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## A REVIEW ON SYNTHESIS OF DIMETHYL ETHER FROM SYNGAS OVER BIFUNCTIONAL/HYBRID CATALYSTS

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**ABSTRACT:** *In this article, dimethyl ether (DME) synthesis from syngas and catalysts for related reactions were reviewed. DME are generally synthesized in a two-step process via methanol so called as indirect methods as state of the art technology, and in order to decrease the cost and increase the conversion, the new studies focused on single step process from syngas by eliminating thermodynamic limitations which comes from syngas-to-methanol equilibrium, called as direct synthesis. In direct DME synthesis, syngas is converted into methanol over a metallic copper-based catalyst, and simultaneously methanol is dehydrated to DME over solid acid catalysts (such as  $\gamma$ -alumina and zeolites), so methanol synthesis and methanol dehydration reactions occur in a single reactor in the presence of bifunctional/hybrid catalysts resulting in an increase in the syngas conversion to DME. In this paper, the effect of bifunctional/ hybrid catalysts and reaction parameters used for direct DME synthesis on syngas conversion, DME yield and selectivity are also summarized.*

**KEYWORDS:** Syngas; Dimethyl ether (DME); Methanol; Bifunctional/Hybrid Catalysts; Syngas to DME

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### INTRODUCTION

The increasing energy requirement due to the rapid development of the industry, the rapid depletion of fossil resources and the problems of global warming caused by the combustion of these resources have accelerated the efforts to develop alternative clean fuel technologies [1-5]. Recently, DME which can be obtained from non-petroleum alternative energy sources (such as biomass, waste, coal, natural gas, various greenhouse gases etc.) has attracted attention with its wide usage area [5,6].

Dimethyl ether (DME,  $\text{CH}_3\text{OCH}_3$ ) known as methoxy methane, is the simplest ethers. DME is in the gas form at standard temperature and pressure and can be liquefied at low pressures at 6 atm or  $-25\text{ }^\circ\text{C}$  [7]. DME is a volatile organic compound, but is non-toxic, non-teratogenic, non-carcinogenic and non-mutagenic [1]. There is an increasing interest in using of DME as a clean alternative fuel and raw material in the chemical industry [8,9]. Besides, DME can be used as environmentally friendly aerosol propellant and refrigerant agent and so it can replace chlorofluorocarbon (CFCs), Freon and R-134, which causes the ozone layer depletion [2,8,10]. DME properties (high cetane number which is about 55-60, ease of storage, transport and distribution) are suitable for its use as an alternative clean fuel in different fields (automotive, domestic and electric power generation) [9]. DME, which has no C-C bond, is an alternative candidate for diesel fuel due to its high cetane number. DME can replace LPG as a heating and cooking fuel or as a blending agent with LPG due to similar physicochemical properties [3, 11]. The advantages of using DME as fuel are high oxygen content (34.8% by mass), low NO<sub>x</sub>, SO<sub>x</sub> and hydrocarbon emissions, less engine noise and near-zero soot

production compared to traditional diesel fuels [13,14]. Physicochemical properties of DME and other different fuels are given in Table 1.

**Table 1.** Comparison of properties of alternative fuel DME and commonly used other fuels [1,11,14]

Properties	DME	Methanol	LPG	Gasoline	Diesel
Chemical Formula	CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>3</sub> OH	C <sub>2</sub> -C <sub>5</sub>	C <sub>4</sub> -C <sub>12</sub>	C <sub>3</sub> -C <sub>25</sub>
Normal Boiling Point, 20°C	-24.9	64	-42	38-204	125-400
Density (g/m <sup>3</sup> , 20°C)	0.661	0.792	0.54	0.71-0.77	0.80-0.86
Cetane Number	55-60	5	5	5-20	40-55
Octane Number	-	110	90-96	90-100	-
Carbon Content (wt.%)	52.2	37.5	82	85.5	87
Sulfur Content (ppm)	0	0	10-50	200	250
Calorific Value LHV, kcal/kg	6925	4800	11950	11110	10800

DME is also used as an intermediate for the production of various chemicals (such as methyl acetate, aromatics, acetic acid, light olefins, gasoline, higher ethers, oxygenates, formaldehyde, ethanol etc.), substituting methanol [11]. Moreover, DME is a potential feedstock to produce diesel and gasoline fuel additives (such as polyoxymethylene dimethyl ethers and dimethoxymethane by oligomerization) [9]. DME is also considered a promising raw material in fuel cells because it can be efficiently converted to hydrogen at low temperatures [15].

### DME Synthesis from Syngas

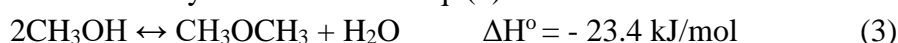
Syngas, as precursor of DME, is produced from gasification of biomass, waste, coal and natural gas reforming or partial oxidation [3]. DME synthesis can be performed from syngas (containing CO, H<sub>2</sub>, CO<sub>2</sub>) by two methods: indirect (two-step process) and direct (single-step process). In the conventional indirect synthesis, firstly methanol is synthesized over copper-based catalyst (mainly, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>) and then DME is synthesized from methanol over solid acid catalyst (most common  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, zeolite, SAPOs), separately. In the direct synthesis method, methanol synthesis and methanol dehydration reactions take place simultaneously in a single reactor at the presence of bifunctional/hybrid catalysts [1, 8,11,16].

In indirect DME synthesis, the methanol synthesis reaction has thermodynamic limitations, and this prevents the conversion of the syngas to methanol. High pressure and large recycle stream are required to ensure high syngas conversion [17]. The direct DME synthesis alleviate the thermodynamic limitations of methanol synthesis by continuously converting methanol to DME, and this provide higher CO conversion and higher DME selectivity. So, the direct DME synthesis is thermodynamically more favorable than the indirect synthesis approach [16,18].

Direct DME synthesis is a highly exothermic reaction process because it consists of methanol formation, methanol dehydration and water-gas shift reactions, which are all highly exothermic. The synthesis of DME from syngas containing CO<sub>2</sub> involves exothermic equilibrium reactions. Methanol synthesis reactions Eq. (1) from CO hydrogenation and Eq. (2) from CO<sub>2</sub> hydrogenation;



Methanol dehydration to DME Eq. (3):



When methanol synthesis and dehydration reactions take place, water gas shift reaction (WGS) Eq. (4) can also occur simultaneously. Relative amount of CO<sub>2</sub> in syngas detects the extent of reverse water gas shift reaction (rWGS).



The direct synthesis of DME from syngas obtain two overall reactions which are Eq. (5) and (6): Eq. (5) considering water-gas shift reaction and Eq. (6) without it.



The direct DME synthesis process provides a simple reactor design that results in a higher CO conversion and lower DME production costs compared to DME production via methanol dehydration process [2].

### Cu-Based Catalysts for Methanol Synthesis

Cu-based catalysts are widely used in methanol synthesis. Researchers have focused on improving the distribution and surface area of Cu and adding different metallic promoters to improve catalyst stability [19]. The methanol synthesis catalyst as metallic function is commonly composed of Cu, Zn, Zr, Cr, Al and sometimes Ti, Mg, Ce, Co, Ga, Mn or other metal. Generally, the methanol synthesis catalysts are prepared by co-precipitation from an aqueous solution of a mixture of metal salts [8, 19].

Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> (CZA) is a typical example of methanol synthesis catalyst, which is generally consisted of 50–70 mol% of CuO, 20–50 mol% of ZnO and 5–20 mol% Al<sub>2</sub>O<sub>3</sub> [11]. Especially Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst has been investigated by many researchers and showed the best results. Active methanol synthesis catalysts have been to increase methanol production and DME yield. Cu-Zn-Al oxide-based metallic catalysts are generally prepared via traditional co-precipitation method for the formation of a hydrotalcite-like precursor [20].

