% CH₃OH selectivity, and a methanol production rate (STY) of 0.95 gmethanol/gcat·h [82].

Other studies have demonstrated the advantages of co-precipitation. A separate study revealed that a catalyst synthesized through impregnation displayed an activity of 12% and a selectivity of 70% towards CH₃OH at 513 K. In contrast, the polyol method yielded a catalyst with 20% CO₂ conversion and 90% CH₃OH selectivity [83]. Additionally, research has shown that the preparation techniques and pretreatment processes significantly influence methanol selectivity [84]. However, deposition-precipitation offers advantages in other areas. Another study identified it as favorable for yielding catalysts with an increased surface area and better control over the size of Au particles [85]. Fig. 4 illustrates the evolution of the catalyst preparation techniques and their influence on catalytic performance.

The methanol space-time yield exhibited an 8.5-fold enhancement for Cu/ZnOx@UiO-66 and a 5.5-fold enhancement for commercially available CZA catalysts compared to those prepared by the traditional impregnation method. The precipitation-coating approach produced the maximum In₂O₃ exposure area, whereas the co-precipitation method produced the lowest In₂O₃ exposure area by causing In₂O₃ to create a bulk dispersion structure with ZrO₂ [87]. In academic research on methanol synthesis catalyst preparation, the impregnation method is a common approach for loading Cu onto supports [75].

Generally, coprecipitation results in greater methanol selectivity than wet impregnation and deposition-precipitation methods [84].

Table 1
Copper-based catalysts commonly employed for methanol synthesis at low pressures.

Company	Catalyst	Composition	Ref
ICI	Cu:Zn:Al:C	58:27:16:1	[79]
Topsoe	Cu:Zn:Al:C	60–52:25–21:15–28:8–6	[79]
Haldor Topsoe (MK-121)	Cu:Zn:Al	55:21–25:8–10	[80]
AIVIGO (CHM-Y)	Cu:Zn:Al	53:26:5.5	[80]
Alfa Aesar	Cu/Zn/Al/Mg	64.2/24.5/9.8/1.3	[39]
INS Pulawy and ZA Tarnów S. A. (TMC-3/1)	Cu:Zn:Al	50:25:10	[80]

3.1.2. Effect of active metal (ratio) and catalyst composition

Regarding the influence of the Cu content on the catalytic performance, the CO₂ conversion increased as the Cu content increased from 10% to 30% but showed a negligible change between 30% and 50%. This suggests that a high Cu loading on Cu–ZrO₂ has a minimal impact on performance [88]. In comparison to catalysts with a higher Zn content, the catalyst containing 30% Zn exhibited improved dispersion and a larger surface area for Cu. The methanol production performance was found to be influenced by the proportion of active Cu and Zn sites, and the best results were achieved using a Cu-ZnO-based catalyst with a composition of 70% Cu and 30% Zn. This catalyst achieved methanol selectivity of 92.1% and CO₂ conversion of 14.2% [89]. It was recently reported that the addition of Zn greatly influences methanol production. Catalysts containing Zn loads of 1.6 and 2.4 wt% exhibit about 1.7 times greater methanol space-time yield (STY) compared to the catalyst with a Zn load of 0.5 wt% [90].

To achieve optimal performance in CO₂ conversion to CH₃OH via hydrogenation, the weight ratio of Al₂O₃ to ZrO₂ in mesostructured Cu–ZnO/Al₂O₃–ZrO₂ (CZAZ) catalysts was adjusted to optimize their microstructure and surface characteristics. Incorporating ZrO₂ into the supports provided a strong basic surface for the catalysts, while the smaller Cu particles enhanced the interfaces of Cu with ZnO, thereby augmenting CH₃OH selectivity [37]. For example, both catalysts achieved a methanol selectivity of 27% at 563 K and 5 MPa, but the catalyst with 8% Si (a Si-rich bifunctional catalyst) exhibited better performance with a CH₃OH content of 6.8% compared to 5.4% for the 4% Si catalyst [91]. A catalytic performance was significantly influenced by the CuZnCeTiOx composition, with optimal results achieved at a Zn/Cu molar ratio of 1.2 and 30 wt% CuO content [92]. In a different scenario, increasing the Ga₂O₃ content led to a significant increase in the inherent reactivity, suggesting the involvement of both Ga₂O₃ and Pd₂Ga phases in methanol synthesis, possibly at bifunctional active sites, where both components contribute to the reaction [93]. Recently, a 5.0%Zn-CdZrOx catalyst with a solid solution structure demonstrated the best catalytic performance at 593 K, achieving CO₂ conversion and CH₃OH selectivity of 8.52% and 80.82%, respectively. These values were 1.9 times higher for conversion and 1.1 times higher for selectivity compared to a 0% Zn-CdZrOx catalyst [94].

As the metal loading increased, there was a notable increase in the dimensions and thickness of the layered particles, which reached a peak at a catalyst loading of 33.61 wt % for both Cu and ZnO [95]. Another recent investigation revealed that doubling the Cu loading led to a quadrupling of CO₂ hydrogenation from 10.8% to 45.6%, along with an improvement in the methanol production rate [39]. The catalyst with a low overall metal content (9.94 wt%) showed noticeably lower methanol preference than the other catalysts. However, this preference increases with higher loading, primarily because of the significantly smaller size of the Cu particles (< 5 nm) and the greater proportion of isolated CuO phase. Furthermore, even with a relatively high total metal content (44.50 wt%), the CZA catalyst maintains consistent catalytic performance, thanks to the formation of a specific layered structure that helps maintain performance [95]. Adding ZnO to a Cu₁MnZr_{0.5} catalyst had a major positive impact on CH₃OH synthesis. As the Cu content increased, the CO₂ conversion rate increased, whereas the methanol selectivity declined. Nevertheless, overall methanol production (STY) improved [96]. A noticeable trend was observed, where a higher silver content consistently resulted in a reduction in methanol selectivity [97].

3.1.3. Effect of precipitation temperatures and synthesis pH

A higher temperature reduces the degree of oversaturation, facilitating precipitation and resulting in a slower precipitation rate [79]. Conversely, decreasing the precipitation temperature during catalyst preparation is beneficial for achieving elevated Cu dispersion, reduced Cu crystal dimensions, and increased activity during the synthesis of CH₃OH [74]. The impact of temperature and pH on catalyst activity can be attributed to the varying Cu and Zn distributions. In particular, the

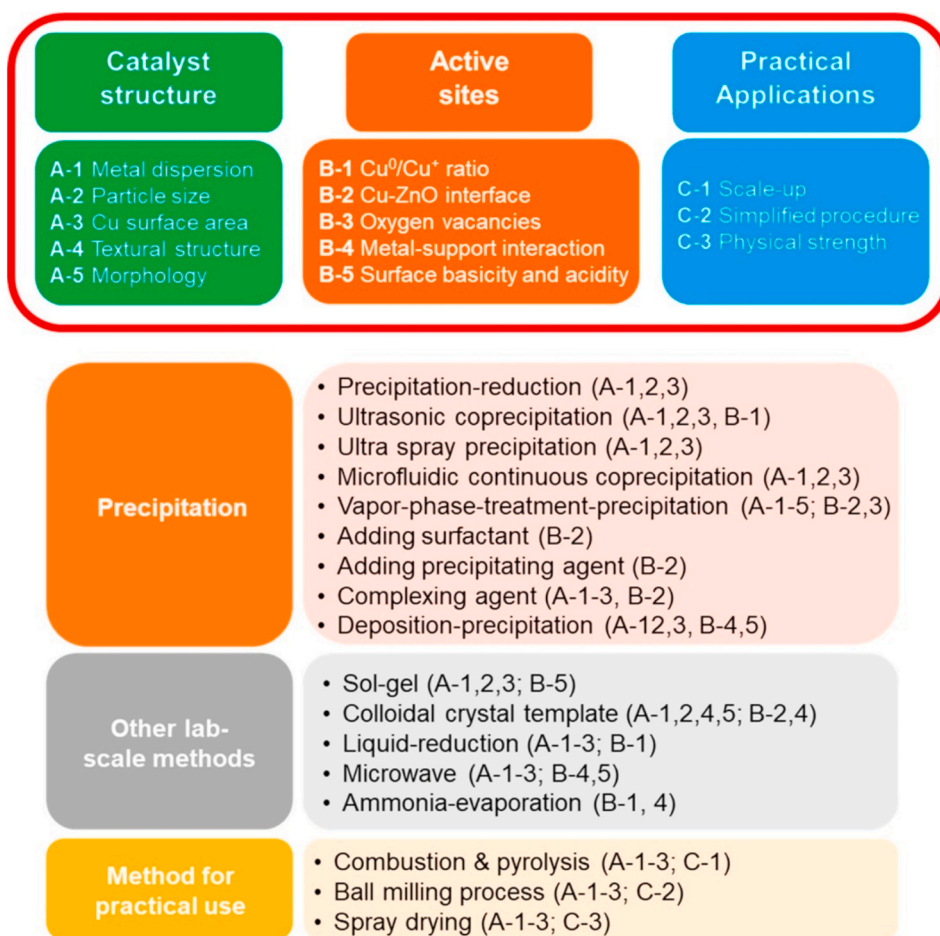


Fig. 4. Developments in catalyst preparation methods and their impact on catalyst activity. Reprinted from Ref. [86]. Copyright (2020), with permission from Elsevier.

pH primarily affects the catalyst by changing the type of precursor material formed, whereas the temperature affects it by altering the precipitation kinetics of precursors with identical compositions. In brief, to achieve a highly active catalyst for CH₃OH synthesis at low pressure using the nitrate route with a high Cu/Zn ratio, it is essential to conduct precipitation at a pH of 7.0 and a temperature of 343 K, followed by aging for approximately 0.5 h at a temperature exceeding 343 K [79].

CZZ catalysts were prepared via co-precipitation at different pH levels, and their performance in CH₃OH synthesis through CO₂ hydrogenation was subsequently evaluated. At pH 8.0, the precipitation process demonstrated the coexistence of Zn-malachite and aurichalcite within the precursor. Consequently, the resultant catalysts exhibited improved performance compared to those formed without Zn-malachite. The observed effect of pH was attributed to its ability to modify the phase compositions of the starting materials. The existence of Zn-malachite within the precursor materials promotes the generation of a more intimate inter-dispersion between ZnO and CuO, leading to the formation of smaller Cu particles after the calcination and reduction stages [98]. Malachite was also detected in Cu/Mg/Al catalysts under acidic conditions (pH 3–7), whereas catalysts synthesized under alkaline conditions (pH 8–11) exhibited XRD patterns, indicating the existence of CuO and Cu₂O phases. This indicated a partial reduction in Cu²⁺ during the co-precipitation process [99]. In another related study, Cu-ZnO catalysts were prepared via the wet impregnation method at different pH values. Subsequently, these catalysts were subjected to calcination and evaluated for methanol synthesis at a temperature of 493–533 K, 3.5 MPa pressure, feed molar ratio of H₂/CO = 2, and space velocity (SV) of 3000 h⁻¹. The catalyst prepared at pH 7.0 demonstrated the highest

activity, with a CO conversion of 35.7% and methanol selectivity of 98.1%, effectively catalyzing the CH₃OH-FPSO (floating production storage offshore) process [100].

3.1.4. Effect of noble and rare-earth metal addition (alternative catalysts to Cu)

Studies exploring alternative catalysts for CO₂ hydrogenation to CH₃OH have shown that silver (Ag) catalysts exhibit a strong and significant preference for methanol production. Research has focused on enhancing the performance of Ag catalysts. Notably, the Al₂O₃-supported catalyst exhibited a substantial increase in methanol production, which was hypothesized to be due to Al₂O₃ effectively preserving Ag in a finely dispersed metallic form. Furthermore, the Ag-ZnO-Ga₂O₃Al₂O₃ catalyst yielded more methanol than the Ag-ZnO/Al₂O₃ catalyst, suggesting that the addition of Ga₂O₃ regulates the electronic state of Ag, shifting it towards a mildly oxidative condition compared to its metallic state [101].

Pd-based catalysts are the most popular noble metals for CO₂ hydrogenation to CH₃OH because of their high activity and selectivity [102]. The introduction of Pd into the CuO-ZnO base of the PCZ catalyst improved the conversion of CO₂ to CH₃OH across all investigated temperatures [103]. Similarly, incorporating gold (Au) nanoparticles into the CuO-ZnO catalysts significantly enhanced both CO₂ conversion and CH₃OH yield, resulting in a two-fold improvement compared to the CuO-ZnO/Al₂O₃ catalyst [104]. However, bulk Au is generally not an effective catalyst owing to its high molecular stability and low adsorption energy. Despite its early recognition as a potential hydrogenation catalyst, Au has rarely been used for this purpose for a long time.

Nonetheless, Au nanoparticles have been documented to be highly effective in numerous catalytic reactions, including CO₂ hydrogenation, the water-gas shift (WGS), and CO oxidation. The substantial impact of various preparation factors on the catalytic performance of gold nanoparticles (Au NPs) underscores their strong dependence on structural characteristics. The heightened reactivity of Au NPs can be attributed to two main factors: (i) the large number of surface sites with low coordination on nanoparticles and (ii) the effects of quantum size. In addition to the nanoparticle size, the efficacy of the Au catalysts is significantly affected by the supporting material. Different oxide materials, including CeO₂, ZrO₂, ZnO, Fe₂O₃, and TiO₂, have been examined as carriers. Studies have indicated that Au generally exhibits greater activity when paired with highly reducible oxides [105].

3.1.5. Role of promoters and supports

In recent years, several interesting studies have been carried out using rare earth metals as efficient promoters to improve the catalytic performance in CO₂ hydrogenation to CH₃OH. The presence of lanthana as a promoter substantially improves the catalytic efficacy, resulting in a significant improvement relative to a Cu-based catalyst without this promotion [4]. For example, various CZZ catalysts have been prepared using various lanthanides (Pr, Nd, Ce, and La) and tested for their ability to catalyze CO₂ conversion. The impact of these modifiers on the physicochemical properties of CZZ catalysts was investigated. La and Ce enhanced the CH₃OH synthesis process, while the addition of Nd and Pr did not have much effect [106]. Using CZA catalysts with varying levels of substitution of Al₂O₃ (0, 25, 50, 75, and 100%) with La₂O₃, the conversion of CO₂ to CH₃OH was examined. A catalytic performance evaluation conducted at atmospheric pressure indicated that introducing La₂O₃ typically results in decreased CO₂ conversion but increased CH₃OH selectivity. The CZA-La50 catalyst yielded optimal performance, exhibiting a 30% increase in CH₃OH production compared to the unpromoted catalyst. This was attributed to the high porosity and specific surface area of the catalyst, facilitating the enhanced adsorption of intermediates and CO₂, which promoted the hydrogenation steps. Additionally, the catalyst effectively maintains a significant portion of Cu in its metallic state during the reaction, further contributing to the observed effects [107].

The selection of catalyst supports for producing hydrocarbons from CO₂ is based on the established relationship between product selectivity and support characteristics, such as specific surface area, pore structure, strength, and the concentration of acid sites. Commonly used supports include boron nitride (h-BN), CeO₂, SiO₂, TiO₂, niobium oxide, ZrO₂, zeolites, and carbon carriers [9]. The hydrophilic metal oxides used as catalyst supports for methanol synthesis have several disadvantages, such as low mechanical strength, poor thermal stability, high toxicity, and a short lifespan. For instance, although SiO₂ offers a large surface area, it transforms into Si(OH)₂ at elevated temperatures in the presence of water vapor, resulting in reduced thermal stability [108]. In addition to their role as supports, SiO₂ and Al₂O₃ can also act as structural promoters [9].

3.1.6. Effect of molecular sieves

The presence of microporous and mesoporous structures in a catalyst can enhance its chemical and thermal stability, thereby improving the overall catalytic performance [109]. For example, incorporating molecular sieve (3A) leads to an enhancement in CH₃OH production from 8.5% to 33.6% by selectively adsorbing water and preventing it from competing for active sites on the catalyst surface [110]. Similarly, a Cu-based catalyst deposited on SBA-15 achieved higher CH₃OH selectivity (91.32%) and CO₂ conversion (13.96%) than alternative oxide supports, while also offering the advantage of being readily reducible [111]. Several catalysts consisting of CZZ-SiO₂ were synthesized through a reverse co-precipitation method (where precursors are mixed before precipitation) involving Zr, Zn, and Cu precursors alongside dispersed colloidal Si-nanoparticles. This study explored the impact of

varying the Si content (0–5 wt%) on both the physicochemical characteristics of the resultant catalysts and their performance in CO₂ hydrogenation. The promotional effect of Si was attributed to geometrical alteration, proving particularly efficient when utilizing small quantities of SiO₂ (≤ 1.5 wt%). Upon the inclusion of 1 wt% SiO₂, a 26% increase in CH₃OH synthesis activity was noted in comparison to the SiO₂-free ternary system. In addition to its impact on methanol synthesis activity, a catalyst prepared with silica exhibited enhanced CO₂ to CO conversion stability [112].

