

Review

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Review

Mini-Review on Recent Developments and Improvements in CO₂ Catalytic Conversion to Methanol: Prospects for the Cement Plant Industry

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Abstract: The cement industry has significant environmental impacts, stemming from natural resources extraction and fossil fuels combustion. Notably, carbon dioxide (CO₂) emissions are a major concern associated with cement production. The cement industry emits 0.6 tons of CO₂ per ton of cement production, which is around 8 % of the total CO₂ emissions in the world. Meeting the 13th United Nations Sustainable Goals, cement plants aim to achieve carbon neutrality by 2050, resulting from reduction in CO₂ emissions (change in the composition of cementitious materials) and the adoption of carbon capture and utilisation (CCU) technologies. A promising approach involves converting CO₂ into valuable chemicals and fuels, such as methanol (MeOH) through the power-to-liquid (PtL) technologies. In this process, CO₂ captured from cement industry flue gas with hydrogen generated from renewable sources through electrolysis of water, catalytically transformed into renewable methanol (e-MeOH), offering a sustainable solution. To achieve this, it is crucial to advance the development of novel, highly efficient catalysts specifically designed for direct CO₂ hydrogenation. In this sense, this review discusses recent developments and improvements in CO₂ catalytic conversion, emphasizing catalyst performance, selectivity, and stability.

Keywords: methanol; CO₂ catalytic conversion; Cu-based catalysts; noble metal-based catalysts; transitional metal carbides catalysts; cement industry

1. Introduction

The excessive utilization of non-renewable energy sources resulting from globalization and industrialization continuously depletes fossil fuels, leading to an imminent energy crisis. Energy production through fossil fuel combustion contributes to a persistent rise in carbon dioxide (CO₂) emissions, intensifying environmental concerns. The escalating atmospheric CO₂ levels have prompted a pursuit of sustainable scientific methods for addressing this convergent challenge. A necessary condition for achieving sustainable growth in renewable energy involves transforming CO₂ into useful materials using effective methods. These approaches show potential for reducing environmental impact within the manufacturing industry, especially in cement production [1].

The cement industry is a significant contributor to CO₂ emissions. About 60 % of these emissions are produced through the calcination of limestone, essential to produce clinker. Since limestone is the primary raw material for cement, the reduction of these emissions poses considerable challenges. Cement plants are required to achieve carbon neutrality by 2050, as outlined in the 13th United Nations Sustainable Goals. One strategy to achieve this goal, involves Carbon Capture and Utilisation (CCU). Among these technologies, converting CO₂ into valuable chemicals like methanol (MeOH) holds immense potential [2–5].

MeOH is an essential and versatile liquid chemical that can be used in various applications, as a solvent, antifreeze or building material. Also, its demand exceeds 108.7 Mtons/year in 2023 (see

Figure 1) due to its role as a chemical intermediate and platform for synthesizing essential commodities such as formaldehyde, olefins, acetic acid, methyl tert-butyl ether (MTBE), dimethyl ether (DME) and gasoline. Additionally, MeOH can serve as a substitute or additive for high-octane fuel and modified diesel engines. Furthermore, MeOH can generate electricity through direct oxidation MeOH fuel cells, making its production from CO₂ environmentally and economically beneficial [6,7]. Leading producers include Methanex (Canada), Lyondell Basel Industries Holdings B.V. (The Netherlands), Methanol Holdings Ltd (Trinidad), BASF SE (Germany), SABIC (Saudi Arabia), Mitsubishi Gas Chemical Co. (Japan), Yanzhou Coal Mining Co. (China), PETRONAS (Malaysia), QAFAC (Qatar Fuel Additives Company), and AMPCO (Atlantic Methanol Production Company, affiliated with the National Gas Company of Equatorial Guinea). The continued interest in MeOH stems from its relatively straightforward production process.

There are different types of MeOH: (i) Brown MeOH: produced from coal, a non-renewable feedstock which is higher in carbon intensity than MeOH produced using natural gas; (ii) Grey MeOH: it is obtained by synthesis reaction from methane (CH₄) present in natural gas (or in some cases, as in China, still from coal), a non-renewable/fossil fuel feedstock; (iii) Blue MeOH: It is also obtained by synthesis derived from natural gas, but includes as part of the process, the CCU of the carbon generated during its production, converting it into a less polluting product; (iv) Green MeOH: it is produced using only renewable energy sources in the process and ensuring that no harmful gases are emitted into the atmosphere. Note that, Green MeOH may be bio-MeOH produced from biomass sources (livestock, agricultural, forestry residues and municipal wastes) or e-MeOH produced from green H₂ (produced from renewable electricity) and captured CO₂. Currently, around 65 % of the world's MeOH is produced from natural gas, and 35 % is produced from coal, with only a small fraction, 0.2 %, coming from biomass, green H₂ and captured CO₂ [8] [9].

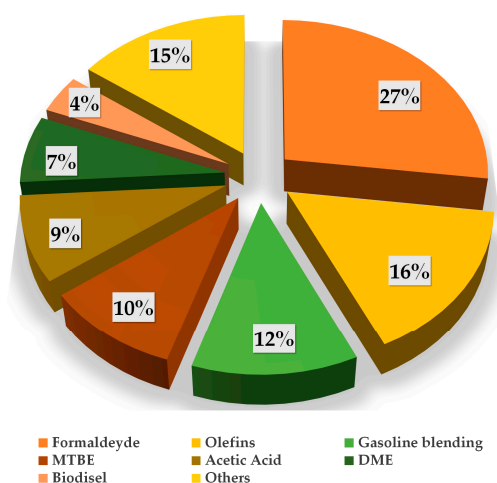


Figure 1. Global demand (108.7 Mtons/year) and world application for MeOH in 2023 [7].

Implementing the Power-to-Liquid (PtL) strategy (see Figure 2), can significantly contribute to reducing the carbon footprint. In this process, CO₂ captured from cement industrial flue gas is combined with H₂ generated by renewable electrolysis (green H₂) and catalytically converted into renewable methanol (e-MeOH) [10,11]. The CO₂ capture processes, for application in the cement industry, are the same as those considered for energy generation in other industrial sectors: pre-combustion, post-combustion and oxy-combustion. The renewable electrolysis can be achieved using solid oxide electrolyzer cells (SOEC), alkaline electrolyzers (AE) and polymer electrolyte membrane electrolyzers (PEM). Note that, according to life cycle assessment (LCA) study on the e-MeOH production, renewable sources use, can reduce the greenhouse gas emissions by 59 % when compared to conventional MeOH production [12].

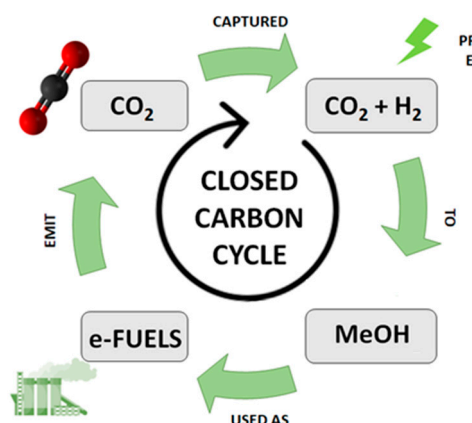


Figure 2. PtL technology in cement industry.