The metallic Cu clusters in Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> constitute the active sites for WSG reactions and methanol synthesis. Metal surface area and Cu distribution affect conversion and selectivity [11]. The role of ZnO is to provide an optimal distribution of metallic Cu, geometric space between Cu nanoparticles, and to prevent sintering of Cu particles as well as to reduce poisoning. Al<sub>2</sub>O<sub>3</sub> in the structure of the catalyst also increases the surface area. The usage of alumina in the Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst is disadvantageous due to the water formed in the synthesis of methanol by CO<sub>2</sub> hydrogenation and because of the strong hydrophilicity of the Al<sub>2</sub>O<sub>3</sub>. To solve this problem, the promoters such as ZrO<sub>2</sub> with lower hydrophilic properties have been developed [11], and so ZrO<sub>2</sub> supports the hydrothermal stability of active sites of CuO-ZnO in the reaction medium containing water. Furthermore, the core shell structure catalysts are suitable for alleviating Cu metal sintering, since the adsorption of water on metallic sites of the catalyst is not desired [20].

Al<sub>2</sub>O<sub>3</sub> is also known to be useful for accelerating the activation and adsorption of CO and inhibiting the sintering of the metal particles, but also increases the stability of the catalyst [21]. The aim of adding M<sup>3+</sup> (e.g. Al<sup>3+</sup>) ions into CuO-ZnO-based catalysts is to enhance both the copper distribution and the surface area, as well as to increase the thermal and chemical stability of the catalyst [2,11].

In the study of Yang et al., although Cu/ZnO catalyst showed better activity at lower temperatures (<523 K) than Zr doped Cu/ZnO catalyst in CO hydrogenation, the Zr-Cu/ZnO catalyst is more active in CO<sub>2</sub> hydrogenation, and the methanol selectivity reached 60.45% at

523 K. In addition, the Zr-Cu/ZnO catalyst showed high activity and selectivity in the hydrogenation of the mixture of CO and CO<sub>2</sub>, and conversion values reached 28% and 55% at 523 K, respectively [22].

Nowadays, the main interests of researchers are catalytic synthesis of methanol and DME by CO<sub>2</sub> hydrogenation [21]. However, the low performance of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> has restricted the effective conversion of hydrogenation of CO<sub>2</sub> to methanol. In addition, CO<sub>2</sub> hydrogenation was suppressed by the strong hydrophilic character of Al<sub>2</sub>O<sub>3</sub> compared to Cu/ZnO/ZrO<sub>2</sub> [23]. In DME synthesis by CO<sub>2</sub> hydrogenation, the metallic function of bifunctional catalysts for methanol synthesis is usually containing Cu/ZrO<sub>2</sub> catalyst instead of common Cu/ZnO [2,23,24].

Wang et al. prepared CuO-ZnO-ZrO<sub>2</sub>-MxOy (CZZM, M=Cr, Mo and W) catalysts by co-precipitation method for CO<sub>2</sub> hydrogenation to MeOH. The results showed that methanol yield and selectivity with CuO-ZnO-ZrO<sub>2</sub> catalyst were increased by the addition of WO<sub>3</sub> and MoO<sub>3</sub>, however slightly reduced with Cr<sub>2</sub>O<sub>3</sub> doping. The difference in methanol yield was correlated with CO<sub>2</sub> adsorption capacities and BET surface areas of catalysts. In addition, methanol selectivity was associated with the ratio of surface contents of Cu and Zn [25].

Guil-López et al. has modified Cu/ZnO methanol synthesis catalyst by the co-modification with Al and Ga (Al+Ga=3% atom). The methanol synthesis carried out at 250 °C and total pressure of 3.0 MPa in a flow reactor using syngas mixture (CO<sub>2</sub>/CO/H<sub>2</sub>/N<sub>2</sub>:4.5/22/58.8/14.7 vol%). The CZ-Al-x-Ga-y catalysts have shown a stable behaviour unlike CZ and higher syngas conversion was achieved compared to CZ. In this regard, Al or Ga monosubstituted catalysts have indicated similar methanol productivity, while Al and Ga co-substituted catalysts has indicated higher production rates [26].

Meshkini et al. prepared Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts by co-precipitation method and modified by adding Mn, Mg, Zr, Cr, Ba, W and Ce oxides to the structure of catalyst. The catalytic activity for CO/CO<sub>2</sub> hydrogenation to methanol was determined at 513 K and 5.0 MPa with of CO/CO<sub>2</sub>/H<sub>2</sub>:1/1/14.5 syngas composition. Mn and Zr supported methanol synthesis catalysts were found to exhibit the most activity. Mn and Zr increased the distribution of Cu particles on the surface and made the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst more stable [27].

Ren et al. prepared by impregnation of Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts modified with ZnO, ZrO<sub>2</sub> and MgO. The results showed that small Cu<sup>0</sup> particles had good dispersion and improved the performance of the catalyst through modification with promoters. It has been showed that a higher reaction temperature on Cu-ZnO-ZrO<sub>2</sub>-MgO/Al<sub>2</sub>O<sub>3</sub> will prevent MeOH synthesis but increase reverse water-gas shift and methanation reactions [28].

### **Solid Acid Catalysts for Methanol Dehydration**

In the literature,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and zeolite catalysts are mostly used in methanol dehydration reaction. Methanol dehydration catalysts are solid acid catalysts of acidic character, usually having mesoporous (2-50 nm), microporous (<2nm) or micro-mesoporous. The acidity of the catalysts seems to be a very important parameter in DME synthesis. The high surface density of the acid sites and the presence of micropores are responsible for the formation of by-products and poisoning of the catalyst with coke deposition [29].

Microporous channels of zeolites, which have less pores than mesoporous materials are considered to be more sensitive to deactivation because of the coke deposition. In addition, much less diffusion restrictions are expected in such mesoporous catalysts. The high Brønsted

acidity of the catalysts has been reported to generally provide the dehydration activity of alcohols. However, the high acidity of the catalyst can lead to high coke formation, which can rapidly deactivate the catalyst. Reducing the strength of the acid regions is usually considered a possible way to hinder coke deposition [30].

Ferrierite, zeolite-Y, mordenite and zeolites of proton and non-proton form (HZSM-5 and ZSM-5) are among the most common zeolites used as acid function in DME synthesis from methanol [31]. Rutkowska et al. tested a new type of hierarchically structured micro-mesoporous ZSM-5 zeolite catalyst for MeOH to DME. The catalytic performance of ZSM-5 was developed by the formation of mesoporosity using the desilication method (alkaline leaching of framework Si). In addition, micro-mesoporous zeolites were more durable to poisoning by coke deposition than conventional ZSM-5 catalyst [29].

The acidity in the zeolites can be reduced by decreasing the aluminum content in the Si/Al ratio [32,33]. In this context, Hassanpour et al. synthesized ZSM-5 catalysts with different ratios of Si/Al content (Si/Al = 25-250) and tested for conversion of methanol at 300 °C and 16 bar. The acidity of catalysts has improved with increasing Si/Al ratio up to 125 and then declined. H-ZSM-5 with Si/Al ratio of 125 was the most convenient catalyst for methanol synthesis with high DME selectivity. The researchers also found by-product generation diminished (e.g., ethylene, propylene) as Si/Al ratio increased [33].

Catizzone et al. investigated the effect of water on FER zeolites (Si/Al = 10, 25 and 45) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> during the MeOH to DME reaction. The results demonstrated superiority of zeolites in terms of water resistance and acidity efficiency. The methanol conversion in the catalytic test was as follows FER10>FER25> $\gamma$ -Al<sub>2</sub>O<sub>3</sub>>FER45 at higher temperatures and FER10>FER25>FER45> $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for temperature up to 200 °C [34].