3.1.7. Effect of calcination temperature

Several factors influence the properties of a catalyst, including the choice of starting materials, preparation method, and calcination temperature. The calcination temperature (heating the catalyst to a high temperature) plays a crucial role in modifying the catalytic behavior for specific reactions [113]. Studies have shown that calcination of Cu-Zn-based catalysts causes phase decomposition, leading to an increased specific surface area and consequently enhanced activity. For example, Cu-Zn-based catalysts were calcined at three different temperatures (573, 673, and 773 K) and their efficiencies in CH₃OH synthesis were examined. These findings indicated that higher calcination temperatures were associated with improved CH₃OH production yields [114]. However, elevated calcination temperatures (>573 K) significantly affect the microstructure of the catalyst by inducing the formation of new phases and diminishing the dispersion of Cu, which is detrimental to CH₃OH production [115]. Certain catalysts subjected to calcination at 673 K exhibited the highest methanol yield (7.0) because they possessed the smallest Cu crystal size and the largest surface area of metallic Cu [116]. In contrast, a lower calcination temperature did not facilitate the movement of Cu²⁺ ions into the crystalline structure of TiO₂, and a higher calcination temperature damaged the facets, leading to a reduced presence of Ti³⁺ [117].

4. CO₂ hydrogenation

Recent progress in CO₂ hydrogenation has led to the development of new catalysts, such as MOFs and single-atom catalysts, designed to address the limitations of traditional ones [3]. Copper (Cu) is the preferred catalyst for CO₂ conversion to CH₃OH because of its high reactivity at lower temperatures, affordability, multiple oxidation states, and strong interaction with various coexisting materials [118]. Transitioning away from traditional catalysts, which often utilize readily available materials such as Cu, Zn, and Al, presents a major challenge [119]. However, there is a demand for catalysts with improved water resistance and extended durability for industrial applications.

While an increased copper concentration enhances catalyst reactivity, it also leads to unfavorable lifetime behavior characterized by minor coke formation on the catalyst surface [74]. One approach to improve Cu-ZnO-based CO₂ to methanol catalysts is to replace Al₂O₃ with alternative support materials such as ZrO₂, which has been extensively studied for this purpose [75]. Recently, there has been a significant focus on and rapid development of catalysts composed of mixed oxide solid solutions [120]. A recent study showed that the surface of CPNs prevents agglomeration and oxidative damage, thus maintaining a uniform dispersion of copper and iron nanoparticles throughout the reaction [121].

The performance and structure of new copper nanoparticle (CuNP) catalysts produced via a novel synthesis method were investigated at low temperatures and pressures (443 K, 3 MPa) for the catalytic conversion of CO₂. This study also reports the first synthesis of a CH₃OH catalyst using a polymer (polyethylene glycol and maleic acid, PEG-MA) as a stabilizing agent and layered hydrotalcite (HTC) as the supporting material [5].

4.1. Catalysts for selective methanol production

Catalysts for methanol synthesis can be classified into three main groups: metal-based (e.g., copper), noble metal co-catalysts (e.g., gold, silver, palladium, and platinum), and oxygen-deficient materials such as In_2O_3 and ZnO . Oxygen vacancy sites serve as active centers for CH_3OH formation in these catalysts. Despite the exploration of various catalysts, copper-based catalysts have remained dominant [122–124]. Prior research has established the relative order of catalytic activity:

$$\text{Au} < \text{Rh} = \text{Ag} = \text{Ir} = \text{Os} < \text{Pt} = \text{Ru} < \text{Ni} < \text{Re} = \text{Pd} = \text{Co} \ll \text{Cu}$$

In other words, CH_3OH synthesis catalysts can be categorized into Cu-based catalysts (e.g., Cu/ZrO_2 and Cu/ZnO), noble metal catalysts (e.g., Pd-In, Pd-Zn, and Pd-Ga), and metal oxide catalysts (e.g., $\text{In}_2\text{O}_3/\text{ZrO}_2$ and ZnO-ZrO_2) [94].

4.2. Catalysts for stable and long-term operation

Industrial-scale CO_2 hydrogenation to CH_3OH using catalysts relies heavily on its stability [125]. Commercial methanol catalysts ($\text{Cu-ZnO-Al}_2\text{O}_3$) are prepared through co-precipitation, resulting in compositions of approximately 5–20% Al_2O_3 , 20–50% ZnO , and 50–70% CuO [126,127]. Catalyst deactivation remains a significant challenge in commercialization. Despite their promising activities, CZA catalysts suffer from stability issues [127]. Like most Cu-based catalysts, their effectiveness deteriorates over time owing to sintering and phase separation [128]. The sintering of Cu nanoparticles on metal oxides at high temperatures significantly challenges the stability of CH_3OH formation via CO_2 hydrogenation [129].

Calcium promotion slightly enhances methanol conversion and improves the catalyst lifetime stability [130]. This exceptional activity and stability arise from the unique microstructure of the catalyst, where ZnO acts as a spatial separator between Cu nanoparticles, ensuring optimal dispersion and abundant active sites [131,132]. The incorporation of Al^{3+} ions further enhance the chemical and thermal stability [133,134].

Over a 720-h reaction time (TOS), investigating the catalytic performance of a CZA catalyst in CO_2 hydrogenation to CH_3OH , the CH_3OH production rate significantly decreased by 34.5%. The primary causes of deactivation were confirmed to be the oxidation of metallic Cu and clustering of ZnO species. Interestingly, the size of the Cu particles remained largely unchanged after 720 h, likely because of the relatively low reaction temperature. This suggests that the Cu particle size is not a major factor in deactivation.

Therefore, enhancing the durability of ZnO and metallic Cu is crucial for extending the lifespan during CO_2 hydrogenation to CH_3OH . It has been suggested that controlling the structural promoter and incorporating a hydrophobic promoter can facilitate the stabilization of the ZnO species and suppress metallic Cu oxidation, thereby fostering superior catalyst stability [135]. An overview of the catalyst stability during methanol synthesis through CO_2 hydrogenation is provided in Table 2.

4.3. Effect of metal-organic frameworks (MOF)

Researchers are becoming increasingly interested in MOF catalysts because of their potential to outperform conventional catalysts [141]. MOFs, which are hybrid materials combining organic and inorganic components, possess well-ordered crystalline lattices with nanopores. Modifying the organic linkers within MOFs allows for easy control of the pore dimensions and overall chemical and physical properties, making them ideal for gas separation membranes. Compared to zeolites, MOFs offer exceptional tunability; their pore size, shape, and overall structure can be varied significantly. Notably, MOFs have 90% higher porosity than zeolites, and some MOFs exhibit remarkable thermal stability, even in the presence of water vapor at elevated temperatures (up to 673 K) [142]. These materials, with their distinctive arrangements of openings

Table 2

Catalyst stability in the hydrogenation process for the conversion of CO_2 to methanol.

Catalyst (composition)	T (°C)	P (MPa)	TOS (h)	Activity loss (%)	Ref
CuZnZr ($\text{Zn}/(\text{Zn} + \text{Zr}) = 0.13$)	250	3.0	250	0	[129]
$\text{In}_{13}/\text{ZrO}_2$	280	3.0	50	0	[125]
MoS_2/C ($\text{C}:\text{Mo} = 45$)	160	3.0	150	0	[136]
10%Pd/ $\text{In}_2\text{O}_3/\text{SBA-15}$	260	5.0	120	0	[137]
CuFe/CPN_1	300	2.0	12	0	[121]
PdZnTi-x (4 wt% Pd, x = $\text{Zn}/\text{Pd} = 7.5$)	250	3.0	12	0	[138]
$\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ ($\text{Cu}/\text{Zn} = 7:3$)	240	4.0	200	1.09*	[95]
$\text{CuZn}_{10}\text{Zr}$	220	3.0	118	0	[139]
CuZnZr (60:29:11)	240	3.0	200	0	[140]
$\text{CuO-ZnO-ZrO}_2\text{-SiO}_2$ (CZZ-1.0Si)	280	2.0	96	0	[112]

and gaps, are promising options for overcoming the limitations of traditional materials [143,144].

The appeal of MOFs in heterogeneous catalysis stems from their ability to serve as excellent supports for dispersing the active metal phases [39]. The production of CH_3OH through CO_2 hydrogenation is influenced by the structure of the catalyst. The composition of the metal and its interaction with the supporting material significantly affect its performance. Many Cu-ZnO catalysts typically exhibit a modest surface area of approximately $30 \text{ m}^2/\text{g}$, limiting their effectiveness in promoting the reaction [145]. In this regard, MOFs offer the advantage of interacting with other catalytically active metals. This is due to their small metal oxide secondary building units (SBUs) at the nanoscale and their ability to adjust their compositions. Consequently, we can systematically explore the impact of the catalytic interface [146]. MOFs also show exceptional promise for water adsorption [147].

Cavka et al. were the first to document UiO-66, a zirconium-based MOF that has attracted significant interest owing to its remarkable thermal and chemical durability, along with its convenient customization potential [145]. A scalable and consistent approach for producing UiO-66- and UiO-67-type MOFs was developed, involving the introduction of HCl into the reaction mixture. This method is significantly faster than previously documented methods, generates remarkable porosities, and is compatible with various linkers [143].

A novel bimetallic MOF-based catalyst (referred to as $\text{Cu-ZnO-MOF-Al}_2\text{O}_3$) was developed to convert CO_2 into CH_3OH through hydrogenation. This newly devised catalyst exhibited remarkable selectivity for CH_3OH production, along with superior performance and durability in CO_2 hydrogenation compared to a standard $\text{Cu-ZnO}/\text{Al}_2\text{O}_3$ catalyst. The $\text{Cu-ZnO-MOF-Al}_2\text{O}_3$ catalyst showed only a small decrease in CO_2 conversion at high temperatures and remained stable at a high conversion level, suggesting minimal deactivation [148].

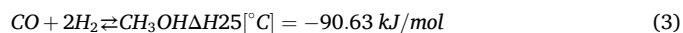
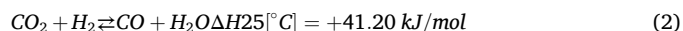
An experimental investigation explored the influence of various materials, including MOFs such as ZIF-8, MIL-101 (Cr), and UiO-66, as well as mesoporous silica (MCF-26), ZrO_2 , and Al_2O_3 , on the performance of Cu catalysts in CO_2 conversion to CH_3OH . These results indicate that UiO-66 is the most effective promoter for Cu-based catalysts, resulting in both exceptional yield and selectivity in the conversion of CO_2 to methanol [146].

Studies examining the impact of structural defects in UiO-66 on its performance in CO_2 hydrogenation to methanol found no correlation between these two factors [145]. Another study investigated Cu nanocrystals encapsulated within UiO-66, ZIF-8, and MIL-101 as catalysts for CO_2 hydrogenation to CH_3OH at 448 K and 1 MPa. They determined that only the catalyst based on Zr-containing UiO-66 exhibited activity. Furthermore, they observed that the placement of Cu within the structure significantly affected catalytic performance. The Cu nanocrystals encapsulated within UiO-66 demonstrated double the activity and

improved stability compared to the Cu deposited onto UiO-66. The improved performance of the latter can be attributed to the enhanced metal-support interactions, facilitating the creation of active Cu sites responsible for converting CO_2 to CH_3OH [146].

5. Reaction kinetics and mechanism

Despite over a century of research on methanol synthesis, the underlying mechanism remains incompletely understood, leading to ongoing debates on various reaction aspects [34,149]. The CO_2 hydrogenation process to synthesize CH_3OH occurs in a catalytic gas phase environment and involves a sequential progression of three fundamental reactions (1)–(3). The first reaction entails the direct conversion of CO_2 through hydrogenation to synthesize CH_3OH (Eq. (1)). Subsequently, the second reaction involves the generation of CO via the r-WGS reaction (Eq. (2)). Lastly, the third reaction encompasses the hydrogenation of CO to produce CH_3OH (Eq. (3)). This multi-step sequence is crucial for the conversion of CO_2 to CH_3OH . The decomposition of the resulting methanol has already been discussed and proven with experiments [150].



The most desired reaction is the hydrogenation of CO_2 to CH_3OH (Eq. (1)). However, this process competes with the r-WGS reaction (Eq. (2)), which rapidly consumes hydrogen (H_2) and produces water (H_2O) as a major byproduct. Water production imposes thermodynamic constraints on the system and deactivates the catalyst [76]. The endothermic properties of the r-WGS reaction favor its equilibrium at elevated temperatures [151].

Significantly, industrial syngas feed (a mixture of CO and H_2) generates more heat compared to CO_2 feed. This is because CO hydrogenation releases more heat than CO_2 hydrogenation [26]. Understanding the reaction kinetics of catalysis is crucial for balancing the desired product with the thermodynamically favored product from the r-WGS reaction [152]. Fig. 5 shows different possible pathways (reaction mechanisms) for producing methanol through the reaction of CO_2 and H_2 .

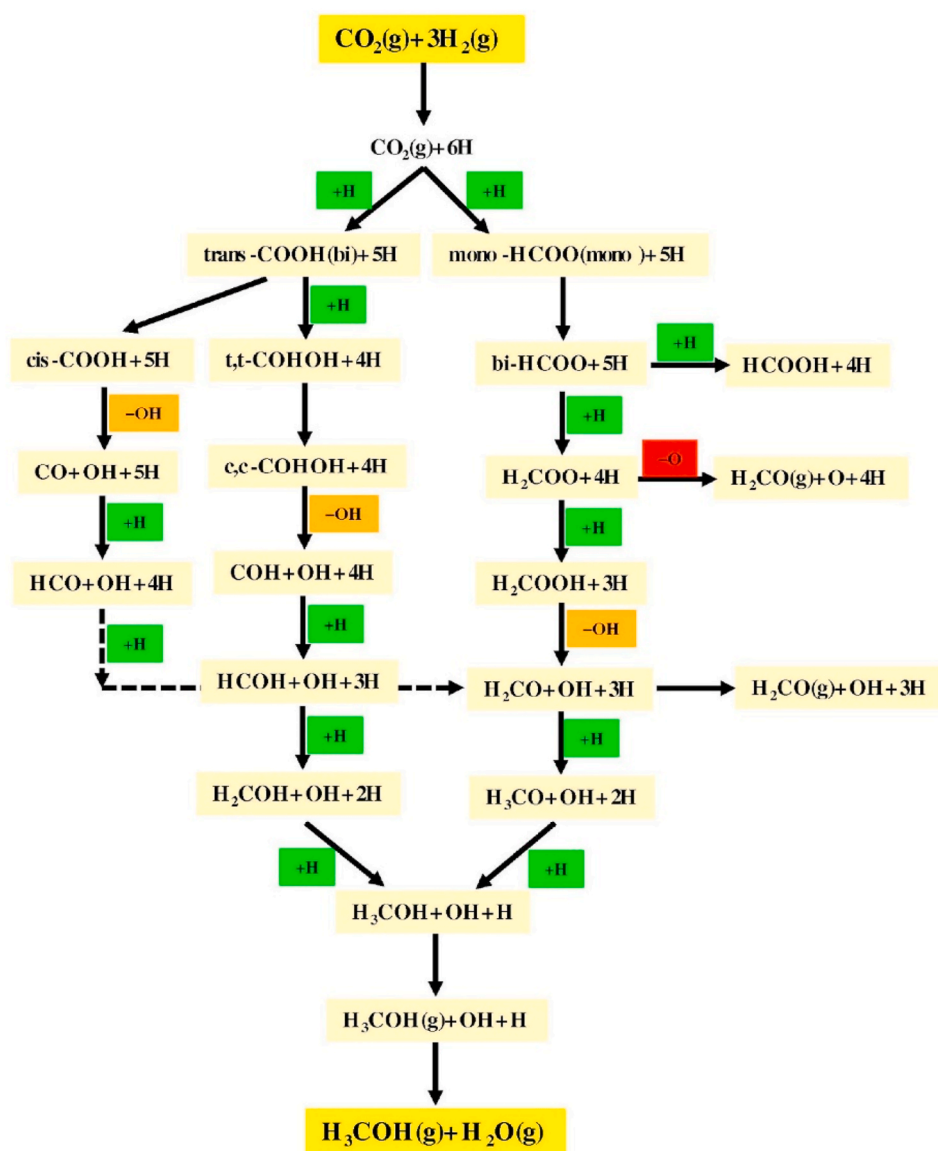


Fig. 5. Reaction mechanism network of methanol synthesis on Cu (111). Reprinted from Ref. [153]. Copyright (2019), with permission from Elsevier.

Upon activation of CO_2 on electron-intensive oxygen vacancy sites, it undergoes a structural change into bent CO_2 species, followed by a hydrogenation reaction, resulting in the formation of a monodentate formate intermediate (HCOO^*) bonded to the catalyst by one oxygen atom. This step is both kinetically and thermodynamically favorable. Subsequent hydrogenation of HCOO^* leads to the production of methanol.

To prevent the unwanted r-WGS reaction and CO byproduct formation, controlling the presence of the key intermediate adsorbed COOH^* (a COOH molecule clinging to the catalyst surface) is crucial [154]. Consequently, Density Functional Theory (DFT) investigations into thermal catalysis have revealed two primary pathways for CO_2 hydrogenation to produce CH_3OH . The r-WGS and formate (HCOO) pathways, in conjunction with the CO-hydro (COOH) pathway, are recognized as the respective routes. Several studies have examined these pathways [133,155,156].

The hydrogenation of CO_2 in the HCOO pathway involves sequential steps. Initially, CO_2 undergoes hydrogenation to form H_2COOH^* or HCOOH^* (another way of representing the formate intermediate). Subsequently, H_2COOH^* or HCOOH^* is further transformed into H_2CO^* , ultimately leading to the formation of CH_3OH [157].

