Catalytic CO_2 conversion to C1 value-added products: Review on latest catalytic and process developments

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ABSTRACT

With the increase in CO_2 emissions in the last decades, CO_2 capture and storage and CO_2 capture and utilization technologies have been interesting topics in literature and industry. CO_2 direct utilization for oil gas recovery is a mature utilization route in the oil and gas industry. CO_2 is the focus of many technological and academic studies for its potential as a source of carbon for producing value-added chemical products and synthetic fuels. CO_2 utilization technologies are grouped based on the production route, such as electrochemical, catalytic, photo-catalytic, photosynthetic, biological, and depolymerization. This review discusses the latest technological innovations in catalyst developments for direct CO_2 utilization to C1 value-added products and fuels. Amongst the various potential products, CO_2 conversion to dimethyl carbonates, methanol, formic acid, syngas, and methane using different homogenous and heterogeneous catalytic systems was discussed. The most recent advancements for process exploitations were highlighted for each utilization route to evaluate the maturity of the proposed systems technically and economically. The review revealed that thermally-driven CO_2 catalytic conversion to methanol, synthesis gas and methane are the most promising for industrial deployment. Furthermore, Green hydrogen and the cost of energy production are the key obstacles to large-scale deployments of CO_2 utilization. However, supported by the latest advancements in renewable energy production, the discussed utilization routes would be more applicable in the near future.

1. Statement of novelty

CO_2 emissions from industry can create serious air pollution problems, harm human health, and contribute to global warming. Many technological and academic investigations focus on CO_2 conversion into value-added products and synthetic fuels. The current study examines the most recent technological advancements and breakthroughs in converting CO_2 to C1 value-added products and fuels. The numerous potential products, required catalysis, predicted yield and conversion, advantages and drawbacks were all investigated and discussed for each conversion pathway. The differences between homogeneous and heterogeneous catalysis were also given and addressed. Furthermore, the most current breakthroughs in process exploitations and the technological and economic maturity of the proposed systems were presented. As a result, this analysis provides scientists and decision-makers with a complete assessment of the future of CO_2 conversion to valuable C1 products.

2. Introduction

2.1. Overview of the importance of CO_2 conversion to value-added products

Controlling and minimizing carbon dioxide (CO_2) emissions has attracted attention to mitigate global warming in recent decades [1]. Although global CO_2 emissions declined by 5.8% during the pandemic in 2020, the emissions surged in 2021 with an increase of 4.9% after the recovery of economic activities [2]. Additionally, the International Panel on Climate Change (IPCC) forecasted an increase in atmospheric CO_2 levels of 579 ppm by the year 2100 [3]. Amongst the different sectors, the use of fossil fuels in transportation and industry is the primary source of environmental concerns due to the massive amount of CO_2 emissions [4]. This necessitates integrating decarbonization systems in industry and transportation to control CO_2 emissions.

The emission of greenhouse gasses (GHG) into the atmosphere exhibits an economic burden and environmental threat due to its

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significant contribution to climate change and global warming [1]. Incorporating CO_2 capture and storage systems with existing fossil-based energy production systems are critically important to mitigate GHG emissions at both economic and environmental levels. However, some developed CO_2 capture and storage technologies are constrained and encounter economic and technical challenges in industrial deployment [5,6]. For example, the commercialized amine process employed to reduce the emissions of CO_2 to the atmosphere has limited capacity, corrosive features, and high-energy demand [7,8]. The injection of CO_2 in deep saline aquifers has no economic value (net cost) and has recently shown issues related to injectivity and induced seismicity. Consequently, integrating CO_2 utilization technologies with CO_2 capture technologies is more economically feasible and contributes to diversifying the product mix of industrial projects. With a Carbon Capture Utilization and Storage (CCUS) technologies capacities of 7 MTPA in 2012, it is crucial to maximize efforts to increase the capacity 100-fold by 2040 to achieve the recommended global two-degree scenario [9,10].

The direct use of captured CO_2 in enhanced oil recovery has been recognized in the oil industry for several decades. This utilization route has been widely used and proved its economic value and commercialization practicality. On the contrary, limited trials have been made to directly use captured CO_2 in food production and other chemical processes. Chemical utilization of CO_2 to value-added products and fuels offers a solution to replace depleted fossil fuels in the market [11,12]. In recent years, developing industrially mature CO_2 capture and utilization technologies for value-added products has been a fundamental area of research for cost-effective CO_2 mitigation to lower the environmental impact. The main value-added chemicals obtained from the conversion of CO_2 by carboxylation or reduction are carbonates, polycarbonate, methanol, synthesis gas, formic and salicylic acid, urea, polymer-building blocks, and fine chemicals as illustrated in Fig. 1 [13]. Furthermore, synthetic fuels such as methane, diesel, and gasoline are potential monetization products produced from captured CO_2 as a building block.

This review aims to present up-to-date research on the catalytic processes used for CO_2 conversion into C1 added-value chemicals and fuels: dimethyl carbonate, methanol, formic acid, synthesis gas, and methane. The latest research advancements on homogenous and heterogeneous catalyst developments for CO_2 utilization routes to products are discussed. Finally, the main opportunities for industrial deployment and challenges encountered in CO_2 utilization processes integration with existing oil and gas infrastructures are addressed and discussed.

2.2. Overview of previous reviews on literature

Several studies focused on overall CO_2 conversion routes to value-added products. Saeidi et al. [14] discussed two different catalytic CO_2 utilization processes into hydrocarbon and methanol through CO_2 hydrogenation wherein the reaction mechanisms and impact of catalyst, reaction conditions, and reactor design on the product efficiency were discussed. The authors highlighted the critical role of catalyst properties, reactor design, and configuration on CO_2 hydrogenation to value-added products. Moreover, different CO_2 thermochemical, electrochemical, photo-electrochemical, and procataleptic CO_2 methanation routes to methane (CH_4) were addressed [15–19]. Younas et al. [3] investigated the electrochemical and thermochemical routes for converting CO_2 to CH_4 by addressing the recent advancements in the reaction mechanism, catalytic materials, and the novel combination of the active metal phase and its synergy. The authors concluded that CO_2 methanation is sensitive to the catalyst's physical and chemical properties, preparation conditions, process route, and reactor design. The authors further reported that the commercialization of only thermochemical methanation was established in developed countries due to the high costs involved with other processing routes such as biological and electrochemical routes. Yang et al. [20] discussed the direct and indirect conversion of CO_2 into C2$^+$ value-added products. The review highlighted two pathways for producing C2$^+$ products: directly from syngas using Fischer-Tropsch synthesis or indirectly from the intermediate methanol. In the latter approach, methanol is initially synthesized from CO_2, then used as an input for producing a wide range of hydrocarbons based on different processes (i.e., methanol to olefin and methanol to propane). Other researchers reviewed the CO_2 conversion to value-added products from a sustainable point of view by evaluating the production routes based on life-cycle assessment and/or carbon footprint [21–23]. Additionally, most recent reviews focused mainly on the conversion of CO_2 to specific value-added products such as methanol, formic acid, synthesis gas, methane, or C2$^+$ hydrocarbons using heterogeneous catalysts [24–34]. However, there has been a lack of comprehensive studies considering different catalytic systems for CO_2 monetization to different C1 products in a single review paper. Hence, this review aims to fill the gap by providing a comprehensive analysis of the most recent studies, published in the literature since 2018, on homogenous and heterogenous catalytic systems and process developments for CO_2 monetization to dimethyl carbonates, methanol, synthesis gas, and methane. Much of the review studies focused extensively on catalytic synergies for small-scale
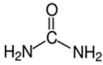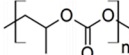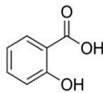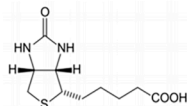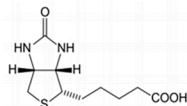
Chemical	Molecular Formula	Chemical	Molecular Formula
Urea		Cyclic carbonate	
Methanol		Ethylene carbonate	
Formaldehyde		Di-methyl carbonate	
Formic acid		Copolymers	
Salicylic acid		Polymer-building blocks	
		Fine chemical: for example, biotin	

Fig. 1. Main industrially produced chemicals from CO_2. [13].

production. The novelty of this work lies in addressing catalytic systems and operational conditions for direct CO_2 utilization to value-added C1 products. Moreover, the technical maturity, economic feasibility, advantages, and drawbacks of the different reported systems were addressed for large-scale industrial deployment.

Search engines such as google scholar and Scopus databases were the primary databases for searching papers. The keywords used for searching the papers were "direct CO_2 utilization to products", "CO_2 utilization to fuels", "homogenous catalysts for CO_2 utilization", "CO_2 hydrogenation", "heterogeneous catalysts for CO_2 utilization", and "CO_2 conversion routes". Section 3 mainly discusses the latest catalytic systems development for direct CO_2 monetization routes to dimethyl carbonate, methanol, formic acid, and synthesis gas. Section 4 discusses CO_2 utilization to fuel methane, while sections 5 and 6 highlight processes performance and the recently deployed industrial applications for CO_2 utilization plants and the challenges encountered for large-scale deployment. Last, the conclusions and recommendations were provided in the previous sections as per the reviewed papers considered in this work.

3. Conversion of CO_2 to products

CO_2 is a crucial building block for chemicals such as carbonates, carboxylic acids, methanol, and synthetic gas. In addition to the economic advantages of CO_2 monetization to value-added products and synthesis gas, synthesis gas could contribute to tackling the fossil fuel depletion concern for synthetic fuels production. Fundamentally, developing cost-effective and highly selective catalysts is the core for large-scale deployment of CO_2 utilization to value-added products. Hence, different homogenous and heterogeneous systems have been examined in the literature to investigate optimal operating conditions and catalyst characteristics.