Ciftci et al. synthesized STA-SiO<sub>2</sub> mesoporous nanocomposite catalyst for MeOH to DME production. The effects of W/Si atomic ratio were investigated, and the best ratio with methanol conversion above 60% and DME selectivity above 99% was determined as 0.33 at 250°C for space time of 0.27 s.g.cm<sup>-3</sup> [35].

Keshavarz et al. used nanocrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Al-N) catalyst having pore size 3.9 nm prepared by sol-gel method for DME synthesis from methanol. When preparing the Al-N catalyst, the addition of cationic surfactant reduced the crystalline size of the catalyst and enhanced the surface area and medium acid sites, which were suitable for DME synthesis from methanol. Al-N prepared using cationic surfactant showed higher methanol conversion (over 80%) than Al-C without surfactant [36].

Hosseini et al. synthesized DME from methanol over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> having pore size 2.9 nm at 2.0 bar and temperature range from 250 to 400 °C.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared using a co-precipitation method. In this study, there was no significant methanol conversion below 270 °C. The methanol conversion at 300 °C reached 82.0%, but at the temperature up to 350 the conversion remained virtually unchanged. DME selectivity and yield reached 99.9% and 81.9% at 300 °C over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively [37].

Tokay et al. performed activity experiment over mesoporous aluminosilicate catalyst (AlSi<sub>3</sub>) and alumina impregnated SBA-15 (Al@SBA-15) for methanol dehydration. The activity of Al@SBA-15 was higher than AlSi<sub>3</sub>. DME selectivity approached 100% above 300 °C and methanol conversion reached 80% at 350 °C for Al@SBA-15. Al@SBA-15 has been found to have quite strong Lewis and Brønsted acid sites. Al@SBA-15 has been reported to have high Brønsted acidity, which eases the formation of DME [30].



Ciftci et al. mesoporous Nafion–silica nanocomposites developed and tested in methanol to DME synthesis. Although Nafion has high acidic strength, it has low surface area. The developed Nafion-silica catalyst was found to have a well-dispersed structure, high surface area and strong Brønsted acid sites rather than Lewis. The DME selectivity has reached approximately 100% at > 180 °C [38].

Varisli et al. prepared mesoporous aluminosilicate catalysts having Al/Si atomic ratios from 0.03 to 0.18 by the hydrothermal synthesis method and tested in DME synthesis by methanol dehydration. The optimum Al/Si ratio was 0.09 in activity tests. Silicotungstic acid (STA) impregnated aluminasilicate (STAMAS) catalyst were also prepared. STAMAS catalyst showed higher activity with 0.8 methanol conversion and high DME selectivity at temperatures as low as 250 °C [39].

Tang et al. stated that ZSM-5/MCM-41 composite material having both microporous and mesoporous permits higher activity and higher stability than ZSM-5 having only microporous structure. The prepared micro-mesoporous ZSM-5/MCM-41 catalyst showed that the best activity ( $X_{\text{methanol}} > 80\%$ ) having 100% DME selectivity and long lifetime was achieved over in the temperature range from 190 to 300 °C [40].

Rutkowska et al. also indicated that hierarchical ZSM-5 (interconnected micro/mesopores) have a lower coke formation rate than ZSM-5 containing microporous [41]. The hierarchical pore structure in the zeolite composite allows easy access of the reactants to the acid region of the catalyst [42].

Wang et al. hierarchically porous composite zeolite (BFZ, with Beta zeolite cores and Y zeolite polycrystalline shells) employed for methanol dehydration. Direct DME synthesis was performed in the presence of CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> and H-form zeolite catalysts (HBFZ or HY). CZA/HBFZ showed higher stability and activity than CZA/HY. CO conversion and the selectivity of DME achieved 94.2% and 67.9% over CZA/HBFZ under 5.0 MPa, 250°C and 1500 h<sup>-1</sup>[43].

### **Bifunctional/Hybrid Catalysts for Direct DME Synthesis**

The various synthesis methods for bifunctional/hybrid catalysts are available in the literature like impregnation, co-precipitation, precipitating sedimentation, coating, sol–gel and wet chemical methods. Among these, the physical mixing and co-precipitation methods are the most commonly used preparation methods [11,16]. Direct DME synthesis takes place in a single reactor by using bifunctional/hybrid catalysts having metallic (such as CuO, ZrO<sub>2</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub>) and acid function (such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, meso-porous SiO<sub>2</sub>, HZSM-5, HY, SAPOs). Conventionally, bifunctional catalysts are used in powder or pellet form [2,16,19].

According to the catalyst activity and the syngas composition, the reaction conditions of one-step DME synthesis generally vary in the temperature range from 200 to 320 °C and pressures from 20 to 100 bar [8,11,44,45]. In reversible exothermic reactions such as DME synthesis from syngas, the reaction temperature is an important parameter. With increasing temperature in DME synthesis, CO conversion is reduced by thermodynamic limitations of the exothermic reaction and Cu sintering, which triggers loss of catalyst activity [2,15,46]. Ereña et al. indicated that the highest oxygenate product concentration for methanol and DME could be achieved in the range of 250-300°C [12]. Above 300°C, there is dominance of hydrocracking reactions that lead to a decrease in selectivity of DME and catalyst deactivation starts at higher temperatures [2, 12, 48]. Moreover, the literature review indicates that the synergy between active sites for methanol synthesis and dehydration reactions plays a significant role for

catalyst stability and activity [16]. In the literature, there are studies of bifunctional catalysts developed with various combinations of methanol synthesis and dehydration catalysts for DME synthesis.

Bayat et al. carried out direct DME synthesis from syngas ( $\text{CO}/\text{CO}_2/\text{H}_2$  in different compositions) using bifunctional catalyst mixtures. Silicotungstic acid impregnated mesoporous alumina (STA@MA) used as a dehydration catalyst and Cu based commercial used as a methanol synthesis catalyst. It has been shown that the high DME selectivity value obtained 0.9 at 275 °C and 50 bar with  $\text{CO}/\text{CO}_2$ :4/1 feed stream containing. The highest value for DME yield reached about 0.55 with  $\text{H}_2/\text{CO}/\text{CO}_2$ :50/10/40 syngas composition. The further increase in the  $\text{CO}_2/\text{CO}$  ratio in the feed stream caused a decrease in DME selectivity as it activated the reverse water gas shift reaction, which resulted in the formation of large amounts of  $\text{H}_2\text{O}$  [48].

Celik et al. synthesized DME from syngas containing different amounts of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$  by using a bi-functional catalyst mixture. The results indicated that DME selectivity of nearly 85.0% was achieved in the presence of a 10%  $\text{CO}_2$  in the temperature range of 250-275 °C at 50 bar over mixed silicotungstic acid (STA) incorporated mesoporous [TRC-75(L)] and a commercial Cu–Zn based catalysts. STA which is one of the HPAs, has been strengthened the Brønsted acid sites of [TRC-75(L)]. HPAs are highly attractive solid acid catalysts that exhibit activity in alcohol dehydration reactions. Since the surface area of HPAs is very low ( $< 1\text{m}^2/\text{g}$ ), they have been incorporated into mesoporous dehydration catalyst [49].

Peláez et al. developed deactivation model for direct DME synthesis from syngas over mixed  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$  catalysts in different ratios. The experimental trials showed that the sudden decrease in activity is reversible and dependent on temperature. Therefore, it is assumed that water results from adsorption on the catalyst. In the stability studies at 250 °C, there was a sudden decrease in conversion due to adsorption of water in the catalyst. When the temperature is increased, water desorbs and hence the conversion increases. The optimum operating temperature is 270°C. It has not been studied due to the deactivation of copper and coke formation at higher temperatures [13].