Nonetheless, in the COOH pathway, the transformation of CO_2 initiates with the r-WGS reaction, wherein CO_2 undergoes the initial conversion to CO^* through COOH^* . Subsequently, CO^* undergoes additional hydrogenation via H_2COH^* , H_2CO^* , H_3CO^* or HCO^* resulting in the ultimate production of CH_3OH [158]. Fig. 6 describes the most widely accepted mechanism of CO_2 hydrogenation on Cu surfaces, as determined by DFT calculations [152]. In the HCOO pathway, HCOO^* is the most important intermediate, while in the rWGS and *trans*- COOH mechanisms, HCOO^* is seen as a dead-end species [72].

It is difficult to convert CO_2 into hydrocarbons or other multi-carbon products using only copper (Cu) catalysts. However, Cu-based catalysts containing other metals like iron (Fe) or nickel (Ni) hold greater promise. This is likely because breaking the carbon-oxygen (C–O) bond to form CH_x ($x = 0\text{--}4$) species, crucial for the subsequent C–C coupling reaction, proves challenging on Cu surfaces. Specifically, breaking the bond between carbon and oxygen in the adsorbed CO^* on Cu is difficult, with a very high energy barrier (>2 eV) compared to Fe catalysts [152].

6. Membrane reactor design and operation

A membrane reactor (MR) is a unit that integrates a chemical reaction process with a membrane-based separation or distribution process

within a single system [44,159]. MRs can achieve high conversion rates of reactants into products in a single pass, particularly for CH_3OH production [160]. Struis et al. pioneered the use of MRs to enhance conversion in CH_3OH synthesis. They conducted reaction tests within a Nafion membrane reactor with lithium content at 473 K and 0.43 MPa, followed by a publication that included both empirical and modeling investigations using the same reactor [42,161]. In a catalytic membrane reactor (CMR), the membrane serves a dual function. It acts both as a separator and a catalyst [162]. Enabling the membrane to actively engage in the chemical reaction occurring within the reactor. Consequently, certain reaction products, particularly those of small size, can permeate selectively through the membrane and exit the reactor via the permeate side.

The concept of catalytic membrane reactors (CMRs) is introduced to overcome the limitations of thermodynamic equilibrium in the CO_2 conversion to CH_3OH . These reactors integrate catalytic reactions and membrane separation into a single system, enabling the continuous and on-site removal of produced steam through selective membranes [43].

This integration of reaction and separation significantly improves chemical processes, ultimately reducing processing costs. Membrane reactors can enhance reaction progress through two main methods:

- selective removal of products: By selectively extracting one or more products from the reaction side through the membrane, the equilibrium of the reaction shifts toward the product side. This leads to an increase in yield, potentially exceeding the thermodynamic equilibrium for reversible reactions.
- Controlled reactant feed: Delivering a specific reactant exclusively to the reaction zone allows for an optimal concentration ratio between the two reactant streams. This improves selectivity by inhibiting unwanted side reactions or product-related secondary reactions [44].

These membrane reactors, which synergistically combine a selective membrane and a catalytic reaction, represent a promising strategy for enhancing the conversion efficiency in CH_3OH synthesis. By utilizing water-selective membranes, water vapor produced during the catalytic process can be promptly removed from the reaction environment. This removal facilitates the advancement of the reaction towards completion, even when operated at lower temperature and pressure conditions [163]. Permeability of H_2O and CH_3OH remained unaffected by CH_3OH feed concentration, except when concentrations were low [46].

Shifting the thermodynamic equilibrium towards increased CH_3OH

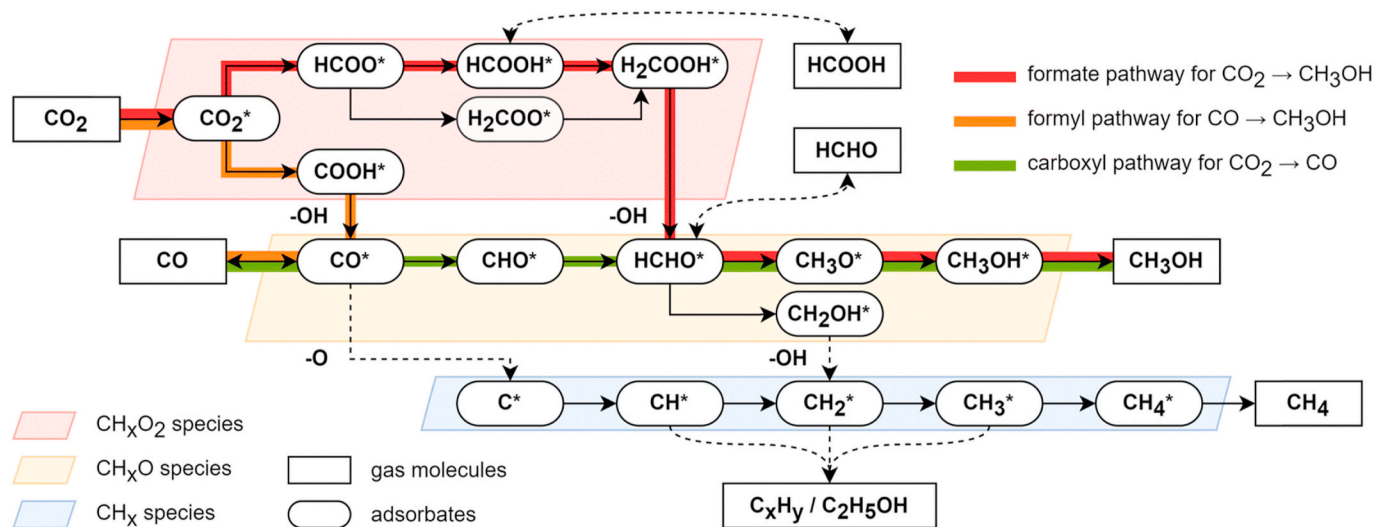


Fig. 6. The potential reaction network and reaction pathway for CO_2 hydrogenations on the Cu surface. Reprinted from Ref. [152]. Copyright (2023), with permission from Elsevier.

yield can be achieved by extracting the products (CH_3OH and H_2O) from the reaction system. Several studies have explored this approach through different reactor designs, including membrane reactors and in situ condensation, but these technologies remain under development and are not yet viable for commercial use [164]. Considering the inherent nature of the CH_3OH production reaction through CO_2 hydrogenation, the strategic elimination of the resultant H_2O from the reaction environment holds the potential to surmount thermodynamic equilibrium constraints by leveraging Le Chatelier's principle. This approach is anticipated to enhance CO_2 conversion and CH_3OH selectivity. To date, there exist only limited instances of successful catalytic membrane reactors (CMRs) employed in the hydrogenation of CO_2 to methanol [43].

The catalytic performance of CO_2 conversion to CH_3OH by hydrogenation in different reaction scenarios is shown in Fig. 7. It can be inferred from the figure that the zeolite membrane reactor achieves higher methanol selectivity than the traditional reactor (TR) at 250 °C and 240 °C, reaching 46% and 73%, respectively, compared to 43% and 67% for TR. This confirms the potential of MR to produce more of the desired product [70].

6.1. Membrane materials and properties

In the context of membrane development for CH_3OH synthesis using MR technology, emphasis should be placed on optimizing materials for atmospheric sweep operation. A key property is high-pressure stability, considering the pressure difference (5–10 MPa) between the retentate

(concentrated solution left behind) and permeate (solution that passes through) sides during operation. This pressure difference significantly impacts the overall performance and efficiency of the membrane system [165].

For CH_3OH synthesis using MR technology, various hydrophilic membranes have been proposed, including zeolite, polymeric, and ceramic types. To maximize water permeation at high CH_3OH reaction temperatures, it is advisable to maintain the lowest possible pressure on the permeate side, typically at atmospheric pressure, owing to the limited water permeance of these materials. Under high temperatures, the prevailing mechanisms by which molecules pass through inorganic porous membranes are anticipated to be Knudsen diffusion and molecular sieving. In membranes featuring a continuous polymeric selective layer, gas permeation is primarily governed by the solution-diffusion mechanism. However, at higher temperatures, particularly with glassy polymers, the dominant factor influencing selectivity becomes diffusion.

H_2O and H_2 , given their relatively small kinetic diameters (0.265 nm and 0.289 nm respectively), readily permeate the reaction system, outcompeting other molecules. This concurrent hydrogen permeation presents a major drawback: the expensive recompression of this low-density gas back to the reactor feed pressure. Overall, there is a need for elevated $\text{H}_2\text{O}/\text{H}_2$ permselectivity (the ability of a membrane to preferentially allow water passage over hydrogen). Yet, current advanced polymeric membranes, whether supported on porous ceramic or thermally stable porous polymeric substrates, typically demonstrate $\text{H}_2\text{O}/\text{H}_2$ permselectivity levels ranging from 1 to 10 at the relevant temperatures. Conversely, ceramic membranes suffer from low

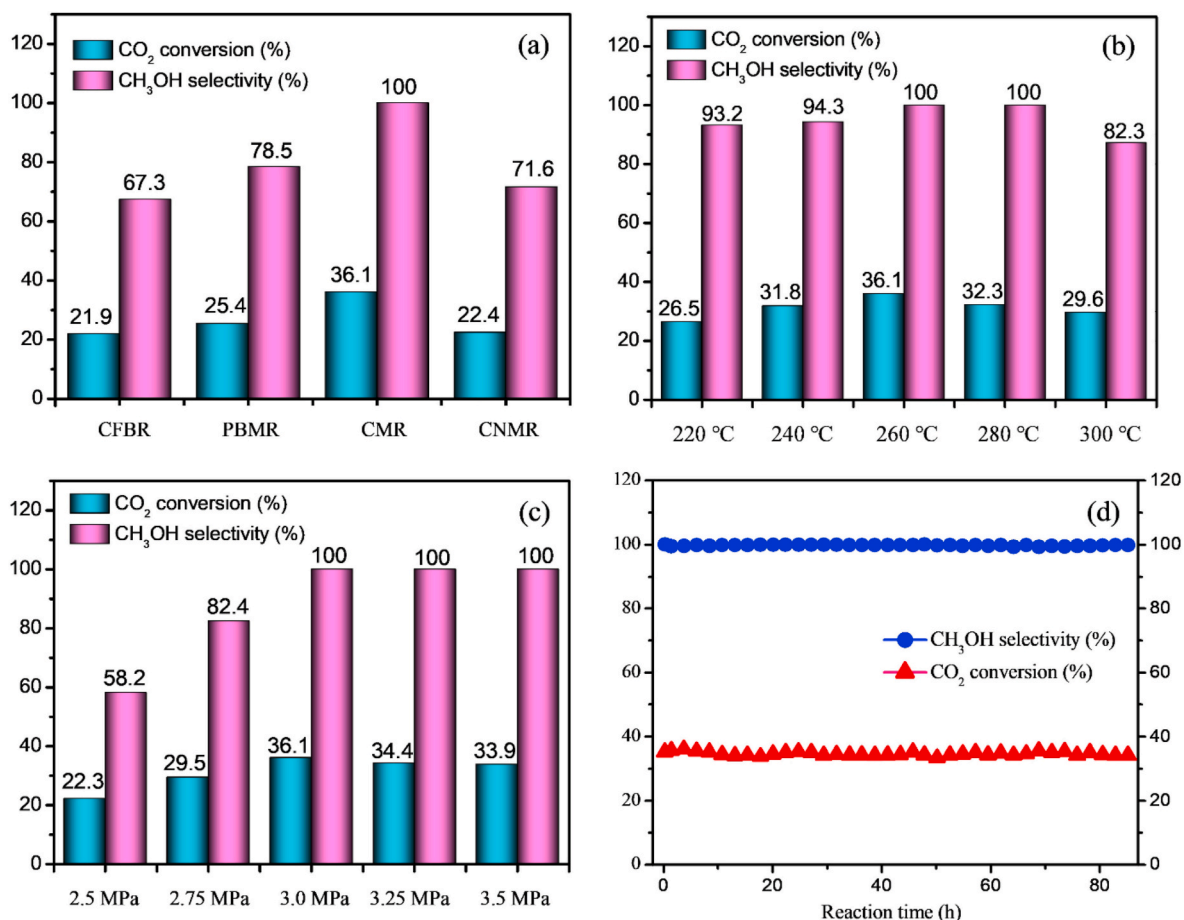


Fig. 7. (A) The performance of catalytic membrane reactors (CMR) in the conversion of CO_2 to methanol was evaluated in comparison to catalytic non-permeable membrane reactor (CNMR) packed bed membrane reactor (PBMR), and catalytic fixed bed reactor (CFBR). The catalytic performance of CMR in the conversion of CO_2 to methanol was also investigated as a function of reaction temperature under a pressure of 3.0 MPa (b) reaction pressures at 260 °C (c) and operation time at 260 °C and 3.0 MPa (d) H_2/CO_2 feed ratio of 3 (GHSV = 3000 h^{-1}). Reprinted from Ref. [43]. Copyright (2021), with permission from John Wiley and Sons.

permselectivity, primarily because their hydrophilic structure degrades at elevated temperatures.

Zeolite membranes, specifically mordenite (MOR) and hydroxy sodalite (H-SOD), have demonstrated significant potential for this specific purpose, owing to their superior $\text{H}_2\text{O}/\text{H}_2$ permselectivities and sufficient mechanical and thermal stabilities under harsh conditions [166].

Recently, a study established sodium ion (Na^+)-gated water conducting nanochannels through a carefully designed approach. This involved assembling NaA zeolite crystals into a seamless, flawless membrane for efficient water removal. This approach facilitated a notable increase in CO_2 conversion and methanol yield during CO_2 hydrogenation to methanol [167].

Most recently, a flawless NaA zeolite membrane was also developed using a template-free method that's cost-effective and easily scalable for future production. The membrane is synthesized on a hollow alumina fiber support. Impressively, it can efficiently separate water from small gas molecules like CO_2 and H_2 even under high conditions (temperatures exceeding 473 K and pressure exceeding 2 Mpa) having a water flux as high as $4.8 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-2}$ and high separation factor for H_2/CO_2 (>10000), $\text{H}_2\text{O}/\text{H}_2$ (>10000), and $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (>300). This exceptional separation ability makes it ideal for applications like CO_2 conversion to methanol via hydrogenation [168].

6.2. Innovations and progress in catalytic membrane reactors (CMR)

The integration of membrane separation and reaction processes offers numerous advantages over conventional methods. Membranes can selectively permeate components in mixtures, acting as barriers or facilitating in situ separation of products and reactants within membrane reactors. Various membrane types have been used, including porous or dense materials made from organic polymers, inorganic materials, or even metals. Asymmetric structures with thin separation layers on strong supports are common for high-throughput applications [165,169].

Different methods exist for categorizing membrane reactors based on factors including the nature of the catalyst, selectivity, and arrangement. This results in six distinct configurations, while the role of the membrane allows further categorization into extractor-type, distributor-type, and contactor-type reactors. Extractor-type membrane reactors utilize membranes to selectively extract products and intermediates, thereby enhancing selectivity and yield [170]. In this regard, various reactor setups have been employed hitherto for the catalytic conversion of CO_2 to CH_3OH .

Reactor design plays a crucial role in CO_2 reduction, impacting catalyst longevity, product quality, production rates, process control, and ultimately effective CO_2 mitigation [171]. Combining a Traditional Reactor (TR) with a Membrane Reactor (MR) consistently yielded higher methanol yields compared to using only the TR. In certain instances, the achieved methanol yield surpassed the value predicted by thermodynamic equilibrium calculations. Although the overall yields were relatively low due to the use of low pressure, these results are deemed as a significant proof-of-concept for the application of this configuration [161].

A recent investigation has introduced a dual-functional catalytic membrane reactor (CMR) designed to efficiently produce CH_3OH from CO_2 . This reactor features a $\text{Cu-ZnO-Al}_2\text{O}_3\text{-ZrO}_2$ layer for catalytic CO_2 hydrogenation that generates CH_3OH , while a nearby hydrophilic LTA zeolite membrane simultaneously removes excess water by-product in real time. This dynamic water removal breaks the constraints imposed by thermodynamic equilibrium, leading to heightened conversion of CO_2 and greater selectivity for CH_3OH . When the CMR operates at 533 K and 3.0 MPa, it attains remarkable outcomes: a 36.1% CO_2 conversion rate and 100% CH_3OH selectivity (Fig. 7). These figures notably surpass those achieved by the CFBR and PBMR methods. Furthermore, the extraction of water from the reaction setup effectively prevents catalyst deactivation and unwanted by-product formation. Consequently, the

CMR's stability throughout operation is significantly enhanced. This positions the CMR as a favorable and promising option for other reactions hampered by the presence of by-product water, whether due to thermodynamic or kinetic limitations [43].

To attain a high degree of CH_3OH purity through a simplified procedure, the selection of a membrane reactor characterized by an exceptional capability to exclusively separate H_2O molecules is imperative. This necessitates the membrane to demonstrate a superior H_2O permselective performance [172].

6.3. Process integration and optimization

The Cu-based catalysts can deactivate due to exposure to water vapor (hydrothermal sintering), highlighting the importance of removing water from the reaction, especially for high CO_2 conversion rates [139]. To address this issue, an internal cooling system that aids in condensing the water and methanol produced from the mixture of gases has shown promise in improving catalyst effectiveness [173].

Membrane-based reactors offer a promising alternative solution. They selectively remove condensable products and potentially shift equilibrium-limited reactions toward desired products. However, selective permeation of H_2O in CO_2 hydrogenation remains challenging due to the similar molecular sizes of the two gases. Zeolite membranes offer advantages due to their stable structure and consistent pore size, leading to improved performance [174]. Gallucci and colleagues demonstrated the effectiveness of combining a zeolite membrane reactor, achieving superior conversion rates compared to conventional reactors [175]. This enhanced efficiency persisted even under a pressure of 2 MPa [42]. Likewise, another study reported an increased CO_2 conversion using a hydrophilic LTA zeolite composite membrane in a membrane reactor [176]. The conversion of CO_2 in this assisted reactor reached 17% at a temperature of 483 K, surpassing the equilibrium value of 6%. Recent research has been geared towards the separation of mixtures comprising water and permeate gases, particularly in high-temperature and high-pressure settings [174].

