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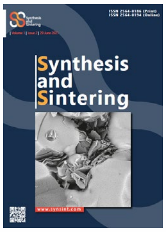

Review article

Direct catalytic production of dimethyl ether from CO and CO_2: A review

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ABSTRACT

Dimethyl ether (DME) is a synthetically produced alternative fuel to diesel-based fuel and could be used in ignition diesel engines due to increasing energy demand. DME is considered extremely clean transportation and green fuel because it has a high cetane number (around 60), low boiling point (-25 °C), and high oxygen amount (35 wt%) which allow fast evaporation and higher combustion quality (smoke-free operation and 90% fewer NO_x emissions) than other alternative CO_2-based fuels. DME can be synthesized from various routes such as coal, petroleum, and bio-based material (i.e., biomass and bio-oil). Dimethyl ether can be produced from CO_2 to prevent greenhouse gas emissions. This review aims to summarize recent progress in the field of innovative catalysts for the direct synthesis of dimethyl ether from syngas ($CO+H_2$) and operating conditions. The problems of this process have been raised based on the yield and selectivity of dimethyl ether. However, regardless of how syngas is produced, the estimated total capital and operating costs in the industrial process depend on the type of reactor and the separation method.

KEYWORDS

Dimethyl ether
Direct synthesis
Catalyst
Syngas
CO_2
Methanol

1. Introduction

Recently, many researchers are looking for alternative fuels due to energy saving and reduction of fuel reserves [1]. Petrochemical products are widely used as energy sources in transportation and industry, but it is difficult to predict when these resources will run out [2]. On the other hand, environmental protection has become a global concern [3] and many research groups are working to develop new low-pollution materials for use in vehicles and internal combustion engines [4, 5].

Finding credible and economical sources of energy depends on converting various waste materials, wasting energy and finding new sources [6]. Developed countries are now replacing conventional petroleum oils with fuels such as biofuels, hydrogen, natural gas, and dimethyl ether (typically abbreviated as DME) [7, 8]. It is an organic compound with the formula CH_3OCH_3, a colorless, volatile, and non-corrosive gas with safe storage and handling that is currently being demonstrated for use in a variety of fuel applications [9]. Due to the similarity of the physical properties of dimethyl ether with LPG (liquified petroleum gas) [10], it can be used as a good alternative to LPG fuel [11, 12]. Dimethyl ether is non-toxic and carcinogenic and uses the same LPG storage and transportation technology [13]. Another reason for the popularity of DME is the production through natural gas and syngas within few hours. Synthesis gas, commonly known as syngas, is a fuel gas mixture consisting primarily of hydrogen, carbon monoxide, and very often some carbon dioxide [14]. Increasing CO_2 from anthropogenic sources is the main reason of global warming [15]. Thus, converting CO_2 is one of the most useful ways to reduce CO_2

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emissions [16]. The reforming reaction of methane with carbon dioxide to produce syngas is a potential technological route for reducing greenhouse gases and ultimately mitigating climate change [17]. However, this process is very endothermic and is often accompanied by the inactivation of the catalyst from carbon curing and deposition. In addition, the use of various dissimilar catalytic systems in dry methane reforming along with their modifications has made it difficult to achieve optimal general conditions for the desired products [18].

Recent investigations suggest two methods for the synthesis of DME, as can be seen in Fig. 1 [19], and focus on the estimation of its physical and thermophysical properties [20, 21] and combustion characteristics [22]. Dimethyl ether can be used as a diesel fuel substitute [23–25] because of its cetane number, high oxygen content (35 wt%), and thermal efficiency. It is worth noting that DME emits very little NO_x, SO_x [26], and soot in the exhaust gas of the diesel engine due to the lack of C–C bond in its structure [27]. Also, because of the non-toxicity of DME, this substance can be a suitable alternative to liquid refrigerants, propellant aerosol, petroleum fuels, and also as intermediates for several oxygenates compounds [28]. DME can be then thought-out a trustful energy vector to introduce renewable energy in the chemical industry as it could recycle CO_2 [29] from biomass [30, 31] or obtain processes in combination with renewable hydrogen. For this purpose, catalytic systems are claimed as active in the activation of CO_2 to perform this reaction. However due to kinetics and the thermodynamic limits, the synthesis of DME requires the development of more effective catalysts.

The purpose of this review is to investigate the direct synthesis of DME as one of the most well-known production methods of carbon dioxide utilization. In this process, catalysts will play a key role, and the research community actually needs a comprehensive outlook on recent insights on this process. In this regard, various types of catalyst and their preparation methods were studied, focusing on process efficiency. Although many aspects of the mechanism of DME synthesis from syngas have not yet been discovered, recent advances in research into H_2 production by DME reforming are increasing interest in effectively closing this H_2 binary loop, given the future green hydrogen economy.

2. Properties and applications of DME

Research shows that dimethyl ether production is increasing with 9 million metric tons annually, so it is important to study its physical and chemical properties. Table 1 provides an overview of some basic properties and combustion characteristics of DME.

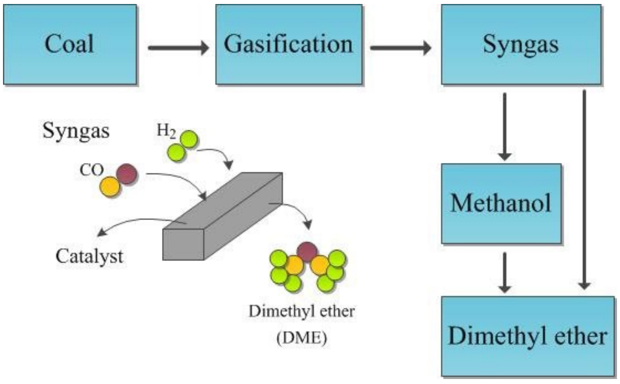

Fig. 1. Main chemical routes for syngas as feedstock to DME synthesis.

At ambient conditions, DME exists in the vapor phase. However, under pressures of greater than 500 kPa, it is liquefied at room temperature. DME, which is a colorless gas with a boiling point of -25 °C, is chemically stable and quickly liquefied under pressure.

DME is an important intermediate in the manufacture of many materials, including petrochemicals, fuels [33], and so on. Therefore, extensive research is needed on the production processes of this potential alternative fuel and the required catalysts. Olefin production from the DME [34] in one step (direct) in the micro-pilot unit was considered by Galanova et al. [35]. DME is commonly utilized in the aerosol industry as a propellant instead of ozone-destroying chlorofluorocarbons and in the chemical industry as a methylation agent. It has shown potential in producing bulk chemicals such as aromatics, acetic acid, and acetone [36]. Ethanol synthesis from syngas (CO/H_2) and DME over catalyst has been one of the most promising, as it employs inexpensively synthesized. Another use of DME is an intermediate in the production of methyl acetate, dimethyl sulfate, and acetic anhydride. DME can also be converted into acetic acid using carbon monoxide and water. Dimethyl ether is a solvent [37], extraction agent [38, 39], and organic extraction solvent for biomass applications. It can also be used as an alternative fuel additive [40] to liquefied petroleum gas to enhance combustion and reduce hazardous emissions.