Researchers have explored both homogeneous and heterogeneous catalytic systems for CO₂ capture and conversion into valuable chemicals, which can serve as essential energy sources in industry. Transition metal-based heterogeneous catalysts have garnered significant attention due to their earth-abundant nature, cost-effectiveness, high activity, selectivity, reusability, and stability in CO₂ utilization technologies. Various heterogeneous catalysts are extensively studied, leveraging their strong adsorption capabilities, large surface-to-volume ratios, metal-metal and metal-support interactions, and synergy between support materials and active metal sites or dopants [9].

Shifting our focus to the cement plant industry, embracing digitization and sustainability is crucial. By doing so, cement players can achieve higher productivity, efficiency, and resilience. An important step, and probably the limiting one in developments to higher TRLs, in the PtL technology in the cement industry, is the catalytic reaction. The development of catalysts suitable for the reaction is under the scope of many researchers. Numerous existing reviews offer comprehensive insights from diverse perspectives. While some reviews concentrate solely on a specific catalyst type [13–15], others cover a wider range of catalyst types [16,17]. Additionally, a review addressing catalyst design, thermodynamics, kinetics, and technical aspects of this reaction has also been published [18–21]. Herein, the focus is on the advancements in heterogeneous catalytic systems, starting with Cu-based catalysts, followed by noble metal-based catalysts, and finally transitional metal carbides, considering recent experimental conditions. Finally, a perspective on the development of CO₂ conversion to MeOH in the cement industry will be emphasized.

2. Heterogeneous Catalytic Systems

In the last years, heterogeneous catalytic systems have played a crucial role in identifying novel routes to synthesize MeOH from CO₂ and are essential for converting CO₂ into valuable chemicals, contributing to greenhouse gas reduction and sustainable chemistry. The production of valuable chemicals, such as e-MeOH, typically involves heterogeneous or homogeneous catalytic conversion, as well as electrochemical, photochemical or photoelectrochemical reduction.

Heterogeneous catalytic conversion of CO₂ can be either a one-step (Equation 1) or a two-step process (Equations 2 and 3), where a one-step process converts CO₂ directly to MeOH, whereas the two-step process converts CO₂/H₂ to CO/H₂O in the first reaction [via reverse water gas shift (RWGS)], followed by the second reaction that combines CO with H₂ to form MeOH. The synthesis of MeOH through one-step is an exothermic reaction and the synthesis of MeOH through RWGS is an endothermic reaction [22].



Figure 3 illustrates how equilibrium CO₂ conversion and MeOH selectivity change in response to variations in temperature [Figure 3 (a)] and pressure [Figure 3 (b)]. Generally, increasing the temperature enhances the rate of CO₂ conversion. This is because higher temperatures provide the necessary energy to overcome activation barriers, leading to more effective collisions between CO₂ and hydrogen (H₂) molecules. However, at lower temperatures, the conversion rate decreases as the reaction kinetics slow down. While higher temperatures increase the conversion rate, they often reduce the selectivity for MeOH. This is because higher temperatures favor the formation of by-products like carbon monoxide (CO) and CH₄ over MeOH. However, lower temperatures tend to favor higher selectivity for MeOH. This is because the reaction pathway leading to MeOH is more thermodynamically favorable at lower temperature [23].

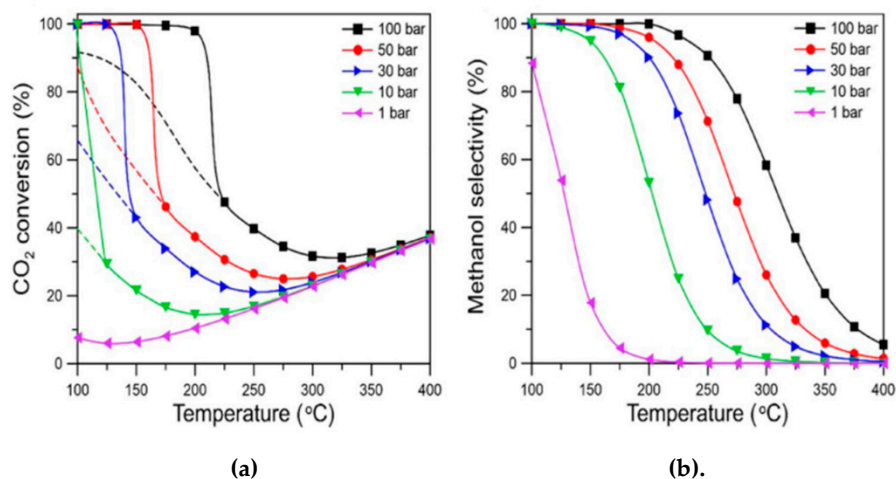


Figure 3. Effect of reaction temperature and pressure on (a) CO₂ conversion; and (b) MeOH selectivity [23].

Currently, industrial processes predominantly use heterogeneous catalytic conversion with copper (Cu)-based catalysts, such as, copper/zinc oxide/aluminium oxide (Cu/ZnO/Al₂O₃) [24]. This industrial process converts syngas to MeOH at a pressure range between 50 and 100 bar and at a temperature range between 200 and 300 °C. According to these conditions and based on thermodynamic equilibrium data for MeOH synthesis from syngas [25], MeOH yields (per pass) are, theoretically, in the range of 55-75 %. However, in practice, conversions are significantly less (ranging from 15-25 % [26] to as high as 40-50 %, with more advanced catalysts [27]).

In the actual context of the decarbonisation of the cement industry, the use of CO₂ emissions as raw material, become an important alternative. As mentioned before, one possibility is the synthesis of MeOH, together with H₂ proceeding from non-CO₂ emitting processes, namely from the water electrolysis process with renewable energy sources (green H₂) [28–31]. Considering the thermodynamic equilibrium for MeOH synthesis from mixtures of H₂ and CO₂, the results indicate that the achievable equilibrium yields are significantly lower (around 10 %) compared to those attainable with syngas (CO/H₂) under similar conditions. Note that, CO₂ hydrogenation consumes more H₂ and generates additional water, accelerating catalyst deactivation (namely related with the sintering of metal active sites). To enhance MeOH yield, modifying the reaction equilibrium (following Le Chatelier's principle) by removing the by-product (H₂O) can shift the equilibrium toward product formation. This can be achieved using several strategies, such as the use of hydrophobic catalyst surfaces, the use of membranes that allow water separation, or the use of dehydration agents [2]. Until now, there have not been developed any "commercial" catalysts, specifically, to be used in CO₂ conversion to MeOH based on Equation 1. In this sense it is of importance to be aware of the reported progress in conventional and new catalysts, with higher catalytic performance and/or "optimal balance" with good CO₂ conversion and MeOH selectivity. According to the literature search, heterogeneous catalysts based on Cu-based catalysts, noble metal-

based catalysts, and transitional metal carbides catalysts have been described in several publications and will be contemplated in this article.