The involvement of membrane technology has opened new doors to enhance process efficiency. Employing a membrane reactor in the synthesis of methanol has proven to be a feasible alternative to overcome the existing challenges of low conversion in traditional packed bed reactors (see Table 3) [177]. Additionally, membrane reactors enable simultaneous reaction and separation, intensifying the overall process [40,178]. Catalytic zeolite membranes containing modified Cu-based catalysts can be used for efficient catalyst deployment and excess water removal from the reaction.

Studt et al. demonstrate that successful catalyst development for CO_2 hydrogenation can be a matter of chance, resulting from a favorable combination of kinetic and thermodynamic properties. Their work underscores the importance of studying the entire chemical system for further improvement. Simply adjusting reaction conditions or catalyst composition in isolation is unlikely to lead to better performance. In the context of CO_2 conversion as a solution to the energy challenge, optimizing the catalyst composition beyond current technologies holds promise for significant performance gains. However, this approach hinges on maintaining the existing material's micro and mesoscopic structures [157].

Li et al. created a model that can predict both the necessary CO_2 permeation level and the appropriate membrane size for specific operating conditions. Furthermore, incorporating a more accurate kinetic model, like the one developed by Pavlišić et al., into this platform could lead to more precise predictions of reactor performance [179].

7. Conclusions from the catalytic operating conditions

Numerous experimental studies have focused on catalyst behavior under specific conditions or the influence of individual factors like pressure or temperature. However, few have investigated the behavior

Table 3Evaluating the effectiveness of Membrane Reactor (MR) and Traditional Reactor (TR) in CO₂ Hydrogenation to Methanol.

Catalyst (composition)	System (reactor)	Membrane (material)	H ₂ /CO ₂ ratio	Temperature (°C)	Pressure (MPa)	Space velocity (mLg ⁻¹ h ⁻¹)	X _{CO₂} (%)	S _{CH₃OH} (%)	Ref
4.5Cu:4.5ZnO:1Al ₂ O ₃	MR	Na-LTA	3:1	240	0.5	-	~15	~0.6	[161]
	TR	-	3:1	240	0.5	-	~13	~0.5	
0.3CuO-0.3ZnO-0.16CeO ₂	MR	Na-LTA	3:1	240	0.5	18,000	-	73	[70]
	MR	Na-LTA	3:1	240	0.7	18,000	-	84	
	TR	-	3:1	240	0.5	18,000	-	67	
	TR	-	3:1	240	0.7	18,000	-	77	
Cu/Zn/Al (Commercial)	MR	LTA	3:1	206	2.0	6000	11.6	75	[42]
	TR	-	3:1	210	2.0	6000	5.0	48	
Cu/Zn (Commercial)	MR	Nafion	3:1	200	0.43	1000	-	-	[180]
	TR	-	3:1	200	0.43	1000	-	-	
1Cu-1ZnO-1Al ₂ O ₃ -0.2ZrO ₂	MR	Na-LTA	3:1	220	3.0	3000	26.5	93.2	[43]
	MR	Na-LTA	3:1	260	3.0	3000	36.1	100	
	MR	Na-LTA	3:1	260	3.5	3000	33.9	100	
	TR	Na-LTA	3:1	260	3.0	3000	21.9	67.3	
Cu/Zn-BTC	MR	Na-LTA	3:1	260	3.0	-	49.1	90.2	[181]
	TR	-	3:1	260	3.0	3000	26.2	50.6	

of the catalyst when exposed to a combination of reactants, such as CO₂ + H₂ or a combination of CO₂ + CO + H₂ [31]. The hydrogenation of CO₂ has been widely reported, with Cu-based catalysts being the most employed (see Table 4). The efficiency of CO₂ hydrogenation reactions depends on the inherent characteristics of the membrane and catalyst in addition to critical process variables, such as feed ratio, pressure, temperature, and gas hourly space velocity (GHSV). In the following subsections, the effects of these operating conditions are discussed critically and in perspective, as this is precisely where the scope for later application in membrane reactors lies.

7.1. Effect of reaction temperature

The exothermicity of the CO₂ conversion to CH₃OH, demonstrated by Eq. (1), indicates that lower temperatures are thermodynamically preferred. However, the high stability of CO₂ necessitates sufficient energy to break its strong bonds. This creates a conflict: thermodynamics favors lower temperatures, but reaction kinetics, the rate of the reaction, accelerates at higher temperatures. Therefore, CH₃OH productivity is governed by both factors [182].

At high temperatures, the formate intermediate, which serves as the primary pathway for methanol synthesis, becomes unstable and breaks down into CO and H₂O via the r-WGS reaction [183]. The optimal temperature range for methanol synthesis lies between 453 and 473 K [74], so the membranes used in this process must be thermally stable. Inorganic membranes are generally preferred for this reason.

An experimental investigation showed that at 513 K, the reaction exhibits a modest CO₂ conversion of 5.7% but a high selectivity of 90% towards CH₃OH. Similarly, at 533 K with all other parameters constant, the CO₂ conversion increases to 18.7%, but the CH₃OH selectivity drops to 53% [128]. In another study, elevating the reaction temperature from 413 to 513 K resulted in a corresponding increase in CO₂ conversion, from 26.3% to 32.6%. This highlights the enhanced catalytic performance of MoS₂-45@C, even at lower operating temperatures [136].

CO₂ conversion also increases with a rise in reaction temperature from 505 to 535 K. CO₂ and CO compete for adsorption sites on the catalyst surface, and CO is more strongly adsorbed at lower temperatures. The resulting CO then reacts with H₂ via the rWGS reaction to form methanol [184].

Conversely, a previous study achieved a CH₃OH yield of 1.9% using Cu/CeO₂ nanorod catalysts at 513 K and 2 MPa. The Cu/CeO₂ nanorod catalyst exhibited the highest CO₂ conversion, reaching a maximum of 6.7% at 573 K. However, with increasing reaction temperatures, CH₃OH selectivity decreased rapidly. The highest selectivity of 89.5% for the

Cu/CeO₂ nanorod catalyst was achieved at 513 K [185].

7.2. Effect of pressure

Pressure is a critical factor in CO₂ conversion to CH₃OH, particularly within membrane reactors, where its importance has been previously underestimated. Future research should focus on optimizing pressure for this application. According to the Le Châtelier-Braun principle, an increase in pressure favors the thermodynamic production of CH₃OH. Conversely, changes in pressure do not impact the r-WGS reaction [186]. The thermodynamic equilibrium of CO₂ favors operation at elevated pressures, making high-pressure conditions advantageous. As the membrane reactor operates at higher pressures, it is anticipated that the system's performance will enhance, leading to improved methanol yield and enhanced membrane selectivity towards water [163].

The impact of varying reaction pressure on both activity and selectivity was investigated using an effective catalyst (CuO/ZnO/Al₂O₃:60/30/10) at 503 K. As the overall pressure rose, the conversion of CO₂ and the selectivity towards CH₃OH increased, but the selectivity for CO decreased with increasing total pressure. CH₃OH selectivity peaked at 7.5 MPa, possibly because the lower pressure resulted in reduced decomposition of the formate species. As a result, raising the pressure can reduce the formation of CO. The ratios of CO to CH₃OH selectivity, when expressed as a function of pressure, exhibit a similar trend to what was observed when they were studied as a function of flow rate. Ultimately, increased pressure and flow rate promote CH₃OH production, but have the opposite effect on CO formation [183].

7.3. Effect of H₂/CO₂ feed ratio

In CO₂ hydrogenation for CH₃OH production, a balanced H₂:CO₂ ratio is 3. If this ratio exceeds 3, it signifies an abundance of H₂ in the feed gas, whereas a ratio below 3 indicates carbon excess. Alternatively, in the CH₃OH synthesis process initiated with CO-based syngas, a balanced CO/H₂ ratio of 2 is necessary. In contrast to the typical syngas-to-methanol approach, hydrogenation of CO₂ demands a greater quantity of hydrogen per unit of carbon, leading to the production of a greater quantity of H₂O as a by-product of the CH₃OH synthesis reaction.

Direct CO₂ hydrogenation leads to lower methanol yields due to two factors. First, a higher CO₂ concentration promotes the reverse water-gas shift reaction (r-WGS reaction, Eq. (2)), generating more H₂O. Second, this additional H₂O (illustrated in Eq. (3)) shifts the hydrogenation reaction equilibrium towards reactants, reducing CH₃OH production. Compared to syngas-to-methanol, this increased H₂O generation can

Table 4
Summary of catalysts and reaction parameters for methanol synthesis.

Catalyst (composition)	Reaction condition				Performance				Ref.
	H ₂ /CO ₂ ratio	Temp (°C)	Pressure (MPa)	Space velocity (mLmin ⁻¹ g ⁻¹ or h ⁻¹)	X _{CO₂} (%)	S _{CH₃OH} (%)	STY	Y _{CH₃OH} (%)	
6Ni(NO ₃) ₂ :4Ga(NO ₃) ₃	3:1	250	5.0	–	95.7	75.4	–	72.2	[1]
Ni/In ₂ O ₃ (10 wt% Ni)	4:1	300	5.0	21000	18.67	~55	0.55	–	[154]
50Cu-20ZnO/Al ₂ O ₃	3:1	200	5.0	15600	7.1	78	–	–	[190]
50Cu-20ZnO/Al ₂ O ₃ -MgO	3:1	200	5.0	15600	8.1	87	–	–	[190]
3.75Cu:1.25Zn:0.25UiO-66	3:1	260	4.0	12000	18.7	52	216.7	9.7	[128]
3.75Cu:1.25Zn:0.25UiO-66	3:1	200	4.0	12000	5.8	92	115.8	5.8	[128]
0.35Cu-0.66Zn-1UiO-66	3:1	250	4.0	12000	3.5	86	74.4	3.0	[191]
6Cu(NO ₃) ₂ -3Zn(NO ₃) ₂ -1Al(NO ₃) ₃	3:1	220	4.0	12000	1.9	94	44.9	1.8	[191]
4.5Cu:4.5ZnO:1Al ₂ O ₃	3:1	240	0.5	–	15	0.6	–	–	[161]
30CuO-49.65ZnO/20.35Al ₂ O ₃	–	300	8.5	7000	30	61.4	–	0.52	[192]
Cu-Zn-Al-K (CZA-K)	3:1	240	3.0	2400	14.0	96.0	–	–	[187]
Cu _{0.25} -In _{0.75} -Zr _{0.5} -O	3:1	250	2.5	18000	1.48	79.7	–	–	[193]
In ₂ O ₃ /ZrO ₂	3:1	280	4.0	15000	16.2	94.4	0.95	15.3	[82]
0.6Cu/0.3ZnO/0.03La ₂ O ₃ /0.07Al ₂ O ₃	4:1	300	8.5	55000	20	65	0.79	–	[4]
30%Cu-ZrO ₂	3:1	240	3.0	9600	24	>80	174.8	–	[88]
40.6CuO-50.3ZnO/9.1Au/Al ₂ O ₃	2.8:1	250	1.5–2.0	–	~10	~60	–	~5	[104]
Cu/ZrO ₂ (10 wt% Cu)	3:1	220	3.0	–	~3	~75	~60	–	[194]
PdZn/TiO ₂ (4 wt% Pd)	3:1	250	3.0	12000	25.6	89.5	–	78.9	[138]
CuZnZr(Zn/(Zn + Zr) = 0, 0.05, 0.13, 0.5, 1)	3:1	250	3.0	9000	23.6	91.2	1.23	–	[129]
2CuZnAl-InO	3:1	250	3.0	30000	~5	~55	~7	–	[195]
CuZnxZr(CuO (60 mol.%))(x = 0, 5, 10, 20, 30)	3:1	250	3.0	6000	14.0	54.4	0.65	–	[139]
1.0PdZn/CeO ₂	3:1	220	2.0	3600	14.07	97.2	165.85	11	[196]
CuO/CeO ₂ (5 wt% Cu)	3:1	–	2.0	–	–	89.5	–	1.9	[185]
8 wt% Cu/ZnAl ₂ O ₄	3:1	220	3.0	9000	11.3	~80	242	–	[197]
In ₂ O ₃ /ZrO ₂ (20In/Zr-X)	3:1	–	2.0	–	~30	–	–	1.57	[198]
CuO-ZnO/γ-Al ₂ O ₃ (1:1)	3:1	230	2.5	1200	24	65	–	4.0	[118]
In ₂ O ₃ -ZrO ₂	4:1	280	5.0	2400	–	~80	9.83	–	[199]
Cu/ZnO/Al ₂ O ₃ /ZrO ₂ (2:1:0.7:0.3)	3:1	230	5.0	8500	18.0	68.4	–	0.38	[200]
Cu ₁ In ₂ Zr ₄ -O	3:1	–	2.0	12000	12.8	72.8	–	9.3	[201]
Pd ₂ Ga(Pd ₂ Ga 2:1)	3:1	210	5.0	–	–	>60	–	–	[93]
CuO-ZnO/Al ₂ O ₃ (mass ratio: 1/1/6)	3:1	270	5.0	3600	14	–	0.28	–	[202]
Cu-Ni/CeO ₂ - Nanotube	3:1	260	3.0	6000	17.8	78.8	18.1	–	[189]
Cu/ZrO ₂ (Cu = 9 wt%)	3:1	270	1.0	–	14.9	~60	–	–	[203]
Au/In ₂ O ₃ -ZrO ₂	3:1	300	5.0	21000	11.3	72.9	0.47	–	[204]
Au/In ₂ O ₃ -ZrO ₂	6:1	300	5.0	21000	14.8	66.0	0.56	–	[204]
Cu/ZnO/Al ₂ O ₃ (45/45/10 mol%)	9:1	–	0.7	2250	13.0	23	9.3	2.7	[74]
Cu/Al ₂ O ₃ CeO ₂ (60 wt% Cu)	3:1	260	3.0	14400	~17	~55	11.9	~10	[178]
CuO-ZnO-CeO ₂ /TNTs (CZC/10TNTs)	3:1	260	3.0	7500	23.3	59.8	9.33	–	[205]
CuO-In ₂ O ₃ (Cu:In 1:2))	3:1	260	3.0	7500	10.3	86.2	5.95	–	[206]
MoS ₂ -45@C	3:1	160	3.0	5670	27.3	95.8	0.54	–	[136]
5CuO:2ZnO:3ZrO ₂	3:1	240	3.0	24000	16.8	41.4	–	7.0	[116]
Cu/ZnO/SBA-15/kaolinite (20 wt% Cu)	3:1	250	2.0	5000	17.5	–	50 mg	–	[90]
Pd _{2.0} /CZZ (2.0 wt% Pd and 10 wt% Zn)	3:1	270	6.0	3600	29.1	43.8	5.11	12.7	[207]
50% In ₂ O ₃ /Co/C-N	–	300	2.0	3000	9.5	88.4	2.5	–	[208]
In ₂ O ₃ /ZrO ₂ (9 wt % In)	4:1	300	5.0	16000	5.2	99.8	0.295	–	[209]
Bi-MnFe ₂ O ₄	3:1	–	0.1	22000	22.0	61	–	–	[171]
Au/ZrO ₂ (0.5–1 wt% Au)	3:1	240	4.0	–	6.8	72.5	1.9	–	[85]
15Cu/6.4ZnO/AlFum MOF	3:1	230	5.0	10000	–	45.6	6.9	–	[39]
Cu/TiO ₂ -ns	3:1	260	3.0	3600	–	64.5	–	5.6	[117]
Mn/Nb/Cu/ZnO/Al ₂ O ₃ -ZrO ₂	3:1	250	2.25	10800	15.9	68.8	–	–	[210]
4Ag6CuZ	3:1	230	3.0	–	–	51	0.72	–	[97]
Pd/SiO ₂ (1, 2, 3, and 4 wt% of Pd)	3:1	200	3.0	–	–	71	–	–	[211]

deactivate conventional Cu/ZnO catalysts, primarily through ZnO agglomeration and metallic Cu oxidation [31].

The ratio of CO₂ to H₂ moles was adjusted within the range of 1:3 to 1:5. When the ratio was set at 1:3, the yield of CH₃OH reached 12.2. However, by utilizing a ratio of 1:5, the highest CH₃OH yield of 14.8 was attained [187]. Au/CeO₂ catalyst was used to evaluate the impact of the H₂/CO₂ feed ratio. The rise in the feed ratio positively influences the rates of formation for all products (CO, CH₄, CH₃OH), albeit to varying degrees. In particular, the CH₃OH production rate experienced a more significant increase when compared to the rates of CH₄ and CO. With an increase in the feed ratio from 3 to 9, there was a substantial increase in selectivity of CH₃OH, from ca. 34% to 62%. The increase in CH₃OH selectivity can be rationalized by considering the stoichiometry of equilibrium reactions (Eq. (1)) - (Eq. (3)). When the H₂/CO₂ feed ratio is

higher, it tends to favor the production of CH₃OH and CH₄ over the r-WGS reaction, as these reactions are more reliant on hydrogen. Certainly, raising the H₂/CO₂ feed ratio resulted in higher rates of CH₃OH and CH₄ formation, with a decrease in CO formation [105].