3.1. Dimethyl carbonates

The functional group carbonate is a base of different chemical compounds comprising one carbonate unit, including dimethyl carbonate, phenyl carbonate, and cyclic carbonates or polycarbonate groups. Nowadays, Dimethyl-carbonate, DMC ($C_3H_6O_3$), is mainly produced in the industry by photo-generation or oxidative carbonylation of methanol [35]. DMC is widely used as a solvent in paints and inks, as an electrolyte in lithium-ion batteries, and as a fuel additive to reduce emissions [21,36]. Additionally, DMC is a synthetic intermediate in medicine, pharmaceuticals, and chemicals [35]. In the last years, utilizing CO_2 to produce DMC has acquired great attention where different process routes were studied with a focus on catalysts and process technologies: (i) direct conversion of CO_2 to methanol and DMC, (ii) indirect conversion of CO_2 to the intermediate CO for DMC production; and (iii) reacting CO_2 with amines to generate carbonylation agent before the formation of carbonate.

In the literature, Zhang et al. [35] discussed the direct DMC by the oxidative carbonylation of methanol following Reaction (1) as an attractive, environmentally friendly, and non-toxic route. A low DMC yield has been generally reported in the literature in earlier studies [37–39]. The low yield was reported to be attributed to factors such as high CO_2 stability, catalyst deactivation, water formation, and limitations in thermodynamic equilibrium [40]. Hence, this necessitated the need to use dehydration agents for water removal from the mixture and the requirement for developing novel catalysts to enhance DMC selectivity and yield in more recent studies [41]. Although both homogenous and heterogeneous catalysts showed effective DMC synthesis from methanol and CO_2, heterogeneous catalysts proved better efficiency for large-scale deployment [42]. The latest innovations in developing effective catalysts, especially heterogeneous catalysts, and process technologies have contributed to overcoming these problems.

$$2CH_3OH + CO_2 \rightleftharpoons C_3H_6O_3 + H_2O \tag{1}$$

A standard molar reaction enthalpy (ΔH°_{298K}) of -17 KJ/mol indicates an exothermic reaction with low heat release [35,43]. Hence, the excessive reaction temperature is unfavorable for DMC synthesis. At equilibrium and according to Le Chatelier's principle, increasing the reaction pressure and lowering the temperature could increase DMC yield. Alternatively, excess CO_2 will be needed to enhance methanol conversion to products. This justifies that the reaction is thermodynamically feasible at optimal moderated operating conditions.

3.1.1. Catalysts for dimethyl-carbonate production

The catalytic systems used for DMC production have been relatively mature since 2015. It was reported that different heterogeneous-based catalysts could be utilized to produce DMC. The most popular catalysts are ionic liquid, alkali carbonate, transition metal oxide, heteropoly acids, and supported catalysts. Ionic liquid catalysts have been known as relatively clean and non-volatile for DMC production. While alkali carbonates proved efficiency for direct DMC synthesis from methanol and CO_2. Hence, recent studies focusing on different catalysts for efficient DMC production were investigated based on process conditions, yield, costs, and energy.

3.1.1.1. Alkali carbonate catalysts and ionic liquids.
The alkali carbonate catalyst K_2CO_3 was reported to be the most effective among different alkali carbonate catalysts in the early 21st century by Fujita et al. [44]. In addition to DMC, a primary byproduct from the direct route of methanol and CO_2 conversion to DMC was dimethyl ether in the presence of methyl iodide and using a K_2CO_3 catalyst. A later study by Yang et al. [45] reported utilizing a K_2CO_3 catalyst for the production of DMC and 1,2-cyclohexene oxide (CHO) under the presence of cyclohexene as a coupling agent. Under optimum CHO: CH_3OH ratio of 1:5, a pressure of 26 bar, and a temperature of 150 °C, a methanol conversion of 16.2% were achieved with DMC selectivity of 38.7% and 55.4% yield. The process required high operating pressure, reflecting the economic burden of scaling up the production process. Hence, a later study by Liu et al. [46] investigated a mild and efficient protocol for the one-pot synthesis of DMC in a one-pot system from CO_2, propylene oxide, and methanol by utilizing K_2CO_3 catalyst at lower pressure. Under optimized conditions of 120 °C and initial pressure of 5 bar, the achieved methanol conversion was 5.8% with DMC selectivity of 42.7% in the presence of ethylene oxide. The reaction yields by-products such as 1-methoxy-2-propanol, 2-methoxy-1-propanol, propylene carbonate, and 1,2-propanediol. Despite the low costs of K_2CO_3 catalyst for DMC production, the maximum reported DMC selectivity was 42.7%. Additionally, the catalytic process required introducing the costly CH_3I as a promoter for enhanced methanol conversion to DMC.

Ionic liquids proved to have low corrosion tendency, low solvent degradation, relatively low regeneration costs and high solubilty of CO2 in capture processes [47,48]. A recent study by Liu & Liu [49] developed a one-pot synthesis of DMC from CO_2, epoxide, and methanol utilizing a binary catalyst system of hydroxyl-functionalized ionic liquids and sodium carbonates under an optimized temperature of 140 °C and pressure of 5 bar. The binary catalyst system proved its efficiency in achieving a high DMC yield of 64% from propylene oxide and a DMC yield of 81% from ethylene oxide after an optimal reaction time of 6 hr. The efficiency of recycling the catalyst for multiple runs was further investigated in the study. At the end of the reaction, products were separated by distillation, and the residue containing the binary catalyst was used for the next run. After three recuses, a DMC yield of 56% was achieved, indicating the practicality of reusing the binary catalyst. The drop in the DMC yield could be attributed to the accumulation of propylene carbonate and 1,2-propanediol in the consecutive recycle, leading to reaction inhibition.

3.1.1.2. Transition metal oxide catalysts and heteropoly acid catalysts.

Metal oxide catalysts have become one of the dominant employed catalysts for producing DMC from CO_2 and methanol. The active parts of the catalyst are resilient to deactivation by oxidation. Consequently, metal oxide catalysts can be stored in the air for a very long time, making them optimal for large-scale deployment in industry. Amongst the different studied catalysts, CeO_2-based catalysts were widely investigated for DMC direct synthesis due to their high catalytic activity and stability [35,50]. Fu et al. [51] reported a new class of TiO_2-promoted CeO_2 nanorod catalysts for DMC synthesis from CO_2 and methanol by addressing a detailed kinetic model for DMC synthesis in a continuous fixed bed reactor. Under optimized reaction conditions of 120 °C and 8 bar, a methanol conversion of 5.38% and DMC selectivity of 83.1% were reported. At higher operational pressure of 50 bar, a slightly higher DMC selectivity of 89.9% was reported by Chiang et al. [52] using the heteropoly acid catalyst $H_3PW_{12}O_{40}/ZrO_2$ for direct DMC synthesis from methanol and CO_2 under conditions of 170 °C, and volumetric CO_2:N_2 ratio of 1:7. While by using the same method and operating conditions, the highest DMC selectivity of 91.4% and methanol conversion of 5.5% was achieved utilizing $H_3PW_{12}O_{40}/Ce_{0.1}Ti_{0.9}O_2$ catalyst by Chiang et al. [53]. The reported DMC selectivity was the highest in the recent literature, reflecting the efficiency of the catalytic systems employed for DMC production. The efficiency of the $H_3PW_{12}O_{40}/Ce_{0.1}Ti_{0.9}O_2$ catalyst promotes it as an effective catalyst for industrial application due to the innumerous oxygen vacancies on its surface, acting as Lewis-acid sites for the catalytic reaction.

3.1.1.3. Supported catalysts. The last group of catalysts reported in the literature for direct synthesis of DMC from methanol and CO_2 is supported catalysts. Supported catalysts consist of a bimetallic active component and a supporter with a large surface area and mechanical strength [35]. Amongst the different reported catalysts in literature, phosphoric acid intercalated Mg-Al hydrotalcite-like compounds and Mg-Al Hydrotaleite/Silica lyogel catalysts achieved the highest DMC selectivity of 99.9% [54–56]. Their results proved that activating methanol on acidic sites enhanced the DMC formation. This is due to the formation of a methyl cation that reacts with methyl carbonate for DMC formation. Furthermore, the presence of Brønsted acid sites showed better activation than Lewis acid sites by promoting the interaction between methanol molecules and Al^{3+}, and decreasing DMC decomposition (i.e., the principle side reaction). For reaction conditions, the reaction kinetics of DMC synthesis from CO_2 and methanol indicate that excess temperature is unfavorable for process efficiency [35]. At certain temperatures, an increase in the yield of carbonate may take place. Other parameters such as catalyst concentration, dehydrating agent, reaction pressure, and temperature are needed to achieve high selectivity, yield, and CO_2 conversion [57]. Considering the influence of different parameters on catalyst performance, a recent study by Faria et al. [55] analyzed activated carbons-based catalysts for DMC production from CO_2 and methanol at different operating conditions for maximum yield and selectivity. A DMC yield of 30% and a selectivity of 100% at optimized reaction conditions of 120 °C and 40 bar were achieved using 0.7 g AC-Fe catalyst in the presence of the promoter CH_3I and molecular sieves as dehydrating agents. Additionally, recycling the catalyst four times for DMC production decreased methanol conversion by 12%.

Several studies investigated catalyst recycling and reuse for DMC production to manage costs [35,58,59]. Al-Darwish et al. [58] investigated nanostructured CeO in different shapes (nanocathedra, nanocubes, nanorods) for DMC synthesis and evaluated the reuse of catalysts for four runs at a reaction temperature of 140 °C, the pressure of 30 bar, reaction time of 3 hr, and catalyst weight of 0.5 g. The reusability results indicate a slight decreased in the catalyst activity by 12.5% in the fourth recycle trial.

Lingaiah, [59] created a series of ZnO-SrO catalysts with varying compositions using the co-precipitation method. An optimal catalyst with a 1:1 mol ratio produced 35% DMC from urea and methanol. Excellent performance was linked to higher activity, which was generated by uniform distributions of moderate to strong basic sites, as well as a significant number of acidic sites. The developed catalyst was easily recovered and reused with consistent activity.

The most popular catalysts for DMC manufacture, including ionic liquids, alkali carbonates, transition metal oxides, heteropoly acids, and supported catalysts, were reviewed by Zhang et al. [35]. Dehydrant catalysts with in-situ hydration can considerably increase DMC yield and catalyst stability. This was attributed to a change in chemical balance and a reduction in the deactivation of catalysts as a result of the removal of the generated water. It was noted that this direction will see a significant breakthrough once the right catalyst and dehydrant combinations are found. Table 1 illustrates the different catalysts and DMC selectivity with employed reaction conditions.