2.1. Cu-Based Catalysts in Direct CO₂ Hydrogenation

The most popular catalysts for CO₂ conversion to MeOH are Cu/ZnO-based catalysts because zinc oxide (ZnO) prevents Cu particle agglomeration and creates a synergistic effect at the Cu and ZnO interface, increasing the amount of Cu surface area required for synthesis and improving the catalysts' overall performance and catalytic activity. However, the short lifetime, low thermal stability, low structural and textural features, and low reactivity are still significant disadvantages of such catalysts. Several studies have been conducted to address the listed limitations [32–34]. Many attempts have been made to improve Cu-based catalysts by adding various modifiers as promoters, supports, or stabilizers using different preparation methods. Currently, Cu-based catalysts can be easily prepared using the impregnation method. However, it is an inappropriate method to produce catalysts with higher metal loadings, such as those with > 10-20 %. Note that, higher metal loadings in catalysts contribute to better performance, selectivity and economic viability. This is because more active sites are available for the reaction, which can improve the overall efficiency. However, increasing the metal loading can lead to lower dispersion of the metal particles, which means fewer active sites are exposed on the surface. This can reduce the catalyst's effectiveness. Additionally, higher metal loadings can block the porosity (specially micropores and possibly mesopores) of the support material, which is essential for the diffusion of reactants and products. To balance these factors, researchers often aim to optimize the metal loading to achieve the best performance without significantly compromising dispersion and porosity. Single-atom catalysts (SACs) are one approach to address these challenges, as they provide high dispersion and maximize the exposure of active sites [35]. The co-precipitation method also solves this issue. It forms separate, crystalline precursor chemicals more successfully than the impregnation technique, leading to the production of metal nanoparticles with uniform support. Co-precipitation is the precipitation of metallic hydroxides or hydroxycarbonates by combining a basic precipitating agent solution (carbonates, bicarbonates, or hydroxides) with a metal precursor solution (such as aqueous nitrates of [Cu, zinc (Zn), and/or aluminium (Al)]). However, the residues from the calcination of the precursors, encourage Cu agglomeration, which lowers the final metal dispersion and reduces catalytic efficiency. In order to overcome this issue, the produced catalyst precursors undergo a thorough water washing to get rid of salt species and nitrates prior to heat treatments. Behrens et al. (2011) [36] reported the synthesis of mixed formates with basic character (Cu_{1-x}Zn_x)₂(OH)₂HCO₃ by co-precipitation from Cu and Zn formate solutions, resulting in a nitrate-free product and avoiding the washing step. A highly active catalyst was successfully synthesized by Prieto et al. (2013) [37] using the co-precipitation of Cu and Zn nitrates with ammonium bicarbonate [(NH₄)HCO₃] instead of sodium carbonate (Na₂CO₃). Na-free hydroxycarbonate precursors were produced by changing the precipitating agent, hence washing treatment was not necessary. The research conducted by Baltes et al. (2008) [38] synthesized a ternary CuO/ZnO/Al₂O₃ catalyst by co-precipitation. The study found that the optimal catalytic performance was achieved when the precursors were precipitated at 70 °C and pH of 6 to 8, aged for 20-60 min, and then calcined at 300 °C. Microwave irradiation has been reported by Fan et al. (2010) [39] to aid in the co-precipitation and aging processes of Cu/ZnO/Al₂O₃ catalyst production. On the one hand, their findings indicated that microwave irradiation during the co-precipitation step would increase the catalyst's activity, but not its stability. However, microwave irradiation during aging demonstrates significant improvements in the catalyst's stability and activity. Exact control of experimental parameters, including pH and temperature is necessary, since all precipitation conditions have a significant impact on the final catalyst's structure and catalytic performances.

On the other hand, the reaction conditions are also important, in order to develop efficient and environmentally friendly catalysts, and therefore, an overview of the catalytic performances, based on reaction conditions [(type of reactor, CO₂/H₂ ratio, temperature, pressure and Gas Hourly Space Velocity) (GHSV)], of some of the most recent Cu/ZnO/Al₂O₃ ternary industrial catalysts, Cu-based

catalysts and novel Cu-based catalyst formulation in direct CO₂ hydrogenation, can be seen in Table 1.

2.1.1. Cu/ZnO/Al₂O₃ Ternary Industrial Catalysts

The Cu/ZnO/Al₂O₃ ternary industrial catalysts are often used as a reference in research and industrial applications for converting syngas to MeOH because these have been extensively tested and validated in various demonstrator units.

Based on the data presented in the Table 1, the influence of type of reactor, CO₂/H₂ ratio, temperature, pressure and GHSV on conversion and selectivity for the Cu/ZnO/Al₂O₃ catalyst is commented [3,40–47]. According to the research conducted by Bansode et al. (2014) [3] the MeOH production through continuous catalytic hydrogenation of CO₂ over co-precipitated Cu/ZnO/Al₂O₃ catalysts in a fixed-bed reactor at high pressures (up to 360 bar) is remarkably efficient. An adjusted range of reaction conditions resulted in outstanding one-pass CO₂ conversion (> 95 %) and MeOH selectivity (> 98 %). The importance of high-pressure in stoichiometric hydrogenation of CO₂ to MeOH was also confirmed by Gaikwa et al. (2016) [46].

For the Cu/ZnO/Al₂O₃ catalyst reported by Li et al. (2014) [44], the fixed-bed reactor at 30 bar and 230 °C, shows a conversion rate of 18.7 % and a selectivity of 43 %. In a tubular reactor at the same pressure but at a higher temperature of 240 °C (see Figure 4), the conversion rate is slightly lower at 16.2 %, with a selectivity of 63.8 %, as reported by Lei et al. (2016) [40]. In the same research conducted by Lei et al. (2016) [40], basically, increasing temperature promotes the conversion of CO₂. However, the selectivity of MeOH decrease with increasing temperature. Hong et al. (2002) [42], in a fixed-bed reactor at 20 bar and 240 °C shows a conversion rate of 20.1 % and a selectivity of 31.3 %. This again highlights the trade-off between conversion efficiency and selectivity with pressure and temperature changes.

An example of catalytic CO₂ hydrogenation to MeOH using Cu/ZnO/Al₂O₃ catalysts prepared according to conventional co-precipitation, was investigated by Lee et (2020) al. [43] in an oil-cooled annulus reactor. The oil-cooled annulus reactor offers several advantages in the conversion of CO₂ to MeOH. One of the primary benefits is its ability to enhance the efficiency of the reaction process. By utilizing an annular design, the reactor can achieve better heat and mass transfer, which is crucial for maintaining the optimal conditions required for the catalytic conversion of CO₂ to MeOH. This design helps in distributing the reactants more evenly and ensures that the catalyst is utilized more effectively, leading to higher catalytic activity (CO₂ conversion and MeOH selectivity of 7.0 % and 98.5 %, respectively). Additionally, the oil-cooled annulus reactor can operate at lower temperatures and pressures compared to conventional reactors. This not only reduces the energy consumption but also minimizes the formation of by-products, making the process more environmentally friendly. The improved thermal management in the oil-cooled annulus reactor also helps in maintaining a stable reaction environment, which is essential for the consistent production of MeOH. Moreover, the oil-cooled annulus reactor's design allows for easier scaling up of the process. Its modular nature means that it can be adapted to different production scales without significant changes to the overall system. This flexibility is particularly advantageous for industrial applications where varying production demands need to be met efficiently [48].

Overall, the Table 1 illustrates that while higher temperatures and pressures can enhance the conversion of CO₂, those may not always favor the selectivity for MeOH. The type of reactor also plays a crucial role, with fixed-bed reactors generally providing a good balance between conversion and selectivity, as validated by research carried out by Liu et al. (2007) [45], Angelo et al. (2015) [49] and Da Silva et al. (2016) [41]. Recently, a simulation study reported by Campos et al. (2023) [50] at moderate pressure (70 bar) and lower temperature (100 °C) demonstrated that incorporating intermediate condensation steps in the process can significantly enhance the catalytic performance of Cu/ZnO/Al₂O₃ ternary industrial catalysts. This approach achieved a single-pass CO₂ conversion rate and MeOH selectivity of 53.9 % and 99.8 %, respectively, which is notably higher than the conventional process. This information is valuable for optimizing industrial processes for MeOH production from direct CO₂ hydrogenation.

