



Study of catalyst bed composition for the direct synthesis of dimethyl ether from CO₂-rich syngas

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ABSTRACT

In this work, we study the direct synthesis of DME using CO₂-rich syngas, with a CO₂/CO ratio similar to that obtained from the gasification of biomass, *i.e.*, 1.9. We used catalytic beds consisting of physical mixtures of the benchmark catalysts used for the synthesis of methanol from syngas and for methanol dehydration to DME, namely Cu/ZnO/Al₂O₃ and γ -Al₂O₃, respectively. Our results show that the ratio between each catalytic phase determines the productivity and selectivity to DME, as well CO and CO₂ conversions. Thus, higher total carbon conversions were obtained with the catalytic bed with the highest content of the Cu/Zn/Al₂O₃ phase. The presence of γ -Al₂O₃ allows to exceed the equilibrium conversion of CO for the syngas to methanol synthesis. The highest DME productivity is obtained with the catalytic bed containing equal amounts of both catalytic phases. In addition, we also show that other reaction variables such as temperature, pressure, and contact time also play an important role in terms of DME productivity. The presence of a high fraction of CO₂ in the syngas results in a high production of H₂O, which after long times on stream result in the deactivation of the Cu/ZnO/Al₂O₃ catalytic phase due to the sintering of the copper particles. The *in situ* removal of H₂O via the addition of an H₂O sorbent, zeolite 3A, into the catalytic bed, results in a significant enhancement of both carbon conversion and DME productivity.

1. Introduction

Dimethyl ether (DME) can be obtained from different feedstocks, including coal and natural gas. More interestingly, DME can be also obtained from organic municipal waste and/or biomass-derived syngas therefore qualifying as a second-generation biofuel. DME is regarded as an alternative clean fuel for several energy sectors, and, for instance, due to their similar physicochemical properties, DME and liquefied petroleum gas (LPG) can be blended in the gas grid and used as cooking or heating gas [1]. DME has a similar cetane number to diesel but cleaner burning properties, lowering emissions of various harmful agents such as soot, hydrocarbons, and NO_x in the exhaust gases of compression-ignition engines [1–3]. In addition, fuel cells can produce energy from DME, either directly or after reforming to produce hydrogen [4]. Consequently, there is a great deal of interest in the use of DME as a second-generation biofuel for the transportation and residential sectors.

The conventional and most mature process to produce DME is the dehydration of methanol over solid acid catalysts such as γ -Al₂O₃, zeolites or silica-modified alumina at temperatures ranging from 250 to 300 °C and pressures between 10 to 20 bar [5–7]. The production of

DME from syngas involves the reactions shown in Eqs. (1)–(4); namely the direct hydrogenation of CO and CO₂ to methanol (Eq. (1) and (2), respectively), the water gas shift reaction (WGSR) (Eq. (3)), and methanol dehydration (Eq. (4)):



Reactions 1, 2 and 3, *i.e.*, the synthesis of methanol from CO or CO₂ and the water gas shift reaction (WGSR) take place in the presence of Cu based catalysts. Consequently, the WGSR will take place during the synthesis of methanol from syngas. The production of DME from methanol is catalyzed by acid catalysts. Both processes take place in different reactors under different reaction conditions. However, the direct synthesis of DME from syngas in a single reactor combining both types of cata-

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Table 1
Overview of the studied catalysts and reaction conditions for the direct synthesis of DME.