3.2. Methanol

Methanol (CH_3OH) is an industrial product used as feedstock in many chemical industries, compounds, and fuel for transportation [28]. In 2016, methanol was one of the top 10 produced chemicals with a total global production of over 85 million MT [60,61]. Fig. 2 illustrates the important applications of methanol in the production of chemicals such as formaldehyde, ethylene, propylene, dimethyl ether (DME), acetic acid, methyl *tert*-butyl ether (MTBE), Tert-amyl methyl ether (TAME), and the production of plastics, paints, and polymers.

Traditionally, syngas produced via gasification of biomass, natural gas, coal, and wastes has been the main source to produce methanol (CH_3OH). Recent studies reported CO_2 conversion into methanol through (a) direct hydrogenation of CO_2 to methanol and (b) subsequent hydrogenation of CO to methanol [28,62,63]. A comprehensive review on the use of non-noble catalysts metal for the production of methanol was presented by Tawalbeh et al. [61]. The study outlines the most commonly used non-noble catalysts for the production of methanol with corresponding mechanisms, recent challenges and opportunities. The direct CO_2 hydrogenation to methanol can be represented as the following:

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad (2)$$

and the competing reverse water gas shift (RWGS) reaction:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (3)$$

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (4)$$

The exothermic CO_2 hydrogenation to CH_3OH (ΔH° = -87 KJ/mol), Reaction (2), depends on temperature, pressure, and reactant ratio, whilst the Reverse Water Gas Shift (RWGS) reaction is endothermic (ΔH° = 41 kJ/mol), Rection (3). Reaction (4) only occurs after the CO is produced from reaction (3) to produce methanol which is more exothermic (ΔH° = -128 kJ/mol) than producing methanol from CO_2. Methanol can be produced from CO_2 in two steps using two reactors based on the CAMMERE process that utilizes a multi-catalyst system. CO_2 is first converted to CO by the RWGS in the first reactor, followed by dehydration. The CO_2/CO/H_2 mixture is fed into another reactor to produce methanol. Previous studies reported that the indirect approach achieved a higher methanol yield at lower operating costs than the direct approach [64–66]. This is mainly attributed to the challenges encountered in the direct route, such as high CO_2 stability and water formation in the RWGS leading to catalyst deactivation and low reaction rate. To overcome these barriers and to exhibit the formation of side products, investigating effective and powerful catalysts has been essential to improve the reaction rate of CO_2 for methanol conversion , [13,67–72]. The latest advances in developing heterogeneous and homogenous catalysts for the hydrogenation of CO_2 to methanol were studied and reported in the literature [28,73–76]. The latest

Table 1
Direct CO2 utilization to DMC using different heterogeneous catalysts.

| Route	Catalyst	Catalyst category	T (°C)	P (bar)	MeOH conversion (%)	DMC selectivity (%)	DMC Yield (%)	Reference
CO_2 + MeOH	imidazolium hydrogen carbonate ionic liquid catalyst [CnCmIm][HCO_3]	Ionic liquid	25	10	74%	97%	Not reported	[40]
CO_2 + epoxide + MeOH	hydroxyl-functionalized ionic liquids (HFILs) and sodium carbonates	Bicomponent catalyst: ionic liquid and alkali carbonates	oil bath at 140	5	propylene oxide conversion of 64% and ethylene oxide conversion of 81%	N/A	64% from propylene oxide and 81% from ethylene oxide	[49]
CO_2 + MeOH + cyclohexane	Potassium carbonate (K_2O_3)	Alkali carbonate	150	26	16.2%	38.7%	Not reported	[45]
CO_2 + epoxide + MeOH	Potassium carbonate (K_2O_3)	Alkali carbonate	120	5	5.8%	42.7%	Not reported	[46]
CO_2 + MeOH	$Ti_{0.04}Ce_{0.96}O_2$ Nanoroad catalyst	Metal oxide	120	8	5.38%	83.1%	Not reported	[51]
CO_2 + MeOH	$H_3PW_{12}O_{40}/ZrO_2$	Heteropoly acid catalysts	170	50	4.5%	89.9%	4%	[52]
CO_2 + MeOH	$H_3PW_{12}O_{40}/Ce_{0.01}Ti_{0.9}O_2$	Heteropoly acid catalysts	170	50	5.5%	91.4%	5%	[53]
CO_2 + MeOH	Phosphoric acid intercalated Mg–Al hydrotalcite-like compounds	Supported catalysts	150	10	2.3%	99.9%	Not reported	[54]
CO_2 + MeOH	Mg-Al Hydrotaleite/Silica Lyogel	Supported catalysts	130	10	15.9%	99.9%	Not reported	Stoain et al. (2013)
CO_2 + MeOH	AC -Fe	Supported catalyst	120	40	23.5%	100	~30%	[55]
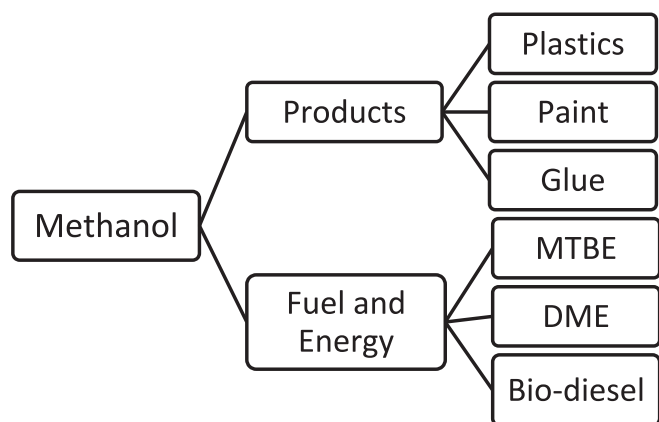
Fig. 2. Methanol monetization routes to products and fuels.

advancements in developing catalysts are discussed and summarized in the following subsections.

3.2.1. Catalysts for methanol production

The reaction pathway for CO_2 conversion to methanol depends on the catalytic system used wherein different side-products can be produced. The most promising heterogeneous catalytic systems are discussed in this review. Especially the commonly investigated Cu/ZnO based due to their effective performance for methanol production and low costs. Moreover, the latest developments in homogenous catalysts were highlighted.

3.2.1.1. Heterogeneous catalysts.

1- Cu-based catalysts

Cu-based catalysts for CO_2 and/or CO hydrogenation to methanol have attracted attention in the literature due to their low cost, low reaction temperature, and high activity. However, maintaining and stabilizing the Cu^+/Cu^0 species during the reaction has been challenging

and directly influences methanol selectivity. In the literature, the addition of metal oxides promoters (i.e., ZnO, ZrO_2, CeO_2, and TiO_2) has been proposed to improve the catalyst selectivity by changing the chemical properties of the catalyst, including ion valence, particle size, and reducibility [77]. Table 2 comprehensively summarizes the latest studies for heterogeneous catalysis for CO_2 hydrogenation to methanol.

a. Cu-ZnO

Different research studies have investigated and developed the conversion of CO_2 to methanol on a pilot scale using heterogeneous

Table 2
Methanol selectivity and CO_2 conversion reported by studies since 2018 for direct CO_2 hydrogenation to methanol using heterogeneous catalysts.

Catalyst	T (°C)	P (bar)	CO_2 conversion (%)	MeOH selectivity (%)	Reference
PdIn(1:1)	210	50	<3%	95%	[78]
Pd-Cu-ZnO	230	45	12%	73%	[79]
	290		6%	69%	
8PdAn-CeO_2	220	20	14%	95%	[80]
AE-Cu-SiO_2	190	30	5.2%	79%	[81]
0.5CaPdZn-ZrO_2	230	30	7.2%	100%	[82]
5PdZn-ZrO_2	230	30	5.7%	100%	[82]
Pt-In_2O_3	300	50	>17%	54%	[83]
$CuZrO_2$ $CuCeO_2$	220	30	N/A	74% 82%	[84]
$CuZrO_2$ $CuCeO_2$	280	30	N/A	30% 72%	[84]
Au-In_2O_3	225	5	1.3%	100%	[85]
Cu-AnO-CeO_2	260	40	~12.5%	61%	[86]
0.58 wt% Pt-In_2O_3	220	20	<0.55%	91.1%	[87]
Cu-SiO_2P	225	30	3.5%	77%	[88]
Cu-MgO	300	50	23%	88%	[89]
Cu-TiO_2	200	30	9.4%	96%	[90]
Cu-ZnO-ZrO_2	275	30	>5%	>85%	[91]
PdZn-ZnO-SiO_2	260	50	3.3%	65.3%	[92]