3. Production of DME

Dimethyl ether can be made from a variety of fossil fuels, including natural gas and coal, as well as renewable biomass and methanol. At present, the catalytic synthesis of DME can be supported simply by the methanol dehydration on acid or by the conversion of syngas through a two-step reaction with methanol as a mediator. Azizi et al. [41] described the synthesis of DME with indirect methods. DME is formed by the dimerization of methanol [32]:

$$2CH_3OH(g) \leftrightarrow CH_3OCH_3(g) + H_2O \qquad \Delta H^o_{rxn} = -16.0\ kJ/gmole \qquad (1)$$

Table 1. Physical properties of dimethyl ether (DME).

Parameter	Quantity	Unit	Refs.
Molar mass	46.07	g/mol	[2]
Liquid density at 20 °C	660	Kg/m^3	[2]
Liquid viscosity at 25 °C	0.12–0.15	Kg/ms	[2]
Viscosity in vapor phase at 20 °C	0.925×10^{-2}	m.Pa.s	[32]
Normal boiling point	-24.9	°C	[3]
Compressibility factor	0.271	-	[32]
Critical temperature	400.1	K	[32]
Critical pressure	5.27	MPa	[32]
Lower heating value	28.43	MJ/mol	[2]
Auto-ignition temperature	508	K	[2]
Flammability range	3.4–18	vol% in air	[11]
Cetane number	55–60	-	[32]
Ignition energy	45	MJ	[32]

DME is produced in two steps, in which methanol is synthesized in the first step from the syngas. After purifying the methanol, it is converted to DME through another process called methanol dehydration in another reactor [42]. The methanol dehydration process is usually preferred at lower temperatures [43] to avoid the formation of other by-products. Process reactions for indirect DME synthesis can be described as follows. Methanol synthesis was obtained as a result of the reaction between carbon dioxide and hydrogen [44]:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^{o}_{298} = -49.6 \text{ kJ/mol} \tag{2}$$

Conversion of carbon monoxide to methanol:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^{o}_{298} = -90.8 \text{ kJ/mol} \tag{3}$$

Dehydration of methanol:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^{o}_{298} = -23.4 \text{ kJ/mol} \tag{4}$$

Water gas shift (WGS):

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^{o}_{298} = -41.2 \text{ kJ/mol} \tag{5}$$

Considering the advantages of performing the reaction, such as easy control of operating conditions and the capability of overcoming the mass transfer limitations, methanol dehydration to DME was investigated by researchers [45–47]. However, the main problem of this two-step DME synthesis is due to the severe thermodynamic limitation of the methanol which results in low gas conversion per pass (15–25%) and therefore high recirculation ratios and high capital and operating costs. To avoid this limitation, researchers began to study the direct synthesis of DME in a single reactor in which the methanol synthesis step is coupled *in-situ* with the dehydration step in a combined process. The direct synthesis of DME from syngas follows mainly two overall reactions [48]:

$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \qquad \Delta H^{o}_{298} = -245.7 \text{ kJ/mol} \tag{6}$$

$$2CO + 4H_2 \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^{o}_{298} = -204.8 \text{ kJ/mol} \tag{7}$$

4. Direct synthesis of DME

Through the direct or one-step synthesis of DME, three reactions occur; methanol formation, water-gas shift reaction, and methanol dehydration. The overall reaction to explain syngas to DME (STD process) is shown in Eq. 6. CO_2 also reacts with hydrogen to produce DME in the STD process. In parallel reaction, methanol as an intermediate product is formed from CO_2 and H_2 and is consumed to DME production as shown in Eqs. 2, 4.

Reverse water gas shift reaction (RWGS):

$$H_2 + CO_2 \leftrightarrow H_2O + CO \qquad \Delta H^{o}_{298} = 41.2 \text{ kJ/mol} \tag{8}$$

The overall reaction of CO_2 hydrogenation to produce DME is determined below:

$$2CO_2 + 6H_2 \leftrightarrow CH_3OCH_3 + 3H_2O \qquad \Delta H^{o}_{298} = -122.2 \text{ kJ/mol} \tag{9}$$

As shown in Fig. 2, the formation of DME is exothermic, while the RWGS reaction is endothermic. The direct method is more economical because a single reactor is required for the direct synthesis of DME. Both reactions are performed together, and obviously, it is advantageous to obtain a high conversion by increasing the reaction rate, but higher reaction temperatures are unfavorable to the formation of DME. Fig. 3 shows the scheme of direct synthesis of DME from CO_2 and H_2. Prior to DME synthesis, it is necessary to adjust the gas composition and purify to remove the acid components [49]. Gases separation can also be done with new technologies such as mixed matrix membrane due to their ecofriendly, process simplicity, and high efficiency [50]. However, key performance indicators, DME break-even price carbon efficiency, and energy efficiency in invested energy should be considered.

A steady-state process model for DME production using coal, containing drying stage, gasification, and DME synthesis, was presented by Kabir et al. [51]. Process efficiency of 32% and CO_2 emissions of 2.91 kg/kg DME were reported. However, the raw materials play the most important role because their composition includes a wide range of hydrogen to atomic carbon (H/C) and oxygen to carbon (O/C) ratios. Depending on these ratios, the produced syngas will be rich in CO or H_2. In both cases, the produced syngas must be upgraded to the suitable H_2 to CO ratio for the DME synthesis [52]. Better DME performance is achieved when CO_2 is removed from the fuel gas before being fed to the synthesis reactor. Based on the simulation, the rationality and practicality of the process can be ensured as much as possible [53, 54]. Green strategies, which are an innovative low-carbon route for DME production in line with the concept of bioeconomics, should be considered [55].

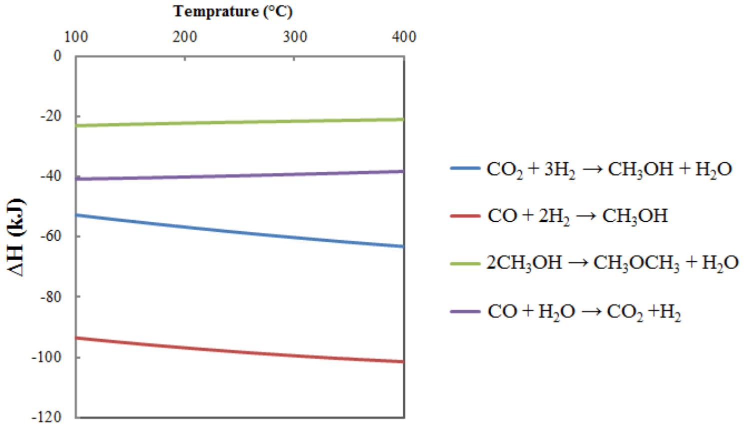

Fig. 2. Effect of temperature on the reactions during DME production.