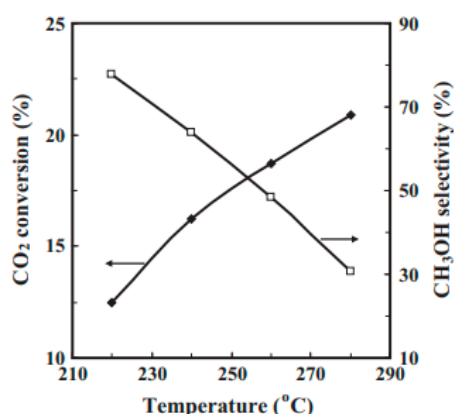


Figure 4. Catalytic performance of Cu/ZnO/Al₂O₃ as a function of the temperature at 30 bar and GHSV = 60 mL min⁻¹g⁻¹ [40].

2.1.2. Cu-Based Catalysts

Researchers are continuously working to enhance the stability, selectivity, and overall performance of Cu-based catalysts by employing advanced synthesis techniques and gaining a deeper understanding of their mechanisms, as previously mentioned.

Other metals, such as zirconium (Zr), cerium (Ce), titanium (Ti), magnesium (Mg) or lanthanum (La) have also been studied, but promoting effect is small. Angelo et al. (2015) [49] studied sol-gel and co-precipitation techniques to produced Cu/ZnO/Al₂O₃ enhanced with zirconium oxide (ZrO₂) and cerium oxide (CeO₂). The ZrO₂ promoted catalyst made by co-precipitation produced the highest results (CO₂ conversion and MeOH selectivity of 23.2 % and 33.0 %, respectively). The catalyst did not benefit from the addition of CeO₂ (CO₂ conversion and MeOH selectivity of 20.4 % and 27.0 %, respectively), and the Cu dispersion was significantly reduced. Xiao et al. (2015) [51] reported the CuO/ZnO catalysts promoted with titanium oxide (TiO₂), ZrO₂, or TiO₂/ZrO₂ mixed oxide were prepared by co-precipitation method and tested for the MeOH synthesis from CO₂ hydrogenation, aiming to improve the catalytic performance of CuO/ZnO catalysts. Based on results, the conversion of CO₂ increases with the addition of promoters and a maximum of 17.4 % is observed over the sample of CuO/ZnO/TiO₂/ZrO₂. The value of MeOH selectivity is 43.8 % over the same sample (CuO/ZnO/TiO₂/ZrO₂), which is 20 % higher than that on the CuO/ZnO catalyst. In order to further improve the performance of the CuO/ZnO/TiO₂/ZrO₂ catalyst, a series of CuO/ZnO/TiO₂/ZrO₂ catalysts were prepared by solid-state method and the effect of adding different assistant complexing agents (citric acid or oxalic acid) on the performance for CO₂ hydrogenation to MeOH reaction was reported by Xiao et al. (2019) [52]. The results suggest that incorporating both citric acid and oxalic acid enhanced the distribution of components, the interaction between CuO and ZnO, and CuO's reducibility. Additionally, it increased the Cu content on the surface and the area of metallic Cu. As a result, CO₂ conversion and MeOH yield significantly improved when citric acid or oxalic acid were added during the preparation process. The highest values were achieved using the catalyst prepared with oxalic acid. The importance of CuO/ZnO catalysts promoted with ZrO₂ mixed oxide was also studied by Li et al. (2015) [53]. In this study, a series of CuO/ZnO/ZrO₂ catalysts was synthesized by a surfactant-assisted co-precipitation method by using quaternary ammonium surfactant [cetyltrimethyl ammonium bromide (CTAB)]. The solid prepared by this new method showed higher MeOH selectivity (54.1 %) This higher selectivity was attributed to the formation of more amounts of active sites resulted from the homogeneous element distribution, intimate interface contact of Cu species with ZnO and/or ZrO₂, and to porous structure with larger pore size. Recently, Marcos et al. (2020) [54] reported the CO₂ hydrogenation mechanism, correlating structure-activity relationships of Cu/ZnO/ZrO₂ catalysts prepared via the surfactant-assisted route with Pluronic P123 (triblock copolymer surfactant) at different surfactant ratios. According to the results, at 250 °C and 30 bar of

pressure, the Cu/ZnO/ZrO₂ catalyst with higher surfactant ratio demonstrated higher catalytic activity with 23.0 % of CO₂ conversion at low GHSV and 75.0 % of MeOH selectivity at high GHSV, and, therefore, the surfactant improves the catalytic activity. In other study, the effect of operating conditions on the conversion of CO₂ to MeOH through the Cu/ZnO catalytic system in conjunction with ZrO₂ polymorph catalysts was also investigated by Marcos et al. (2022) [55]. According to thermodynamics results, the increase of pressure favours MeOH production at the equilibrium conditions. A series of catalysts derived from perovskite-type precursors were prepared via sol-gel method, as reported by Zhan et al. (2014) [56]. The results show that perovskite catalysts doped with magnesium (Mg) provide regular dispersion for Cu species, which lead to improve MeOH selectivity (65.2 %) and CO₂ conversion (9.1 %) at 50 bar of pressure and 250 °C of temperature. Note that, the perovskite catalysts without Mg shows MeOH selectivity of 57.9 % and CO₂ conversion of 6.4 %.

The comparison of experimental conditions and according to the research conducted by Marcos et al. (2020) [54], reducing pressure (up to 30 bar) and temperature (up to 250 °C) allows the achievement of high CO₂ conversion (around 23 %) and high selectivity towards MeOH (around 75 %) with Cu/ZnO/ZrO₂ catalysts as shown in the Figure 5. Note that the Cu/ZnO/ZrO₂ catalyst obtained from the higher surfactant ratio (0.06), exhibited the highest and close to equilibrium CO₂ conversion at low GHSV.

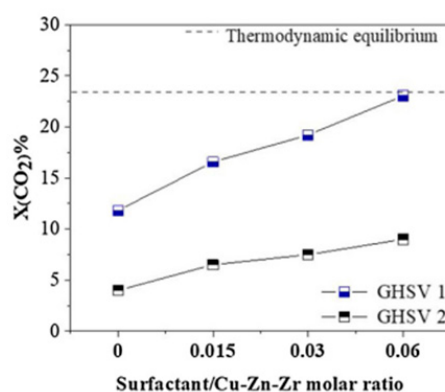


Figure 5. Effect of surfactant ratio on CO₂ conversion in comparison to equilibrium conversion, 30 bar, 250 °C, and CO₂/H₂ = 1:3, GHSV 1=100 mL min⁻¹ g⁻¹ and GHSV 2 = 400 mL min⁻¹ g⁻¹ [54].

2.1.3. Novel Cu-Based Catalyst Formulation

Despite the advances reported in the literature, the development of new Cu-based catalysts has not yet been fully exploited. The most widely used hydrophobic catalytic supports are carbon materials, such as activated carbon (AC) [57], graphene [58], as well as carbon nanotubes (CNTs) [59] [60]. Currently, these catalytic supports have become the most studied, because these supports provide a hydrophobic nature, large surface area, and strong thermal stability. In addition, the large surface area can greatly promote the anchoring of the metal by the carbon surface's functionalization [61]. In this sense, an overview of the catalytic performances, based on reaction conditions (type of reactor, CO₂/H₂ ratio, temperature, pressure and GHSV) of some of the most recent novel Cu-based catalyst formulation, can be seen in Table 1.