catalysts [21,30,93,94]. Amongst the various heterogeneous catalysts, the most conventionally studied catalyst for methanol synthesis was Cu-ZnO [28,70,95,96]. In the Cu-ZnO catalyst, ZnO acts as a dispersant and stabilizer for Cu, and the Cu-ZnO interactions activate the catalyst's active sites for methanol synthesis [97]. However, CO_2 conversion using Cu-ZnO catalysts remains low, with less than 20% conversion, due to the high CO_2 stability and the limited process kinetics [98–100]. Hence, introducing promoters and additives (i.e., Aluminum (Al), Lead (Pd,) Silver (Ag), Platinum (Pt)), and oxygen-deficient materials (i.e., Indium Oxide (In_2O_3), and Aluminum oxide (Al_2O_3)) proved to increase the efficiency of the Cu-ZnO based systems to produce methanol from CO_2 [70,78,101,102]. In industry, Al_2O_3 has commonly been used as a promoter to enhance and improve the stability and activity of the Cu-ZnO catalyst. Cu-ZnO-Al_2O_3 catalysts have been widely used in which: (a) the promotor ZnO provides a high dispersion and stabilization level of Cu active sites, hence, contributing to enhancing methanol production reaction and (b) the metal oxide (Al_2O_3) provides support for the catalyst [103–105]. On the other hand, researchers showed that replacing Al_2O_3 with ZrO_2, CeO_2, MgO, and TiO_2 has shown good performance in enhancing the catalytic performance of Cu-ZnO based catalyst [84,98,100,106–109]. In a study by Angelo et al. [110], Al_2O_3 was substituted with other supporters such as ZrO_2, CeO_2, and CeO_2-ZrO_2 to understand the influence of the supporter on the catalytic performance of the CuO-ZnO based catalyst. Cu-ZnO-ZrO_2 catalyst exhibited the best catalytic performance at investigated reaction conditions of 280 °C and 50 bar, where methanol selectivity reached 33%. The ZrO_2 acts as a modifier to increase catalyst activity by improving CO_2 adsorption due to the high basicity of the final catalyst. The addition of ZrO_2 further allows the catalyst to favor the selectivity to methanol due to the higher CO_2 adsorption over the basic sites and its subsequent hydrogenation on the Cu–ZnO active sites [111,112]. Table 3 compares metal oxides (ZrO_2, CeO_2, and Al_2O_3) used for Cu-ZnO modification where ZrO_2 has shown the best catalytic activity [110]. Although the interface between the metal and oxides in the Cu-ZnO-ZrO_2 catalyst was reported to be efficient for direct CO_2 hydrogenation to methanol, the various roles of using Cu as an active phase and oxides, particularly ZrO_2, as support remain suboptimal [30,113]. The kinetic aspects of the operating parameters for the thermal catalytic conversion of CO_2 to methanol using Cu-ZnO-ZrO_2 were investigated by Marcos et al. [91]. The authors reported that the crystal phases of ZrO_2 (i.e., polymorphs, monoclinic tetragonal, and cubic) significantly influence the physical properties of the catalyst and its selectivity for methanol production. Moreover, the results revealed that Cu-ZnO-ZrO_2-I catalyst (100 wt% Tetragonal, 27 wt% Cu, and 15 wt% Zn) at H_2:CO_2 ratio of 4:1 M at 275 °C and 30 bar showed the best performance for methanol production with methanol rate formation of greater than 55 g_{MeOH}/$kg_{cat.h}$ selectivity. The catalyst further proved its durability for up to 7 reuse cycles at 225C, 40 bar, and 6 hr; justifying its practicability for industrial deployment. However, the requirement of high hydrogen flowrate must be put into consideration for economic large-scale deployment depending on the hydrogen production source.

On the other hand, a recent study by Guo et al. [86] studied CO_2 hydrogenation using a ternary CuO-ZnO-CeO_2 catalyst prepared using plasma decomposition. CeO_2 enhanced the catalytic performance of the catalyst for CO_2 adsorption due to the formation of oxygen vacancies, large surface area, and the improved interaction between the metal and CeO_2. An approximate CO_2 conversion of 12.5% and methanol selectivity of around 61% were achieved at 260 °C and 40 bar.

b. Cu-ZrO_2

Among different oxides, Zirconia (ZrO_2) showed exceptional properties as a promoter or supporter for synthesizing methanol from CO_2 due to its hydrophilic characteristic that enhanced desorption of the water formed from the RGWS reaction, enhancing methanol selectivity and yield [114]. Introducing ZrO_2 to the Cu-based catalyst enhances the overall performance of the catalyst by (1) providing greater surface area and increasing dispersion of Cu particles and (2) enhancing the catalytic performance and efficiency of the Cu-based catalyst [70,115]. However, the catalytic performance and CO_2 activation mechanisms are mainly impacted by the nature of the ZrO_2 crystal phase [91,116]. A study by Marcos et al. [116] proved that the ZrO_2 preparation method had a substantial impact on the specific surface area, the surface acidic/basic characteristics of ZrO_2, and crystallographic phase composition when preparing ZrO_2 catalysts using reflux and hydrothermal methods. Additionally, different additives were investigated for improving the activity and efficiency of the Cu-ZrO_2 catalyst, such as Gallium Oxide (Ga_2O_3) to form Ga_2O_3-Cu-ZrO_2 catalyst for methanol production [91,117,118]. The enhanced performance of using the promoter Ga_2O_3 with a Cu-based catalyst is due to the small particle size of Ga_2O_3 that favors forming an intermediate state of copper between Cu^0 and Cu^{2+} [118,119].

Although studies proved that binary catalyst Cu-ZnO-ZrO_2 showed better methanol selectivity and CO_2 conversion than Cu-ZnO-Al_2O_3 [91,120], a greater performance was achieved by mixing both promoters, ZrO_2 and Al_2O_3, together to form the catalyst system Cu-ZnO-ZrO_2-$Al2O_3$ [121]. Combining both systems together resulted in increasing the thermal stability, basicity, and surface area of the catalytic system [122]. Moreover, the catalyst system Cu-ZnO-ZrO_2-Al_2O_3 resulted in greater water poisoning resistance than Cu-ZnO-Al_2O_3 and Cu-ZnO-ZrO_2 catalysts by reducing the reversible adsorption of water and CO [122]. A study by Gao et al. [99] reported that Cu-AnO-ZrO_2-Al_2O_3 catalyst with 5 wt% ZrO_2 showed a methanol yield of 80% greater than that by the commercial catalyst Cu-ZnO-Al_2O_3.

c. Cu-CeO_2

Cerium oxide (CeO_2) was also investigated by combining it with Cu to enhance the performance of the Cu catalyst for effective CO_2 hydrogenation to methanol. Wang et al. [84] studied CO_2 hydrogenation over Cu-supported catalysts on ZrO_2 and CeO_2. The reaction took place at 30 bar and temperature between 240 and 300 °C revealed that Cu-CeO_2 catalysts exhibited higher methanol selectivity than Cu-ZrO_2 catalysts. The authors concluded that the improved interaction at the Cu-CeO_2 interface leads to improved Cu particles dispersion and enhanced concentration of oxygen vacancies, which in turn strengthens CO_2 adsorption and stabilizes carbonate intermediates for methanol formation. It was reported that methanol selectivity decreased while increasing temperature. Additionally, the by-product CO selectivity increases due to the increase of the RWGS reaction.

d. Cu-TiO_2

Titanium oxide (TiO_2) has also been explored as a supporter of the Cu-based catalyst for CO_2 hydrogenation to methanol [90,123,124]. This is mainly due to its high thermal and chemical stability, in addition

Table 3
Effect of modification of Cu-ZnO catalysts with promoters: ZrO_2, CeO_2, Al_2O_3 over the activity of methanol synthesis at 280 °C and 50 bar [110].

Sample	M^a (wt.%)			CO_x Conversion (%)	CH_3OH Yield (mmol/g_{cat} hr)	CH_3OH Selectivity (%)
	Al	Zr	Ce			
CZ-Al_2O_3	100	–	–	19.5	9707	37
CZ-CeO_2	–	–	100	12.8	6554	37
CZ-ZrO_2	–	100	–	23.2	10,331	33

[a] Nominal composition (wt.%) Cu/Zn/Me (Me: Al, Ce,s and/or Zr) = 30/41/29.

to the redox properties of the TiO_2 that promote the formation of oxygen vacancy sites which improves CO_2 adsorption. Additionally, TiO_2 facilitates the dispersion of Cu particles [109]. Hence, promoting CO_2 activation in the interfacial sites of $Cu-TiO_2$ following a similar reaction mechanism of the Cu-ZnO based catalyst for CO_2 hydrogenation to methanol [125]. A study by Sharma et al. [90] tested $Cu-TiO_2$ catalyst prepared by hydrothermal and impregnation methods for CO_2 hydrogenation to methanol. The catalyst prepared by the hydrothermal method exhibited better activity, stability, and enhanced methanol selectivity of 96% with a CO_2 conversion of 9.4% at 200 °C and 30 bar. However, further assessments of the catalytic systems are needed to investigate the durability of the catalyst for industrial applications.

e. Cu-MgO

Magnesium Oxide (MgO) was also investigated to improve the catalytic performance of Cu-based catalysts for methanol production due to its basicity that enhances the adsorption of CO_2 [126]. Additionally, MgO contributes to forming dispersed Cu particles that play an essential role in enhancing the catalytic performance and improving methanol synthesis [106]. In recent literature, Kleiber et al. [89] studied the effect of the calcination temperature and duration on the catalytic performance of the Cu-MgO catalyst for CO_2 hydrogenation to methanol. The study provided the first results in the literature for methanol production from CO_2 in a semi-continuous tank reactor using Cu-MgO catalyst. The experimental analysis was conducted under three main phases with different temperatures and pressures where CO_2 hydrogenation took place over 48 h to achieve a maximum yield of 28%, methanol selectivity of 88%, and CO_2 conversion of 23% at operation conditions of 50 bar and 300 °C. Additionally, the authors concluded that a steady-state activity of the catalyst was not obtained after 48 h of operation. However, the influence of catalyst preparation methods on the performance of Cu-MgO catalyst is still under investigation, reflecting the system's immaturity for large-scale deployment [127,128].

2- Non-Cu catalysts, Metal-based catalysts: Au, Ag, Pd, Pt, La and Ni

Other active base metals have been investigated as catalysts for CO_2 hydrogenation to methanol, such as Silver (Ag), Gold (Au), Palladium (Pd), and Platinum (Pt). The following subsections briefly discuss the latest innovations in incorporating non-Cu catalysts for direct CO_2 hydrogenation to methanol.

a. Au and Ag – based catalysts

Different studies have shown the efficiency of Au and Ag catalysts for CO_2 hydrogenation to methanol. Hartadi et al. [129] kinetically studied the selectively supported Au-ZnO catalyst for CO_2 hydrogenation to methanol and investigated the effect of total pressure and the influence of CO on the reaction. The authors reported that compared to the Cu-ZnO-Al_2O_3 catalyst, Au-ZnO catalyst showed better methanol formation rate and selectivity at 240 °C and the studied pressure range between 5 and 50 bar. Additionally, higher CO concentration resulted in decreasing methanol formation rate. A later study by Hartadi et al. [130] studied the role of CO in influencing the methanol formation from CO_2/H_2 mixture using the Au-ZnO catalyst. The authors concluded that for CO_2 hydrogenation at 240 °C and 5 bar, the methanol formation was higher for mixtures with greater CO_2 concentration. Whilst for mixtures containing both CO and CO_2, the methanol formation increased with low CO concentrations, justifying that CO_2 is the main source for methanol formation. However, when increasing the temperatures between 240 and 300 °C, CO becomes the dominant carbon source for methanol formation rather than CO_2. Additionally, a recent study by Abdel-Mageed et al. [131] investigated the impact of water vapor on the reaction behavior of CO_2 hydrogenation to methanol under Au-ZnO catalyst at 5 bar, temperature range between 270 and 350 °C, and

various amounts of water vapor (2-8 vol%) in a TAP reactor. Adding water vapor to the CO_2/H_2 mixture decreased methanol selectivity on the Au-ZnO catalyst at a temperature of 270 °C and pressure between 5 and 20 bar. Additionally, water vapor addition influenced the activity of the catalyst. However, when increasing the pressure, the negative effect of water vapor on the reaction was mitigated and decreased. The highest achieved methanol selectivity of 100% was reported using $Au_+^\delta–In_2O_{3−x}$ at an operating temperature below 225 °C and 5 bar [85]. The substantial interaction between Au and the supporter enhanced the catalytic performance of Au, which opens the door for further investigation on the practicability and durability of Au catalysts.