| Catalyst | Syngas | M ¹ | T | P | GHSV | C conversion | DME selectivity | Reference | |
|--|--|---|------------------------------------|-----|---------|--------------|---|--------------------------|------|
| MSC ² | DSC ³ | MSC/DSC ratio ⁴ | CO/CO ₂ /H ₂ | °C | bar | % | | | |
| CuO/ZnO/Al ₂ O ₃ 50/40/10 | γ-Al ₂ O ₃ | 1-5 | 1/0.5/0.9 | 0.3 | 250 | 40 | 11000 h ⁻¹ | - | [29] |
| CuO/ZnO/Al ₂ O ₃ 6/3/1 | γ-Al ₂ O ₃ | 1, 2 and 3 | 1/0.13/2 | 1.7 | 200-260 | 20 | 2400 mL/h/g _{catalyst} | - | [30] |
| Cu/ZnO/Al ₂ O ₃ 6/2/1 | γ-Al ₂ O ₃ | CuO/γ-Al ₂ O ₃ 1.75 | 1/0/2 | 2 | 250 | 50 | 2000 L/kg _{catalyst} /h | X _{CO} = 50 | [21] |
| CuO/ZnO 62.5/20.8 | γ-Al ₂ O ₃ | CuO/γ-Al ₂ O ₃ 3.7 | 1/0/2 | 2 | 250 | 50 | 4000 mL/g _{catalyst} /h | X _{CO} = 66 | [22] |
| Cu/La/Zr 1/0.08/1 | γ-Al ₂ O ₃ | 3 | 1/0.2/1 | 0.7 | 260 | 40 | 1500 h ⁻¹ | X _{CO} = 73 | [12] |
| Cu/ZnO/Al ₂ O ₃ (Mn) 6/2.5/1.5 | γ-Al ₂ O ₃ | 1 | 1/0/1.5 | 1.5 | 240-270 | 41.3 | 6000 h ⁻¹ | X _{CO} = 85 | [23] |
| Commercial | γ-Al ₂ O ₃ | 2.3 | 1/0/1.5 | 1.5 | 250 | 30 | 0.20 kg/h/Nm ³ | X _{CO} = 28 | [31] |
| | | 12.3 | 1/0/1.5 | 1.5 | 270 | | 0.20 kg/h/Nm ³ | X _{CO} = 44 | 64 |
| | | 5.7 | 1/0.19/1.5 | 1.1 | 270 | | 0.164 kg _{cat} /h/Nm ³ | X _{CO} = 39 | 72 |
| CuO/ZnO/Al ₂ O ₃ (Zr) | γ-Al ₂ O ₃ | 1.5 vol. ratio | 1/1/2.2 + CH ₄ 0.6 | | 270 | 50 | 1500 h ⁻¹ | X _{CO} = 79 | [32] |
| | | | | | | | | X _{CO2} = 5 | |
| Cu | γ-Al ₂ O ₃ | 5% Cu mole | 1/0/2 | 2 | 310 | 50 | 1080 mL/h/g _{catalyst} | X _{CO} = 72 | [52] |
| Cu/Zn/Al 6/3/1 (mole) | | 2 | 1/0.13/2.2 | 1.8 | 260 | 40 | 1500 mL/h/g _{catalyst} | X _{CO} = 95 | [33] |
| | SO ₄ ²⁻ -modified γ-Al ₂ O ₃ | | | | | | | | |
| Cu, ZnO | γ-Al ₂ O ₃ | 2/1/6 Cu/Zn/Al | 1/0.16/2.06 | 1.6 | 270 | 30 | 2000 h ⁻¹ | X _{CO} = 57 | [24] |
| Cu, ZnO | γ-Al ₂ O ₃ | 1 | 1/0.25/1.25 | 0.8 | 250 | 50 | | X _{CO} = 7 | [25] |
| | HSiW | | 1/0/1 | 1 | 250 | | | X _{CO} = 10 | 58 |
| | HSiW | | 1/0.25/1.25 | 0.8 | 270 | | | X _{CO} = 14 | 70 |
| CZA | γ-Al ₂ O ₃ | 2 | 1/0/2 | 2 | 275 | 40 | 33.33 g _{catalyst} /h/mol | X _{CO} = 95 | [26] |
| | γ-Al ₂ O ₃ | 2 | 0/1/8 | 7 | | | | X _{CO2} = 32 | 35 |
| | NaHZSM5 | 4 | 0/1/8 | 7 | | | | X _{CO2} = 50 | 70 |
| Cu/Zn/Al 6/3/1 (mole) | Mg modified HZSM5 | 2 | 1/0.13/2.2 | 1.8 | 260 | 40 | 1500 mL/h/g _{catalyst} | X _{CO} = 96 | [27] |
| Commercial | HSiW over mesoporous alumina | - | 1/0/1 | 1 | 275 | 50 | 7500 mL/h/g _{catalyst} | X _{CO+CO2} = 30 | [53] |
| | | | 1/0.25/1.25 | | | | | X _{CO+CO2} = 35 | 88 |
| | | | 1/1/2 | | | | | X _{CO+CO2} = 46 | 80 |
| | | | 1/4/5 | | | | | X _{CO+CO2} = 70 | 76 |
| Cu-Mn | Zeolite Y | 1 | 1/0/1.5 | 1.5 | 245 | 20 | 1500 h ⁻¹ | X _{CO} = 25 | [28] |
| CuO/ZnO/Al ₂ O ₃ 47/24/3 | ZSM5 | 2.5 - 5 | 1/0.17/2 | 1.6 | 225 | 40 | | X _{CO} = 30 | [34] |
| Cu/Zn/Al | SiO ₂ /Al ₂ O ₃ | | 1/0.5/1.5 | 0.7 | | | | X _{CO} = 60 | 90 |
| Cu/Zn/Zr Cu/Zn/Mn | SAPO-11 | 1 - 10 | 1/0/3 | 3 | 275 | 30 | 10.18 g _{catalyst} • h (mol C) ⁻¹ | X _{CO+CO2} = 38 | [11] |
| | | | 1/0.3/3.9 | 2.8 | | | | X _{CO+CO2} = 28 | 90 |
| | | | 1/0.7/5.1 | 2.6 | | | | X _{CO+CO2} = 20 | 88 |
| | | | 1/1/6 | 2.5 | | | | X _{CO+CO2} = 18 | 88 |
| Cu/Zn/Zr 2/1/1 atomic | SAPO-11 | 0.5-2 | 1/1/6 | 2.8 | 275 | 30 | 7.60 g _{catalyst} • h (mol C) ⁻¹ | X _{CO+CO2} = 10 | [54] |
| Cu/ZnO/ZrO ₂ | Ferrierite | 2 | 0/1/3 | 2 | 260 | 30 | 8800 NL/kg _{cat} /h | X _{CO2} = 5 | [55] |
| CZA Katalco 51-8 | γ-Al ₂ O ₃ | 9 | 1/1.9/7.7 | 2 | 270 | 25 | 5000 h ⁻¹ | X _{CO+CO2} = 10 | 2 |
| | | | | | | | 7500 h ⁻¹ | X _{CO+CO2} = 9 | 1 |
| | | | | | | | 5000 h ⁻¹ | X _{CO+CO2} = 24 | 1 |
| | | | | | | | 7500 h ⁻¹ | X _{CO+CO2} = 21 | 1 |
| | | | | | | | 5000 h ⁻¹ | X _{CO+CO2} = 9 | 29 |
| | | | | | | | 7500 h ⁻¹ | X _{CO+CO2} = 7 | 32 |
| | | | | | | | 5000 h ⁻¹ | X _{CO+CO2} = 16 | 22 |
| | | | | | | | 7500 h ⁻¹ | X _{CO+CO2} = 15 | 16 |
| | | 0.11 | | | | | 5000 h ⁻¹ | X _{CO+CO2} = 3 | 53 |
| | | | | | | | 7500 h ⁻¹ | X _{CO+CO2} = 3 | 41 |
| | | | | | | | 5000 h ⁻¹ | X _{CO+CO2} = 4 | 64 |
| | | | | | | | 7500 h ⁻¹ | X _{CO+CO2} = 3 | 40 |