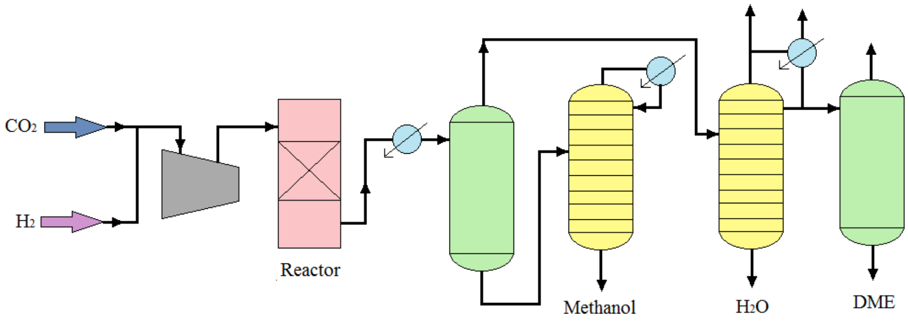

Fig. 3. The process scheme of direct synthesis of DME from CO_2 and H_2.

5. Catalysts for DME production

At present, innovative strategies for the synthesis of DME from different syngas and catalysts in different reactors and operating parameters have been reported [56]. The catalyst used in the direct synthesis of DME from synthesis gas must have essentially two functions, for example, methanol synthesis and methanol dehydration [57]. Catalyst inactivation one of the most important challenges in the synthesis of single-stage DME from syngas is the combination of methanol synthesis and water-deficiency properties in a catalyst without negatively interfering with their performance. It is an inescapable fact that cleaning the syngas is essential to prevent methanol synthesis catalyst poisoning. This operation raises capital cleaning and operating costs. Developing and using a suitable catalyst in the gas supply stage can be one way to minimize the concentration of these gases. Another solution could be to design and develop a bifunctional catalyst [58] that could control higher concentrations of these toxic gases. Therefore finding the right formulation for a bifunctional catalyst is also important for better process performance.

5.1. Methanol formation reaction

5.1.1. Bifunctional hybrid catalysts

Direct synthesis of DME requires highly efficient bifunctional catalytic systems that combine the hydrogenation function of carbon monoxide for methanol synthesis and the acidic function for methanol dehydration (Fig. 4). Therefore, the crucial issue in catalyst design could be the optimization of the catalyst composition and interaction between these catalyst components. The activity of the bifunctional catalysts decreases with time on stream owing to the deactivation by water. Therefore, water plays a major role in the acidic activity of catalysts, as it determines the strength and availability of methanol to these acidic sites and can be altered by thermal treatments or modification of metal-oxygen clusters in local structures [59]. The advanced adsorption process shows that, by choosing the right water absorber, it is possible to overcome the thermodynamic constraint [60]. Direct DME catalysts are susceptible to deactivation by oxidation, sintering, coke deposition, and contamination to impurities in the syngas, affecting the acidic sites of methanol dehydration [61, 62].

Copper catalysts have been used in various chemical processes, such as water gas shift reactions [63]. Currently, the most efficient methanol synthesis catalysts are copper-based and hence widely used in industry. As mentioned earlier, methanol synthesis is an exothermic reaction, and a volumetric contraction accompanies the preferred reaction conditions are, therefore, low temperatures and high pressures according to Le Chatelier's principle [64]. Cu-ZnO-based catalysts [65], combined with solid acid catalysts such as zeolites and γ-Al_2O_3, have been studied in CO_2 hydrogenation to produce DME, and the results showed increases CO_2 conversion [66–68]. In hybrid bifunctional catalysts, defects in Cu particles, changes in Cu particle morphology, dispersion, crystallite size, and interaction of Zn atoms with metallic Cu particles are important factors that define the activity of methanol synthesis components. Nature (Brønsted or Lewis), acid strength (weak to moderate) as well as the textural properties (mesoporosity) of acidic sites play a basic role in the performance of methanol dehydration. Various catalysts for CO_2 hydrogenation have been investigated, including [69–76], Pd-based catalysts [77–80], and bimetallic catalysts such as Pd-Ni, Fe-Ni, Cu-Ni, and Pd-Zn as effective couple for methanol production [81–85]. Among these catalysts, Cu-ZnO-based catalysts are the most widely used [86–90] because the Cu and ZnO loadings play a critical role in the physicochemical properties and catalytic performance of catalysts [91]. Different preparation methods, such as co-precipitation [92, 93], sol-gel, citrate method, and saturation method, have been used [70, 94]. Recently, the Cu-Zn-Al (CZA) catalyst for methanol synthesis has been successfully developed [95]. Zn is usually considered an active phase for methanol synthesis; however, the specific interaction at the Cu/ZnO interface may influence the catalytic performance. Also, Al_2O_3 is a hydrophilic substance that may absorb water produced by the CO_2 hydrogenation reaction, thereby accelerating copper sintering and reducing catalyst activity [96]. Therefore, finding new and very efficient catalysts for this reaction is very desirable.

Meanwhile, the CuO-ZnO-ZrO_2 (CZZr) catalyst has relatively good performance and stability, therefore has been widely used in last decade [97]. To increase the efficiency of the CZZr catalyst, new methods to preparation, such as CTAB-assisted co-precipitation, combustion synthesis, solid-state reaction, precipitation reduction, and hydrothermal synthesis, have been studied [65, 98–101]. In addition, many reports have suggested that additives are also a good way to improve the performance of the CuO-ZnO-ZrO_2 catalyst. Słoczyski et al. [102] reported that the addition of both Mg and Mn oxides increased the dispersion of the active site and the specific surface of the catalyst, which lead to increase the activity of the CZZr catalyst. Afterward, they compared several promoters such as B, Gd, Ga, In, Y, Mn, and Mg. The results showed that the catalyst with Ga_2O_3 mixing has the lowest Cu particle size and therefore achieves maximum methanol production [103]. Altogether, the activity of these catalysts

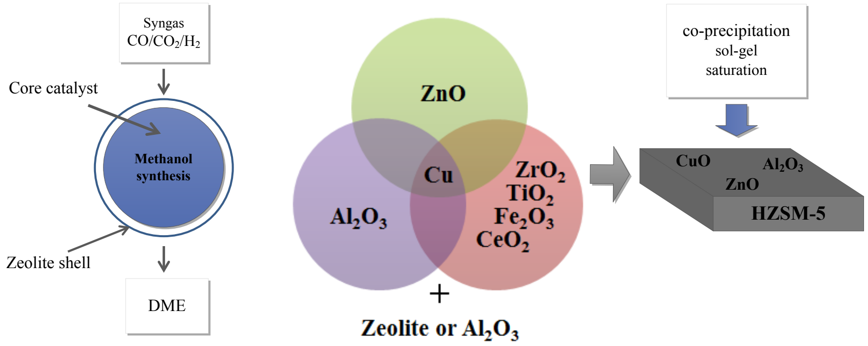

Fig. 4. Bifunctional catalysts and zeolite for direct synthesis of DME.

results from the high surface area and dispersion of Cu, indicating that these are important factors for developing fundamental mechanical insights into synthesis performance.