Deerattrakul et al. (2016) [62] study the impact of incorporating graphene oxide into Cu/ZnO catalyst prepared by impregnation method, for the CO₂ hydrogenation to MeOH. Note that, the catalysts were prepared with 5,10, 20, and 30 wt% of Cu-Zn metals. According to the results, at 250 °C and 15 bar of pressure, the catalyst with graphene oxide based on loading 10 wt% of metals demonstrated catalytic activity with 26.0 % of CO₂ conversion and 5.1 % of MeOH selectivity. The authors observed that, when increasing the loading beyond 10 wt%, the CO₂ conversion decreased and increase the MeOH selectivity, because the agglomeration of active metals led to reduced Cu oxides. Note that, the catalyst with graphene oxide based on loading 30 wt% of metals demonstrated catalytic activity with 20.0 % of CO₂ conversion and 15.6 % of MeOH selectivity. This enhanced

performance was attributed to the increased specific surface area of catalyst with graphene oxide and the enhanced adsorption capacity of H_2 and CO_2 due to the presence of graphene oxide.

Witoon et al. (2018) [63] study the impact of incorporating graphene oxide into $CuO/ZnO/ZrO_2$ catalyst prepared via a reverse co-precipitation method, for the CO_2 hydrogenation to MeOH. According to the results, at 200 °C and 20 bar of pressure, the catalyst with graphene oxide demonstrated catalytic activity with 4.5 % of CO_2 conversion and 75.9 % of MeOH selectivity. Note that, according to the results, at same conditions, the catalyst without graphene oxide demonstrated catalytic activity with 3.4 % of CO_2 conversion and 68.0 % of MeOH selectivity.

Fan et al. (2016) [58] study the impact of incorporating graphene oxide into $CuO/ZnO/ZrO_2/Al_2O_3$ catalyst prepared by co-precipitation method, for the CO_2 hydrogenation to MeOH. The authors concluded that the graphene-supported on Cu-based catalyst inhibit the sintering of the catalyst, which increased the CO_2 conversion and MeOH selectivity. According to the results, at 240 °C and 20 bar of pressure, the catalyst with graphene oxide demonstrated catalytic activity with 14.7 % of CO_2 conversion and 74.0 % of MeOH selectivity. Note that, according to the results, at same conditions, the catalyst without graphene oxide demonstrated catalytic activity with 13.2 % of CO_2 conversion and 70.0 % of MeOH selectivity. Wang et al. (2015) [64] discusses the synthesis of MeOH from CO_2 hydrogenation using Cu/ZrO_2 catalysts supported on CNTs with different functional groups. According to the results, at range temperature of 220-260 °C and 30 bar of pressure, the catalyst doped with CNTs demonstrated catalytic activity between 4.10-16.3 % of CO_2 conversion and 36.5-68.5 % of MeOH selectivity. It highlights the catalyst with nitrogen-containing groups on the CNTs surface showing the highest MeOH activity and the potential for reducing CO_2 emissions through the conversion of CO_2 into valuable chemicals like MeOH. The CO_2 hydrogenation using Cu/ZrO_2 catalysts supported on CNTs (in this study doped with pyridine) was also study by Sun et al. (2018) [65]. According to the results, at 200 °C and 30 bar of pressure, the catalyst doped with CNTs demonstrated catalytic activity with 5.0 % of CO_2 conversion and 82.0 % of MeOH selectivity. Note that, according to the results, at same conditions, the catalyst without CNTs demonstrated catalytic activity with 2.0 % of CO_2 conversion and 95.0 % of MeOH selectivity. They concluded that the pyridine nitrogen was found to increase the dispersion of CuO, facilitate its reduction, decrease the size of Cu particles, improve H_2 adsorption, and produce the most active sites.

Recently, Luo et al. (2020) [66] study an activated carbon-supported Cu/ZnO catalyst prepared by plasma decomposition at moderate temperature (around 140 °C), for CO_2 hydrogenation to MeOH. A fixed-bed reactor was used to assess the catalysts' catalytic performance between 230 and 290 °C at 40 bar of pressure. In the catalytic evaluation of catalysts, the catalyst produced by cold plasma. According to the results, a range temperature of 230 and 290 °C and 40 bar of pressure, the catalyst prepared by cold plasma demonstrated catalytic activity between 2.7-7.5 % of CO_2 conversion and 80.0-50.0 % of MeOH selectivity. Note that, according to the results, at same conditions, the catalyst prepared by calcination demonstrated catalytic activity with 3.0-5.5 % of CO_2 conversion and 80.0-45.0 % of MeOH selectivity.

Comparing the studies (see Table 1) of novel Cu-based catalyst formulation, offers several advantages for MeOH production: (i) enhanced reactivity and selectivity (carbon materials' large surface area and high compatibility with functional groups allow for the design of tailored catalysts. This can lead to improved reactivity and selectivity in MeOH synthesis reactions; (ii) cost-effectiveness (carbon materials is more affordable than other catalyst materials like noble metals; and (iii) stability and regenerability: carbon materials supported Cu catalysts exhibit excellent stability during MeOH production. Additionally, spent catalysts can often be regenerated and reused. The presence of ZrO_2 in $CuO/ZnO/ZrO_2$ /Graphene catalytic system led to the process with higher selectivity (75.9 %) for MeOH formation and lower CO_2 conversion (4.5 %). However, the presence of Al_2O_3 did affect the overall MeOH formation in the $Cu/ZnO/ZrO_2$ /Graphene catalyst, resulting in an increase in CO_2 conversion (around 14.7 %) and similar selectivity of MeOH (around 74 %). Incorporation of ZrO_2 to Cu/ZrO_2 /CNTs enhanced the catalytic performance with high selectivity (around 82 %) values for MeOH. In contrast, comparatively low conversion (2.7 %) of CO_2 and higher selectivity (around 80 %) to MeOH was reported when ZnO was incorporated to $Cu/ZnO/AC$ under

similar conditions (40 bar of pressure and 230 °C of temperature) with Cu-based catalysts, as show in Figure 6.

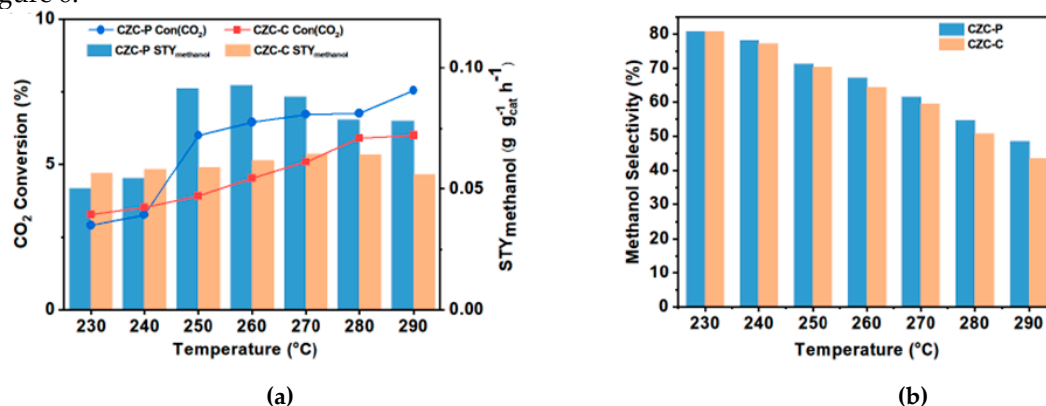


Figure 6. Catalytic performance of activated carbon (AC) supported Cu/ZnO catalysts at different temperatures, pressure of 40 bar, GHSV = 100 ml·min⁻¹ g⁻¹ and CO₂/H₂ = 1:3 [66].