¹ M = ([H₂] - [CO₂]) / ([CO] + [CO₂]) ² MSC: methanol synthesis catalyst. ³DSC: DME synthesis catalyst. ⁴ Unless stated otherwise, MSC/DSC mass ratio.

lysts has been proposed recently. The direct process is simpler and it has been stated that the variety of sources and processes through which syngas can be produced, confers to this direct synthesis economic advantage [4]. For the direct synthesis of DME from syngas, the catalytic bed should comprise a mixture of both catalytic phases. The optimum reaction conditions for the methanol synthesis from syngas over copper-zinc-alumina (CZA) catalysts range between 220 and 280 °C, typically 250 °C, and between 50 and 100 bar [8–10]. These conditions do not coincide with the optimum ones for the industrial production of DME via methanol dehydration, which takes place above 280 °C and over 10 bar [7]. Consequently, a trade-off between both processes should be reached to maximize DME productivity. The nature of these catalysts and the operating conditions for the direct synthesis of DME have been object of study in several recent publications (see Table 1 for comprehensive details). All studies in the literature report the use of Cu/ZnO/Al₂O₃ (CZA) catalysts, in some cases doped with zirconia or lanthanum, although the

promotional effect of the latter oxides is not clearly demonstrated [11–13]. Methanol dehydration to DME proceeds over acid based catalysts, such as alumina [4,14], zeolites [15,16], heteropolyacids [17–19] or doped activated carbons [20]. Among those, γ-Al₂O₃ and zeolites are by far the most studied catalysts for the methanol dehydration reaction, giving DME selectivity values as high as 85%. However, most studies for the direct synthesis of DME from syngas report significantly lower DME productivities than the ones obtained in the two step-process using Cu/ZnO/Al₂O₃ and γ-Al₂O₃ as catalysts [21–28]. This observation suggests that the syngas to DME process is not only the lineal combination of both processes, syngas to methanol and methanol to DME, and that the system must be optimized.