Catalyst support plays an important role in metal catalysts, as it demonstrates the ability of the catalytically active site. In addition, the adsorption properties of the reactants (H_2, CO_2, and CO) that lead to different reaction functions can be modified by the interaction between the metal and the support [104]. In the CO_2 hydrogenation process, catalyst support requires several basic features: high surface area to facilitate dispersion and reduction of the active phase, morphological stability, and high mechanical strength [105]. Ideally, both properties in a catalyst mixture should lead to a positive performance, which is possible by selecting the appropriate chemical properties and the desired degree of intimacy. However, achieving the right combination without negative interference remains a challenge in these multifunctional catalytic systems.

5.1.2. Photocatalysis technology

Recently, sunlight has been studied as a photocatalytic technology to convert CO_2 to hydrocarbon fuels such as CH_3OH and CH_4 using a semiconductor. A commercial TiO_2 (P25) catalyst is a standard semiconductor and is most commonly used as a photocatalyst due to its low cost, non-toxic, and stable catalysts. Unfortunately, a major drawback of TiO_2 is the rapid combination of electron-hole pairs. It has been reported that metal cation doping on TiO_2 catalysts can reduce electron-hole pair composition [106]. To accomplish the improved photoactivity, many researchers tried to modify TiO_2 by doping with metal.

The saturation method was applied in Ni/TiO_2 catalysts preparation, using TiO_2 as support and $Ni(NO_3)_2.6H_2O$ as a precursor of Ni [107]. A batch reactor equipped with a 60 W-UV light source was used for the experiments. After 3 hours, the highest amount of methanol was obtained, but decreased slightly due to oxidation of methanol. Therefore, Ni/TiO_2 catalyst can be used as a suitable and effective catalyst to converting CO_2.

Ti-MCM-41 can be used for hydrogen production under visible light irradiation, which is justified due to the high specific surface of Ti-MCM-41 and the further dispersion of TiOx in the zeolite [108]. Also, the methanol selectivity would be increased by further loading the noble metal, Pt or Pd nanoparticles, as active sites. The results showed that the regulation of the initial surface and active site of microporous zeolites is a very suitable method to modify the photocatalytic production of methanol from CO_2.

5.2. Methanol dehydration reaction

5.2.1. Zeolites

Zeolite is a mineral composed mainly of aluminosilicate with a mixed crystallographic structure giving rise to specific molecule-sized pores [109] and is widely used in industry as a catalyst. Zeolites application is probably the most significant economic and embraces two main areas-acid and redox catalysis. Zeolites are used on a huge scale in the petrochemicals industry and exploit the acidity of zeolites due to both frameworks, Brønsted acid centers, but also, in some cases, extra-framework Lewis acid sites [110]. Zeolites are typically prepared by hydrothermal treatment of alumina and silica solutions [111] with sodium hydroxide. As the Si to Al ratio increases, catalytic activity tends to exceed the maximum due to two opposing effects: increasing the effectiveness of each acid center on the one hand and decreasing the number of acid centers on the other [112]. Zeolites are generaly used in DME synthesis [29, 113, 114] because of the acid sites [115], and great hydrothermal stability, and good reactivity at low temperatures [116]. However, zeolites have some disadvantages such as coke production [117] and low-molecular-weight hydrocarbons [118], which reduce DME selectivity and catalyst life.

Ferrierite-H named HZSM-5, a ferrierite group of zeolite (the FER structure), can be used as a catalyst in the MTD (methanol to DME) process, which could be synthesized from fume-based geopolymer precursors, a cost-effective and eco-friendly approach [119]. One of the catalysts used for the synthesis of DME is the CeO_2-CaO-Pd/HZSM-5 catalyst, which was tested in a microporous fixed bed reactor of sulfur-containing syngas [120]. The catalytic stability of the CeO_2-CaO-Pd/HZSM-5 hybrid catalyst was investigated to ensure that the experimental kinetic results were not significantly affected by the induction period and catalytic deactivation. Characterization analysis revealed that the sulfur tolerance of Pd/CeO_2 was due to the ability of CeO_2 to convert H_2S to SO_x [121]. Thus, active Pd sites for methanol synthesis are protected against sulfur poisoning, which was the main reason for the deactivation of Pd/Al_2O_3 catalysts. Instead, the HZSM-5 surfaces are known to be the active methanol dehydration reaction center [122]. Therefore, this catalyst has good sulfur tolerance, activity and exhibited excellent catalytic performance for DME synthesis. The results showed that the CO conversion rate and DME selectivity increase with increasing temperature, while the DME selectivity decreases when it is more than 300 °C. Studies on MFI type zeolite have shown that this structure has good stability but with lower efficiency of DME and higher coke formation due to larger pore structure than FER type zeolite structure [123].

Modified zeolite catalysts, such as KHZSM-5 [118], ZSM-5/MCM-41 [124], P/ZSM-5 [125], Na/HZSM-5 [116] have been studied to improve coke resistance and hydrothermal stability in the MTD reaction (methanol to DME). However, as shown in Table 2, most studies in the literature focus on HZSM; the methanol dehydration reaction was performed in a fixed bed down-flow reactor by Kim et al. [118]. Increasing the water content during feeding causes the reaction to take place over a wider temperature range. Despite the decrease in low-temperature methanol conversion, the methanol and DME conversion options were more than 50 and 99, respectively. It was found that catalyst inactivation due to coke formation depends on the amount of water in the feed stream. Coke as covering the catalyst particle surface deactivates the catalyst. Aromatic compounds trapped in pores affect the acidity, pore-volume, surface area as well as conversion. Although catalyst deactivation due to dealumination caused a 20% decrease in the methanol conversion, the stability of K-HZSM-5 is expected to be improved by the addition of a proper amount of water in the feed. Deactivation of the K-HZSM-5 catalyst resulted from coke formation or dealumination under specific reaction conditions. Catalyst deactivation due to dealumination, which caused a 20% drop in the methanol conversion during the initial period of the reaction, depends on the amount of water in the feed stream. Furthermore, simple-structured oxygenates develop on the surface of the catalyst when using water-containing methanol as the feed.