Song et al. synthesized Cu–ZnO– $\text{Al}_2\text{O}_3$ – $\text{ZrO}_2$  (CZAZ) catalysts with different ratios of Zr by a co-precipitation method as methanol synthesis catalyst and then physically mixed with  $\gamma\text{-Al}_2\text{O}_3$  dehydration catalyst. Zirconia has been investigated as an effective promoter in methanol synthesis catalysts for  $\text{CO}$  and  $\text{CO}_2$  hydrogenation.  $\text{CO}$  conversion, DME selectivity and space time yield reached 79.3 (mol%), 85.8 (C-mol%) and 5.08 mol/L/h at 270 °C and 5 MPa for syngas ( $\text{H}_2/\text{CO}/\text{CO}_2/\text{CH}_4=52/24/23/1$ ) to DME synthesis. The  $\text{CO}$  conversion first increased and then decreased, while the Zr content increased between 0 and 10 mol%. Among the Zr loading methanol synthesis catalysts, the highest surface area of about 123  $\text{m}^2/\text{g}$  was seen in the 3 mol% Zr loading catalyst. The highest  $\text{CO}$  conversion of 79.3% was achieved with CZAZ(3)/A, whereas the lowest  $\text{CO}$  conversion of 67.8% was achieved with CZAZ(10)/A [50].

Hua et al. prepared CuO–ZnO– $\text{MO}_x$  (M =Zr, Al, Cr, Ti) catalysts by co-precipitation method and mixed physically with HZSM-5 for direct DME synthesis. The catalytic activity decreases  $\text{CZZ}/\text{HZSM-5} > \text{CZA}/\text{HZSM-5} > \text{CZC}/\text{HZSM-5} > \text{CZT}/\text{HZSM-5}$ , respectively.  $\text{CO}$  conversion 55.2%, DME yield 33.9% and DME selectivity 61.4% was achieved over CZZ/HZSM-5 at 250 °C, 3.0 MPa for syngas of  $\text{H}_2/\text{CO}/\text{CO}_2/\text{N}_2=36/36/18/10$  (molar %). It was observed that large amount of  $\text{CO}_2$  was produced with the formation of hydrogen through the WGS reaction [51].

Cai et al. investigated the effect of hybrid catalyst having a wide variety of zeolite particle sizes on the production of syngas to DME at 260 °C, 20 bar and H<sub>2</sub>/CO:2/1. CO conversion decreases CZA-ZSM-5@95 > CZA-ZSM-5@110 > CZA-ZSM-5@80 > CZA-ZSM-5@65 > CZA-ZSM-5@500 > CZA-ZSM-5@800, respectively. ZSM-5@500 and ZSM-5@800 zeolites indicated lower CO conversion. Hybrid catalysts containing smaller zeolite crystallites showed higher CO conversion and higher DME productivity [44].

Bonura et al. evaluated the catalytic behavior of CuZnZr-FER hybrid catalyst, ferrierite samples of different acidity and grain size in the CO<sub>2</sub>-DME hydrogenation reaction at 220–260 °C and 3.0 MPa. The decay in the CO<sub>2</sub> conversion curves is related to the sintering of the metal on the copper particles by adsorbing the water released during the reaction. The size of ferrierite particles plays an important role in the interaction of active sites responsible for CO<sub>2</sub> activation and dehydration of MeOH to DME and on catalytic behavior [52].

Xu et al. investigated the effect of bifunctional catalyst containing commercial JC207 (CuO-ZnO/Al<sub>2</sub>O<sub>3</sub>) for methanol synthesis and HZSM-5 for methanol dehydration on direct DME synthesis. HZSM-5 catalyst was used at different Si/Al ratios (Si/Al = 25, 38, 50, 150). JC207/HZSM-5 [Si/Al=38] bifunctional catalyst indicated the best performance at 3.0 MPa and 250-270°C [53].

Asthana et al. performed direct DME synthesis from syngas (CO/H<sub>2</sub>) in the presence of Cu-based methanol synthesis catalyst containing different proportions of ZnO and MgO, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> methanol dehydration catalyst. The maximum effectiveness has achieved with 37% CO conversion and 83% DME selectivity over CZM (20)- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> hybrid catalyst containing 20% MgO [54]. Mao et al. revealed that MgO helps to neutralize the stronger acid sites to weaker sites. The strong acidic sites are informed to increase degradation of DME into lower hydrocarbons [55].

Recently; the advantages of the catalysts used in the core shell-like structure for DME synthesis have been investigated. Core-shell catalysts contain methanol synthesis catalyst in the core and methanol dehydration catalyst in the shell. The methanol formed in the core diffuses outwards and turns into DME in the shell. Core-shell structured bifunctional catalysts have been developed and it is aimed to reduce thermodynamic limitations by performing different reactions in different regions of these catalysts. The addition of both functions into the same catalyst particle structure relieves the synergy of reactions catalyzed by each function [19]. In the literature, core-shell catalysts having different compositions such as Cr/ZnO-SAPO-46 [56], CuO-ZnO@HZSM-5 [57], Cr-ZnO-S-H-ZSM-5 [58], H-ZSM-5/Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> [59], CuO-ZnO-Al<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [45] and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/SAPO11 [60] have been studied for DME synthesis.

Wang et al. have investigated the effect of CuO-ZnO-Al<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> core-shell catalyst and physically mixed hybrid catalyst on DME selectivity and CO conversion. This core-shell catalyst indicated excellent performance in a fixed bed reactor at 5.0 MPa, 260 °C, and 1500 mL/(h.gcat). DME selectivity and CO conversion were 28.3% and 51.6% over core shell catalyst, while were 71.1% and 61.9% over physically mixed catalyst [45].

Phienluphon et al. compared the catalytic activity of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/SAPO11 prepared by physical coating (core-shell structure) and mixing methods in a fixed bed reactor at 250 °C and 5.0 MPa. The syngas composition was H<sub>2</sub>/CO/CO<sub>2</sub>/Ar:58.10/33.80/5.10/3.09. Core-shell capsule Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/SAPO11 was more active catalyst in terms of CO conversion (92.0% vs 64.9%), DME selectivity (90.3% vs 46.6% C-mol) and DME yield (83.1% vs 30.2%) [60].



Liu et al. prepared HZSM-5 membrane packed CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst for CO<sub>2</sub> hydrogenation to DME. CO<sub>2</sub> conversion, DME selectivity and yield reached 48.3%, 48.5% and 23.4% at 3.0 MPa, 270 °C and volume ratio of CO<sub>2</sub>/H<sub>2</sub> to 1:3 [46].

Yang et al. synthesized double-shell capsule Cr/ZnO–S–Z catalyst for DME production from syngas (Ar/CO/CO<sub>2</sub>/H<sub>2</sub>:3.02/32.6/56/59.22 mol%) at 5.0 MPa and 573-623 K. Cr/ZnO–S–Z core-shell catalyst was prepared by dual-layer method. Silicate-1 zeolite (S) was initially synthesized on the Cr/ZnO catalyst as an intermediate layer, and then H-ZSM-5 (Si/Al = 50) zeolite (Z) shell was formed on the surface. The selectivity of DME improved from 45.42% to 50.84% with the reaction temperature rising from 573 K to 623 K, while the selectivity of methanol reduced [58].

## DISCUSSION

DME is synthesized from syngas obtained from different sources such as biomass, waste, coal, natural gas and various greenhouse gases. DME synthesis can be performed by two methods; one is direct synthesis method and the other is indirect synthesis method. In the indirect synthesis method, the methanol synthesis reaction has thermodynamic limitations which decrease the conversion of the syngas. In the direct synthesis method, methanol synthesis and dehydration reactions are carried out simultaneously in the presence of bifunctional/hybrid catalysts in a single reactor. The using bifunctional/hybrid catalysts have both metallic function for methanol synthesis and solid acid function for methanol dehydration. Catalysts are generally used for DME synthesis in powder form or in pellet form to prevent pressure drop. Indeed, each catalyst particle will act as an individual DME synthesis reactor for both reactions. So, the direct DME synthesis method allows for higher syngas conversion by alleviating thermodynamic limitations, and the process results in lower DME production costs compared to methanol dehydration.