A study examined H₂ consumption within a CO₂ hydrogenation reaction using a tri promoted CZA catalyst. While increasing the H₂:CO₂ ratio led to a higher CO₂ conversion, a ratio exceeding 6.5–10.0 resulted in a significant decrease in CH₃OH selectivity and a rise in methyl formate production [188]. Perhaps, there is a requirement to fine-tune the operating parameters to achieve a more effective utilization of H₂ for the best possible performance of the catalyst in the CH₃OH synthesis.

The use of membranes as distributors is suitable for setting suitable, homogeneous H₂:CO₂ ratios and concentrations along the catalyst bed. Selectivity shifts towards methanol appear realistic in this way.

7.4. Effect of space velocity (SV)

Gas Hourly Space Velocity (GHSV) is a critical parameter that measures the volumetric flow rate of gas (under standard conditions) relative to the catalyst bed volume [165]. It significantly impacts catalyst activity and concentration profiles. The rate of CH₃OH production exhibits a direct proportionality to the GHSV of CO₂.

In catalytic reactions, reactants undergo a series of steps to be converted into the final product [74]. Raising the GHSV equates to decreasing the reactor volume or the number of reactor tubes for a specific feed rate. Consequently, enhancing energy efficiency by lowering the GHSV entails a substantial increase in the number of tubes within the reactor, thereby increasing investment costs [165].

After initial optimization of reaction parameters, a CuNi₂ alloy supported on CeO₂–NT achieved a CO₂ conversion of 117.8% and a CH₃OH space-time yield of 18.1 mmol/gcat·h. Notably, this catalyst performs exceptionally well across a broad range of space velocities, with variations in GHSV not significantly impacting CO₂ hydrogenation [189].

This is where the distributor principle of a membrane can be advantageous. By introducing fresh reactants along the reactor bed, particularly towards the outlet where unreacted CO₂ remains due to spent reactants, the entire catalyst can be utilized more efficiently, leading to increased productivity.

8. Challenges and opportunities

In general, CH₃OH synthesis via CO₂ hydrogenation is acknowledged for its cost-efficiency and eco-friendliness. Nevertheless, this process faces limitations because of the low reactivity and inherent stability of CO₂ [212]. Some published works that highlight the conversion of CO₂ to CH₃OH in a membrane reactor are presented in Table 5.

8.1. Catalyst deactivation

Catalyst deactivation is a major challenge in CO₂ hydrogenation, necessitating a deep understanding of the deactivation mechanisms to develop strategies for improving catalyst stability [3]. The catalyst lifetime and the plant end-of-run rate are limited by catalyst deactivation. Cu-based catalysts used in CH₃OH synthesis can deactivate due to sintering and poisoning, with sintering being the more common cause. Sintering is a diffusion-controlled process, so its rate increases with temperature [213]. The literature highlights factors contributing to the deactivation of Cu-based catalysts by water, including the obstruction of hydrogen adsorption sites, alterations in the Cu morphology, and oxidation of the active Cu phase [25].

The CO₂ hydrogenation efficiency of CZA catalysts is hindered by water-induced catalyst deactivation and crystallization of Cu and ZnO. To improve stability and efficiency, other metal oxides are introduced as promoters in the catalyst composition. Studies have investigated the addition of metals such as Zr, La, Ce, Pd, Ga, V, Al, and Mn in Cu–Zn-based catalysts for CO₂ conversion to CH₃OH [128,214]. It also involves a molecular-reducing reaction, indicating that higher pressures enhance its thermodynamic favorability. Numerous catalysts have been proposed to achieve optimal CO₂ conversion across varying pressure ranges [215,216].

It is suggested that when H₂O is present during the process of CH₃OH synthesis, it speeds up the metal oxide crystal growth, leading to catalyst deactivation and hindering CO₂ adsorption [217]. Dehydrating membranes could counteract this effect, and the impact on methanol catalyst lifetime would be of fundamental interest.

Generally, a good catalyst for CH₃OH synthesis needs a large surface area of Cu. This is achieved by using small Cu nanoparticles, usually 2–10 nm in diameter [213]. Given that methanol synthesis through CO₂ hydrogenation depends on catalyst structure, and since this structure is influenced by its environment, it's crucial to monitor the catalyst's

Table 5

Report of previous works on CO₂ hydrogenation to methanol using membrane reactor.

Title	Summary	Findings	Ref.
Application of NaA Membrane Reactor for Methanol Synthesis in CO ₂ Hydrogenation at Low Pressure	For all reaction conditions, the membrane reactor (MR) performs better than the traditional reactor (TR), achieving higher methanol yields and selectivity.	The MR achieves a significantly higher CH ₃ OH yield (1.4–1.7 times) compared to the TR, particularly under milder conditions (lower GHSV and temperatures between 493 and 513 K).	[70]
Zeolite membranes: Comparison in the separation of H ₂ O/H ₂ /CO ₂ mixtures and test of a reactor for CO ₂ hydrogenation to methanol	The experiment investigated the ability of various zeolite membranes, such as zeolite T, Ti-Chabazite, chabazite, mordenite, and zeolite A, to separate water from mixtures containing H ₂ , CO ₂ , and H ₂ O at specific reaction temperatures.	Zeolite A exhibited the highest separation factor between H ₂ O and H ₂ . Initial tests compared a conventional reactor to a setup comprising both a TR and an MR. These tests demonstrated a higher CH ₃ OH yield. In one instance, the yield exceeded the maximum achievable through thermodynamic equilibrium in a standard reactor.	[161]
Highly Selective CO ₂ Conversion to Methanol in a Bifunctional Zeolite Catalytic Membrane Reactor	A catalytic membrane reactor (CMR) with dual functionality was designed to enhance the effective production of CH ₃ OH from CO ₂ . Within this CMR, CH ₃ OH synthesis occurs through catalytic hydrogenation of CO ₂ within the CZA layer, while simultaneously, the by-product H ₂ O is selectively eliminated in situ by the adjacent hydrophilic zeolite LTA membrane.	Operating the CMR at 533 K and 3.0 MPa allows for a CO ₂ conversion rate of 36.1% and 100% CH ₃ OH selectivity, significantly surpassing the results achieved in both the CFBR and PBMR. Additionally, efficiently eliminating H ₂ O from the reaction system serves to prevent catalyst deactivation and the formation of by-products, ultimately ensuring the CMR's long-term stability during continuous operation.	[43]
A membrane reactor for methanol synthesis	An assessment was conducted on a perfluorinated cation exchange material (Nafion, DuPont) for suitability as a vapor permeation membrane in environments with temperatures reaching 473 K. The perm-selectivities for CH ₃ OH and H ₂ O relative to H ₂ are influenced by the type of counter ion within the polymer, and they decline as temperature increases.	Lithium emerges as the most suitable choice for a counter ion, offering perm-selectivity values of 32 for H ₂ O and 5.6 for CH ₃ OH. Moreover, as the partial pressures of CH ₃ OH and H ₂ O vapors rise, both permeability and perm-selectivity increase.	[180]
Na ⁺ -gated water-conducting nanochannels for boosting CO ₂	It is highly desirable to develop durable nanochannels for conducting water that	The remarkably effective removal of water in real-time through these water-	[167]

(continued on next page)

Table 5 (continued)

Title	Summary	Findings	Ref.
conversion to liquid fuels	can effectively separate water from small gas molecules like hydrogen (H ₂), especially under high temperature and pressure conditions. These nanochannels are essential for enhancing numerous critical reactions significantly hindered by water, which is the primary by-product, in terms of thermodynamics and kinetics. The challenge lies in identifying and creating these nanochannels within large-area separation membranes without introducing additional defects.	conduction nanochannels resulted in a significant enhancement of CO ₂ conversion and CH ₃ OH yield during the process of CO ₂ hydrogenation for CH ₃ OH production.	
An experimental study of CO ₂ hydrogenation into methanol involving a zeolite membrane reactor	This study investigates the potential for a zeolite membrane reactor (MR) to improve CO ₂ to methanol conversion compared to conventional catalytic setups. Zeolite membrane reactors combine catalytic reactions with the separation characteristics of zeolite membranes.	Comparing the outcomes of this study to existing literature data for both the MR and the TR, with a focus on CO ₂ conversion, methanol selectivity, and yield at feed ratios (H ₂ /CO ₂) of 3 and 7, it becomes evident that employing a zeolite membrane reactor result in achieving greater CO ₂ conversion, as well as higher levels of CH ₃ OH selectivity and yield in comparison to a TR.	[42]

evolution from its inception to its end, as depicted in Fig. 8 [218].

8.2. Economic viability

The production cost of methanol and dimethyl ether (DME) from renewable feedstocks is determined by various factors such as feedstock type, production technology, energy requirements, production capacity, operating conditions, and product purity [212]. Methane (CH₄) and CO₂ are relatively affordable, with the latter possibly having a negative cost. As a result, transforming these compounds into more valuable chemical goods offers significant economic advantages [233].

Global methanol production has grown significantly in recent years, with installed production capacity expanding at an annual rate of 10% and actual production steadily growing at 7%. This growth led to a total production of 60 billion kilograms in the year 2012 [28]. The potential future of the industrial-scale process lies in the economic feasibility of using heterogeneous catalytic methods to convert pure CO₂ into CH₃OH. Methanex Corp. estimates that the current market price of CH₃OH is €370 per metric ton [219].

Significant progress has been achieved through advancement in Cu/Zn-catalyst technology, which has revolutionized CH₃OH synthesis. These catalysts now play a dominant role and have enabled lower reaction temperatures. The enhanced conversion rate facilitated by these lower temperatures has been advantageous economically by enabling operation at reduced pressure, known as the "low-pressure process." It's evident that consistently removing the products from the reactor would substantially enhance CH₃OH yield, thereby decreasing the need for extensive gas recycling and synthesis pressure [180].

By performing life cycle analyses and techno-economic assessments of various process intensifications for CH₃OH synthesis, including membranes, adsorption, condensation, and absorption, the most appropriate reactor for a particular application can be chosen [160].

The idea of a Methanol-based economy has been introduced, highlighting the importance of methanol within a circular economy. As a result, policies have been shifting towards embracing the methanol economy concept in both the fuel and chemical sectors. At present, the advancement of projects involving the conversion of CH₃OH into paraffin and olefin compounds has increased the demand for CH₃OH in the market. Thus, understanding catalyst design for CH₃OH production is crucial, given the rapid growth of the CH₃OH market and the consistent rise in production output [220].

A suitable membrane technology would reshuffle the cards, not least because dehydrating membranes would make complex distillation steps

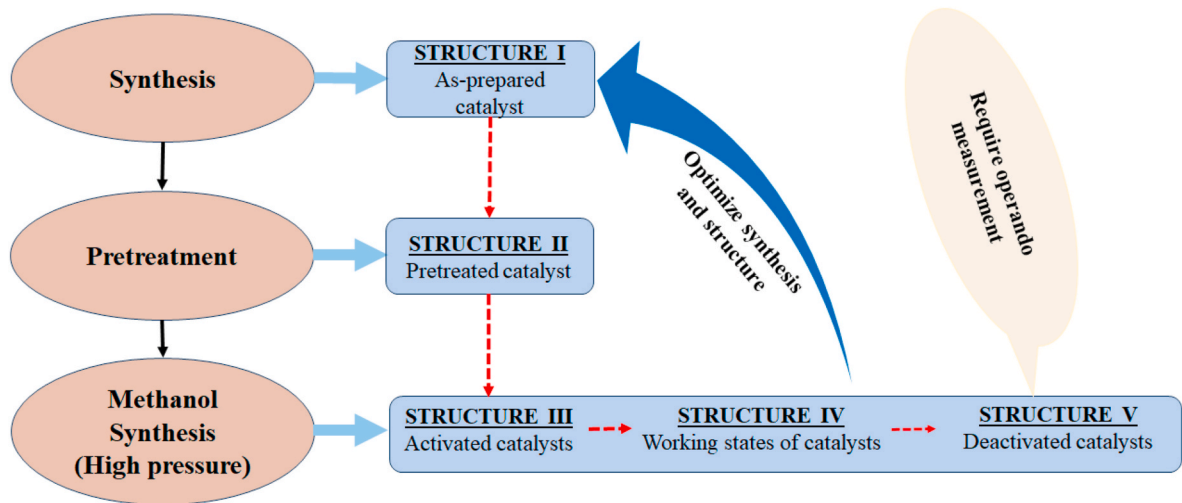


Fig. 8. The diagram illustrates the stages in the lifespan of a catalyst used in the production of methanol. A current obstacle is the absence of comprehensive in-situ studies that encompass multiple modes, making it difficult to explore catalyst behavior under high-pressure reaction conditions and impeding progress in enhancing catalytic properties [218].

of CH₃OH/H₂O mixtures much easier economically.

8.3. Environmental impact

In practice, various thermochemical methods exist that can convert CO₂ into valuable products like hydrogen, methanol, and ethanol [221], but Commercial technology must balance performance with environmental benefit [222]. Developing efficient hydrogen conversion technologies can significantly reduce harmful CO₂ emissions, contributing to a reduction in carbon emissions and the pursuit of carbon neutrality.

A notable example is the extensive research and application of hydrogen fuel cells, which offer several advantages: (i) The sole byproduct of the chemical reaction is water, with no involvement of other pollutants, particularly greenhouse gases. (ii) Hydrogen is safe in compliance with safety standards. (iii) These fuel cells are easily transportable and storable. Hence, the effective utilization of hydrogen fuel cells holds great importance [2].

Advancing renewable electrolytic hydrogen is the crucial solution for effectively implementing the technology based on economic analysis. Additionally, considering “blue hydrogen” during the transition to greener production processes is important [223].

Nguyen et al. explored using CO₂ for CH₃OH production via different routes. They found that, from an environmental perspective, hydrogenation technology using renewable hydrogen sources outperforms other methods by sequestering more CO₂ than it releases. Consequently, CH₃OH production involving CO₂ hydrogenation with renewable hydrogen stands out as the most promising approach to achieving the long-term goal of near-zero emissions [224].

Efficient technology is desirable, and this review has provided the necessary input.

9. Conclusion and future outlook

Utilizing CO₂ as a carbon feedstock for methanol synthesis effectively integrates this greenhouse gas into the chemical industry. However, efficient catalyst systems are crucial to facilitate CO₂ conversion to CH₃OH through hydrogenation, with a focus on enhanced selectivity, stability, and activity.

This review highlights advancements and challenges in using future membrane technologies with potential Cu-based catalysts for direct CO₂ conversion to CH₃OH. Alternative catalyst production methods and integration of zeolite membranes can achieve high methanol selectivity and productivity, catalyst stability, and most importantly, increased CO₂ conversions across all reaction parameters. Enhanced reactor productivity and process economics can be achieved through advancements in active catalysts, membrane designs, and reactor configurations.

With continued research and development, membrane reactors have the potential to become a major player in the synthesis of CH₃OH from CO₂. This would be a remarkable advancement in efforts to mitigate climate change and develop a carbon-cycle economy.

In this review, the progress made and perspective in CO₂ conversion to methanol using membrane reactors were discussed in detail. However, the necessary basic principles were also examined, which are:

- i. Enhancing the permeability and selectivity of membrane materials hinges on understanding their fundamental properties and structures. Several strategies can improve the microstructure of these materials. Optimizing synthesis methods to minimize defects and enhance uniformity is crucial. Additionally, exploring novel fabrication techniques can lead to more controlled structures. Finally, tailoring the composition and morphology of membrane materials through material design and surface modification can further improve their properties.
- ii. The development of new, highly active, and selective catalysts is crucial for efficiently converting CO₂ to methanol. Like membrane materials, catalyst stability is a primary concern due to the

harsh operating conditions. Therefore, balancing stability with catalytic activity is crucial for developing effective catalytic membrane systems. This can be achieved through material optimization, surface modification, and the incorporation of robust support structures.

- iii. The development of membrane reactor configurations that can maximize the efficiency of the membrane reactor. As for reactor configurations, Hollow fiber membranes offer high surface area-to-volume ratios, making them suitable for processes requiring compact designs and high throughput.

Continued research and development efforts hold the potential to fine-tune the reactor design, optimize catalyst and membrane formulations, and improve overall process economics. As researchers strive to address challenges such as catalyst stability, membrane selectivity, and reactor scalability, we anticipate the emergence of even more efficient and viable strategies for converting CO₂ emissions into valuable chemicals (e.g., CH₃OH).

Data availability

No data was used for the research described in the article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Mustapha Grema Mohammed: Writing – original draft, Project administration, Investigation. **N. Awanis Hashim:** Writing – review & editing, Supervision. **Wan Mohd Ashri Wan Daud:** Writing – review & editing, Supervision. **Unalome Wetwatana Hartley:** Resources, Funding acquisition. **Mohamed Kheireddine Aroua:** Resources, Conceptualization. **Sebastian Wohlrab:** Writing – review & editing, Validation.

Acknowledgments

The authors would like to express their gratitude to the UM International Collaboration Grant (IMG004-2022), SouthEast Asia-Europe Joint Funding Scheme for Research and Innovation, KMUTNB (KMUTNB-FF-66-52) and JFS (B48G660108) for financial support throughout this research.