2.2. Noble Metal-Based Catalysts

Noble metal-based catalysts, such as palladium (Pd), gold (Au), and platinum (Pt), have also been tried in production of e-MeOH. Because of their strong H₂ adsorption and dissociation activity, these metals have a lot of attention in the CO₂ to MeOH conversion process [67]. An overview of the catalytic performances, based on reaction conditions (type of reactor, CO₂/H₂ ratio, temperature, pressure and GHSV), of some of the most recent noble metal-based catalyst, can be seen in Table 1.

Bahruji et al. (2016) [67] focuses on controlling the form of the Pd nanoparticles deposited onto the ZnO support. The authors used two preparation methods, one an impregnation method and the second is based on the colloidal formation of preformed Pd nanoparticles and their immobilisation on the ZnO support. Based on the results, the catalytic performance of the Pd/ZnO catalysts is crucially dependent on these methods and on the resulting physical characteristics. The results show how important it is to monitor the size of Pd/Zn particles and their surface structure in order for the catalysts to reach high selectivity levels of around 60 % MeOH and 11 % conversion at 250 °C and 20 bar. The authors concluded that the sol-immobilized method for Pd/ZnO synthesis presents a more eminent way of controlling Pd and Pd/Zn particles size than the impregnation method, resulting in a higher catalytic activity. Xu et al. (2016) [68] also affirmed the importance of the Pd/Zn alloy in MeOH synthesis from CO₂ and H₂. However, the presence of alumina (Al₂O₃) did affect the overall MeOH formation in the catalyst, resulting in a decrease in CO₂ conversion (about 2.4 %) and similar selectivity of MeOH (about 74.9 %).

Collins et al. (2021) [69] showed more recently that Pd/Ga-supported mesoporous silica oxide (SiO₂) is an effective catalyst for producing MeOH from CO₂. Thin layer gallium oxide (Ga₂O₃) promotes CO₂ adsorption to generate polydentate carbonate species, which are then converted into MeOH, according to characterization using in situ transmission infrared spectroscopy. Authors claimed that the improvement of the catalytic performance requires the closeness of the Ga₂O₃ and dipalladium gallium (Pd₂Ga) surfaces. Choi et al. (2017) [70] studied a CO₂ hydrogenation to MeOH with a series of CeO₂-supported Pd/Cu catalysts, which were synthesized using a deposition-precipitation method. As a result, it is reported that the Pd addition on MeOH catalyst, Cu/CeO₂, could enhance the catalytic activity due to the improvement of the Cu site reducibility through hydrogen spillover property. Pd promotion enhanced MeOH productivity by increasing CO₂ conversion (8.8 to 17.8 %) in tested temperature range (190-270 °C) and 30 bar of pressure. Note that, Cu/CeO₂ catalyst (without Pd) shows a lower CO₂ conversion (1.8 to 6.4 %) in same temperature range.

The research on Ga₂O₃ supported palladium catalyst (Pd/Ga₂O₃) was reported by Fujitani et al. (1995) [71]. In their studied, the co-precipitation approach was used to prepare the catalyst. The catalytic activity was realized on fixed-bed reactor at 250 °C of temperature and 50 bar of pressure. The result showed that Pd/Ga₂O₃ catalyst (CO₂ conversion of 19.6 % and MeOH selectivity of 51.5 %)

generates better results than Cu/ZnO (CO₂ conversion of 11.7 % and MeOH selectivity of 36.1 %). Additionally, compared Pd with other metal [Al, chromium (Cr), Ti, Zn, and Zr] oxide support materials, this result is lower. It can be seen from Table 1 that for other metal oxides the CO₂ conversion and MeOH selectivity values were in the range of 0.4-15.5 % and 4.3-37.5 %, respectively.

Rui et al. (2020) [72] describe a novel gold/indium oxide (Au/In₂O₃) catalyst for the selective hydrogenation of CO₂ to MeOH. The results show that the MeOH selectivity is 100 % and over 70 % at temperatures below 225 °C and 275 °C, respectively. This result is almost 20 times higher than the Au catalyst supported by other oxides, such as ZnO, ZrO₂, CeO₂, TiO₂, Al₂O₃. Sagar et al. (2022) [73] studied the effect of different preparation methods on the catalyst surface and catalytic performance of Au/ZrO₂. Results showed that the higher CO₂ conversion (6.8 %) was obtained for the catalyst prepared by deposition rather than the impregnation method (CO₂ conversion of 2.5 %) was since it produces a high loading Au with controllable particle size and large surface area. Note that, the activity tests were conducted in a temperature of 240 °C, high pressure (40 bar) and stainless-steel tubular fixed-bed reactor.

Catalytic performance of Pt/indium oxide (Pt/In₂O₃) has been reported by Sun et al. (2020) [74] for CO₂ hydrogenation. Interestingly, Pt/In₂O₃ catalyst shown significant activity and selectivity for the hydrogenation of CO₂ to MeOH. The results demonstrate that the reaction proceeds with about 100 %, 74 %, and 54 % MeOH selectivity at <225 °C, 275 °C, and 300 °C, respectively. Also, the Pt/In₂O₃ catalyst achieves a 17.3 % CO₂ conversion at 300 °C. Han et al. (2021) [75] also reported the Pt/In₂O₃ catalysts for MeOH synthesis from CO₂ hydrogenation. The results shown that the catalytic activity may be improved by adding a small amount of Pt to In₂O₃ by co-precipitation method. The selectivity can be increased from 72.2 % (In₂O₃) to 91.1 % (Pt/In₂O₃) at 220 °C. Additionally, the CO₂ conversion can be increased from 4.4 % (In₂O₃) to 8.3 % (Pt/In₂O₃) at 300 °C.

Comparing noble metal-based catalysts (see Table 1) and considering the same condition reactions (50 bar at 250 °C) for MeOH synthesis from mixtures of H₂ and CO₂, the results indicate that achievable CO₂ conversion is higher (around 19.6 %) compared to those obtained with Cu-based catalysts. On the other hand, the MeOH selectivity is relatively smaller (around 51.5 %). However, according to the literature, in the presence of noble metal-based catalysts reducing pressure (up to 30 bar) and temperature (up to 180 °C), it is possible to achieve a higher selectivity of MeOH (around 79 %). Furthermore, research by Rui et al. [72] demonstrates that the intrinsic chemical activity of In₂O₃ and the strong Au/In₂O₃ interaction may be utilized to greatly increase the catalytic performance of Au catalysts (around 100 %), as show in Figure 7.

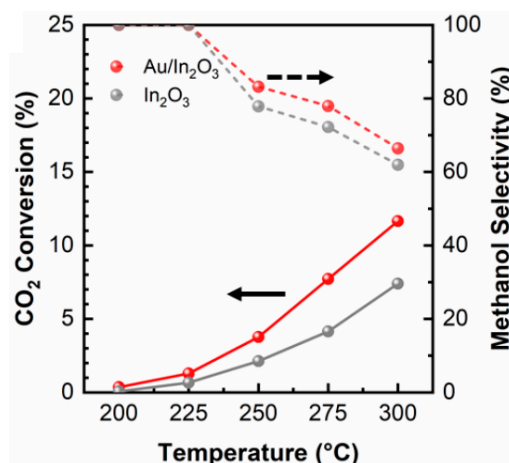


Figure 7. CO₂ conversion and MeOH selectivity versus temperature over In₂O₃ and Au/In₂O₃ catalyst [72].