A summary of the studies conducted on direct DME synthesis, the applied catalysts and operating conditions are given in Table 2. From the table, it can be concluded that most of the studies are generally carried out at a temperature range of 200-300 °C and pressures up to 80 bars, mostly between 30-50 Bars. The effect of the reaction parameters used in the activity tests of the related catalysts used for DME synthesis on syngas conversion, DME yield and selectivity were also reviewed the mentioned table.

Recently, the development of core-shell structured catalysts as a bifunctional catalyst for DME synthesis has been on the agenda. Since sequential reactions take place in the same structure of the catalyst particle, this eliminate individual equilibrium limitation from the intermediate (methanol) formation, by reducing total thermodynamic limitations. In addition, it has been mentioned that H<sub>2</sub>O generated in the dehydration reaction will not influence the formation of methanol on the metallic function of the core-shell catalyst [11]. The present studies emphasize the importance of core-shell structure catalyst due to the greater availability of acid sites in the shell for the higher conversion of methanol to DME. Methanol that is synthesized within the core and expanding to the shell of the catalyst particle continuously converted to DME [19] and so, the methanol synthesis equilibrium reaction shifts towards the right side as this reaction irreversible-one-way reaction. These properties of the core shell structure make it more attractive for two step equilibrium reactions compared to other forms including hybrid catalysts structures.

In Cu-based methanol synthesis catalyst, particle size of copper and optimal distribution of metallic copper particles is an important parameter for catalyst activity. Oxides such as Zn, Zr, Mg, Ga, Al etc. are incorporated to the catalyst for this purpose as well as to increase the thermal stability and surface area of the Cu-based catalyst. Solid acid catalysts, mainly  $\text{Al}_2\text{O}_3$  and zeolites, are used in methanol dehydration to selectively synthesize DME. The methanol dehydration reaction is thought to be catalyzed by weak or moderate acid sites as Brønsted and Lewis [16]. However, the high acidity of the catalyst can lead to high coke formation, which can rapidly deactivate the catalyst by Cu sintering [30]. Most of the researchers also claim that strong acid sites are responsible for the generation of hydrocarbons [33].

Water molecules formed in methanol dehydration and  $\text{CO}_2$  hydrogenation are adsorbed on the Lewis sites of the  $\gamma\text{-Al}_2\text{O}_3$  catalyst used, due to the strong hydrophilicity of the alumina. To overcome this disadvantage different zeolites and SAPOs (as SAPO-18) are used, and their strong acidity must be limited to minimize hydrocarbon formation when preparing these catalysts. In contrast, the adsorption effect of water is much less important for H-ZSM5 due to its more hydrophobic property and the superiority of Brønsted type acidity [10, 19, 51, 63].

The slender and narrow microporous structure of the zeolites may prevent DME from rapidly diffusing through the pores [2]. As a result, zeolites may rapidly lose their catalytic activity and selectivity due to the formation of by-products and the accumulation of carbonaceous compounds [2]. In general, zeolites have a higher surface area from microporous crystal interfaces when compared to other catalysts. The main strategies for overcoming these disadvantages and increasing the transport of molecules in microporous crystals are to shorten the length of the microporous channels of the zeolite or to increase its pore diameter. Furthermore, it can be also achieved by reducing the crystal size of zeolites or by adding pore system such as meso into the individual zeolite crystal [42].

**Table 2.** Effect of different bifunctional/hybrid catalyst and reaction parameters on DME synthesis

Catalysts	Reactor Type*	Temperature °C	Pressure MPa	Feed Composition, Space Velocity, Space Time	Conversion (X), Yield(Y), Selectivity (S)	Authors
CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> with NH <sub>4</sub> ZSM-5, HZSM-5 or $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Fixed Bed Reactor	200-260	2	H <sub>2</sub> /CO/CO <sub>2</sub> /Ar=62/31/4/3 SV= 2400 mL gcat <sup>-1</sup> h <sup>-1</sup>	Y <sub>DME</sub> =100%	Abu-Dahrieh et al. [7]
CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> (CZA)/SAPO-18 CuO-ZnO-ZrO <sub>2</sub> (CZZr)/SAPO-18 CuO-ZnO-MnO(CZMn)/SAPO-18	Fixed-bed isothermal reactor system	275	3	CO <sub>2</sub> /CO=0-1 and H <sub>2</sub> /CO <sub>x</sub> =3-4 Space time=10.18 gcat h (mol <sub>C</sub> ) <sup>-1</sup>	S <sub>DME</sub> ≈90% Y <sub>DME</sub> ≈25%	Ateka et al. 2016 [10]
Cu-ZnO-Al <sub>2</sub> O <sub>3</sub> /ZSM5	Tube Reactor	175-250	4	H <sub>2</sub> /CO/CO <sub>2</sub> /N <sub>2</sub> = 61/30/5/4 0.2 g of ZSM5 cat SV=15000 mL gcat <sup>-1</sup> h <sup>-1</sup>	Y <sub>DME</sub> =1.89 g (gcat h) <sup>-1</sup> S <sub>DME</sub> = 90%	Chen et al. [15]
Hybrid (CuO-ZnO-ZrO <sub>2</sub> /S-11) Core-shell (CuO-ZnO-ZrO <sub>2</sub> @S-11)	Fixed Bed Reactor	275	3	CO <sub>2</sub> /CO <sub>x</sub> = 0.5 H <sub>2</sub> /CO <sub>x</sub> = 3 Space time= 7.60 gcat h mol <sub>C</sub> <sup>-1</sup>	X <sub>CO<sub>x</sub></sub> ≈ 11-8.6% Y <sub>DME</sub> = 8.7-6.8%	Sanchez et al. [19]
CZA/Zr-HFer	Tubular fixed-bed reactor	250	5	H <sub>2</sub> /CO=2/1 Total flow 24 mL min <sup>-1</sup>	X <sub>CO</sub> = 37.6% S <sub>DME</sub> ≈65%	Flores et al. [20]
CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> /HZSM-5	Fixed Bed Reactor	260	2	H <sub>2</sub> /CO= 2/1 GHSV = 3600-14400 mL/gcat h	X <sub>CO</sub> = 82.2% S <sub>DME</sub> = 71.4%	Cai et al. [44]
Core-shell structure catalyst CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Fixed Bed Reactor	220-320	2-6	H <sub>2</sub> /CO= 2/1 GHSV = 1000-4000 mL/(h gcat)	X <sub>CO</sub> =71.1% (mol) S <sub>DME</sub> = 61.9% (mol)	Wang et al. [45]
CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> /NaHZSM-5	Fixed Bed Reactor	275	4	H <sub>2</sub> /CO= 2/1 space time 67 (gcat) h/mol H <sub>2</sub> /CO <sub>2</sub> = 3/1 space time= 67 (gcat) h/mol	Y <sub>DME</sub> = 78 % S <sub>DME</sub> = 80 % X <sub>CO<sub>2</sub></sub> =35 % S <sub>DME</sub> =75%	Ereña et al. [47]
Cu based MSC + STA@MA	Fixed Bed Reactor	180-300	5	H <sub>2</sub> /CO/CO <sub>2</sub> : 50/10/40 Space time: 0.48 s gcat /mL	X <sub>CO<sub>2</sub>+CO</sub> = 70% S <sub>DME</sub> = 80%	Bayat et al. [48]
Cu-ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> and $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Fixed Bed Reactor	270	5	H <sub>2</sub> /CO/CO <sub>2</sub> /CH <sub>4</sub> : 52/24/23/1 GHSV = 1500 h <sup>-1</sup>	X <sub>CO</sub> = 79.3 % (mol) X <sub>CO<sub>2</sub></sub> = 5.37 % (mol) S <sub>DME</sub> = 85.8 % (C-mol)	Song et al. [50]