Bi-functional catalyst, Cu-Zn/ZrO_2, HZSM5, and Cu-Zn/ZrO_2, K-HZSM5 into a plug flow reactor was tested. Prachumsai et al. [126] showed that catalytic production of DME increased by mixing $CuZnZrO_2$ and KHZSM5, with a high selectivity towards DME. Because of the difference in surface chemistry of HZSM5 and K-HZSM5, mixing the $CuZnZrO_2$ and HZSM5 catalysts led to a higher yield of valuable products, and hydrocarbons were observed [126]. HZSM-5 catalysts are among the most important solid acid-base materials for the direct synthesis of DME [122]. HZSM-5 catalysts have high acidity (which includes both Lewis and Br Lewnsted acid sites) and molecular selectivity, great thermal resistance and wide surface area. Compared with the other solid acid catalysts, HZSM-5 evidenced more stability in the presence of water [127]. Researches have introduced various synthesis methods with different sources and patterns for the preparation of HZSM-5 zeolites. The physical properties and catalytic activity of HZSM-5 zeolite depend on the synthesis temperature. Karaman and Octar used HZSM-5 hierarchical catalysts by steam crystallization (SAC) method to increase its surface acidity. They showed that the increase in the content of heteropoly acid (HPA) as a catalyst had increased DME selectivity and CO conversion. In the presence of this catalyst, DME selectivity of 57% and CO conversion of 46% were attained at the best reaction temperature of 275 °C. In addition, the methanol obtained was not entirely converted to DME, and result the selectivity of DME remained 57% [128].

Yang et al. [129] studied two different zeolite membrane hydrothermal synthesis methods; the traditional acidic HZSM-5 zeolite membrane synthesis method with the aluminum resource in the precursor solution and the close-to-neutral Silicalite-1 zeolite membrane preparation method without an aluminum resource [129]. The core catalyst, Cu/ZnO/Al_2O_3 (CZA), was prepared by the co-precipitation method. In successive direct DME synthesis reactions from syngas, zeolite capsule catalysts exhibit an excellent selectivity for DME compared to conventional hybrid catalysts and more DME dehydration suppression for the formation of alkane/alkene by-products. Thus, the concept of a zeolite capsule catalyst with the effect of equilibrium shift, shape selectivity, and synergistic constraints promises to be widely used for many sequential reactions such as multistage organic synthesis. The CZA-ZSM-5(25)-A that hierarchical ZSM-5(25)-A sample was synthesized by alkaline desilication has the higher catalytic stability and higher initial activity [130].

A bifunctional catalyst, consisting of Fe-modified CZZA and HZSM-5 with various Fe loadings, was prepared using a co-precipitation method and then loaded into a fixed-bed reactor for DME synthesis by Fan et al. [131]. A reduction process was carried out at 250 °C for 10 h with 20 ml/min of pure H_2 under atmospheric pressure. The catalytic performance of all Fe-modified CZZA catalysts, with different Fe loadings, was slightly lower due to the coverage of the Cu surface area, but the stability of Fe-CZZA catalysts was greatly enhanced because of much lower loss of Cu surface area, as compared to that of the CZZA catalyst. Nearly a 1.4% (absolute value) loss of DME yield, with reference to the initial yield for 0.5Fe-CZZA/HZSM-5 bifunctional catalysts in a 100 h run of reaction, was obtained [131].

H-mordenite zeolite (HM) was investigated as a catalyst for methanol dehydration in a three-phase slurry reactor by Khandan et al. [132]. H-mordenite (HM), modified with aluminum oxide, was prepared by the wet impregnation method with aqueous solutions of aluminum nitrate. These results revealed that the hybrid catalyst composed of Cu–ZnO–ZrO_2 and Al-modified H-mordenite with 8 wt% aluminum oxide had good stability for the direct synthesis of DME from synthesis gas. Recent studies have shown that zirconia has a synergistic effect on DME production [133–135]. Independent of the fact that Cu surfaces or Cu-ZnO interfaces can serve as the standard active phase for CO_2-based catalytic technologies, nevertheless new synthetic methods for Achieving better synergies in this field are a welcome step in the composition of the combined catalyst [136]. The advanced behavior of the Cu-ZnO-ZrO_2 system is related to the weak hydrophilic character of zirconium oxide, which prevents the intense absorption of water and increases the initial surface, which facilitates the absorption of CO_2 and, therefore, the efficiency of methanol. Physico-chemical properties of Cu-Zn-Zr systems can be controlled by varying composition and preparation methods [137].

HBFZ as a hierarchically porous composite zeolite with beta zeolite cores and Y-zeolite polycrystalline shells was used in CZA as a methanol dehydration catalyst to synthesize DME from syngas in a fixed bed reactor by Wang et al. [138].

Sulfated zirconia with adding 1% Mn by sol-gel (Mn/SZ-S) and impregnation method (Mn/SZ-I) on the methanol conversion process was tested by El-Desouki et al. [139], and it was found that Mn/SZ SZ-S catalyst has better catalytic performance. High catalytic activity has been attributed to high surface area and high acidity due to the high Lewis acidity of zirconium sulfate.

Today, more than 100 heteropoly acids of various compounds and structures are known. Heteropoly acid (HPA), as a green catalyst, is frequently used to obtain higher selectivity due to higher activity. The catalytic effect of HPAs in reactions depends on the acidity, heteropoly anion structure, and type of reaction [140]. A series of bifunctional hybrid catalysts based on phosphotungstic acid ($H_3PW_{12}O_{40}$) supported on TiO_2 combined with Cu-ZnO(Al) catalyst have been prepared, characterized, and tested for direct DME synthesis from syngas in a fixed-bed reactor. Activity tests were performed in a fixed-bed reactor loaded with hybrid catalysts diluted with SiC (1:3 vol). The overall methanol and DME yield on CZA-HPW/Ti hybrids was, in all cases, lower than the methanol yield achieved on the CZA reference [141].

For the direct synthesis of DME from syngas, semi-formed MFI zeolite mixed with copper-zinc-aluminum catalyst was used. The DME synthesis reaction was carried out in a fixed-bed stainless-steel tubular reactor with CuO–ZnO–Al_2O_3 catalyst (Cu:Zn:Al = 60:30:10 atomic ratio). In addition, the hybrid catalyst with embryonic zeolite (EZ) with a relatively low Si/Al (< 50) ratio was prepared [142].