On the contrary, only a few studies focused on Ag-based catalysts for CO_2 hydrogenation to methanol. This is attributed to the fact that Ag is less active in methanol synthesis than Cu. Słoczyński et al. [132] investigated the catalytic performance of the $M−ZnO−ZrO_3$ catalyst for M = Cu, Au, and Ag. The results revealed the high catalytic performance of Cu compared with Ag and Au at 220 °C and 80 bar. Cu showed the best CO_2 conversion, whereas methanol selectivity was as follows: Au > Ag > Cu. Furthermore, Ag has been investigated as a promoter in catalysts to enhance the efficiency of catalysts for CO_2 hydrogenation to methanol. Grabowski et al. [133] reported the enhancement of the selectivity of CO_2 hydrogenation to methanol after adding Ag to a Cu-ZrO_2 catalyst. Tada et al. [125] also reported the influence of adding Ag to the CuO-ZrO_2 catalyst for improving methanol selectivity. Interestingly, the results indicated that the formation of Ag-Cu alloy particles and their selectivity played an essential role in CO_2 hydrogenation to methanol.

b. Pd, Pt – based catalysts

Compared to Cu-based catalysts, Palladium (Pd) based catalysts exhibited better stability and catalytic activity for CO_2 hydrogenation to methanol [80,134]. Different supporters/promoters have been studied with Pd-catalyst, such as metal oxides including ZnO, CeO_2, SiO_2, Al_2O_3, In_2O_3, ZrO_2, and carbon nanotubes (CNT). Malik et al. [82] reported a methanol selectivity of up to 100% at 230 °C and 30 bar using 5PdZn-ZrO_2 and 0.5CaPdZn-ZrO_2. This is relatively less than the maximum selectivity of 73% reported by Hu et al. [79] Pd-Cu-ZnO catalyst at 230 °C and 45 bar. On the other hand, PdZn-X catalysts (X = SiO_2, Al_2O_3, ZnO-SiO_2) showed a maximum selectivity of 49.8% and CO_2 conversion of 4.4% at experimental conditions of 260 °C, 30 bar, and H_2:CO_2 rate of 3:1 [92]. While increasing the operating pressure to 50 bar boosted the selectivity of PdZn-ZnO-SiO2 up to 65.3%. Indicating that PdZn alloy itself does not provide active sites for CO_2 conversion to methanol. On the other hand, Han et al. [87] introduced Platinum (Pt) into In_2O_3 to investigate the influence of Pt on CO_2 hydrogenation to methanol. The results of testing different Pt concentrations revealed that 0.58 wt% Pt-In_2O_3 catalyst resulted in a maximum methanol selectivity of 91.1%, much higher than the methanol selectivity of 72.2% achieved when using the In_2O_3 catalyst alone. For Pt and Pd-based catalysts, further assessment of catalyst recycling is needed to assess the durability of the catalyst for cost-effective methanol production.

c. Other catalyst systems (In_2O_3, La, and Ni)

Other studies in literature investigated using Lanthanum (La) and Nickel (Ni) based catalysts for direct methanol synthesis from CO_2. Kuang et al. [135] studied La:Cu:Zn:X (X = Zr, Al, Al + Zr) perovskite-like catalysts, prepared using co-precipitation preparation method, with ratios of (1:0.7:0.3:0), (1:0.7:0.2:0.1), (1:0.7:0.2:0.1), and (1:0.7:0.1:0.1:0.1) labeled LCZ, LCZZ, LCZA, and LCZZA, respectively. The catalysts were tested for CO_2 hydrogenation to methanol using a fixed bed reactor at 250 °C and 50 bar. The results revealed that LCZA possessed the highest CO_2 conversion of 13.2% and methanol selectivity of 42.4%, while LCZ catalyst had the highest methanol selectivity of 59% and CO_2 conversion of 10.8%. A study by Poerjoto et al. [136]

revealed that $La_{0.9}Sr_{0.1}CuO$ catalyst exhibited a maximum CO_2 conversion of 8.59% and methanol selectivity of 49% at 300 °C and 30 bar. The high methanol selectivity and CO_2 conversions achieved using La-based catalysts encourage further theoretical and experimental analysis of perovskite-based catalysts for CO_2 hydrogenation to methanol.

Furthermore, In_2O_3 was a highly reported oxide for CO_2 conversion to methanol [83,102,113,137,138]. However, the catalyst displayed insufficient activity at low reaction temperatures. Recent strategies investigated adding a metal component, such as Pt, Pd or Ni, or a metal oxide, such as ZrO_2, as a promoter to enhance the catalytic performance. Compared to the commercial catalyst Cu-ZnO-Al_2O_3, ZrO_2 supported on In_2O_3 has shown better stability and enhanced methanol selectivity up to 100% [115,139]. Additionally, replacing Pd with the abundant metal Nickel (Ni) supported on In, and In_2O_3 catalysts have been investigated experimentally and/or theoretically for CO_2 hydrogenation to methanol [137,140–143]. The studies mainly focused on surface characterization tests and density functional theory calculations to observe the Ni-In synergy. In comparison with other 5 wt% Co, Cu, and Pd based In_2O_3 catalysts, 5 wt% Ni-In_2O_3 exhibited the greatest methanol selectivity of 53% and CO_2 conversion of 2.8% evaluated for CO_2 hydrogenation at 250 °C and 30 bar using down-flow stainless steel reactor [144]. Moreover, loading Iridium (Ir) supported on In_2O_3 significantly improved the activity and selectivity for CO_2 hydrogenation to methanol at 300 °C and 50 bar [145]. The experimental study reported a CO_2 conversion of 17.7% achieved on a 10 wt% Ir-In_2O_3 with methanol selectivity over 70%.

3.2.1.2. Homogenous catalysts. The first utilization of a homogenous metal catalyst for CO_2 hydrogenation to methanol was reported in 1995 by Tominaga et al. [146], who used $Ru_3(CO)_{12}$ and potassium iodide (KI) in an N-methyl pyrrolidone solution at 240 °C and 80 bar. Following the first study, only a few studies demonstrated homogenous catalytic systems for direct CO_2 hydrogenation to methanol in the literature. Fundamentally, most reported homogenous catalysts remain inefficient for industrial deployment and require a long way to becoming practical and cost-efficient [147,148]. Nonetheless, previously developed homogenous catalysts displayed the ability of CO_2 hydrogenation at milder conditions than heterogeneous catalysts. Temperatures as low as 80 °C and 90 °C were sufficient for CO_2 hydrogenation to methanol using C-scorpionate iron(II) catalyst ($FeCl_2(\kappa^3$-HC(pz)$_3$)) and cobalt-based catalyst. $Co(acac)_2$ in an additive-free system [149,150]. However, further optimizations are needed to develop a water-resistant homogenous catalytic system.

3.3. Formic acid

Formic acid (HCOOH) is a common commodity in the chemical, agricultural, leather, textile, rubber, and pharmaceutical industries. Nowadays, formic acid is a promising hydrogen storage material, providing a safer and easier transport of hydrogen to markets. Formic acid is dehydrogenated at receiving terminals to CO_2 and H_2 under mild conditions. Historically, formic acid production has been produced from biomass, Tartaric acid, Oxalic acid, Hydrocyanic acid, and Carbon monoxide [151]. Moreover, multiple formic acid production technologies from CO and methanol have been developed in literature and in the industry [152–154]. The hydrolysis of methyl format based on a two-stage process was reported as the most common route for conventional formic acid production [21,155]. On the contrary, the technical and economic feasibility of CO_2 conversion to formic acid has been assessed in literature for CO_2 transition to a low carbon product [156–158]. Two approaches could be utilized for formic acid synthesis from CO_2: (i) generation of CO followed by formic acid synthesis via the carbonylation process; and (ii) direct CO_2 hydrogenation to formic acid. In the latter approach, formic acid can be produced via CO_2 hydrogenation per the following reaction:

$$CO_2 + H_2 \rightleftharpoons HCOOH \tag{5}$$

Thermodynamic constraints have limited the development of direct hydrogenation of CO_2 to formic acid industrial processes due to high CO_2 stability and entropic contribution with a $\Delta G°$ value of $+ 33$ kJ/mol in the gaseous reaction [159]. Hence, formic acid synthesis from CO_2 is more favorable in an aqueous solution ($\Delta G° = -4$ kJ/mol) [160]. Different catalytic systems were investigated to enhance the feasibility of the process. A recent study by Mardini & Bicer, [161], modeled and simulated CO_2 hydrogenation to formic acid by Aspen plus. The study reported a reactor conversion of 19% at a temperature of 123 °C. Hence, concluding that CO_2 hydrogenation to formic acid is thermodynamically unfavorable where further advancements would be needed for designing a cost-effective industrial process.

3.3.1. Catalysts for CO_2 hydrogenation to formic acid

In the direct conversion of CO_2 to formic acid, the conversion of gaseous reactants to liquid products is entropically unfavorable. To shift the reaction towards product formation, bases such as ammonia and triethylamine can be introduced. Moreover, changing reaction operating conditions such as temperature, CO_2 pressure, pH, and base type can influence the reaction equilibrium [162]. Different homogenous and heterogeneous catalytic systems have been evaluated in the literature for direct CO_2 hydrogenation to formic acid under the effect of different promoters, temperatures, pressures, solvents, and ligands.