References

- [1] Chiang CL, Lin KS, Lin YG. Preparation and characterization of Ni₂Ga₃ for methanol formation via CO₂ hydrogenation. *Top Catal* 2017;60:685–96.
- [2] Wang L, Wang D, Li Y. Single-atom catalysis for carbon neutrality. *Carbon Energy* 2022;4:1021–79.
- [3] Boretto A. Carbon dioxide hydrogenation for sustainable energy storage. *Int J Hydrogen Energy* 2024;58:1386–95.
- [4] Ali S, Kumar D, Khader MM, Mondal KC, El-Naas MH. Synthesis and evaluation of lanthana modified Cu-based catalysts for CO₂ hydrogenation to value added products. *Mol Catal* 2023;543.
- [5] Ye L, Xiao P, Scales P, Webley P, Singh R, Li GK. Improved copper-based catalysts for alcohol-assisted CO₂ hydrogenation: a comparative study between novel nano-stabilized and deposition-precipitation method. *Mol Catal* 2023;547.
- [6] Lu Z, Wang J, Sun K, Xiong S, Zhang Z, Liu C-j. CO₂ hydrogenation to methanol over Rh/In₂O₃-ZrO₂ catalyst with improved activity. *Green Chemical Engineering* 2022;3:165–70.
- [7] Haruna A, Tanimu G, Ibrahim I, Garba ZN, Yahaya SM, Musa SG, et al. Mitigating oil and gas pollutants for a sustainable environment – critical review and prospects. *J Clean Prod* 2023;416.
- [8] Meesattham S, Kim-Lohsoontorn P. Low-temperature alcohol-assisted methanol synthesis from CO₂ and H₂: the effect of alcohol type. *Int J Hydrogen Energy* 2022;47:22691–703.
- [9] Minyukova TP, Dokuchits EV. Hydrogen for CO₂ processing in heterogeneous catalytic reactions. *Int J Hydrogen Energy* 2023;48:22462–83.

- [10] Zhang M, Li F, Dou M, Yu Y, Chen Y. The synergetic effect of Pd, in and Zr on the mechanism of Pd/In₂O₃-ZrO₂ for CO₂ hydrogenation to methanol, vol. 7. Reaction Chemistry & Engineering; 2022. p. 2433–44.
- [11] UN. 27th session of the conference of the Parties of the UNFCCC (COP 27). 2022.
- [12] Sen R, Koch CJ, Galvan V, Entesari N, Goeppert A, Prakash GKS. Glycol assisted efficient conversion of CO₂ captured from air to methanol with a heterogeneous Cu/ZnO/Al₂O₃ catalyst. J CO₂ Util 2021;54.
- [13] Artz J, Müller TE, Thenert K, Kleinekorte J, Meys R, Sternberg A, et al. Sustainable conversion of carbon dioxide: an integrated review of catalysis and life cycle assessment. Chem Rev 2018;118:434–504.
- [14] Halilu A, Hayyan M, Aroua MK, Yusoff R, Hizaddin HF, Basirun WJ. Hybridized Fe/Ru-SiMWCNT-ionic liquid nanofluid for CO₂ conversion into carbamate using superoxide ion. J Environ Chem Eng 2021;9.
- [15] Halilu A, Hadj-Kali MK, Hashim MA, Yusoff R, Aroua MK. Bifunctional ionic deep eutectic electrolytes for CO₂ electroreduction. ACS Omega 2022;7:37764–73.
- [16] Halilu A, Hadj-Kali MK, Hashim MA, Ali EM, Bhargava SK. Electroreduction of CO₂ and quantification in new transition-metal-based deep eutectic solvents using single-atom Ag electrocatalyst. ACS Omega 2022;7:14102–12.
- [17] Megia PJ, Vizcaíno AJ, Calles JA, Carrero A. Hydrogen production technologies: from fossil fuels toward renewable sources. A mini review. Energy Fuel 2021;35:16403–15.
- [18] Muradov N. Low to near-zero CO₂ production of hydrogen from fossil fuels: status and perspectives. Int J Hydrogen Energy 2017;42:14058–88.
- [19] Boretti A. Promoting further discussion of methanol and ammonia energy storage ecosystems. Int J Hydrogen Energy 2024;51:29–32.
- [20] Boretti A. There are hydrogen production pathways with better than green hydrogen economic and environmental costs. Int J Hydrogen Energy 2021;46:23988–95.
- [21] Bajzadeh H, Rahimpour MR, Khorram M, Mohammadzadeh S. Mathematical modeling the methanol production process for direct CO₂ hydrogenation over a gallium (Ga₃Ni₅) catalyst. Chemical Engineering and Processing - Process Intensification 2023;183.
- [22] Battaglia P, Buffo G, Ferrero D, Santarelli M, Lanzini A. Methanol synthesis through CO₂ capture and hydrogenation: thermal integration, energy performance and techno-economic assessment. J CO₂ Util 2021;44.
- [23] Jarvis SM, Samsatli S. Technologies and infrastructures underpinning future CO₂ value chains: a comprehensive review and comparative analysis. Renew Sustain Energy Rev 2018;85:46–68.
- [24] Brix F, Desbuis V, Piccolo L, Gaudry E. Tuning adsorption energies and reaction pathways by alloying: PdZn versus Pd for CO₂ hydrogenation to methanol. J Phys Chem Lett 2020;11:7672–8.
- [25] Bukhtiyarova M, Lunkenbein T, Kaehler K, Schloegl R. Methanol synthesis from industrial CO₂ sources: a contribution to chemical energy conversion. Catal Lett 2017;147:416–27.
- [26] Abashar MEE, Al-Rabiah AA. Highly efficient CO₂ hydrogenation to methanol via in-situ condensation and sorption in a novel multi-stage circulating fast fluidized bed reactor. Chem Eng J 2022;439.
- [27] Yang R-X, Chuang K-H, Wey M-Y. Hydrogen production through methanol steam reforming: effect of synthesis parameters on Ni–Cu/CaO–SiO₂ catalysts activity. Int J Hydrogen Energy 2014;39:19494–501.
- [28] Szima S, Cormos C-C. Improving methanol synthesis from carbon-free H₂ and captured CO₂: a techno-economic and environmental evaluation. J CO₂ Util 2018;24:555–63.
- [29] Cannizzaro F, Hensen EJM, Filot IAW. The promoting role of Ni on In₂O₃ for CO₂ hydrogenation to methanol. ACS Catal 2023;13:1875–92.
- [30] Daifeng L, Zhen Z, Yinye C, Lingxing Z, Xiaochuan C, Xuhui Y, et al. The Co-In₂O₃ interaction concerning the effect of amorphous Co metal on CO₂ hydrogenation to methanol. J CO₂ Util 2022;65.
- [31] Lombardelli G, Mureddu M, Lai S, Ferrara F, Pettinau A, Atzori L, et al. CO₂ hydrogenation to methanol with an innovative Cu/Zn/Al/Zr catalyst: experimental tests and process modeling. J CO₂ Util 2022;65.
- [32] Cheng D, Negreiros FR, Apra E, Fortunelli A. Computational approaches to the chemical conversion of carbon dioxide. ChemSusChem 2013;6:944–65.
- [33] Fujitani T. Enhancement of the catalytic performance and active site clarification of Cu/ZnO based catalysts for methanol synthesis by CO₂ hydrogenation. J Jpn Petrol Inst 2020;63:43–51.
- [34] Ahmad K, Abi Jaoude M, Upadhyayula S, Polychronopoulou K, Ravaux F. Kinetics of greenhouse gas CO₂ hydrogenation over K-promoted Cu/ZnO/Cr₂O₃ catalyst towards sustainable aviation fuel production. Fuel 2023;337.
- [35] Flores JH, Peixoto DPB, Appel LG, de Avillez RR, Silva MIPd. The influence of different methanol synthesis catalysts on direct synthesis of DME from syngas. Catal Today 2011;172:218–25.
- [36] Chen H, Cui H, Lv Y, Liu P, Hao F, Xiong W, et al. CO₂ hydrogenation to methanol over Cu/ZnO/ZrO₂ catalysts: effects of ZnO morphology and oxygen vacancy. Fuel 2022;314.
- [37] Guo Q, Li S, Li J, Hu Y, Duanmu C. Enhanced CO₂ hydrogenation to methanol on the mesostructured Cu–ZnO/Al₂O₃–ZrO₂ catalyst. ACS Appl Energy Mater 2021;4:8311–21.
- [38] Zhao D, Ortner N, Holena M, Wohlrab S, Kondratenko EV. Identifying catalyst property descriptors for CO₂ hydrogenation to methanol via big-data analysis. ACS Catal 2023;13:10547–59.
- [39] Duma ZG, Moma J, Langmi HW, Louis B, Parkhomenko K, Musyoka NM. Towards high CO₂ conversions using Cu/Zn catalysts supported on aluminum fumarate metal-organic framework for methanol synthesis. Catalysts 2022;12.
- [40] Huang Y, Zhu L, He Y, Wang Y, Hao Q, Zhu Y. Carbon dioxide utilization based on exergoenvironmental sustainability assessment: a case study of CO₂ hydrogenation to methanol. Energy 2023;273.
- [41] Struis R, Stucki S, Wiedorn M. A membrane reactor for methanol synthesis. J Membr Sci 1996;113:93–100.
- [42] Gallucci F, Paturzo L, Basile A. An experimental study of CO₂ hydrogenation into methanol involving a zeolite membrane reactor. Chemical Engineering and Processing-Process Intensification 2004;43:1029–36.
- [43] Yue W, Li Y, Wei W, Jiang J, Caro J, Huang A. Highly selective CO₂ conversion to methanol in a bifunctional zeolite catalytic membrane reactor. Angew Chem Int Ed Engl 2021;60:18289–94.
- [44] Li K. Ceramic membranes for separation and reaction. John Wiley & Sons; 2007.
- [45] Padinjarekutt S, Sengupta B, Li H, Friedman K, Behera D, Lecaros R, et al. Synthesis of Na⁺-gated nanochannel membranes for the ammonia NH₃ separation. J Membr Sci 2023;674.
- [46] Liu Q, Noble RD, Falconer JL, Funke HH. Organics/water separation by pervaporation with a zeolite membrane. J Membr Sci 1996;117:163–74.
- [47] Feng C, Khulbe K, Matsuura T, Farnood R, Ismail A. Recent progress in zeolite/zeotype membranes. Journal of Membrane Science and Research 2015;1:49–72.
- [48] Chen G, Zhang J, Geng M, Sunarso J, Wong NH, Ma T, et al. Design and direct preparation of a novel silicon carbide support for zeolite membrane. Appl Water Sci 2022;12.
- [49] Martinez Galeano Y, Tarditi AM, Cornaglia LM. NaA zeolite membranes on modified porous stainless steel supports: a comparative study of different SiO₂ sources. Braz J Chem Eng 2020;37:383–97.
- [50] Xu R, Pang W, Yu J, Huo Q, Chen J. Chemistry of zeolites and related porous materials: synthesis and structure. John Wiley & Sons; 2009.
- [51] Sano T. CHA zeolite membrane. Encyclopedia of membranes. 2014. p. 1–3.
- [52] Liu B, Kita H, Yogo K. Preparation of Si-rich LTA zeolite membrane using organic template-free solution for methanol dehydration. Sep Purif Technol 2020;239.
- [53] Huang A, Wang N, Caro J. Seeding-free synthesis of dense zeolite FAU membranes on 3-aminopropyltriethoxysilane-functionalized alumina supports. J Membr Sci 2012;389:272–9.
- [54] Chau JH, Tellez C, Yeung KL, Ho K. The role of surface chemistry in zeolite membrane formation. J Membr Sci 2000;164:257–75.
- [55] Schneider H, Schindel LK, Gomes LB, Tessaro IC, Marcilio NR. Template-free ZSM-5 membrane preparation on alumina support by secondary hydrothermal synthesis. Current Research in Green and Sustainable Chemistry 2021;4.
- [56] Huang A, Liang F, Steinbach F, Caro J. Preparation and separation properties of LTA membranes by using 3-aminopropyltriethoxysilane as covalent linker. J Membr Sci 2010;350:5–9.
- [57] Grand J, Awala H, Mintova S. Mechanism of zeolites crystal growth: new findings and open questions. CrystEngComm 2016;18:650–64.
- [58] Li Y, Yang W. Microwave synthesis of zeolite membranes: a review. J Membr Sci 2008;316:3–17.
- [59] Ma J, Shao J, Wang Z, Yan Y. Preparation of zeolite NaA membranes on macroporous alumina supports by secondary growth of gel layers. Ind Eng Chem Res 2014;53:6121–30.
- [60] Gui T, Zhang F, Li Y, Cui X, Wu X, Zhu M, et al. Scale-up of NaA zeolite membranes using reusable stainless steel tubes for dehydration in an industrial plant. J Membr Sci 2019;583:180–9.
- [61] Sathupanya M, Gulari E, Wongkasemjit S. The effect of starting material ratio, heating temperature and time on the morphology of NaA zeolite. Journal of Metals, Materials and Minerals 2003;12:41–50.
- [62] He Qiu, Zhang Y, Kong L, Kong X, Tang X, Meng D, et al. High performance SSZ-13 membranes prepared at low temperature. J Membr Sci 2020;603.
- [63] Hazrati H, Rostamizadeh M, Omidkhah MR, Sadeghian Z. Influence of synthesis and operating parameters on silicalite-1 membrane properties. Compt Rendus Chem 2018;21:19–26.
- [64] Gao X, Deng S, Kawi S. Zeolite-based catalytic membrane reactors for thermo-catalytic conversion of CO₂. iScience 2022;25:105343.
- [65] Li Z, Deng Y, Wang Z, Hu J, Haw KG, Wang G, et al. A superb water permeable membrane for potential applications in CO₂ to liquid fuel process. J Membr Sci 2021;639.
- [66] Sato K, Nakane T. A high reproducible fabrication method for industrial production of high flux NaA zeolite membrane. J Membr Sci 2007;301:151–61.
- [67] Zhang F, Zheng Y, Hu L, Hu N, Zhu M, Zhou R, et al. Preparation of high-flux zeolite T membranes using reusable macroporous stainless steel supports in fluoride media. J Membr Sci 2014;456:107–16.
- [68] Yu J, Pan Y, Wang C, Lai Z. ZIF-8 membranes with improved reproducibility fabricated from sputter-coated ZnO/alumina supports. Chem Eng Sci 2016;141:119–24.
- [69] Chen M, Guo W, Kong X, Tang X, Yang S, Meng D, et al. Efficient and facile preparation of pure silica CHA zeolite membranes by gel-less method. J Membr Sci 2023;666.
- [70] TriVan T, Nguyen L-P, Thu Hoai N, Tung Thanh D, Phuong Thuy N, Duc Anh N. Application of NaA membrane reactor for methanol synthesis in CO₂ hydrogenation at low pressure. Int J Chem React Eng 2018;16.
- [71] Santana CS, Rasteiro LF, Marcos FCF, Assaf EM, Gomes JF, Assaf JM. Influence of Al, Cr, Ga, or Zr as promoters on the performance of Cu/ZnO catalyst for CO₂ hydrogenation to methanol. Mol Catal 2022;528.
- [72] Qaderi J. A brief review on the reaction mechanisms of CO₂ hydrogenation into methanol. International Journal of Innovative Research and Scientific Studies 2020;3:33–40.