Geopolymers are aluminosilicate materials made from solid materials containing alumina and silica and are activated by alkaline or alkaline silicates at ambient temperature or above. Geopolymers can be considered as amorphous analogues of some synthetic zeolites, and the synthesis of aluminosilicate zeolites is possible using traditional hydrothermal techniques. The raw materials of silica fume (SF) and metakaolin (MK) with ZSM-35 zeolite were studied in a stainless steel fixed-bed reactor [119].

FER- and MFI-type zeolites are recognized as stable catalysts for DME synthesis. The application of nano-sized MFI allows obtaining a DME selectivity similar to FER [143], but with a higher DME production rate and lower coke deposition. Catizzone et al. [123] synthesized a micro-sized FER sample (M-FER) with pyrrolidine as structure-directing agent (SDA) by adopting the 0.6 Pyrrolidine–0.08 Na_2O–0.05 Al_2O_3–1 SiO_2–20 H_2O gel molar composition: A Nano-sized FER sample (N-FER) was synthesized by using seeds prepared by adopting the same condition of M-FER but with the addition of sodium lauryl sulfate (SLS) with an SLS/Al_2O_3 molar ratio equals 0.3. Catalytic tests were performed in an experimental tubular reactor. The results show that crystal size plays an essential role in terms of DME production, DME selection, and coke deposition. Nano-sized crystals perform better than tiny crystals [123].

Bedoya et al. [144] investigated Al-MCM-41 nanospheres with variable size had been synthesized by the sol-gel method. The catalytic activity results showed that all samples tested reached 100% of selectivity towards DME. The smallest Al-MCM-41 nanospheres achieved 78% of DME yield at 300 °C and good catalytic activity performance below 300 °C. The stability of the fresh and regenerated Al-MCM-41 nanospheres was evaluated for 48 h time-on-stream. High values of DME yield (> 60%) were maintained during 48 h time-on-stream showing the possibility for recycling the material [144]. Three-dimensional microporous zeolites have attracted much attention in catalysis because of their large BET surface area and abundant pores. Seker et al. [145] mixed the commercial CuO–ZnO–Al_2O_3, an MSC specifically designed for syngas conversion, with MCM-41-supported tungstophosphoric acid (SAC component) and optimized the mixing ratios and reaction conditions for the highest rate in DME synthesis from CO_2 hydrogenation in a single-pass flow reactor. The high density of acidic sites with very high performance for methanol dehydration to DME allows operations at very high space velocities, which provides a very significant DME synthesis rate. This record-high rate presents the broad potential of supported HPAs as acid function in single-pass conversion of CO_2 to DME. It offers opportunities for developing high-performance catalysts for direct conversion of CO_2 into fuels, enabling CO_2 hydrogenation as a valuable strategy for renewable energy utilization [145].

The fabrication by a physical coating of a bifunctional core-shell-structured catalyst (CZZr@S-11) has been studied using CuOZnO-ZrO_2 (CZZr) as metallic function and SAPO-11 as acid function [146]. The effects of calcination temperature and mass ratio between metal and acidic functions on their kinetic behavior for DME synthesis from syngas have been evaluated. Indicators considered: the conversion of CO_x ($CO+CO_2$) and CO_2; yields and selectivity of DME, methanol, and hydrocarbons; and stability. CZZr@S-11 catalyst prepared under suitable conditions revealed better reaction indices than the hybrid catalyst (CZZr/S-11), prepared by a physical mixture of the individual functions, especially interesting for the valorization of CO_2. Besides, the core-shell structure is suitable for debilitation Cu sintering, as the adsorption of H_2O on the metallic sites is disfavored. On the other hand, coke deposition in acid function is reduced by minimizing the contribution between coke formations, which is faster in metal yield than in acid yield. [147]. Also, phosphate alumina has more weakly-held water, which may help protect the resistance of Cu/ZnO via inverse spillover.

5.2.2. γ-Al_2O_3

Methanol dehydration usually is carried out using Al_2O_3 as catalysts [148, 149]. It is used due to its great specific surface area, uniform pore size distribution, high thermal resistance, and high DME selectivity. Al_2O_3 enhances thermal and chemical stability. However, this material presents weak to medium surface acidity and therefore presents low catalytic activities along with its super-hydrophilic behaviour [150] and thus undergoes a fairly rapid and reversible deactivation. However, Al_2O_3 has a low activity at temperatures lower than 200 °C where no hydrocarbons are formed, thus giving a total selectivity for DME of 100%.

The direct synthesis of DME from syngas has been studied on three mixtures with different catalyst ratios for the synthesis of methanol (CZA) and DME (γ-Al_2O_3). Mixtures with equal value of both catalysts provided the highest DME efficiency, while mixtures with the highest CZA/γ-Al_2O_3 mass ratios of 9 have the highest selectivity of DME. Comparison between the results showed that the presence of a large part of CO_2 in syngas strongly affects the catalytic performance and leads to a reduction in the total carbon conversion and DME efficiency. It can be explained that the presence of CO_2 in the syngas leads to high efficiency of H_2O in the catalyst bed, which leads to the accumulation of copper particles, thus leading to lower CO conversion and deactivation of the γ-Al_2O_3 catalyst and reduced conversion of methanol to DME. Removal of water by an adsorbent in the catalytic bed leads to high efficiency of DME. However, this is a temporary effect and total carbon conversion and DME efficiency decreases again after adsorbent saturation. Nevertheless, the results show the positive effect of in-situ water removal for direct synthesis of DME from syngas and pave the way for the development of strategies to maintain H_2O removal operations during DME synthesis [151].

WO_3 supported on γ-Al_2O_3 were investigated for the dehydration of methanol to DME at 230 °C in a fixed bed flow type reactor at atmospheric pressure using nitrogen or air as a carrier gas by Said et al. [152]. The role of WO_3 added to γ-Al_2O_3 is modulating the number and type of acidic sites. The results revealed that the WO_3 modified γ-Al_2O_3 has good stability for the synthesis of DME from methanol under inert and oxidative atmospheres, and the maximum yield of DME was obtained. The catalyst exhibits good stability toward methanol dehydration reaction for a long operation time.

The comparative catalytic performance of η-Al_2O_3 and γ-Al_2O_3 catalysts prepared from two common precursors, aluminum nitrate (AN) and aluminum chloride (AC), respectively, were investigated by

Osman et al. [153] and the impact of calcination temperature was evaluated in order to optimize both the precursor and pre-treatment conditions for the production of DME from methanol in a fixed bed reactor. All catalysts prepared from AN (η-Al_2O_3) showed higher activity than those prepared from AC (γ–Al_2O_3) at all calcium temperatures.This catalyst showed high resistance and was found to have twice activity of the commercial γ-Al_2O_3 or 87% of the activity of commercial ZSM-5 at 250 °C.