3.3.1.1. Homogeneous catalysts. The discovery of Phosphine-based Ruthenium (Ru) complexes for CO_2 hydrogenation to formic acid under relatively mild conditions and the presence of triethylamine by Inoue et al. [163] has opened the door for further homogenous catalytic developments in the field. Extensive research studies on Iridium (Ir), Rhodium (Rh), Ru, Pd, Ni and their derivatives have been reported for direct formic acid production from CO_2 [164–169]. For the first time, Montandon-Clerc & Laurenczy [170] reported Fe(II) catalyst using *meta*-trisulfonated-tris[2-(diphenyl-phosphino)-ethyl]phosphone ligand (Fe(II)-PP3TS) for direct CO_2 hydrogenation to formic acid at mild conditions and acidic aqueous solutions. The study revealed that the catalyst is robust to be utilized for multiple cycles for direct formic acid production. A recent study tested a series of Ir catalysts bearing amide-based ligands for CO_2 hydrogenation to formic acid [171,172]. The studies revealed that homogenous catalysts exhibit challenges in terms of separation and recycling. Hence, the performance and efficiency of heterogeneous catalytic systems were evaluated and studied for more efficient formic acid production.

3.3.1.2. Heterogeneous catalysts. Several studies focused on the heterogeneous hydrogenation of CO_2 to formic acid as a promising approach for CO_2 utilization and hydrogen storage. Compared to homogenous catalysts, heterogeneous catalysts demonstrated better separation of catalysts from the reaction mixture and the possibility of reusing the catalysts for multiple runs. However, heterogeneous catalysts usually result in lower catalytic activity than homogenous catalysts due to the poor atom utilization efficiency. A new concept of idealized catalysts combining the advantages of the homogenous catalysts (i.e., high selectivity) and heterogeneous catalysts (i.e., high stability) in a single catalytic system known as single-atom catalysts based on Ni, Cu, Pd, and Ru embedded in graphene was reported in most recent research studies [173–175]. However, the studies for single-atom catalysts are first principle calculations where the stability of the catalyst for CO_2 hydrogenation to formic acid is preliminarily assessed. A new strategy of utilizing Al-Sn-CNTs composite for electrocatalytic reduction of CO_2 to formic acid was reported by (Jinrui Guo et al. [176]). In the study, a methanol selectivity of 88.9% was reported within 1 hr under optimized conditions of pH of 9.0, Cl$^-$ concentration of 10 mmol/L, Al-Sn-CNTs dosage of 2 g/L, and temperature of 25 °C. The novel developed
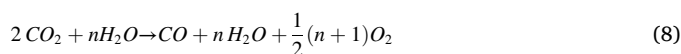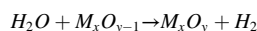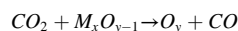
hybrid catalytic systems pose better activity and lower costs for CO_2 heterogeneous catalysis to formic acid. Furthermore, nano-scale metal catalysts (i.e., Pd, Rh, Ru, Au, Ag) were developed and discussed from a surface chemistry point of view for CO_2 hydrogenation to formic acid at a temperature between 80 and 90 °C and at atmospheric pressure [177,178]. The studies concluded that the catalytic performance of nano-catalysts mainly depends on the metal component, supporter, additive, reaction temperature, and pressure.

Since direct CO_2 hydrogenation to formic acid is thermodynamically unfavorable, bases were commonly added to the reaction mixture to shift the thermodynamic equilibrium towards formic acid synthesis [179,180]. However, the formation of formate adducts and salts increases the complexity of purification and the overall costs and waste management [180–182]. Former CO_2 hydrogenation to formic acid studies reported basic properties of solvents [159,183,184]. The studies concluded that high pressure was required to overcome thermodynamic and kinetic limitations, resulting in lower catalytic activity than operating under mild conditions. Consequently, subsequent studies investigated using basic ionic liquids as buffers for optimizing the catalyst performance, efficiency, and stability [185]. One major limitation to ionic liquids utilization is the high costs involved in the separation, recycling and processing of ionic liquids. A recent study by Kim et al. [186] investigated base-free catalytic hydrogenation of CO_2 to formic acid using a Pd-C_3N_4 catalyst in a batch reactor at 40 °C, 50 bar, a reaction time of 16 hr and CO_2:H_2 ratio of 1:1. The researchers reported that over Pd-C_3N_4 catalyst, hydrogen is activated on Pd and CO_2 on basic sites of C_3N_4. Moreover, the acid treatment of the Pd-C3N4-MW catalyst significantly improved the reaction rate. A reaction rate expressed in palladium time yield based on the total Pd in the catalyst was used to calculate the catalyst efficiency, where a remarkable value of 1325 μ mol$_{HCOOH}$/mol$_{Pd}$s for the Pd-C_3N_4-MW-Acid catalyst. This represents the highest value reported in the literature for base-free CO_2 hydrogenation to formic acid. Moreover, electrochemical and photocatalytic approaches for CO_2 hydrogenation to value-added products are potential promising routes [178,187–190],. Those technologies are in the early design stages with limited efficiency and high costs arising from renewable resources; further advancements would be needed for large-scale implementation.

3.4. Synthesis gas

Synthesis gas (i.e., syngas) encompasses a mixture of CO, CO_2 and H_2 that has been traditionally produced by: (i) partial oxidation of methane using Pt catalysts, (ii) steam reforming of methane using Ni catalysts, or (iii) using carbon feedstock from coal and/or heavy hydrocarbons gasification. Syngas is a fundamental feedstock to produce clean fuels, chemicals, and products. These products include the production of waxes, olefines, diesel, and gasoline through the Fischer-Tropsch process. Other vital products that utilize syngas as input include isobutane, ethanol, hydrogen gas, and methanol [191]. Over the last few years, CO_2 has become a fetching feedstock for syngas production due to its abundance. Different methods have been developed for the direct conversion of CO_2 to syngas, including (i) RWGS reaction with $\Delta H^{\circ}_{298K} = 42.1 kJ/mol$, Reaction (3); (ii) dry reforming of methane with $\Delta \Delta H^{\circ}_{298K} = 247 kJ/mol$, Reaction (6); (iii) thermochemical dissociation reaction driven by solar energy Reaction (7); and (iv) high-temperature electrolysis, Reaction (8). Compared to the thermal route, the process illustrated in Reaction (7) uses a thermochemical approach for CO_2 and H_2O decomposition at appropriate lower temperatures by combining endothermic and exothermic reactions using metal oxide redox pairs, such as Zn/ZnO, and FeO/Fe_3O_4, following a two-step thermochemical metal/oxide cycles for splitting CO_2 and H_2O. While the reaction route expressed in Reaction (8) is known as the solid oxide co-electrolysis process, wherein syngas is produced at the cathode side, and the by-product, oxygen, is produced at the anode side. At the cathode side, a

gas stream of CO_2 and H_2O is supplied to receive electrons from an external power to synthesize syngas (CO_2 and H_2), and oxygen anions. The negative oxygen ions are then transferred through the electrolyte under applied voltage to the anode side to be oxidized to oxygen gas. Different catalytic systems have been studied in literature since 2018 for converting CO_2 to syngas, with a significant focus on heterogeneous catalysts.

$$CO_2 + CH_4 \rightleftarrows 2CO + 2H_2 \tag{6}$$

$$M_xO_y \rightarrow M_xO_{y-1} + \frac{1}{2}O_2 \tag{7}$$

$$CO_2 + M_xO_{y-1} \rightarrow O_y + CO$$

$$H_2O + M_xO_{y-1} \rightarrow M_xO_y + H_2$$

$$2 CO_2 + nH_2O \rightarrow CO + n H_2O + \frac{1}{2}(n+1)O_2 \tag{8}$$

3.4.1. Homogenous catalysts for syngas production

Non-noble metal-based catalysts such as Ni and Cobalt (Co) were commonly evaluated for industrial-scale deployment due to their low costs and availability [192]. Moreover, the addition of supporters and promoters was analyzed to enhance the catalytic activity of the catalyst and to prevent catalyst deactivation due to carbon deposition. Wang et al. [193] employed Nickel (II) Tripodal complex as a homogeneous electro-catalyst for carbon dioxide and water reduction. In the presence of 5 M of H_2O in N,N'-dimethylformamide (DMF) for 6 hr in a one-room cell, a CO selectivity of 96% was reported with negligible evolution of H_2 gas. The study revealed the robustness of the catalyst with a high turnover number (TON) of 1.90×10^6 in a one-day operation with negligible deactivation. On the other hand, Co(II) complex ($Co_5(btz)_6(NO_3)_4(H_2O)_4$) showed high stability and reactivity for CO_2 photo-reduction to syngas in both pure and diluted CO_2 as reported by Sun et al. [194]. The multi-nuclear complex showed a 212-fold boost, up to 2748 TONs, compared to the mono-nuclear cobalt complex, with broad H_2 and CO ratio flexibility from 16:1 to 2:1. The authors further revealed that this reactivity could be maintained for more than 200 hr. A recent study by Ren et al. [195] reported a self-assembly cobalt-based photocatalyst, C1@CD-CuInS2/ZnS quantum dots (QDs), to produce syngas in CO_2 saturated water under the presence of light. In comparison with the non-assembled system and pristine CuInS$_2$/ZnS QDS system, the reported assembled catalyst showed better efficiency, CO selectivity, and syngas production activity for more than 200 hr. However, the former studies mainly focused on the surface characterization of the catalysts for syngas synthesis. More assessments will be needed to evaluate the techno-economic feasibility of homogenous catalysts for industrial production.