2.3. Transitional Metal Carbides Catalysts

A new class of catalysts generated from metals with carbon integrated into the metal lattice are called transitional metal carbides. These resemble Pd, Au, Pt, and other noble metals in their physico-

chemical characteristics, which include high melting point, high hardness, high mechanical and high thermal stability. An overview of the catalytic performances, based on reaction conditions (type of reactor, CO_2/H_2 ratio, temperature, pressure and GHSV), of some of the most recent transitional metal carbides catalyst, can be seen in Table 1. Recently, the molybdenum carbide (Mo_2C) catalyst system's was assessed by Dongil et al. (2020)[76]. The authors found that adding Mo_2C could enhance their catalytic activity in the production of MeOH. The CO_2 conversion and MeOH selectivity reached 3.4 % and 60.0 %, respectively, at 150 °C and 20 bar of pressure for Mo_2C catalyst. While, the CO_2 conversion and MeOH selectivity reached 3.0 % and 50.0 %, respectively, at same conditions for Cs/ Mo_2C catalyst.

Some other catalysts have also received a lot of attention lately. For instance, Zhang et al. (2022) [77] synthesized a Mo-Co-C-N catalyst using a Metal-Organic Frameworks (MOFs), ZIF-67, precursor at 275 °C and 20 bar of reaction pressure. The catalyst's MeOH selectivity and CO_2 conversion were 9.2 % and 58.4 %, respectively. This is mostly due to the fact that the addition of N created a large number of oxygen vacancies, which made it easier for CO_2 to dissociate and adsorb and further increased MeOH selectivity. Box-like assemblages of quasi-single-layer molybdenum disulfide (MoS_2) nanosheets were created by Zhou et al. (2022) [78] and edge-blocked by zinc sulfide (ZnS) crystallites (referred to as $h\text{-MoS}_2/\text{ZnS}$) using a MOF-engaged technique. MeOH selectivity of 67.3 % and CO_2 conversion of 13.0 % may be attained by the $h\text{-MoS}_2/\text{ZnS}$ catalyst at reaction conditions of 260 °C and 50 bar.

The comparison of experimental conditions, of these studies (see Table 1) revealed that, between Cu-based catalysts and noble metal-based catalysts, catalytic tests realized under similar conditions, transitional metal carbide catalysts (see Figure 8) have moderate CO_2 conversion (around 13.0 %) and MeOH selectivity (around 67.3 %).

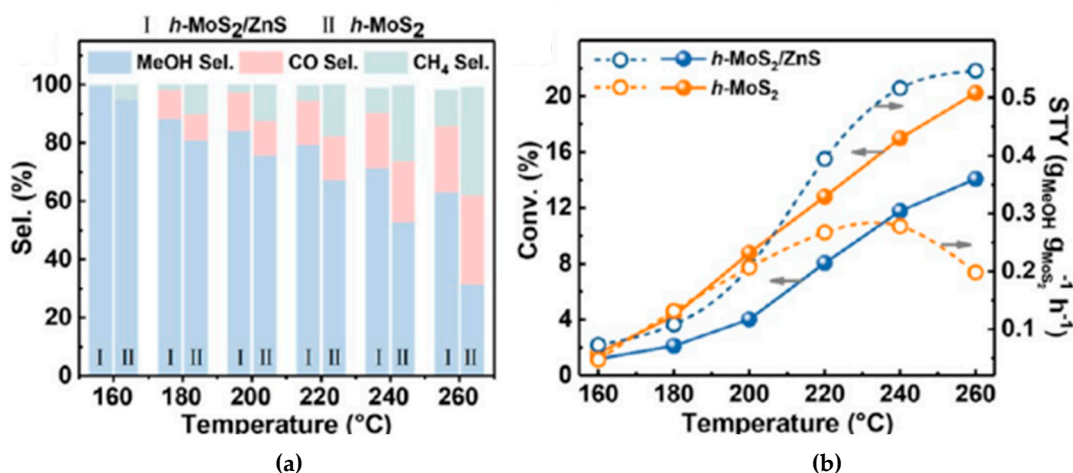


Figure 8. (a) Selectivity and (b) conversion for CO_2 hydrogenation of transitional metal carbides catalysts ($h\text{-MoS}_2/\text{ZnS}$ and $h\text{-MoS}_2$) at different reaction temperatures, pressure of 50 bar, GHSV = 60 $\text{ml}\cdot\text{min}^{-1}\text{g}^{-1}$ and $\text{CO}_2/\text{H}_2 = 1:3$ [78].

Table 1. Reaction conditions and catalytic performance of selected catalysts in direct CO₂ hydrogenation to MeOH.

Catalyst	Type of reactor	CO ₂ /H ₂ ratio	GHSV / ml·min ⁻¹ g ₁	Conditions / bar; °C	Conversion / %	Selectivity / %	Reference
Cu-based ternary industrial catalysts							
Cu/ZnO/Al ₂ O ₃	Fixed-bed	1:14	175	360; 260	95.7	98.2	[3]
Cu/ZnO/Al ₂ O ₃	Fixed-bed	1:3	167	442; 280	65.3	91.9	[46]
Cu/ZnO/Al ₂ O ₃	Fixed-bed	1:3	60	20; 240	20.1	31.3	[42]
Cu/ZnO/Al ₂ O ₃	Fixed-bed	No info	No info	30; 230	18.7	43.0	[44]
CuO/ZnO/Al ₂ O ₃	Tubular	1:3	60	30; 240	16.2	63.8	[40]
Cu/ZnO/Al ₂ O ₃	Annulus	5:64	100	30; 250	7.0	98.5	[43]
Cu/ZnO/Al ₂ O ₃	Slurry	No info	No info	50; 170	5.2	11.9	[45]
Cu/ZnO/Al ₂ O ₃	Fixed-bed	1:4	167	50; 240	7.3	51.0	[49]
Cu/ZnO/Al ₂ O ₃	Fixed-bed	1:4	167	50; 260	15.5	36.0	[49]
Cu/ZnO/Al ₂ O ₃	Tubular	1:3	No info	50; 270	12.7	65.0	[41]
Cu/ZnO/Al ₂ O ₃	Flow model	1:3	30-667	70; 100	53.9	99.8	[50]
Cu-based catalysts							
Cu/ZnO/Al ₂ O ₃ /ZrO ₂	Fixed-bed	1:4	167	50; 280	23.2	33.0	[49]
Cu/ZnO/Al ₂ O ₃ /CeO ₂	Fixed-bed	1:4	167	50; 280	20.4	27.0	[49]
CuO/ZnO	SS tubular	22:66	40	30; 270	16.1	36.5	[51]
CuO/ZnO/TiO ₂	Tubular	22:66	40	30; 270	16.4	38.8	[51]
CuO/ZnO/ZrO ₂	Tubular	22:66	40	30; 270	17.0	41.5	[51]
CuO/ZnO/TiO ₂ /ZrO ₂	Tubular	22:66	40	30; 270	17.4	43.8	[51]
CuO/ZnO/TiO ₂ /ZrO ₂	Fixed-bed	22:66	60	30; 270	8.1	47.1	[52]
CuO/ZnO/TiO ₂ /ZrO ₂ /citric acid	Fixed-bed	22:66	60	30; 270	16.1	43.7	[52]