Mejía et al. [154] studied niobium phosphate ($NbOPO_4$) and niobic acid ($Nb_2O_5.nH_2O$) while a Cu-based catalyst and γ-Al_2O_3 were applicated as reference material. Combining the methanol synthesis catalyst with the solid acid resulted in high CO conversion compared to methanol synthesis catalysts without solid acid or regular in a stacked substrate configuration with solid acid downstream of the methanol synthesis catalyst. In addition, the stability of all mixtures varies depending on the nature of the solid acid, which indicates different inactivation mechanisms. Higher acidity and more acidic sites may be the reason for the catalytic activity of NbP. The number of copper crystals in catalyst grew under reaction conditions, but their growth was similar in different mixtures, so the loss of copper surface alone could not explain deactivation. However, other structural changes in the Cu-based catalyst cannot be completely excluded; one of the Cu-based catalysts mixed with γ-Al_2O_3 after the reaction showed an additional diffraction peak related to the ZnO nanostructure, indicating these methanol catalysts can be prone to structural changes during DME synthesis. The γ-Al_2O_3 accumulates more coke compared to niobium base catalyst, which may partly clarify the low yield of DME production, especially for γ-Al_2O_3.

5.2.3. HMS supported catalysts

The hexagonal mesoporous silica (HMS) has a simple preparation method that can be extracted without pollution but preparation parameters affected on morphology and characteristics of HMS [155]. Among the various types of solid acids used for methanol dehydration, H-ZSM-5 has been extensively studied on laboratory and commercial scales. Al-HMS (Aluminated hexagonal mesoporous silica) as a solid acid catalyst for various reactions has been reported to methanol dehydration to DME [156]. The effects of incorporating Al into the HMS framework on the activity, selectivity, and durability in the methanol dehydration were studied by Sabour et al. [156] and showed that the Si/Al ratio of 10 for Al-HMS is the best for DME production. As the Si/Al ratio increased, the conversion increased, but the DME selectivity decreased.

5.2.4. Vermiculite

Vermiculite is a hydrous phyllosilicate mineral that was used with alumina pillared and modified with titanium as a catalyst for dehydration of methanol to DME [157]. Modification of vermiculite significantly increased its specific surface area as well as partial leaching of Al^{3+} and Fe^{3+} cations from clay layers. Acid treatment of vermiculite let to its activation in methanol dehydration processes. Catalytic activity was evaluated using different hourly space velocities, in the absence and presence of water in the feed, in the temperature range of 250–450 °C. Modified vermiculite was shown to be active and selective in methanol dehydration. The Al pillaring leads to more active catalysts than TiO_2. The addition of water has a negative effect on the activity of the catalyst and leads to faster deactivation of the catalyst. The effect of methanol hourly velocity has no significant effect on methanol conversion but changes strongly to DME selectivity at the beginning of the reaction. Increasing the temperature reduces the selectivity of DME from 100% to 70%.

5.3. Reverse water gas shift reaction

In contrast to the direct synthesis of methanol and DME, CO is obtained from an endothermic reaction (Eq. 8). Because CO is much more reactive than CO_2, the RWGS reaction is often seen as the initial intermediate stage for many other CO_2 hydrogenation processes such as CO_2 methanation or conversion of CO_2 to methanol [158]. Therefore, it is preferred to produce suitable catalysts synthesized with efficient techniques, which allow high conversion at low reaction temperatures [159]. In CO_2 hydrogenation, large amounts of water are produced, which may lead to catalyst poisoning. Because this reaction always operates at moderate or high temperatures, catalysts with excellent water tolerance are attractive for practical use. Supported metal catalysts typically show severe sintering conditions under high-temperature treatment conditions. Noble metals such as Pt, Pd, Rh, and Ru show good properties for proper performance in RWGS reaction [160, 161]. Corrosion resistance, as well as intense activity in H_2 separation, can improve the stability and performance of CO_2 conversion on noble metal-based catalysts.

Cu-based catalysts, previously widely used in the industrial WGS reaction, are the most studied for reverse reaction due to their high activity and lower cost. In fact, the effect of Cu lies in increasing its adsorption capacity for reaction intermediates [162]. For example, ternary catalysts containing Cu (such as Cu/ZnO based on Al_2O_3) are among the most widely used catalysts for this process because they display a high selectivity of CO, especially at low temperatures [163–165]. The effect of support composition on the performance of Cu-based catalysts has been reported in various works [165, 166]. The Cu/$CeO_{2-\delta}$ catalyst with a load of 8.0% by weight copper showed the highest CO_2 conversion rate in the RWGS reaction. Cu/$CeO_{2-\delta}$ composite material is a superior catalyst for the RWGS reaction due to its high CO_2 conversion and selectivity of 100% CO [167]. Molybdenum carbide catalysts are also chosen to activate the RWGS reaction [168]. Research has shown that they are more active and much more selective to CO compared to TiC, ZrC, NbC, TaC, or WC [169].

Table 2. Summary of the studied catalysts and reaction conditions for the direct synthesis of DME.

Catalyst	**Temp. (°C)**	**Press. (bar)**	**GHSV ($mL/g_{cat}.h$)**	**H_2/CO_2 mole ratio**	**H_2/CO mole ratio**	**X_{CO2} (%)**	**X_{CO} (%)**	**S_{DME} (%)**	**Y_{DME} (%)**	**Ref.**
CuO-ZnO-ZrO_2/HZSM-5	200	30	60000	3		< 5%		90		[136]
CZA/HBFZ	250	50		12.67	2.23		94.2	67.9		[138]
CZA–EZ	260	20	3600		2		74	75		[142]

Table 2. Continued.