Catalysts	Reactor Type*	Temperature °C	Pressure MPa	Feed Composition, Space Velocity, Space Time	Conversion (X), Yield(Y), Selectivity (S)	Authors
CuO-ZnO-MOx (M = Zr, Al, Cr, Ti)/HZSM-5 hybrid catalyst	Fixed Bed Reactor	180-270	3	H <sub>2</sub> /CO/CO <sub>2</sub> /N <sub>2</sub> = 36/36/18/10 GHSV = 4800 h <sup>-1</sup>	X <sub>CO</sub> =55.2% Y <sub>DME</sub> =33.9% S <sub>DME</sub> =61.4%	Hua et al. [51]
JC207/HZSM-5 [Si/Al]= 25, 38, 50, 150]	Fixed Bed Reactor	250-290	3	H <sub>2</sub> /N <sub>2</sub> /CO/CH <sub>4</sub> /CO <sub>2</sub> = 42.1/13.4/33.9/5.0/5.6 SV = 1300 L/(kg.h)	X <sub>CO</sub> ≈ 77% S <sub>DME</sub> ≈ 76%	Xu et al. [53]
JC207 (CuO-ZnO- Al <sub>2</sub> O <sub>3</sub> )	Fixed-bed tubular reactor	240-260	3-5	H <sub>2</sub> /CO=1-3 Space Velocity (WHSV)=2000-4000 mL/gcat h	X <sub>CO</sub> =37% S <sub>DME</sub> = 83%	Asthana et al. [54]
Core-shell structure catalyst Cr/ZnO@SAPO-46	Fixed Bed Reactor	350	5	H <sub>2</sub> /CO/CO <sub>2</sub> /Ar=58.10/33.80/5.10/3.09 W <sub>Cu/ZnO</sub> /F <sub>Syngas</sub> = 10 g mol/h	X <sub>CO</sub> =6.9% S <sub>DME</sub> = 37%	Pinkaew et al. [56]
Double shell capsule catalyst Cr/ZnO-S-Z (S=Neutral Silicate-1 zeolite layer; Z=HZSM-5 layer)	Fixed Bed Reactor	300-350	5	Ar/CO/CO <sub>2</sub> /H <sub>2</sub> =3.02/32.6/5.16/59.22 W <sub>Cu/ZnO</sub> /F <sub>Syngas</sub> = 13.6 g h mol <sup>-1</sup>	S <sub>DME</sub> = 50.84%	Yang et al. [58]
Core (Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> ) – shell (SAPO-11) zeolite capsule	Fixed Bed Reactor	250	5	H <sub>2</sub> /CO/CO <sub>2</sub> /Ar=58.10/33.80/5.10/3.09 W <sub>Cu/ZnO</sub> /F <sub>Syngas</sub> = 10 g. mol/h	Y <sub>DME</sub> = 83.1% X <sub>CO</sub> = 92% S <sub>DME</sub> =90.3% (C-mol)	Phienluphon et al. [60]
Cu-ZnO-ZrO <sub>2</sub> /Al-modified H-mordenite	Three-phase slurry reactor	220-270	2.5-5	H <sub>2</sub> /CO=2/1 Feed rate= 100-400 mL/min	S <sub>DME</sub> = 82% X <sub>CO</sub> = 68%	Khandan et al. [61]
CuO-ZnO-MnO/ SAPO-18	Fixed Bed Reactor	250-325	3	H <sub>2</sub> :CO <sub>x</sub> =3; CO <sub>2</sub> :CO <sub>x</sub> = 0-0.5 Space time= 5.02 gcat. h mol <sub>c</sub> <sup>-1</sup>	Y <sub>DME</sub> = 21% S <sub>DME</sub> = 94%	Ateka et al. [62]
Cu-ZnO-Al <sub>2</sub> O <sub>3</sub> /Zr-Ferrierite	Fixed Bed Reactor	250	4	CO/CO <sub>2</sub> /H <sub>2</sub> =41/21/38 SV=5500 L/(kgcat h)	X <sub>CO</sub> = 49% (mol) S <sub>DME</sub> = 58.2% (mol)	Bae et al. [63]
Cu-ZnO-ZrO <sub>2</sub> /H-ZSM5	Fixed Bed Reactor	200-240	3	CO <sub>2</sub> /H <sub>2</sub> /N <sub>2</sub> =3/9/1 SV= 10000 h <sup>-1</sup>	Y <sub>DME</sub> =0.225 kg <sub>DME</sub> /kgcat/h	Frusteri et al. [64]
Cu-ZnO colloidal catalysts + γ-Al <sub>2</sub> O <sub>3</sub>	Autoclave reactor (Parr)	260	5	H <sub>2</sub> /CO/CO <sub>2</sub> =70/24/6 SV=7.4 Lsyngas/g <sub>CuZn</sub> /h	X <sub>CO</sub> =56% S <sub>DME</sub> = 65% (C %)	García-Trenco et al. [65]