An obvious feature expected to influence strongly the performance of the syngas to DME process is the ratio between the two types of catalysts in the reactor. However, as shown in Table 1, most studies in the literature focus on catalytic beds with high CZA contents, ranging be-

tween 50 and 92 % [11,12,30–34,21–23,25–29], with very few studies reporting CZA to acid catalyst ratios below 1 [13,24,26]. Surprisingly, the selectivity to DME does not seem to be strongly affected by the small fraction of acid catalyst in the catalytic bed. For instance, as shown in Table 1, a DME selectivity of 64 % can be obtained with a catalytic bed containing only 7% of γ -Al₂O₃ [31]. As also shown in Table 1, similar values are obtained with catalytic beds containing a higher content of the acid catalyst.

DME production from syngas is not only affected by the nature and relative amount of each catalyst in the bed, but the reaction conditions are critical as well. For instance, catalyst mixtures with similar ratios between the methanol synthesis catalyst and the DME synthesis catalyst (MSC:DSC) show total carbon conversions, as high as 96 % [26,27,33]. However, those results were obtained at low spatial velocities and, more importantly, with CO₂-lean syngas. On the other hand, the range of temperatures and pressures at which most of the cited works were carried out are rather narrow (mainly 240–275 °C and 20–50 bar), suggesting that the optimum temperature may be contained within those values.

As shown above, most studies concerning the direct synthesis of DME from syngas focus on the effect of catalyst nature and reaction conditions (P, T, GHSV) using either CO₂-free syngas or syngas with a low CO₂ content. The presence of CO₂ is known to affect strongly the performance of the CZA catalyst. First, it is widely accepted that a small fraction of CO₂ must be present in the syngas mixture in order to increase the production rate of methanol from syngas; otherwise, the activity of the catalyst would decrease due to an over reduction of the Cu particles [35–37]. Despite the optimum amount of CO₂ has been identified to be as low as 2.4 % vol. [38], CO₂ is usually considered as the source of methanol [10]. This view has been disputed in a recent publication that claims that the actual source of methanol, CO₂ or CO, depends on the reaction conditions [39]. However, an excess of CO₂ in the syngas results in a high fraction of Cu²⁺ species in the surface of the catalyst, resulting in slower reaction rates [37]. In view of this, it is reasonable to assume that the composition of the syngas, namely the CO₂ to CO ratio, will influence the catalytic performance for the direct synthesis of DME from syngas. Some mathematical models have been developed to study this effect [40,41].

When syngas is produced from biomass (or organic waste), the volumetric content of CO₂ in the syngas obtained can be significantly higher than that of CO, depending on the type of biomass and on the gasification process [42,43]. This deviation from the optimum composition for the methanol synthesis reaction could affect the production of DME in the direct synthesis process. However, a very narrow range of syngas compositions has been studied in the syngas to DME literature. Particularly, most studies have been conducted using syngas compositions with very low CO₂/CO ratios, close to the optimum ones for the production of methanol from syngas. Clearly, experimental data for the direct synthesis of DME using a wider range of syngas compositions, including those with high contents in CO₂, would be required for the development of new technologies of direct synthesis of DME that use biomass-derived syngas.

Finally, it is also known that the activity of both catalysts used in the direct synthesis of DME from syngas, *i.e.*, the copper-based catalyst and the acid catalysts (γ -Al₂O₃) decline in the presence of water [44–46]. Sadly, during the direct synthesis of DME from syngas several sources of water production exist, namely: *i*) CO₂ hydrogenation to methanol, *ii*) reverse WGS, and *iii*) methanol dehydration to DME, resulting in a H₂O-rich environment. To minimize the limiting effect of water presence in this process, several strategies have been proposed, such as the use of selective membranes [41,47], a partial transformation of CO₂ into CO prior to the methanol synthesis reaction [48] or the use of water sorbent solids in the reaction medium [49].

In this work, we report the catalytic activity for the direct synthesis of DME from CO₂-rich syngas, with a CO₂/CO vol. ratio of 1.9, using three catalytic beds with different loadings of the benchmark catalyst for the synthesis of methanol and DME. This CO₂/CO ratio has been

reported to be obtained from municipal solid waste through sorption-enhanced gasification [50]. The effect of reaction conditions, namely pressure, temperature, and spatial velocity has been explored. In addition, the effect of in-situ water removal has been assessed by adding a H₂O-sorbent zeolite in the catalytic bed.