Catalyst	Type of reactor	CO ₂ /H ₂ ratio	GHSV / ml·min ⁻¹ g ₁	Conditions / bar; °C	Conversion / %	Selectivity / %	Reference
Cu-based catalysts							
CuO/ZnO/TiO₂/ZrO₂/oxalic acid	Fixed-bed	22:66	60	30; 270	17.8	46.1	[52]
CuO/ZnO/ZrO₂	Quartz tubular	1:3	60	30; 240	12.1	54.1	[53]
Cu/ZnO/ZrO₂	Quartz	1:3	100	30; 250	23.0	75.0	[54]
Cu/ZnO/ZrO₂	Fixed-bed	No info	62	30; 250	5.0	70.0	[55]
La/Cu/Mg/ZnO	Quartz	1:3	60	50; 250	9.1	65.2	[56]
La/Cu/ZnO	Quartz	1:3	60	50; 250	6.4	57.9	[56]
Novel Cu-based catalyst formulation							
Cu/ZnO/Graphene	Fixed-bed	1:3	40	15; 250	26.0	5.1	[62]
CuO/ZnO/ZrO₂/Graphene	Fixed-bed	3:9	No info	20; 200	4.5	75.9	[63]
CuO/ZnO/ZrO₂/Al₂O₃/Graphene	Fixed-bed	1:3	101	20; 240	14.7	74.0	[58]
Cu/ZrO₂/CNT_s	Fixed-bed	23:69	60	30; 200	5.0	82.0	[65]
Cu/ZrO₂/CNT_s	Fixed-bed	23:69	60	30; 260	16.3	68.5	[64]
Cu/ZnO/AC	Fixed-bed	1:3	100	40; 230	2.7	80.0	[66]
Cu/ZnO/AC	Fixed-bed	1:3	100	40; 290	7.5	50.0	[66]
Noble metal-based catalysts							
Pd/ZnO	Fixed-bed	1:3	No info	20; 250	11.0	60.0	[67]
Pd/ZnO/Al₂O₃	Fixed-bed	23:69	60	30; 180	2.9	79.4	[68]
Pd/Ga₂O₃/SiO₂	Glass micro	1:3	No info	30; 250	1.9	65.0	[69]
Pd/Cu/CeO₂	Fixed-bed	22:66	No info	30; 270	17.8	23.7	[70]

Catalyst	Type of reactor	CO ₂ /H ₂ ratio	GHSV / ml·min ⁻¹ g ₁	Conditions / bar; °C	Conversion / %	Selectivity / %	Reference
Pd/Al ₂ O ₃	Fixed-bed	1:3	No info	50; 250	3.4	29.9	[71]
Pd/Cr ₂ O ₃	Fixed-bed	1:3	No info	50; 250	2.1	22.4	[71]
Pd/Ga ₂ O ₃	Fixed-bed	1:3	No info	50; 250	19.6	51.5	[71]
Pd/TiO ₂	Fixed-bed	1:3	No info	50; 250	15.5	3.0	[71]
Pd/ZnO	Fixed-bed	1:3	No info	50; 250	13.8	37.5	[71]
Pd/ZrO ₂	Fixed-bed	1:3	No info	50; 250	0.4	4.3	[71]
Au/In ₂ O ₃	Fixed-bed	19:76	350	50; 225	1.3	100.0	[72]
Au/In ₂ O ₃	Fixed-bed	19:76	350	50; 250	3.8	83.2	[72]
Au/In ₂ O ₃	Fixed-bed	19:76	350	50; 275	7.7	78.0	[72]
Au/In ₂ O ₃	Fixed-bed	19:76	350	50; 300	11.7	67.8	[72]
Au/ZrO ₂	SS tubular fixed-bed	No info	No info	40; 240	6.8	75.0	[73]
Pt/In ₂ O ₃	Quartz-lined fixed-bed	24:72	No info	20; 300	8.3	41.0	[75]
Pt/In ₂ O ₃	Vertical fixed-bed	19:76	350	50; 300	17.3	54.0	[74]
Transitional metal carbides catalysts							
Mo ₂ C	Fixed-bed	1:3	127	20; 150	3.3	60.0	[76]
Cs/Mo ₂ C	Fixed-bed	1:3	127	20; 150	3.0	50.0	[76]
Mo-Co-C-N	Fixed-bed	23:68	100	20; 275	9.2	58.4	[77]
h-MoS ₂ /ZnS	Fixed-bed	1:4	100	50; 260	13.0	67.3	[78]

3. Conclusions and Outlook

The conversion of CO₂ into MeOH has garnered significant attention as a potential solution for mitigating greenhouse gas emissions and utilizing CO₂ as a valuable feedstock. In recent years, researchers and industrial stakeholders have made substantial progress in developing efficient catalysts and understanding the underlying mechanisms of CO₂ hydrogenation to MeOH. This mini-review explores the latest advancements in this field. By harnessing CO₂ emissions from cement production and converting them into MeOH, it is simultaneously addressed environmental concerns and created a sustainable pathway for chemical synthesis. In this context, the prospects for integrating CO₂ to e-MeOH technologies within cement plants hold promise for a greener and more resource-efficient future. However, two key points to note: (i) the need for a very high recirculation flow rate to achieve acceptable conversions; and (ii) the use of membrane reactors, which, by removing H₂O from the system, allow for high CO₂ conversions at moderate pressures.

The review shows advances in heterogeneous catalysis (e.g., Cu-based, novel Cu-based formulation, noble metal-based and transitional metal carbide catalysts) for MeOH synthesis via direct CO₂ hydrogenation. Researchers have made significant progress in this area, aiming to address environmental challenges and utilization of renewable energy. Despite numerous research efforts, challenges remain in improving the activity, selectivity, and stability of catalytic systems for large-scale industrialization of CO₂-based MeOH synthesis. However, the catalysts require overcoming thermodynamic equilibrium limitations. Researchers must consider reaction conditions (such as high-pressure hydrogenation and low-temperature MeOH synthesis) and reactor design (including novel approaches like selective membrane reactors). Improving catalyst stability (e.g., water tolerance) remains crucial; Cu-based catalysts suffer from poor activity and stability due to Cu oxidation and ZnO agglomeration. However, strategies like incorporating suitable structural promoters or hydrophobic promoters can enhance Cu-based catalyst stability.

In the context of heterogeneous catalysis for direct CO₂ conversion, the cement industry's future shows significant promise for reducing carbon emissions and achieving carbon neutrality. Since cement production companies have been developing a solution for the conversion of waste gases from blast furnaces into high value-added chemicals, it is important to explore the advances in catalysts to develop an efficient, environmentally friendly, and economically viable process. Researchers are actively exploring structure-performance correlations of catalytic materials using advanced chemical characterizations, aiming to improve catalytic selectivity while maintaining stability at industrially relevant CO₂ conversion rates. This involves activating CO₂ molecules and stabilizing specific reaction intermediates. Suitable promoters and supports can enhance the stability of these intermediates through metal-support interactions. Additionally, understanding the structural evolution of the catalyst and its active sites during the reaction is crucial. Factors like morphology, particle shape, size, and phase composition significantly impact the electronic structure and activity of the catalyst. Achieving these goals will contribute to a more sustainable cement industry and a greener future.

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