Catalysts	Reactor Type*	Temperature °C	Pressure MPa	Feed Composition, Space Velocity, Space Time	Conversion (X), Yield(Y), Selectivity (S)	Authors
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> & HZSM-5 (modified with MgO, CaO, BaO)	Fixed Bed Reactor	260	4	H <sub>2</sub> /CO/CO <sub>2</sub> /N <sub>2</sub> : 59.93/27.33/4.12/8.62 GHSV = 1500 mL h <sup>-1</sup> g <sup>-1</sup>	X <sub>CO</sub> = 93.8% (C-mol) S <sub>DME</sub> = 64.4% (C-mol)	Mao et al. [66]
CuZnZr-FER hybrid catalyst	Fixed Bed Reactor	220-260	5	CO <sub>2</sub> /H <sub>2</sub> /N <sub>2</sub> : 3/9/1 GHSV: 8800 NL/kgcat/h	X <sub>CO2</sub> = 23.6 % S <sub>DME</sub> = 47.0 %	Bonura et al. [67]
Pd-modified CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /HZSM-5	Fixed Bed Reactor	200	3	H <sub>2</sub> /CO <sub>2</sub> = 3.3/1 (v/v) GHSV = 1800 h <sup>-1</sup>	X <sub>CO2</sub> = 18.67% (C-mol) S <sub>DME</sub> = 73.56% (C-mol)	Sun et al. [68]
Cu/Zn/Al/HZSM-5	Pilot scale plant-fixed bed tubular	200-230	4-4.2	H <sub>2</sub> /N <sub>2</sub> /CO/CH <sub>4</sub> /CO <sub>2</sub> /C <sub>2</sub> .3 = 26-28/16-21/26-31/3-4/19-24/<0.7 GHSV = 1000 h <sup>-1</sup>	X <sub>CO</sub> = 61.4-71 % Y <sub>DME</sub> = 90.4-155kg m <sub>cat</sub> <sup>-3</sup> h <sup>-1</sup>	Yuping et al. [69]
Cu-Zn-Al/γ-Al <sub>2</sub> O <sub>3</sub>	Multitubular fixed bed reactor	220-260	2.2-2.5	GHSV = 1000-1400 h <sup>-1</sup>	X <sub>CO</sub> = 45%	Wang et al. [70]
CuO/ZnO/ Al <sub>2</sub> O <sub>3</sub> -HZSM-5	Fluidized bed reactor	260	3	H <sub>2</sub> /CO = 1/1 (v/v) GHSV = 3000 mL/ (g. h)	X <sub>CO</sub> = 66.8 % S <sub>DME</sub> = 46.2 %	Teng et al. [71]
Cu-Zn-Al-M/γ-Al <sub>2</sub> O <sub>3</sub> (M=Ga, La, Y, Zr)	Fixed Bed Reactor	250-280	4.13	H <sub>2</sub> /CO = 1.5/1 GHSV = 6000-12000 h <sup>-1</sup>	Y <sub>DME</sub> = 47.7%	Venugopal et al. [72]
CuO/ZnO/Al <sub>2</sub> O <sub>3</sub> + HZSM-5	Slurry phase autoclave reactor	240	3.5	H <sub>2</sub> /CO = 1-2 SV = 500-1300 mLn/ (g-cat·h)	X <sub>CO</sub> = 89.1 % Y <sub>DME</sub> = 50.4% S <sub>DME</sub> = 57.6 %	Moradi et al. [73]
CuO-Fe <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /HZSM-5	Fixed Bed Reactor	240-280	2-3.5	H <sub>2</sub> /CO <sub>2</sub> = 5/1 (mol ratio) GHSV = 1500-3000 mL.gcat <sup>-1</sup> .h <sup>-1</sup>	X <sub>CO2</sub> = 28.4% S <sub>DME</sub> = 64.5%	Liu et al. [74]
CuO-ZnO-ZrO <sub>2</sub> /HZSM-5	Fixed Bed Reactor	250	3	CO <sub>2</sub> /H <sub>2</sub> /N <sub>2</sub> = 22/66/12 CO <sub>2</sub> /H <sub>2</sub> = 1/3 (v/v) GHSV = 3600 mL g <sup>-1</sup> h <sup>-1</sup>	X <sub>CO2</sub> = 22.2% S <sub>DME</sub> = 67.6% Y <sub>DME</sub> = 15%	Li et al. [75]
Cu/ZnO/HZSM-5 sputtering catalyst	Fixed Bed Reactor	250	5	CO/CO <sub>2</sub> /Ar = 32.5/5.2/3.1, balanced with H <sub>2</sub> W <sub>cat</sub> /F <sub>syngas</sub> = 10 g h mol <sup>-1</sup>	X <sub>CO</sub> = 13% (C-mol) S <sub>DME</sub> = 93.5% (C-mol)	Zeng et al. [76]
CuO-TiO <sub>2</sub> -ZrO <sub>2</sub> /HZSM-5	Fixed Bed Reactor	250	3	CO <sub>2</sub> /H <sub>2</sub> /N <sub>2</sub> = 23.3/64.5/12.2 WHSV = 1500 h <sup>-1</sup>	X <sub>CO2</sub> = 15.60 % Y <sub>DME</sub> = 7.41% S <sub>DME</sub> = 47.5 %	Wang et al. [77]



Catalysts	Reactor Type*	Temperature °C	Pressure MPa	Feed Composition, Space Velocity, Space Time	Conversion (X), Yield(Y), Selectivity (S)	Authors
CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub> , ferriite or HZSM-5	Tubular reactor	200-260	4	H <sub>2</sub> /CO/CO <sub>2</sub> /N <sub>2</sub> =48-64/0-32/0-32/4 (vol %) SV=15000 mL (gcat h) <sup>-1</sup> H <sub>2</sub> /CO=1/1 SV=15000 mL (gcat h) <sup>-1</sup>	X <sub>CO</sub> =63% S <sub>DME</sub> =60% Y <sub>DME</sub> =2.12 g (gcat h) <sup>-1</sup> Y <sub>DME</sub> =2.3 g (gcat h) <sup>-1</sup>	Huang et al. [78]
Cu-ZnO-ZrO <sub>2</sub> /H-ZSM5	Fixed Bed Reactor	180-240	3	CO <sub>2</sub> /H <sub>2</sub> /N <sub>2</sub> =3/9/1 GHSV= 10000 NL kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Y <sub>MeOH</sub> =430 gtotal MeOH kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> X <sub>CO<sub>2</sub></sub> =16.1% S <sub>DME</sub> =33.9%	Bonura et al. [79]
Cu-ZnO-ZrO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub> -HZSM-5	Fixed Bed Reactor	220-300	7.5-8	H <sub>2</sub> /CO/N <sub>2</sub> /CO <sub>2</sub> /CH <sub>4</sub> =39.8/14.7/37.2/5.9/2.4 H <sub>2</sub> /CO/N <sub>2</sub> /CO <sub>2</sub> /CH <sub>4</sub> =41/13.4/37.7/5.6/2.3 SV=500-3000 h <sup>-1</sup>	X <sub>CO</sub> =90% S <sub>DME</sub> =80%	Hengyong et al. [80]
CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> /pseudo-boehmite	Fixed Bed Reactor	220-260	4	H <sub>2</sub> /CO/CO <sub>2</sub> (molar ratio) = 1/1/0.08 GHSV=1500 h <sup>-1</sup>	X <sub>CO</sub> =81.51% (C-mol) S <sub>DME</sub> = 67.01% (C-mol) Y <sub>DME</sub> = 54.62% (C-mol) Y <sub>DME</sub> = 42%	Li et al. [81]
Cu/Zn/Al citric/TPA-K10	Fixed Bed Reactor	280-360	4	CO/CO <sub>2</sub> /H <sub>2</sub> =30/5/65 GHSV= 3600 h <sup>-1</sup>	Y <sub>DME</sub> = 42%	Šliwa et al. [82]
CuO-ZnO- Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /HZSM-5 (SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub> =25)	Fixed Bed Reactor	260	3	H <sub>2</sub> /CO <sub>2</sub> =3/1 GHSV= 1600 h <sup>-1</sup>	X <sub>CO<sub>2</sub></sub> =25% S <sub>DME</sub> = 23 %	Zhao et al. [83]
Hybrid CuZnAl/HZSM-5	Fixed Bed Reactor	260	4	90 vol% syngas H <sub>2</sub> /CO/CO <sub>2</sub> = 66/30/4 and 10 vol% Ar GHSV = 1.7 L <sub>syngas</sub> gcat <sup>-1</sup> h <sup>-1</sup>	X <sub>CO</sub> =89.4 % Y <sub>DME</sub> = 56.9 % C S <sub>DME</sub> = 63.7 % C	García-Trenco et al. [84]
Cu-ZnO-Al <sub>2</sub> O <sub>3</sub> /SAPO-18	Fixed Bed Reactor	275	3	H <sub>2</sub> :COx =3 and 4; CO <sub>2</sub> :CO <sub>x</sub> = 0-0.5 Space time= 10.18 gcat h (molc) <sup>-1</sup>	X <sub>CO<sub>2</sub></sub> = 10% S <sub>DME</sub> = 80%	Ateka et al. [85]
C301/HZSM-5 C301/ γ-Al <sub>2</sub> O <sub>3</sub>	Slurry Reactor	230-270	4-8	H <sub>2</sub> /(CO+CO <sub>2</sub> ) = 2/1 GHSV = 3060 mL/gcat . h	X <sub>CO</sub> = 50% Y <sub>DME</sub> = 40%	Wang et al. [86]
Core-shell structure catalyst CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> @Al <sub>2</sub> O <sub>3</sub>	Fixed Bed Reactor	260	5	H <sub>2</sub> /CO=2/1 GHSV= 1500 mL.h <sup>-1</sup> gcat <sup>-1</sup>	X <sub>CO</sub> =35.2% S <sub>DME</sub> = 61.1%	Wang et al. [87]