2. Experimental

2.1. Catalyst mixtures preparation

Cu/ZnO/Al₂O₃ (Katalco 51-8), referred to as CZA, and γ -Al₂O₃ (Alfa Aesar bimodal 70-5000 Å, 220–280 m²/g) were used for the catalytic tests. Known masses of each catalyst were weighed, mixed, sieved, and pressed to form tablets. Then, they were crushed again and sieved to obtain grains with a particle size between 250 and 300 µm. The CZA/ γ -Al₂O₃ ratios studied were 10/90, 50/50 and 90/10 by weight.

2.2. Characterization

Fresh and used catalyst mixtures were characterized by X-ray diffraction (XRD) and Raman spectroscopy. XRD data were collected in a powder X-ray X Pert Pro PANalytical with a configuration θ -2 θ , using CuK α radiation. A coupled reaction chamber allows treating the samples in a controlled atmosphere and under controlled temperature. Copper particle sizes, d_{Cu} , in nm, of the fresh and used catalysts were determined parting from the data of the collected diffractograms and using Eq. (5), corresponding to the Scherrer equation.

$$d_{Cu} = \frac{K\lambda}{\beta \cos \theta} \quad (5)$$

In Eq. (5), assuming spherical copper crystal with cubic symmetry, the value of the Scherrer constant, K, is equal to 0.94. The wavelength corresponding to the used x ray source (λ) is 0.15418 nm. β and θ are the full width at half maximum (FWHM) and the position of the peaks of the copper reflections, respectively. Parting from the calculated particle sizes of the materials, the corresponding surface area of the Cu particles was calculated with Eq. (6)

$$S_{Cu}(XRD) = \frac{6000}{\rho_{Cu} \cdot d_{Cu}} \quad (6)$$

Where S_{Cu} is the copper surface area of the particles in m²/g of Cu, ρ_{Cu} is the density of copper in m³cm⁻³, which is 8.92 for a fcc crystalline structure, and d_{Cu} is the average particle size of the Cu° crystals.

Raman spectra were collected to determine whether coke deposits are formed in the used catalysts. A Renishaw Raman Microscope spectrometer equipped with two lasers emitting at 532 nm with a 1800 lines/mm grating monochromator, and 785/532 nm and 300 mW with a 1200/1800 lines/mm grating monochromator, respectively, was used. The scattered photons were simultaneously collected on a CCD camera. The spectral resolution was 1 cm⁻¹ using a 50x objective.

2.3. Catalytic activity

The performance of the mixtures of CZA and γ -Al₂O₃ catalysts with different weight ratios for the direct synthesis of DME from CO₂-rich syngas has been studied in a fixed-bed stainless-steel tubular reactor with an intern diameter of 9 mm. The reactor is heated in an electric furnace, and its temperature is measured by a thermocouple placed in the middle of the catalytic bed. The catalytic performance of the mixtures for the synthesis of DME from syngas was assessed under different reaction conditions; 270–290 °C, 25 and 50 bar and 5000 and 7500 NmL_{syngas}/h/mL_{catalytic bed} (henceforth, h⁻¹). Finally, the addition of a H₂O-sorbent (zeolite 3A, UOP MS-1018 1/16" extrudates) in the reactor bed has been also assessed. For each experiment, 0.2 g of the mixture of CZA and γ -Al₂O₃ catalysts in the desired ratios, namely 90:10, 50:50, and 10:90, were mixed with SiC (SiC/catalyst ratio 3/1 v/v) to ensure

isothermal conditions along the whole reaction bed. The approximate height of the catalytic bed was 1.5 cm. Previous to the catalytic test, the catalyst was treated in a H₂/N₂ 20/80 vol. stream at 1 bar and 250 °C for 2.5 h, with a heating rate from 25 to 250 °C of 2 °C/min. The purpose of this treatment is to reduce the CuO to Cu⁰. The outlet gases were analysed on-line with a Varian CP-3800 gas chromatograph equipped with a Hayesep Q packed column connected to a thermal conductivity detector (TCD) and a Rtx-1 capillary column connected to a flame ionization detector (FID), for the analysis of the inorganic gases and methanol and DME, respectively. Traces of C₂H₄ were observed in some experiments; however, the signal was too weak for proper quantitation.