Catalyst	Temp. (°C)	Press. (bar)	GHSV ($mL/g_{cat}.h$)	H_2/CO_2 mole ratio	H_2/CO mole ratio	X_{CO2} (%)	X_{CO} (%)	S_{DME} (%)	Y_{DME} (%)	Ref.
CZZ(C)/FER (co-precipitation)	250	20	1800	3		17.5		28.4	5	[143]
CZZ(G)/FER (sol-gel)	250	20	1800	3		18.0		24.6	4.4	[143]
CZA/TPA ($H_3PW_{12}O_{40}$)/MCM-41	250	45	40000	3		8.9		23.1		[145]
CuO-ZnO-ZrO_2/SAPO-11	250	50	8400		2					[146]
CuO-ZnO-ZrO_2/SAPO-11	275	30		6	3		30		8	[147]
CZA/ Al_2O_3	270	50	5000	4 (v/v)	7.7 (v/v)	9	32	23		[151]
$Nb_2O_5.nH_2O$, $NbOPO_4/\gamma$–Al_2O_3	260	40	15000		2 (v/v)		75	65	49	[154]
CuO-ZnO-Al_2O_3/HZSM-5	275	10–40	600		2		64		59	[170]
CuO–ZnO/HZSM-5	260	20	6000		2		54	69.6		[171]
CuZZrA/HZSM-5	250	50	6000	3		30.9			21.2	[172]
CuO-ZnO-Al_2O_3/HZSM-5	260	42	1525	3		21.4		55.5	21.9	[173]
CuO-ZnO-Al_2O_3/HZSM-5	275	40	18000		2		39	34	34	[174]
CuO-ZnO-Al_2O_3/HZSM-5	260	30	346	3		27.3		67.1	18.3	[175]
CuO-TiO_2-ZrO_2/HZSM-5	250	30	1500	~2.8		15.6		47.5	7.41	[176]
CuO-Fe_2O_3-ZrO_2/HZSM-5	260	30	250	5		28.4		64.5		[177]
CZA/HZSM 5(80)	260	20	2400		2		20		98.71	[178]
CZA/γ–Al_2O_3	260	20	2400		2				54.19	[178]
Cu-Zn-Al-La/HZSM-5	250	30	3000	3		43.8		71.2		[179]
Cu-Mo/HZSM-5	240	20	1500	3		12.36		77.19		[180]
CuO-Fe_2O_3-CeO_2/HZSM-5	260	30	1500	4		20.9		63.1	13.2	[181]
Cu-Fe-Ce/HZSM-5	260	30	1500	4		18.1		52	9.4	[182]
Cu-Fe-La/HZSM-5	260	30	1500	4		17.2		51.3	8.8	[182]
Cu-Fe-Ce/HZSM-5	260	30	1500	4 (v/v)		20.9		63.1	13.2	[183]
Plasma, Cu-Fe-Ce/HZSM-5	260	30	2000	4 (v/v)		24.3		69.5	16.9	[183]
CuO-ZnO-Al_2O_3/NaHZSM-5	275	40			2:1			80	78	[184]
CuO-ZnO-Al_2O_3/HZSM-5	270	30	4200	3		30.6		49.2	15.1	[185]
Cu-Zn-Al/Al_2O_3	260	50	750	3		20		82		[186]
Cu/ZSM-5	260	20.26	9000		2		65	64		[187]
Cu-Zn-Al-Zr/ZSM-5	260	30	400	3		25		23.3	5.8	[188]
PdZn/TiO_2/ZSM-5	270	20	720	3		11		32.3		[189]
CZA/FER	200	50	2000	66:9	66:21	95		88		[190]
CuZnZr/ FER	260	50	8800	3		23.6		47		[191]
CZZ/FER	280	50	2030	3		30		62		[192]
CuZnZr/WO_x/Al_2O_3	260	30	3000	3		18.9		15.3		[193]
CuO-ZnO-ZrO_2/WO_x/ZrO_2	260	30	1000	3		21.5		29	6.88	[194]
Cu-Zn-Zr/MFI	240	50	2307	3		24		49.3	11.6	[195]
Cu-Zn-Ga/FER	260	30	2030	3		21.1		34.9		[196]
Cu-Zn-Al/ZSM5,CNTs	262	30	1800	3		46.2		45.2	20.9	[197]
CuO-ZnO-ZrO_2/SO_4^{2-} ZrO_2	260	20	3750	3		17.2		25.6		[198]
Cu-Zn-Zr-V/ZSM-5	270	30	4200	3		32.5		58.8	19.1	[199]
Cu-Zn-Zr-Pd/ZSM-5	200	30	1800	3		18.67		73.56		[200]
Cu/Zn/Al Amorphous Si-Al	266	30	1800	3		47.1		42.4	19.9	[201]
Cu-Mn-Zn/zeolite-Y	245	20	1500		1.5 (v/v)		53.6	63.5		[202]

6. Conclusions

Dimethyl ether (DME) is one of the multi-purpose alternative fuels that have attracted a lot of interest to use due to its potential as the next-generation bio-fuel. DME is a green fuel with high-efficiency compression combustion that can be used as a diesel substitute. The good properties of DME in terms of low toxicity and high energy density make it possible to replace LPG, methanol, and petroleum. To develop the use of DME, it is crucial to building the infrastructure needed for the raw material supply chain, the DME synthesis process, and the development of the machinery industry. This work aimed to collect the state-of-the-art DME production as a sustainable fuel and find the technological challenges in converting CO_2 to DME as a direct production route. A large amount of greenhouse gases (CO and CO_2) have been produced due to the extensive use of fossil-based fuels, and to combat this pollution, the technology of mitigation of these gases must be developed. However, the utilization of biomass feedstocks herein can only be sustainable when supported by the DME synthesis process with a high production capacity. Much research has been performed to find the most suitable operating conditions for DME synthesis. DME as a biofuel can be used as an attractive energy source instead of diesel which produces very little exhaust gas, almost zero CO_2 emissions, and therefore, no need to absorb and separate CO_2 in the DME plant.

The most important process for direct synthesis of DME is syngas and CO_2, but this process occurs in two stages. One of the associated problems herein is the inactivation of the catalyst due to water formation and deposition of coke on the surface of the catalyst. The most widely used syngas hydrogenation catalyst is $Cu/ZnO/Al_2O_3$ (CZA), and acid catalysts are required for the methanol dehydration reaction. Compared to the DME production from syngas, the synthesis of DME from CO_2 produces more water, which poisons the catalyst as most catalysts are hydrophilic. A wide range of catalysts has been tested for acid performance for the methanol dehydration reaction. Catalyst preparation methods also have a significant effect on catalyst properties.

Various operational parameters affect the synthesis process of DME. The direct synthesis of DME has been carried out in the temperature range of 120–300 °C and pressure range up to 50 bar. The molar ratio of H_2/CO_2 also has a huge effect on DME selectivity and CO_2 conversion. A few studies have been performed on the synthesis of DME on a pilot plant scale. More research needs to be done to develop robust catalytic systems to achieve the most active, reusable, economic, and highly water-resistant. Syngas cleaning is essential to prevent methanol synthesis catalyst poisoning, so cleaning operations impose additional capital and operating costs. Process simulation allows one to consider different technological types related to the feasibility of this technology installation, examine the effect of process parameters on production efficiency, and minimize energy consumption or costs associated with process execution. Research on such models can improve energy efficiency and reduce the energy consumption process of this green technology. Sensitivity analysis to examine the impact of some important economic parameters showed a great challenge on the way to achieving a circular economy in general. However, research suggests that this environmentally friendly choice is not far behind the present market features. Nonetheless, attempts to develop economically appealing green processes must be stepped up.

CRediT authorship contribution statement

Asieh Akhoondi: Writing – original draft.
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Data availability

As this is a review article, no new data were generated or analyzed. All information and data sources referenced are publicly available or cited appropriately within the article.

Declaration of competing interest

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