- [73] Hengne AM, Yuan DJ, Date NS, Saih Y, Kamble SP, Rode CV, et al. Preparation and activity of copper–gallium nanocomposite catalysts for carbon dioxide hydrogenation to methanol. *Ind Eng Chem Res* 2019;58:21331–40.
- [74] Lo IC, Wu H-S. Methanol formation from carbon dioxide hydrogenation using Cu/ZnO/Al₂O₃ catalyst. *J Taiwan Inst Chem Eng* 2019;98:124–31.
- [75] Zhu J, Ciolca D, Liu L, Parastaev A, Kosinov N, Hensen EJM. Flame synthesis of Cu/ZnO-CeO₂ catalysts: synergistic metal-support interactions promote CH₃OH selectivity in CO₂ hydrogenation. *ACS Catal* 2021;11:4880–92.
- [76] Poto S, van Berkel DV, Gallucci F, D'Angelo MFN. Kinetic modelling of the methanol synthesis from CO₂ and H₂ over a CuO/CeO₂/ZrO₂ catalyst: the role of CO₂ and CO hydrogenation. *Chem Eng J* 2022;435.
- [77] Zhou Z, Gao P. Direct carbon dioxide hydrogenation to produce bulk chemicals and liquid fuels via heterogeneous catalysis. *Chin J Catal* 2022;43:2045–56.
- [78] Cai D, Cai Y, Tan KB, Zhan G. Recent advances of indium oxide-based catalysts for CO₂ hydrogenation to methanol: experimental and theoretical. *Materials* 2023;16.
- [79] Li J-L, Inui T. Characterization of precursors of methanol synthesis catalysts, copper/zinc/aluminum oxides, precipitated at different pHs and temperatures. *Appl Catal Gen* 1996;137:105–17.
- [80] Ledakowicz S, Nowicki L, Petera J, Nizioł J, Kowalik P, Gołębowski A. Kinetic characterisation of catalysts for methanol synthesis. *Chem Process Eng* 2013;34:497–506.
- [81] Borovinskaya ES, Trebbin S, Alscher F, Breitung C. Synthesis, modification, and characterization of CuO/ZnO/ZrO₂ mixed metal oxide catalysts for CO₂/H₂ conversion. *Catalysts* 2019;9.
- [82] Zain MM, Mohammadi M, Kamiuchi N, Mohamed AR. Development of highly selective In₂O₃/ZrO₂ catalyst for hydrogenation of CO₂ to methanol: an insight into the catalyst preparation method. *Kor J Chem Eng* 2020;37:1680–9.
- [83] Allam D, Bennici S, Limousy L, Hocine S. Improved Cu- and Zn-based catalysts for CO₂ hydrogenation to methanol. *Compt Rendus Chem* 2019;22:227–37.
- [84] Xu J, Su X, Liu X, Pan X, Pei G, Huang Y, et al. Methanol synthesis from CO₂ and H₂ over Pd/ZnO/Al₂O₃: catalyst structure dependence of methanol selectivity. *Appl Catal Gen* 2016;514:51–9.
- [85] Sagor TV, Zavašnik J, Finšgar M, Novak Tušar N, Pintar A. Evaluation of Au/ZrO₂ catalysts prepared via postsynthesis methods in CO₂ hydrogenation to methanol. *Catalysts* 2022;12.
- [86] Jiang X, Nie X, Guo X, Song C, Chen JG. Recent advances in carbon dioxide hydrogenation to methanol via heterogeneous catalysis. *Chem Rev* 2020;120:7984–8034.
- [87] Wei Y, Liu F, Ma J, Yang C, Wang X, Cao J. Catalytic roles of In₂O₃ in ZrO₂-based binary oxides for CO₂ hydrogenation to methanol. *Mol Catal* 2022;525.
- [88] Chang X, Han X, Pan Y, Hao S, Chen J, Li M, et al. Insight into the role of Cu–ZrO₂ interaction in methanol synthesis from CO₂ hydrogenation. *Ind Eng Chem Res* 2022;61:6872–83.
- [89] Zabidi NAM, Tasfy S, Shaharun MS. Hydrogenation of CO₂ to methanol using copper/zinc oxide-based catalyst: effect of active metal ratio. In: 4th international conference on fundamental and applied sciences (ICFAS) held as part of world engineering, science and technology congress (ESTCON). Kuala Lumpur; 2016, MALAYSIA.
- [90] Abelniece Z, Kampars V, Piirsoo H-M, Mändar H, Tamm A. The influence of Zn content in Cu/ZnO/SBA-15/kaolinite catalyst for methanol production by CO₂ hydrogenation. *Energy Rep* 2022;8:625–9.
- [91] Carvalho DF, Almeida GC, Monteiro RS, Mota CJA. Hydrogenation of CO₂ to methanol and dimethyl ether over a bifunctional Cu–ZnO catalyst impregnated on modified γ -alumina. *Energy Fuel* 2020;34:7269–74.
- [92] Chang K, Wang T, Chen JG. Methanol synthesis from CO₂ hydrogenation over CuZnCeTi mixed oxide catalysts. *Ind Eng Chem Res* 2019;58:7922–8.
- [93] García-Trenco A, White ER, Regoutz A, Payne DJ, Shaffer MSP, Williams CK. Pd₂Ga-Based colloids as highly active catalysts for the hydrogenation of CO₂ to methanol. *ACS Catal* 2017;7:1186–96.
- [94] Ma X, Li X, Yang X, Tian X, Zhan H, Wang W, et al. Zn–CdZrO₄ solid solution catalysts for hydrogenation of CO₂ to methanol. *Fuel* 2023;346.
- [95] Zhang C, Yang H, Gao P, Zhu H, Zhong L, Wang H, et al. Preparation and CO₂ hydrogenation catalytic properties of alumina microsphere supported Cu-based catalyst by deposition-precipitation method. *J CO₂ Util* 2017;17:263–72.
- [96] Wang S, Yang J, Wang S, Zhao N, Xiao F. Effect of Cu and Zn on the performance of Cu–Mn–Zn/ZrO₂ catalysts for CO₂ hydrogenation to methanol. *Fuel Process Technol* 2023;247.
- [97] Alotaibi MA, Din IU, Alharthi AI, Bakht MA, Centi G, Shaharun MS, et al. Green methanol synthesis by catalytic CO₂ hydrogenation, deciphering the role of metal-metal interaction. *Sustainable Chemistry and Pharmacy* 2021;21.
- [98] Gao W, Qu G, Xu M, Chang S, Na W. Effect of pH on Co-precipitated Cu–ZnO–ZrO₂ catalysts used in CO₂ hydrogenation: the role of Zn-malachite in the precursors. *Fuel Cell* 2021;21:31–8.
- [99] Dasireddy VDBC, Stefancic NS, Likozar B. Correlation between synthesis pH, structure and Cu/MgO/Al₂O₃ heterogeneous catalyst activity and selectivity in CO₂ hydrogenation to methanol. *J CO₂ Util* 2018;28:189–99.
- [100] Lee JH, Lee SH, Moon DJ. Preparation and characterization of Cu-based catalysts for methanol synthesis in MeOH-PPSO process. *J Nanosci Nanotechnol* 2013;13:4398–400.
- [101] Sugawa S, Sayama K, Okabe K, Arakawa H. Methanol synthesis from CO₂ and H₂ over silver catalyst. *Energy Convers Manag* 1995;36:665–8.
- [102] Yang H, Zhang C, Gao P, Wang H, Li X, Zhong L, et al. A review of the catalytic hydrogenation of carbon dioxide into value-added hydrocarbons. *Catal Sci Technol* 2017;7:4580–98.
- [103] Melian-Cabrera I, Lopez-Granados M, Fierro JLG. Effect of Pd on Cu–Zn catalysts for the hydrogenation of CO₂ to methanol: stabilization of Cu metal against CO₂ oxidation. *Catal Lett* 2002;79:165–70.
- [104] Kim K-J, Ahn H-G. Effect of gold nanoparticles addition to CuO–ZnO/Al₂O₃ catalyst in conversion of carbon dioxide to methanol. *J Nanosci Nanotechnol* 2017;17:2724–7.
- [105] Vourros A, Garagounis I, Kyriakou V, Carabineiro SAC, Maldonado-Hódar FJ, Marnellos GE, et al. Carbon dioxide hydrogenation over supported Au nanoparticles: effect of the support. *J CO₂ Util* 2017;19:247–56.
- [106] Ban H, Li C, Asami K, Fujimoto K. Influence of rare-earth elements (La, Ce, Nd and Pr) on the performance of Cu/Zn/Zr catalyst for CH₃OH synthesis from CO₂. *Catal Commun* 2014;54:50–4.
- [107] Kourteles M, Kousi K, Kondarides DI. CO₂ hydrogenation to methanol over La₂O₃-promoted CuO/ZnO/Al₂O₃ catalysts: a kinetic and mechanistic study. *Catalysts* 2020;10.
- [108] Din IU, Shaharun MS, Naeem A, Tasleem S, Ahmad P. Revalorization of CO₂ for methanol production via ZnO promoted carbon nanofibers based Cu–ZrO₂ catalytic hydrogenation. *J Energy Chem* 2019;39:68–76.
- [109] Ojelade OA, Zaman SF. CO₂ hydrogenation to methanol over PdZn/CeO₂ catalyst. *Chemistry Catalysis* 2019;72:732–9.
- [110] Boonamnuay T, Kim-Lohsoontorn P. Multifunctional catalyst of Cu/ZnO and molecular sieve for low temperature CO₂ conversion to methanol. In: 5th international conference of chemical engineering and industrial biotechnology (ICCEIB). City Univ Hong Kong: ELECTR NETWORK; 2020.
- [111] Tasfy S, Zabidi NAM, Shaharun MS, Subbarao D. Methanol production via CO₂ hydrogenation reaction: effect of catalyst support. *Int J Nanotechnol* 2017;14:410–21.
- [112] Phongamwong T, Chantaprasertporn U, Witoon T, Numpilai T, Poo-Arpon Y, Limphirat W, et al. CO₂ hydrogenation to methanol over CuO–ZnO–ZrO₂–SiO₂ catalysts: effects of SiO₂ contents. *Chem Eng J* 2017;316:692–703.
- [113] Din IU, Shaharun MS, Subbarao D, Naeem A. Synthesis, characterization and activity pattern of carbon nanofibers based copper/zirconia catalysts for carbon dioxide hydrogenation to methanol: influence of calcination temperature. *J Power Sources* 2015;274:619–28.
- [114] Vali SA, Markeb AA, Moral-Vico J, Font X, Sánchez A. A novel Cu-based catalyst supported in chitosan nanoparticles for the hydrogenation of carbon dioxide to methanol: from the optimization of the catalyst performance to the reaction mechanism. *Catal Commun* 2023;182.
- [115] Gesmanee SK-aW. Catalytic hydrogenation of CO₂ for methanol production in fixed-bed reactor using Cu–Zn supported on gamma-Al₂O₃. In: Procedia E, editor. International conference on alternative energy in developing countries and emerging economies. Thailand: Bangkok; 2017. p. 739–44.
- [116] Chen D, Mao D, Wang G, Guo X, Yu J. CO₂ hydrogenation to methanol over CuO–ZnO–ZrO₂ catalyst prepared by polymeric precursor method. *J Sol Gel Sci Technol* 2019;89:686–99.
- [117] Bao Y, Huang C, Chen L, Zhang Yd, Liang L, Wen J, et al. Highly efficient Cu/ anatase TiO₂ {001}-nanosheets catalysts for methanol synthesis from CO₂. *J Energy Chem* 2018;27:381–8.
- [118] Santiago RG, Coelho JA, de Lucena SMP, Musse APS, Portilho MF, Rodriguez-Castellon E, et al. Synthesis of MeOH and DME from CO₂ hydrogenation over commercial and modified catalysts. *Front Chem* 2022;10:903053.
- [119] Bowker M. Methanol synthesis from CO₂ hydrogenation. *ChemCatChem* 2019;11:4238–46.
- [120] Hussain S, Liu T, Hou L, Yang J, Li Q. First principles investigations of structural and electronic properties of Ga-doped ZnZrO solid solutions for catalytic reduction of CO₂. *Mol Catal* 2023;537.
- [121] Azoulay A, Garcia Baldovi A, Alberio J, Azaria N, Tzadikov J, Tashakory A, et al. Carbon-phosphorus-nitrogen materials as highly thermally stable catalyst supports for CO₂ hydrogenation to methanol. *ACS Appl Energy Mater* 2022;6:439–46.
- [122] Li F, Zhan H, Zhao N, Xiao F. CO₂ hydrogenation to methanol over La–Mn–Cu–Zn–O based catalysts derived from perovskite precursors. *Int J Hydrogen Energy* 2017;42:20649–57.
- [123] Wang P, Zha F, Yao L, Chang Y. Synthesis of light olefins from CO₂ hydrogenation over (CuO–ZnO)-kaolin/SAPO-34 molecular sieves. *Appl Clay Sci* 2018;163:249–56.
- [124] Xiao J, Mao D, Guo X, Yu J. Effect of TiO₂, ZrO₂, and TiO₂–ZrO₂ on the performance of CuO–ZnO catalyst for CO₂ hydrogenation to methanol. *Appl Surf Sci* 2015;338:146–53.
- [125] Sharma P, Ho PH, Shao J, Creaser D, Olsson L. Role of ZrO₂ and CeO₂ support on the In₂O₃ catalyst activity for CO₂ hydrogenation. *Fuel* 2023;331.
- [126] Ramli MZ, Syed-Hassan SSA, Hadi A. Performance of Cu–Zn–Al–Zr catalyst prepared by ultrasonic spray precipitation technique in the synthesis of methanol via CO₂ hydrogenation. *Fuel Process Technol* 2018;169:191–8.
- [127] Ren S, Fan X, Shang Z, Shoemaker WR, Ma L, Wu T, et al. Enhanced catalytic performance of Zr modified CuO/ZnO/Al₂O₃ catalyst for methanol and DME synthesis via CO₂ hydrogenation. *J CO₂ Util* 2020;36:82–95.
- [128] Xu Y, Gao Z, Peng L, Liu K, Yang Y, Qiu R, et al. A highly efficient Cu/ZnO_x/ZrO₂ catalyst for selective CO₂ hydrogenation to methanol. *J Catal* 2022;414:236–44.
- [129] Wang J, Liu H, Wang T, Xi Y, Sun P, Li F. Boosting CO₂ hydrogenation to methanol via Cu–Zn synergy over highly dispersed Cu, Zn-codoped ZrO₂ catalysts. *Catal Today* 2023;410:205–14.
- [130] Malik AS, Zaman SF, Al-Zahrani AA, Daous MA, Driss H, Petrov LA. Selective hydrogenation of CO₂ to CH₃OH and in-depth DRIFT analysis for PdZn/ZrO₂ and CaPdZn/ZrO₂ catalysts. *Catal Today* 2020;357:573–82.