In some experiments, a H₂O-sorbent material, namely zeolite 3A, crushed and sieved to a particle size between 250 and 300 μm, was added to the catalyst bed in order to study the effect of water removal during the syngas to DME process.

The CO, CO₂, and total carbon (CO+CO₂) conversions were calculated according to Eqs. (7)–(9), respectively.

$$X_{\text{CO}} = \frac{(\text{CO}_{\text{in}} - \text{CO}_{\text{out}})}{\text{CO}_{\text{in}}} \times 100 \quad (7)$$

$$X_{\text{CO}_2} = \frac{(\text{CO}_{2,\text{in}} - \text{CO}_{2,\text{out}})}{\text{CO}_{2,\text{in}}} \times 100 \quad (8)$$

$$X_{\text{CO+CO}_2} = \frac{(\text{CO}_{\text{in}} + \text{CO}_{2,\text{in}} - \text{CO}_{\text{out}} - \text{CO}_{2,\text{out}})}{\text{CO}_{\text{in}} + \text{CO}_{2,\text{in}}} \times 100 \quad (9)$$

Where CO_{in} and CO_{2,in} are the molar flows at the inlet of the reactor, and CO_{out} and CO_{2,out} are the molar flows at the outlet, all of them expressed in moles per minute. Selectivity towards methanol and DME were obtained using Eqs. (10) and (11).

$$S_{\text{MeOH}} = \frac{\text{CH}_3\text{OH}_{\text{out}}}{\text{CH}_3\text{OH}_{\text{out}} + 2 \text{CH}_3\text{OCH}_3_{\text{out}}} \quad (10)$$

$$S_{\text{DME}} = \frac{2 \times \text{CH}_3\text{OCH}_3_{\text{out}}}{(\text{CH}_3\text{OH}_{\text{out}} + 2 \times \text{CH}_3\text{OCH}_3_{\text{out}})} \quad (11)$$

CH₃OH_{out} and CH₃OCH_{3,out} represent the mole flows of the corresponding product (methanol or DME) at the outlet, expressed in moles per minute. Eventually, the productivities of methanol and DME, expressed in moles of the corresponding product per minute and gram of mixture, were calculated using Eqs. (12) and (13).

$$\text{Productivity}_{\text{MeOH}} = \frac{C_{\text{in}} \times \frac{\chi_{\text{CO+CO}_2}}{100} \times S_{\text{CH}_3\text{OH}}}{m_{\text{CZA}+\gamma\text{Al}_2\text{O}_3}} \quad (12)$$

$$\text{Productivity}_{\text{DME}} = \frac{C_{\text{in}} \times \frac{\chi_{\text{CO+CO}_2}}{100} \times S_{\text{CH}_3\text{OCH}_3}}{2 \times m_{\text{CZA}+\gamma\text{Al}_2\text{O}_3}} \quad (13)$$

C_{in} is equal to CO_{in}+CO_{2,in}, representing the total carbon flow fed to the reactor, and m_{CZA + γAl₂O₃} is the total mass of the mixture of catalysts in the reactor in grams.

3. Results and discussion

3.1. Effect of CZA:γ-Al₂O₃ ratio

Fig. 1 shows the CO, CO₂, and CO+CO₂ conversions obtained with the CZA:γ-Al₂O₃ catalytic mixtures studied in this work (90:10, 50:50 and 10:90) during the syngas to DME processes at 270 °C, 25 and 50 bar and 5000 and 7500 h⁻¹. The thermodynamic equilibrium values of CO and CO₂ conversions for the methanol synthesis reaction and for the direct synthesis of DME are shown for comparison.

As observed in Fig. 1, CO₂ conversions are not strongly affected by reaction conditions and they remain close to the equilibrium value for the direct DME synthesis, regardless of the reaction conditions studied in this work. The higher CO₂ conversion reached at 50 bar accounts to a higher equilibrium conversion rather than, or in addition to, kinetics

effects. Nevertheless, a slight decrease of CO₂ conversion with the decreasing content of CZA in the catalytic bed can be observed in Fig. 1. It should be noted that the experimental CO conversions exceeds the CO equilibrium conversions for the StM process (7 and 40 % at 25 and 50 bar, respectively), especially with the 90:10 mixture. This observation proves that it is possible to overcome the thermodynamic limitations of the methanol synthesis reaction in the direct synthesis of DME.