3.4.2. Heterogeneous catalysts for syngas production

Ni-based and Co-based catalysts were further investigated for heterogeneous catalysis in recent research studies. Phan et al. [196] studied the hydroxyapatite-supported Co and Ni catalyst in the dry reforming of methane for the first time. The reaction was carried out in a fixed-bed reactor at 700 to 750 °C and pressure of 1.6 bar with a molar feed composition of CH_4 (20%), CO_2 (20%), and N_2 (60%). The study revealed that the activity of the catalyst was stable for up to 50 or 160 hr of time on stream with H_2 and CO selectivity up to 80–90%. At the same feed compositions, Arkatova et al. [197] tested the catalytic activity of the new metallic Ni_3Al matrix modified with the implantation of Pt and Ru at 600 °C and 900 °C and atmospheric pressure. The study showed that the presence of Pt and Ru enhanced the catalytic activity, wherein increased activity was directly linked to an increase in Pt and Ru content. The catalyst Pt-Ni_3Al was reported to be the most efficient among the different tested catalytic systems as it was robust to deactivation by coke. Mozammel et al. [198] studied Rh and Co addition to Ni-based

catalyst supported on mesoporous alumina for dry reforming methane to syngas. The formed bimetallic (NiCo-MAl) and trimetallic (NiCoRh-MAI) catalysts showed better catalytic activity and enhanced the catalyst's resistance to coking. Moreover, Nikolaraki et al. [199] reported the impacts of gamma-Alumnia (γ-Al_2O_3), ceria-zirconia (CeO_2-ZrO_2), and alumina-ceria-zirconia (Al_2O_3- CeO_2-ZrO_2) on dry reforming of methane activity, resistance against coke formation and selectivity at a temperature between 500 and 750 °C. The researchers found that stable performance was shown by Ir-alumina-ceria-zirconia (Ir-Al_2O_3- CeO_2-ZrO_2), and Ir-ceria-zirconia catalysts (Ir- CeO_2-ZrO_2) amongst the different examined catalysts.

Other authors reported palladium nanoparticles-decorated silicon nanosheets (Pd@SiNS) for CO_2 reduction to syngas via RWGS under light irradiation [200], nanoporous Cr_2O_3-Cu catalyst for syngas production via RWGS [201], molybdenum nitride (Mo_2N) for photo-assisted CO_2 reduction to CO via RWGS in the presence of UV light [202]. Using light attributed to overcoming the high thermal energy requirement for syngas production and revealed a promising approach for further investigation for large-scale deployment.

4. Conversion of CO_2 to fuel: Methane

Production of synthetic natural gas (methane) from CO_2 achieved ever-increasing attention in the last ten years. As a major part of natural gas, methane has been used as an energy source for decades. Many methane monetization pathways have been adopted commercially to convert methane into more useful chemicals and fuels, such as the production of syngas, ethylene, methanol, and higher hydrocarbons, as illustrated in Fig. 3.

Conversion of CO_2 into methane through methanation is a prominent method for using energies stored in chemical bonds. The reaction is commonly known as the Sabatier Reaction for producing methane and water from a reaction of carbon dioxide with hydrogen at elevated temperatures between 300 and 400 °C and in the presence of a catalyst [203]. Alternatively, the process of methanation can also be carried out at low temperatures (<70 °C) utilizing biological methods in stirred-tank and trickle-bed reactors [204,205]. The overall Sabatier reaction for methane synthesis from CO_2 can be represented by the exothermic reaction ($\Delta H^{\circ}_{298K} = -165\,kJ/mol$):

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad (9)$$

Methanation over different metal catalysts, including Ni, Ru, and Al

has been investigated in literature for efficient and cost-effective production. The catalytic systems can be classified into homogenous and heterogeneous catalysts as highlighted in the following subsections.

4.1. Homogenous catalysts

The control of the performance of single-site catalysts during synthesis and design has been a challenging aspect when developing homogenous catalysts. Luconi et al. [206] prepared and characterized alkyl/amido complexes of neutral Hf (IV) and Zr (IV). The complexes were stabilized by N-ligand, containing heterodendate fragment, and checked for their catalytic activity for the *tandem* carbon dioxide hydrosilylation to methane. The complex $\kappa^3\{N$-$,N,N$-$\}Zr(IV)(Bn)_2$ catalyzed the reaction selectively to methane with a turnover frequency of 272 hr^{-1} at 96% substrate conversion. Nie et al. [207] reported the conversion of CO_2 to CH_4 using two Ni catalysts, i.e. [(4,4'-dimethyl-2,2'-bipyridine)$_2Ni_2Cl_4(H_2O)_2$] and [(2,2'-bipyridine)$_2Ni_2Cl_4(H_2O)_2$], in the presence of photosensitizers. The cost-effective catalysts were easily synthesized and preserved and exhibited a methane selectivity of up to 81% under LED blue light irradiation for 7 hr and 6 mL of CO_2-saturated MeCN/TEOA/H_2O solution. In addition, Nganga et al. [208] investigated electrochemical methane synthesis from CO_2 using Rhenium complex catalysts. The authors reported three Rhenium tricarbonyl complexes coordinated by diamine ligands: 2-(isoquinolin-3-yl)-4,5-dihydrooxazole, 2-(quinolin-2-yl)-4,5-dihydrooxazole, and 2-(iso-quinolin-1-yl)-4,5-dihydrooxazole. In the presence of 2,2,2-trifluoroe-thanol and an applied potential of −2.5 V, the electrolysis experiment produced methane with TON ranging from 1.3 to 1.8. The assessments reveal that electrocatalytic homogenous conversion of CO_2 to methane is still under development for optimizing catalyst characteristics and operating conditions for larger applications. Further recent studies mainly evaluated heterogeneous catalysts for direct CO_2 conversion to syngas.

4.2. Heterogeneous catalysts

Light-driven heterogeneous catalysis has been a promising perspective and cost-effective for CO_2 conversion to methane. Quan et al. [209] evaluated the hydrogenation of CO_2 to methane using light on a Ru-CeO_2 catalyst and reported CO_2 conversion of 99% and methane selectivity of 100% in the presence of light. The results concluded that this method is more efficient than thermal heating. At a temperature of
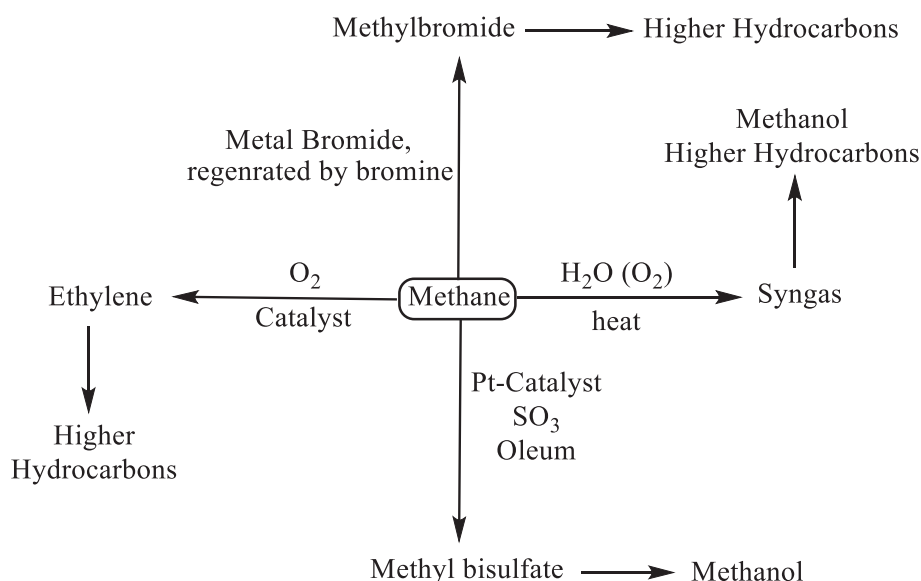
Fig. 3. Methane monetization routes to fuels and products.

160 °C, a reaction rate six times greater than that of the thermal heating process was reported. Additionally, the activation energy for CO_2 under illumination (74.8 kJ/mol) was found to be less than the activation energy needed under heating (92.2 kJ/mol), indicating that activation energy reduction is favored by light irradiation. Regarding catalyst stability, the catalyst was robust to degradation in a continuous 30 hr light-driven reaction, while the thermal catalytic route reported a 24% degradation. Moreover, Barrio et al. [210] demonstrated using light as a renewable energy source with Ni nanoparticles supported on graphitic carbon nitride for low-temperature CO_2 methanation at 150 °C. Graphic carbon was further investigated by Cui et al. [211], who tested Co-MnO heterostructured nanoparticles inside porous graphitic carbon (Co/MnO@PGC). The results revealed that the catalyst could synthesize methane from CO_2 at 160 °C with methane product selectivity of greater than 99%. On the other hand, Li et al. [212] tested bimetallic Ni-Pd alloy catalysts for CO_2 hydrogenation to methane. The authors revealed that the bimetallic catalyst showed comparatively more significant catalytical activity than the monometallic Pd or Ni-supported SBA-15 catalyst, wherein the $Ni_{0.75}Pd_{0.25}$-SBA-15 catalyst exhibited the optimal catalytic performance with CO_2 conversion of 96.1% and CH_4 yield of 93.7% at 430 °C. The high catalytic activity was attributed to surface dispersion of Ni. Moreover, heterogeneous metal-free-ligand-free nano-catalysts for CO_2 conversion to methane have been reported by Mishra et al. [213]. The unique approach revealed that defect-containing nano-silica is an effective alternative to expensive Nobel-based metal catalysts and complex organometallic-based catalysts for CO_2 hydrogenation to methane.

The rarely reported Ir-based heterogeneous catalyst for CO_2 reduction to methane has been studied by Tang et al. [214]. The authors reported a novel photo-catalyst with Ir nanoparticles dispersed on TiO_2 nano-sheets resulting in increased CO_2 adsorption and better methane selectivity. Moreover, Riani et al. [215] investigated the impact of 37 wt % La_2O_3 addition on the activity of Ni-SiO_2- γ-Al_2O_3 for CO_2 conversion to methane wherein a methane selectivity of 100% was reported at low temperatures and atmospheric pressure. The authors confirmed that the promoter lanthanum allows stronger CO_2 adsorption, hence enhanced catalytic performance. Additionally, Zhang et al. [35] further investigated solar-driven photocatalytic reduction for methane production using carbon nano-layer coated TiO_2. In this approach, CO_2 and H_2O were used as feedstock, forming the by-product CO.

Apart from methane production, CO_2 hydrogenation to Fischer-Tropsch products, liquid hydrocarbons, via Gas to Liquid (GTL) process utilizing heterogeneous catalysts has been a prominent route for producing higher hydrocarbons such as kerosene, diesel, and gasoline. CO_2 is utilized in the first production stage in the proposed production routes, where CO_2 is converted to CO via RWGS reaction before being fed to the GTL process. The studied catalytic systems and the latest advancements in CO_2 conversion to C2 + products and fuels are out of the scope of this review and have been reported in previous review studies [29,32,216].