- [131] Hartadi Y, Widmann D, Behm RJ. Methanol formation by CO₂ hydrogenation on Au/ZnO catalysts – effect of total pressure and influence of CO on the reaction characteristics. *J Catal* 2016;333:238–50.
- [132] Samson K, Sliwa M, Socha RP, Góra-Marek K, Mucha D, Rutkowska-Zbik D, et al. Influence of ZrO₂ structure and copper electronic state on activity of Cu/ZrO₂ catalysts in methanol synthesis from CO₂. *ACS Catal* 2014;4:3730–41.
- [133] Dang S, Gao P, Liu Z, Chen X, Yang C, Wang H, et al. Role of zirconium in direct CO₂ hydrogenation to lower olefins on oxide/zeolite bifunctional catalysts. *J Catal* 2018;364:382–93.
- [134] Chen P, Tao L, Zhu J, Zhao G, Liu Y, Lu Y. Morphology-controllable hexagonal-phase indium oxide in situ structured onto a thin-felt Al₂O₃/Al-fiber for the hydrogenation of CO₂ to methanol. *Energy Technol* 2019;7.
- [135] Liang B, Ma J, Su X, Yang C, Duan H, Zhou H, et al. Investigation on deactivation of Cu/ZnO/Al₂O₃ catalyst for CO₂ hydrogenation to methanol. *Ind Eng Chem Res* 2019;58:9030–7.
- [136] Cui P, Sun R, Xiao L, Wu W. Exploring the effects of the interaction of carbon and MoS₂ catalyst on CO₂ hydrogenation to methanol. *Int J Mol Sci* 2022;23.
- [137] Jiang H, Lin J, Wu X, Wang W, Chen Y, Zhang M. Efficient hydrogenation of CO₂ to methanol over Pd/In₂O₃/SBA-15 catalysts. *J CO₂ Util* 2020;36:33–9.
- [138] Quilis C, Mota N, Pawelec B, Millán E, Navarro Yerga RM. Intermetallic PdZn/TiO₂ catalysts for methanol production from CO₂ hydrogenation: the effect of ZnO loading on PdZn-ZnO sites and its influence on activity. *Appl Catal B Environ* 2023;321.
- [139] Sun X, Jin Y, Cheng Z, Lan G, Wang X, Qiu Y, et al. Dual active sites over Cu-ZnO-ZrO₂ catalysts for carbon dioxide hydrogenation to methanol. *J Environ Sci (China)* 2023;131:162–72.
- [140] Bonura G, Cordaro M, Cannilla C, Arena F, Frusteri F. The changing nature of the active site of Cu-Zn-Zr catalysts for the CO₂ hydrogenation reaction to methanol. *Appl Catal B Environ* 2014;152:152–61.
- [141] Shi Y, Su W, Wei X, Song X, Bai Y, Wang J, et al. Highly active MIL-68(In)-derived In₂O₃ hollow tubes catalysts to boost CO₂ hydrogenation to methanol. *Fuel* 2023;334.
- [142] Feng C, Khulbe K, Matsuura T, Farnood R, Ismail A. Recent progress in zeolite/zeotype membranes. *Journal of Membrane Science and Research (JMSR)* 2014;1.
- [143] Katz MJ, Brown ZJ, Colon YJ, Siu PW, Scheidt KA, Snurr RQ, et al. A facile synthesis of UiO-66, UiO-67 and their derivatives. *Chem* 2013;49:9449–51.
- [144] Vellingiri K, Kumar P, Deep A, Kim K-H. Metal-organic frameworks for the adsorption of gaseous toluene under ambient temperature and pressure. *Chem Eng J* 2017;307:1116–26.
- [145] Stawowy M, Ciesielski R, Maniecki T, Matus K, Łużny R, Trawczyński J, et al. CO₂ hydrogenation to methanol over Ce and Zr containing UiO-66 and Cu/UiO-66. *Catalysts* 2019;10.
- [146] Rungtaweeworani B, Baek J, Araujo JR, Archanjo BS, Choi KM, Yaghi OM, et al. Copper nanocrystals encapsulated in Zr-based metal-organic frameworks for highly selective CO₂ hydrogenation to methanol. *Nano Lett* 2016;16:7645–9.
- [147] Furukawa H, Gandara F, Zhang YB, Jiang J, Queen WL, Hudson MR, et al. Water adsorption in porous metal-organic frameworks and related materials. *J Am Chem Soc* 2014;136:4369–81.
- [148] Qi T, Zhao Y, Chen S, Li W, Guo X, Zhang Y, et al. Bimetallic metal organic framework-templated synthesis of a Cu-ZnO/Al₂O₃ catalyst with superior methanol selectivity for CO₂ hydrogenation. *Mol Catal* 2021;514.
- [149] Abbas I, Kim H, Shin C-H, Yoon S, Jung K-D. Differences in bifunctionality of ZnO and ZrO₂ in Cu/ZnO/ZrO₂/Al₂O₃ catalysts in hydrogenation of carbon oxides for methanol synthesis. *Appl Catal B Environ* 2019;258.
- [150] Ortner N, Zhao D, Mena H, Weiss J, Lund H, Bartling S, et al. Revealing origins of methanol selectivity loss in CO₂ hydrogenation over CuZn-containing catalysts. *ACS Catal* 2023;13:60–71.
- [151] Trifan B, Lasobras J, Soler J, Herguido J, Menéndez M. Modifications in the composition of CuO/ZnO/Al₂O₃ catalyst for the synthesis of methanol by CO₂ hydrogenation. *Catalysts* 2021;11.
- [152] Shi Y-F, Ma S, Liu Z-P. Copper-based catalysts for CO₂ hydrogenation: a perspective on active sites. *EES Catalysis* 2023;1:921–33.
- [153] Dang S, Yang H, Gao P, Wang H, Li X, Wei W, et al. A review of research progress on heterogeneous catalysts for methanol synthesis from carbon dioxide hydrogenation. *Catal Today* 2019;330:61–75.
- [154] Jia X, Sun K, Wang J, Shen C, Liu C-j. Selective hydrogenation of CO₂ to methanol over Ni/In₂O₃ catalyst. *J Energy Chem* 2020;50:409–15.
- [155] Kattel S, Yan B, Chen J, Rodriguez J, Liu P. Tuning activity and selectivity toward CO₂ conversion: going from metal, metal alloy to metal-oxide. *Abstr Pap Am Chem Soc* 2017;253.
- [156] Liu C, Liu P. Mechanistic study of methanol synthesis from CO₂ and H₂ on a modified model Mo₂S₈ cluster. *ACS Catal* 2015;5:1004–12.
- [157] Studt F, Behrens M, Kunkes EL, Thomas N, Zander S, Tarasov A, et al. The mechanism of CO and CO₂ hydrogenation to methanol over Cu-based catalysts. *ChemCatChem* 2015;7:1105–11.
- [158] Wu C, Lin L, Liu J, Zhang J, Zhang F, Zhou T, et al. Inverse ZrO₂/Cu as a highly efficient methanol synthesis catalyst from CO₂ hydrogenation. *Nat Commun* 2020;11.
- [159] Chen GW, Yuan Q. Methanol synthesis from CO₂ using a silicone rubber/ceramic composite membrane reactor. *Separ Purif Technol* 2004;34:227–37.
- [160] Van Kampen J, Boon J, van Sint Annaland M. Separation enhanced methanol and dimethyl ether synthesis. *J Mater Chem A* 2021;9:14627–9.
- [161] Raso R, Tovar M, Lasobras J, Herguido J, Kumakiri I, Araki S, et al. Zeolite membranes: comparison in the separation of H₂O/H₂/CO₂ mixtures and test of a reactor for CO₂ hydrogenation to methanol. *Catal Today* 2021;364:270–5.
- [162] Algieri C, Coppola G, Mukherjee D, Shammam MI, Calabro V, Curcio S, et al. Catalytic membrane reactors: the industrial applications perspective. *Catalysts* 2021;11.
- [163] Sea B, Lee KH. Methanol synthesis from carbon dioxide and hydrogen using a ceramic membrane reactor. *React Kinet Catal Lett* 2003;80:33–8.
- [164] Lacerda de Oliveira Campos B, John K, Beeskow P, Herrera Delgado K, Pitter S, Dahmen N, et al. A detailed process and techno-economic analysis of methanol synthesis from H₂ and CO₂ with intermediate condensation steps. *Processes* 2022;10.
- [165] Dieterich V, Wein N, Spliethoff H, Fendt S. Performance requirements of membrane reactors for the application in renewable methanol synthesis: a techno-economic assessment. *Advanced Sustainable Systems* 2022;6.
- [166] Hamed H, Brinkmann T, Shishatskiy S. Membrane-assisted methanol synthesis processes and the required permselectivity. *Membranes* 2021;11.
- [167] Li H, Qiu C, Ren S, Dong Q, Zhang S, Zhou F, et al. Na⁺-gated water-conducting nanochannels for boosting CO₂ conversion to liquid fuels. *Science* 2020;367:667–71.
- [168] Deng Y, Li Z, Chen T, Bian Z, Lim K, Dewangan N, et al. Low-cost and facile fabrication of defect-free water permeable membrane for CO₂ hydrogenation to methanol. *Chem Eng J* 2022;435.
- [169] Song G, Zhou W, Li C, Wang Z, Hu F, Wang T, et al. Semi-hollow LTA zeolite membrane for water permeation in simulated CO₂ hydrogenation to methanol. *J Membr Sci* 2023;678.
- [170] Li MM-J, Zeng Z, Liao F, Hong X, Tsang SCE. Enhanced CO₂ hydrogenation to methanol over CuZn nanoalloy in Ga modified Cu/ZnO catalysts. *J Catal* 2016;343:157–67.
- [171] Bibi M, Ullah R, Sadiq M, Sadiq S, Khan I, Saeed K, et al. Catalytic hydrogenation of carbon dioxide over magnetic nanoparticles: modification in fixed-bed reactor. *Catalysts* 2021;11.
- [172] Seshimo M, Liu B, Lee HR, Yogo K, Yamaguchi Y, Shigaki N, et al. Membrane reactor for methanol synthesis using Si-rich LTA zeolite membrane. *Membranes* 2021;11.
- [173] Wu W, Xie K, Sun D, Li X, Fang F. CuO/ZnO/Al₂O₃ catalyst prepared by mechanical-force-driven solid-state ion exchange and its excellent catalytic activity under internal cooling condition. *Ind Eng Chem Res* 2017;56:8216–23.
- [174] Sawamura K-I, Shirai T, Takada M, Sekine Y, Kikuchi E, Matsukata M. Selective permeation and separation of steam from water-methanol-hydrogen gas mixtures through mordenite membrane. *Catal Today* 2008;132:182–7.
- [175] Gallucci F, Basile A. A theoretical analysis of methanol synthesis from CO₂ and H₂ in a ceramic membrane reactor. *Int J Hydrogen Energy* 2007;32:5050–8.
- [176] Tavolaro A, Tavolaro P. LTA zeolite composite membrane preparation, characterization and application in a zeolitic membrane reactor. *Catal Commun* 2007;8:789–94.
- [177] Muharam Y, Fardiansyah AB. Hydrogenation of carbon dioxide into methanol on a Cu/Zn/Al₂O₃ catalyst in a fixed-bed reactor. 4th International Symposium on Applied Chemistry (ISAC). Bumi Serpong Damai. INDONESIA 2018;2024.
- [178] Li S, Guo L, Ishihara T. Hydrogenation of CO₂ to methanol over Cu/AlCeO catalyst. *Catal Today* 2020;339:352–61.
- [179] Salehi M-S, Askarishahi M, Gallucci F, Godini HR. Selective CO₂-Hydrogenation using a membrane reactor. *Chemical Engineering and Processing-Process Intensification* 2021;160.
- [180] Struis Jozef RPW, Stucki S, Wiedorn M. A membrane reactor for methanol synthesis. *J Membr Sci* 1996;113:93–100.
- [181] Tian C, Huang A. Synthesis of a Cu/Zn-BTC@LTA derivatived Cu-ZnO@LTA membrane reactor for CO₂ hydrogenation. *J Membr Sci* 2022;662.
- [182] Din IU, Shaharun MS, Naeem A, Alotaibi MA, Alharthi AI, Nasir Q. Effect of reaction conditions on the activity of novel carbon nanofiber-based Cu/ZrO₂ catalysts for CO₂ hydrogenation to methanol. *Compt Rendus Chem* 2020;23:57–61.
- [183] Allam D, Cheknoun S, Hocine S. Operating conditions and composition effect on the hydrogenation of carbon dioxide performed over CuO/ZnO/Al₂O₃ catalysts. *Bull Chem React Eng Catal* 2019;14:604–13.
- [184] Tian Hf, Yu L, Ding J, Zha F, Tang Xh, Chang Y. Synthesis of hollow CuO/ZnO/Al₂O₃ composite microspheres for catalysing carbon dioxide hydrogenation. *Micro & Nano Lett* 2019;14:932–6.
- [185] Ouyang B, Tan W, Liu B. Morphology effect of nanostructure ceria on the Cu/CeO₂ catalysts for synthesis of methanol from CO₂ hydrogenation. *Catal Commun* 2017;95:36–9.
- [186] Salomone F, Sartoretto E, Ballauri S, Castellino M, Novara C, Giorgi F, et al. CO₂ hydrogenation to methanol over Zr- and Ce-doped indium oxide. *Catal Today* 2023;423:114023.
- [187] Pasupulety N, Al-Zahrani AA, Daous MA, Podila S, Driss H. A study on highly active Cu-Zn-Al-K catalyst for CO₂ hydrogenation to methanol. *Arab J Chem* 2021;14.
- [188] Berahim NH, Zabidi NAM, Ramli RM, Suhaimi NA, Seman AA, Yasin NH. Effect of feedstock composition on the methanol synthesis via the CO₂ hydrogenation process. In: Othman MB, Abdul Karim SA, Wilfred CD, Lee KC, Sokkalingam R, editors. Proceedings of the 1st international conference of new energy. Singapore: Springer Nature Singapore; 2023. p. 1–9.
- [189] Tan Q, Shi Z, Wu D. CO₂ hydrogenation to methanol over a highly active Cu-Ni/CeO₂ - nanotube catalyst. *Ind Eng Chem Res* 2018;57:10148–58.
- [190] Guo T, Guo Q, Li S, Hu Y, Yun S, Qian Y. Effect of surface basicity over the supported Cu-ZnO catalysts on hydrogenation of CO₂ to methanol. *J Catal* 2022;407:312–21.

- [191] Yang Y, Xu Y, Ding H, Yang D, Cheng E, Hao Y, et al. Cu/ZnO_x@UiO-66 synthesized from a double solvent method as an efficient catalyst for CO₂ hydrogenation to methanol. *Catal Sci Technol* 2021;11:4367–75.
- [192] Ali S, Kumar D, Mondal KC, El-Naas MH. Development of highly active Cu-based CO₂ hydrogenation catalysts by solution combustion synthesis (SCS): effects of synthesis variables. *Catal Commun* 2022;172.
- [193] Yao L, Shen X, Pan Y, Peng Z. Synergy between active sites of Cu-In-Zr-O catalyst in CO₂ hydrogenation to methanol. *J Catal* 2019;372:74–85.
- [194] Witoon T, Chalorntham J, Dumrongbunditkul P, Chareonpanich M, Limtrakul J. CO₂ hydrogenation to methanol over Cu/ZrO₂ catalysts: effects of zirconia phases. *Chem Eng J* 2016;293:327–36.
- [195] Stangeland K, Chamssine F, Fu W, Huang Z, Duan X, Yu Z. CO₂ hydrogenation to methanol over partially embedded Cu within Zn-Al oxide and the effect of indium. *J CO₂ Util* 2021;50.
- [196] Ojelade OA, Zaman SF, Daous MA, Al-Zahrani AA, Malik AS, Driss H, et al. Optimizing Pd:Zn molar ratio in PdZn/CeO₂ for CO₂ hydrogenation to methanol. *Appl Catal Gen* 2019;584.
- [197] Song L, Wang H, Wang S, Qu Z. Dual-site activation of H₂ over Cu/ZnAl₂O₄ boosting CO₂ hydrogenation to methanol. *Appl Catal B Environ* 2023;322.
- [198] Numpilai T, Kidkhunthod P, Cheng CK, Wattanakit C, Chareonpanich M, Limtrakul J, et al. CO₂ hydrogenation to methanol at high reaction temperatures over In₂O₃/ZrO₂ catalysts: influence of calcination temperatures of ZrO₂ support. *Catal Today* 2021;375:298–306.
- [199] Frei MS, Mondelli C, Cesarini A, Krumeich F, Hauert R, Stewart JA, et al. Role of zirconia in indium oxide-catalyzed CO₂ hydrogenation to methanol. *ACS Catal* 2019;10:1133–45.
- [200] Gao P, Yang H, Zhang L, Zhang C, Zhong L, Wang H, et al. Fluorinated Cu/Zn/Al/Zr hydrotalcites derived nanocatalysts for CO₂ hydrogenation to methanol. *J CO₂ Util* 2016;16:32–41.
- [201] Gao J, Song F, Li Y, Cheng W, Yuan H, Xu Q. Cu₂In nanoalloy enhanced performance of Cu/ZrO₂ catalysts for the CO₂ hydrogenation to methanol. *Ind Eng Chem Res* 2020;59:12331–7.
- [202] Tursunov O, Kustov L, Tilyabaev Z. Methanol synthesis from the catalytic hydrogenation of CO₂ over CuO-ZnO supported on aluminum and silicon oxides. *J Taiwan Inst Chem Eng* 2017;78:416–22.
- [203] Tada S, Oshima K, Noda Y, Kikuchi R, Sohmiya M, Honma T, et al. Effects of Cu precursor types on the catalytic activity of Cu/ZrO₂ toward methanol synthesis via CO₂ hydrogenation. *Ind Eng Chem Res* 2019;58:19434–45.
- [204] Lu Z, Sun K, Wang J, Zhang Z, Liu C. A highly active Au/In₂O₃-ZrO₂ catalyst for selective hydrogenation of CO₂ to methanol. *Catalysts* 2020;10.
- [205] Shi Z, Tan Q, Wu D. Enhanced CO₂ hydrogenation to methanol over TiO₂ nanotubes-supported CuO-ZnO-CeO₂ catalyst. *Appl Catal Gen* 2019;581:58–66.
- [206] Shi Z, Pan M, Wei X, Wu D. Cu-In intermetallic compounds as highly active catalysts for CH₃OH formation from CO₂ hydrogenation. *Int J Energy Res* 2022;46:1285–98.
- [207] Alabsi MH, Chen X, Wang X, Zhang M, Ramirez A, Duan A, et al. Highly dispersed Pd nanoparticles supported on dendritic mesoporous CeZrZnO_x for efficient CO₂ hydrogenation to methanol. *J Catal* 2022;413:751–61.
- [208] Fang T, Liu B, Lian Y, Zhang Z. Selective methanol synthesis from CO₂ hydrogenation over an In₂O₃/Co/C-N catalyst. *Ind Eng Chem Res* 2020;59:19162–7.
- [209] Martin O, Martin AJ, Mondelli C, Mitchell S, Segawa TF, Hauert R, et al. Indium oxide as a superior catalyst for methanol synthesis by CO₂ hydrogenation. *Angew Chem Int Ed Engl* 2016;55:6261–5.
- [210] Zulkifli NI, Zabidi NAM, Merican ZMA, Tasfy SFH. Effects of promoter's composition on the physicochemical properties of Cu/ZnO/Al₂O₃-ZrO₂ catalyst. *Catalysts* 2022;12.
- [211] Alharthi AI, Ud Din I, Alotaibi MA, Bagabas A, Naeem A, Alkhalifa A. Low temperature green methanol synthesis by CO₂ hydrogenation over Pd/SiO₂ catalysts in slurry reactor. *Inorg Chem Commun* 2022;142.
- [212] Goepfert A, Czaun M, Jones JP, Surya Prakash GK, Olah GA. Recycling of carbon dioxide to methanol and derived products - closing the loop. *Chem Soc Rev* 2014;43:7995–8048.
- [213] Cul Y, Fish A, Glen P, Macleod N, Mistry N, Nicholson M, et al. Latest catalyst provides more methanol for longer. 2022.
- [214] Qi T, Li W, Li H, Ji K, Chen S, Zhang Y. Yttria-doped Cu/ZnO catalyst with excellent performance for CO₂ hydrogenation to methanol. *Mol Catal* 2021;509.
- [215] Abelniece Z, Kampars V. Preparation of Cu/ZnO/SBA-15 catalyst for methanol synthesis via CO₂ hydrogenation at low pressure: effect of calcination temperature. In: *Proceedings of the 7th world congress on civil, structural, and environmental engineering*; 2022.
- [216] Anderson JT, Abelniece Z, Kampars V, Piirsoo H-M, Tamm A. Effects of Al and Co promoters on CuO/SBA-15/Kaolinite catalyst properties and CO₂ hydrogenation at low pressure. *E3S Web of Conferences* 2021;259.
- [217] Arena F, Barbera K, Italiano G, Bonura G, Spadaro L, Frusteri F. Synthesis, characterization and activity pattern of Cu-ZnO/ZrO₂ catalysts in the hydrogenation of carbon dioxide to methanol. *J Catal* 2007;249:185–94.
- [218] Li Y, Wu Z. A review of in situ/operando studies of heterogeneous catalytic hydrogenation of CO₂ to methanol². *Catal Today* 2023;420.
- [219] Din IU, Shaharun MS, Alotaibi MA, Alharthi AI, Naeem A. Recent developments on heterogeneous catalytic CO₂ reduction to methanol. *J CO₂ Util* 2019;34:20–33.
- [220] Zhang Z, Cheng S, Liu W, Chen B, Gao X, Wang P, et al. Unraveling the regulation of Mn in Cu-ZnO_x formation during methanol synthesis from syngas over Cu/ZnO/Al₂O₃-Mn catalysts. *Appl Catal B Environ* 2023;338.
- [221] Saleh HM, Hassan AI. Green conversion of carbon dioxide and sustainable fuel synthesis. *Fire* 2023;6.
- [222] Saleh TA. Nanomaterials and hybrid nanocomposites for CO₂ capture and utilization: environmental and energy sustainability. *RSC Adv* 2022;12:23869–88.
- [223] Wu T-W, Chien IL. A novel energy-efficient process of converting CO₂ to dimethyl ether with techno-economic and environmental evaluation. *Chem Eng Res Des* 2022;177:1–12.
- [224] Nguyen TBH, Zondervan E. Methanol production from captured CO₂ using hydrogenation and reforming technologies_ environmental and economic evaluation. *J CO₂ Util* 2019;34:1–11.