CO conversions are affected by both the reaction conditions and the composition of the catalytic bed. Thus, higher CO conversions are recorded at high pressure (50 vs 25 bar) and low space velocities (5000 vs 7500 h⁻¹). When compared at similar reaction conditions, Fig. 1 shows that CO conversions decrease with the decreasing content of CZA in the mixture. Thus, whereas ~ 50 % CO conversion is obtained over the mixture with the highest CZA content in the series of 90:10, a negative CO conversion (higher CO_{out} than CO_{in}) is obtained using the 10:90 CZA:γ-Al₂O₃ mixture. This observation indicates that under such reaction conditions the reverse WGS (r-WGS), whereby CO₂ is converted into CO, is faster than the CO hydrogenation reaction. As also observed in Fig. 1, the CO conversion achieved with the mixtures with the highest CZA:γ-Al₂O₃ ratios studied in this work, 90:10 and 50:50, increase with reaction pressure. This feature is not observed over the catalytic bed with the lowest amount of CZA (10:90) showing similar CO conversions at 25 and 50 bar. Finally, CO conversion decreases with the space velocity, although again this feature is more evident over the 90:10 and 50:50 catalytic beds.

It is worth to state that both methanol and DME are produced under all conditions studied in this work, including the experiments conducted with the mixtures with the lowest CZA:γ-Al₂O₃ ratio in the series, under which a net production of CO is observed. This observation indicates that in addition to being converted into CO, CO₂ acts as carbon source for the methanol production, either directly (Eq. 2 and Eq. 3 occurring in parallel) or with CO as intermediate (Eqs. (3), and (1) occurring consecutively). Either way, the r-WGS appears to play the key role in the overall process.

Fig. 2 shows the productivities of methanol and DME normalized to the mass of the catalytic bed. The maximum theoretical DME productivity at each reaction condition, based on the molar flow at the inlet of the reactor and the equilibrium conversions, are indicated in Fig. 2.

Fig. 2 shows an evident relation between the methanol productivity and the CZA content catalytic bed. Thus, methanol productivity decreases with the decreasing fraction of CZA in the mixture. The observed trend goes in line with the evolution of carbon conversion (Fig. 1). This feature is more evident at 50 bar than at 25 bar. As also observed in Fig. 2, DME productivity presents a maximum (of around 2 mmol/h/g_{mixture}) with the CZA:γ-Al₂O₃ 50:50 mixture at every reaction condition considered in this work. On the one hand, DME productivity over the 90:10 mixture is very low (almost negligible) under all reaction conditions studied in this work. On the other hand, the productivity of DME over the 10:90 mixture is slightly lower than that obtained over the 50:50 mixture, even though CO+CO₂ conversion and methanol productivity are significantly smaller under this reaction condition. The high productivity of methanol and the low selectivity to DME in the experiments conducted over the 90:10 catalyst mixture indicates that methanol dehydration over the γ-Al₂O₃ phase is not taking place. This feature cannot be ascribed to the low intrinsic activity of the acid phase, since γ-Al₂O₃ is known to be display catalytic activity for methanol dehydration at 270 °C and 1-10 bar. Nevertheless, at this temperature, the space velocity of the methanol over the γ-Al₂O₃ is the parameter that controls the catalytic performance [14]. Although it cannot be measured, since methanol productivity is higher over the mixtures with high fraction of CZA, the space velocity of the methanol over γ-Al₂O₃ would increase with the decreasing content of acid catalyst in the bed. Another possible explanation to the observed low DME productivity over the 90:10 mixture can be the inhibition of the γ-Al₂O₃ by water. As discussed above, the 90:10 mixture presents the highest CO₂ and CO con-