5. Performance evaluation

In recent literature, the direct route of CO_2 conversion to value-added products has acquired significant interest. The high kinetic inertness and thermodynamic stability ($\Delta G^0 = - 394.38$ kJ/mol) of CO_2 have limited its practical uses at its entire power for chemicals or fuel synthesis. To overcome the CO_2 stability barrier, many primary assessments focused on developing catalysts, studying reaction mechanisms, and investigating the influence of the catalyst preparation method on the catalytic performance. Most of the investigated technologies for direct synthesis utilized thermo-catalytic, photo-catalytic, and electro-assisted technologies for product synthesis in a continuous fixed bed reactor or one-pot batch reactor [35,207,217]. In addition to utilizing expensive dehydrating agents for water dehydration, a few studies reported using membrane reactors and in-situ separation techniques to remove water formed in the direct CO_2 hydrogenation to DMC or methanol [218–220]. Hence, enhancing the product yield and catalyst robustness to deactivation for durable operation. Membrane reactors and fixed-bed reactors investigations reflect the maturity of the process for large-scale deployment. However, parameters such as pressure, temperature, time, catalyst amount, and dehydrating agent type must be further optimized for enhanced economic production.

From a reaction kinetics perspective, the solid–gas reaction favors a high operating pressure to limit the movement of the gaseous reactant molecules at oxygen vacancies on the catalyst surface. Hence, high operating pressure in the range of 20–50 bar was reported in the literature for direct CO_2 hydrogenation to methanol. While for DMC production, an operating pressure between 5 and 50 bar was reported depending on the catalytic system used for effective production. Fundamentally, more focus on electro-assisted and photo-catalytic technologies was reported for syngas and methane production to provide activation energy for promoting CO_2 activation. The studies mainly focused on computational assessments and reaction mechanisms, indicating that more studies are needed to report the techno-economic feasibility of such technologies and catalytic systems.

6. Opportunities and challenges

Amongst the different CO_2 hydrogenation routes, technological advancements for CO_2 hydrogenation to methanol have been the major focus for researchers in the literature. Different authors have investigated optimal operating conditions, economic analysis, and lifecycle assessment for CO_2 to methanol plant simulated using commercial chemical process simulation software such as Aspen Plus and ChemCAD [105,221–231]. Barbera et al. [222] reported a technical comparison of process simulation of CO_2 conversion to formic acid or syngas using Aspen plus. Whilst other studies reported simulation-based analysis for CO_2 conversion to products such as syngas, methane, and formic acid [221,225,232–234]. The simulation-based studies discussed that the economic success of the processes for industrial exploitation mainly depends on H_2 source and cost.

6.1. Methanol

For industrial deployment in the European continent, the first industrial-scale direct conversion of CO_2 to methanol plant was launched by Carbon Recycling International (CRI) in Iceland in 2012 with a renewable methanol production capacity of 4000 tons/year sold as a gasoline additive. The plant utilizes captured CO_2 from flue gases and H_2 produced via alkaline water electrolysis using renewable grid electricity [235,236]. More recently, the same technology for the CO_2 to methanol plant was launched in Anyang, Henan, province of China, to recycle industrial waste gases. The process, designed and licensed by CRI, recycles over 160,000 tons/year of CO_2 and is operated and handled by the owner, the Shunli joint venture company, to sell green methanol to the local chemical and transport market [237–239]. It was also reported that the production costs of methanol using CRI technology are twice that of the natural gas-derived methanol production route [236]. In Qatar, the Qatar Fuel Additives Company (QAFAC), in partnership with Mitsubishi Heavy Industries, deployed a CO_2 recovery plant in 2014 to recover CO_2 emissions from the methanol plant for reinjection into methanol production. The deployed plant does not produce green methanol from captured CO_2. However, it increases methanol production by 250 million tons/day and reduces CO_2 emissions by 500 million tons/day [240].

6.2. Formic acid

For industrial deployment, BASF process was first developed by Schaub & Paciello [180] for CO_2 hydrogenation to formic acid and tested on a pilot scale. The reported process consists of three main

sections: (1) hydrogenation in the presence of $NHex_3$ and diols; (2) catalyst extraction; and (3) formic acid separation. Moreover, in 2012, a CO_2 to formic acid process was developed by the Leitner group, which was later used to develop a pilot-scale formic acid project by the Reactwell (*Pilot & Test Center ReactWell*, n.d.; [182,241]. In the proposed biphasic system, CO_2 at supercritical conditions is mixed with an ionic liquid containing a Ruthenium catalyst and a nonvolatile base for producing formic acid.

6.3. Syngas

For the production of syngas, Linde built a pilot dry reforming process to synthesize syngas from methane and CO_2 in Munich, Germany, in 2015 [242]. Linde partnered with BASF for catalyst development and Karlsruhe Institute of Technology (KIT) for developing simulations. In 2019, Linde further reported success in developing the DRYREF™ technology in collaboration with BASF for cost-effective and energy-efficient steam reforming [243]. The commercial process utilizes an innovative catalyst developed by BASF and unique process technology to reduce the amount of steam required for the reforming process for syngas production. Additionally, Chiyoda corporation developed a CO_2 reforming technology, CT-CO2AR®, utilizing CO_2 for producing syngas at different H_2/CO ratios by varying the feed gas steam/carbon ratio and CO_2/carbon ratio [244]. The technology enables utilizing CO_2-containing natural gas or CO_2 emitted from various industrial applications for syngas production. Moreover, the process was successfully demonstrated in Niigata, Japan GTL project, in 2011 for syngas production.

6.4. Methane

Researchers at the Department of Energy's Pacific Northwest National Laboratory (PNNL) have developed a method to convert captured CO_2 to methane gas using a PNNL-water-lean post-combustion capture solvent (2-EEMPA). The researchers reported that using 2-EEMPA reduced the energy requirement for fueling the CO_2 to methane reaction. This is mainly due to 2-EEMPA's ability to dissolve CO_2 easily, converting more than 90% of captured CO_2 to methane under mild reaction conditions and the heterogeneous Ruthenium-based catalysts [245]. The researchers further revealed that the integrated system could reduce capital costs by 32%, operating costs by 35%, and the synthetic natural gas selling price by 12% [246]. Furthermore, the initial results of a pilot plant for CO_2 conversion to methane using hydrogen from water electrolysis and CO_2 captured from flue gases using amine absorption were discussed by Chwoła et al. [247]. The process was built by Taurnon Wytwarzanie S.A Łaziska Power Plant in Poland and demonstrated using a microchannel reactor. At a pressure of 1.5–3 bar and temperature between 280 and 350 °C, a maximum of 98% CO_2 conversion to synthetic natural gas consisting of 82% of CH_4, 13% of H_2, and 5% CO_2 was achieved.

6.5. Challenges for large-scale deployment

CO_2 utilization as a feedstock in industrial processes has been challenging due to the stability of CO_2 molecules, wherein large energy content is required to transform CO_2 into valuable products [203]. So far, thermal routes have been reported as the most significant for low-energy intensive production. However, with the increased electricity costs and unsustainability of using nonrenewable energy resources, the use of renewable energy resources such as wind and solar enhances the economic attractiveness of deploying energy-intensive processes on large scale. For low temperature and low pressure operations, photo-catalytic and electro-assisted technologies appear more attractive for industrial applications. Although photocatalytic systems have been explored to overcome the high thermal energy requirement for CO_2 processing to value-added products and fuels, no pilot-scale processes have been reported. Further work would be required to examine the

efficiency of photo-catalytic systems in real-life CO_2 utilization processes. On the other hand, amongst the different monetization routes, CO_2 to methanol and DMC appears to be more mature. However, the combination of operating temperature and pressure, H_2:CO_2 ratio, catalyst type, and dehydration type must be considered for optimal synthesis.

The co-reactant H_2, generally generated by water electrolysis, plays a significant role in commercializing CO_2 conversion processes to value-added products. This is attributed to the high energy requirement and resources for the water electrolysis processes [3]. Hence, many studies evaluated techno-economic and lifecycle assessments to justify the overall system maturity and performance of CO_2 utilization routes for the industrial implementation considering the H_2 production costs [14,105,248–252].

7. Conclusion and recommendations

CO_2 conversion by a catalytic reaction to produce value-added products has become an attractive approach to mitigate environmental issues and support a sustainable chemical industry. Furthermore, hydrogenating CO_2 to value-added products is a reliable approach for hydrogen storage from renewable resources and transportation to distant markets. Amongst the different C1 monetization products, methanol molecules have the highest theoretical hydrogen content (12.6 wt%) and are currently the most advanced option. Different direct and indirect routes exist for CO_2 monetization to value-added products. In this work, direct CO_2 conversion routes to dimethyl carbonate, methanol, formic acid, methane, and syngas were evaluated by considering the latest innovations in heterogeneous and homogenous catalyst systems development. Several technological developments have been highlighted in this review paper to better understand the processes involved in the conversion of CO_2 to various C1 chemicals. This is demonstrated by elucidating the development of heterogeneous catalysts, kinetics, and reaction mechanism. After thoroughly reviewing the reactions, it is possible to conclude that catalysts are critical for the process to be economically viable. Given the advancements in technological developments, many heterogeneous catalyst systems show sufficient performance yet high costs for industrial deployments. On the other hand, the high costs of hydrogen production and process energy requirement, especially in RWGS-based processes, are significant limitations for large-scale process deployment. In the thermal-driven catalytic conversion, apart from the cost constraints, there is no technical barrier to exploiting thermal-driven catalytic CO_2 conversion to useful C1 products. Additionally, with the latest developments in renewable energy production technologies, renewable energy-driven CO_2 conversion to C1 products and fuels will become more applicable in the near future. Further studies shall investigate pilot-scale production and/or simulation-based analysis for the proposed catalytic systems to evaluate the technical and economic efficiency of large-scale deployment. On the other hand, further studies are needed to optimize catalytic systems and reaction conditions for syngas and methane production.

Author contributions

All authors contributed equally to this review.

Data availability

The datasets generated during and/or analyzed during the current study are available upon request.

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.

Data availability

Data will be made available on request.

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