Catalysts	Reactor Type*	Temperature °C	Pressure MPa	Feed Composition, Space Velocity, Space Time	Conversion (X), Yield(Y), Selectivity (S)	Authors
CuO-ZnO-ZrO <sub>2</sub> @SAPO-11 core-shell (mass ratio of 1/2)	Fixed Bed Reactor	250-325	1-5	CO <sub>2</sub> /COx=0-1 H <sub>2</sub> /COx= 2.5 - 4 Space-time=1.25-15 g h mol <sup>-1</sup> c <sup>-1</sup>	S <sub>DME</sub> ≈72% Y <sub>DME</sub> ≈ 6% X <sub>CO2</sub> ≈23% X <sub>COx</sub> ≈ 8% (For CO <sub>2</sub> /COx=0.75)	Sanchez et al. [88]
Mesoporous Cu/Al <sub>2</sub> O <sub>3</sub>	Fixed Bed Reactor	260-320	5	H <sub>2</sub> /CO=2/1 GHSV= 1500 mL/(h . gcat)	X <sub>co</sub> =52.9% S <sub>DME</sub> = 66.1%	Wang et al. [89]
UiO-66 encapsulating STA	Fixed Bed Reactor	290	3	H <sub>2</sub> /CO/N <sub>2</sub> =2/1/3 GHSV= 3000 mL/gcat . h	X <sub>co</sub> = 2% S <sub>DME</sub> = 68.7%	Li et al. [90]
Cu/Zn/Al slurry catalysts	Slurry Bed Reactor	280	4	H <sub>2</sub> /CO=1/1	X <sub>co</sub> = 54.32% S <sub>DME</sub> = 69.74%	Sun et al. [91]
CeO <sub>2</sub> -CaO-Pd/HZSM-5	Fixed Bed Microreactor	240-300	3-4	H <sub>2</sub> /CO=2 - 3 H <sub>2</sub> +CO/N <sub>2</sub> /H <sub>2</sub> S = 75/24.5/0.5 GHSV= 2000-3000 L kg <sup>-1</sup> h <sup>-1</sup>	X <sub>co</sub> ≈75% S <sub>DME</sub> ≈67%	Chu et al. [92]
Cu-ZnO-ZrO <sub>2</sub> -WO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	Fixed Bed Reactor	260	3	CO <sub>2</sub> /H <sub>2</sub> /N <sub>2</sub> =3/9/1 Flow rate = 65 mL min <sup>-1</sup> 0.3 g of hybrid catalysts	X <sub>CO2</sub> = 18.9% S <sub>DME</sub> = 15.3% Y <sub>DME</sub> = 165.6 g <sub>DME</sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Suwannapichat et al. [93]
CZA/HZSM-5 nanocatalysts	Fixed Bed Reactor	200-300	4	H <sub>2</sub> /CO=2/1 GHSV= 18000-45000 mL/gcat h	X <sub>co</sub> = 32% S <sub>DME</sub> = 82%	Allahyari et al. [94]
CZA-ZrFER(Na) CZA-ZrFER(K) CZA-ZrFER(NH <sub>3</sub> )	Fixed Bed Reactor	250	4	CO/CO <sub>2</sub> /H <sub>2</sub> = 41/21/38 SV= 5500 L/(kgcat h)	X <sub>co</sub> = 59.4% (mol) S <sub>DME</sub> = 62.9% (mol)	Bae et al. [95]
CuO-ZnO-ZrO <sub>2</sub> + WO <sub>x</sub> /ZrO <sub>2</sub>	Fixed Bed Reactor	260	3	CO <sub>2</sub> /H <sub>2</sub> /N <sub>2</sub> =3/9/1 SV= 4333 mL gcat <sup>-1</sup> h <sup>-1</sup>	X <sub>CO2</sub> = 21.5% Y <sub>DME</sub> = 6.88% Y <sub>DME</sub> =271.2 g <sub>DME</sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Witoon et al. [96]
Cu/mesoAl	Fixed Bed Reactor	250	5	H <sub>2</sub> /CO=2/1 SV= 2000 L/(kgcat . h)	X <sub>co</sub> = 9.6% (mol) S <sub>DME</sub> = 78.5% (mol)	Ham et al. [97]

In order to achieve higher syngas conversion, DME selectivity and yield, the direct DME synthesis method is supported by many researchers with the valorization of CO<sub>2</sub> co-feed with syngas [6, 10, 85]. The selectivity and conversion of CO<sub>2</sub> co-feed with syngas to DME is quite higher than direct CO<sub>2</sub> hydrogenation. The increase of CO<sub>2</sub>/CO ratio in the CO<sub>2</sub> co-feed with syngas will reduce the DME selectivity because water is formed by the activation of rWGS reaction [11, 48].

Low conversion of CO in CO<sub>2</sub>-containing syngas at low temperatures (less than 275°C) has been resulted from the competitive adsorption between CO and CO<sub>2</sub> to the metallic functional catalyst used. The reduction in conversion at temperatures above 275°C is associated with thermodynamic limitations due to the exothermic of the reactions and partial loss of activity with Cu sintering. In addition, hydrocracking reactions are favored above 300°C, and DME selectivity decreases [47]. The use of copper catalysts at high temperatures (above 280–300 °C) is known to result in the sintering of copper particles and coke formation [13].

## CONCLUSION

The recent research has emphasized that DME can be utilized as an intermediate to produce biofuel and valuable products (gasoline, aromatics and olefin etc.) [98-101], also used as an individual alternative fuel for diesel engines and power generation in gas turbine [102]. The current studies show that the development of durable, long-lasting and stable catalysts with higher activity for DME synthesis has been continued on lab-scale. The production of DME from syngas via direct synthesis method has attracted attention in the literature and many researches are available. Since the limitation of the current state of the art indirect DME from methanol related reaction, direct DME synthesis studies, including the development of related bifunctional/hybrid catalysts, have accelerated. Active catalyst pairs and bifunctional catalysts that can be scaled up for commercialization with high syngas conversion, DME selectivity and yield in direct DME synthesis are still under investigation. The novel bifunctional/hybrid catalysts continue to be developed for better synergistic effect with different combinations of metallic and acidic functions to catalyze DME synthesis reactions. The optimization of catalyst structures and creation of kinetic models through density functional theory (DFT) is essential for understanding the mechanism of DME synthesis reactions and this supports the production of efficient DME. The direct synthesis method in the presence of bifunctional/hybrid catalysts which have two active functions is thermodynamically more favorable than indirect synthesis since syngas to methanol and methanol to DME reactions are simultaneously synthesized in the single reactor. Mainly Cu-based bimetallic or multimetallic catalysts are used for the synthesis of methanol, while solid acid catalysts such as Al<sub>2</sub>O<sub>3</sub>, HZSM-5, SAPOs and SiO<sub>2</sub> are often used for methanol dehydration. In preparing bifunctional catalysts, physical mixing and co-precipitation are commonly used preparation methods, as well as preparation methods like impregnation, precipitating sedimentation, sol-gel, coating and wet chemical. In addition to determining the optimum experimental parameters in direct DME production, the aim is to optimize the components of different metallic and acidic functions in the preparation of active bifunctional catalysts and to provide synergies between them for higher catalytic activity [16, 24].

### Nomenclature:

DME	Dimethyl ether
MeOH	Methanol

CZA	CuO-ZnO-Al <sub>2</sub> O <sub>3</sub>
CZZ	CuO-ZnO-ZrO <sub>2</sub>
CZC	CuO-ZnO-Cr <sub>2</sub> O <sub>3</sub>
CZT	CuO-ZnO-TiO <sub>2</sub>
CZAZ	CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> -ZnO
GHSV	Gas Hourly Space Velocity
WHSV	Weight Hourly Space Velocity
SV	Space Velocity
W/F	Weight of Catalyst/ Feed Flow of Syngas

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