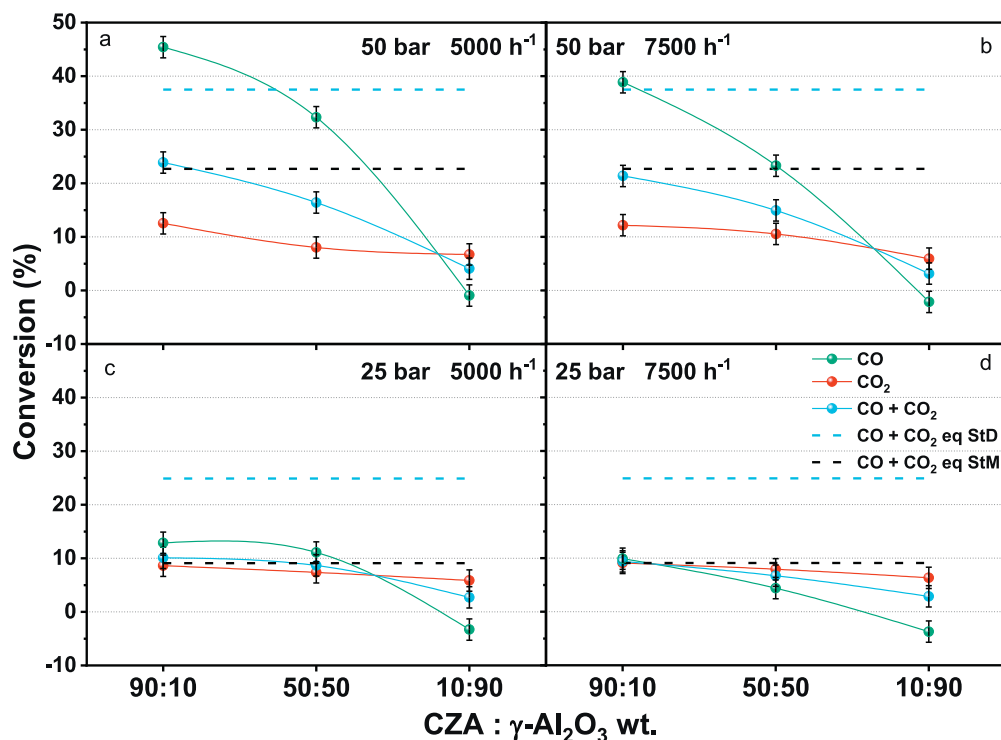


Fig. 1. CO, CO₂ and CO+CO₂ conversion values obtained with the CZA:γ-Al₂O₃ mixtures at different reaction conditions. Syngas composition: CO/CO₂/H₂=1/1.9/7.7 vol. Reaction temperature 270 °C. StD: syngas to DME. StM: syngas to methanol.

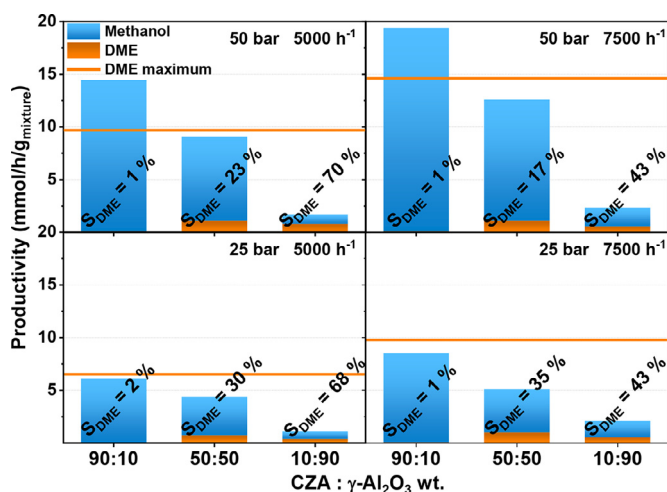


Fig. 2. Methanol and DME productivities obtained with the CZA:γ-Al₂O₃ mixtures at different reaction conditions. Syngas composition: CO/CO₂/H₂=1.0/1.9/7.7 vol. Reaction temperature 270 °C.

version values in the series, therefore resulting in a high concentration of H₂O in the reaction media therefore inhibiting methanol dehydration to DME over γ-Al₂O₃. This effect, i.e., the negative effect of large amounts of water in the DME synthesis from methanol over γ-Al₂O₃ has been reported elsewhere. This deactivation has been ascribed to a blockage of the acid sites by water molecules or to a phase transition of the γ-Al₂O₃ to bohemite [45,51].

Whereas the highest DME productivities have been obtained with the 50:50 mixture (equal amounts of CZA and γ-Al₂O₃), the best results in terms of DME selectivity were achieved with the 10:90 mixture. This observation seems to be consistent with the discussion above; due to the lower content of CZA in this mixture, total carbon conversion and methanol production are the lowest in the series, consequently, the pro-

duction of water is low resulting in a lower deactivation of γ-Al₂O₃. Moreover, the space velocity of the methanol over the acid phase in the 10:90 mixture is expected to be low, thus favouring DME production.

The highest CO₂+CO conversion value reached in our work is ca. 22 %, with a maximum DME productivity of ca. 2.5 mmol_{DME}/h/g_{catalyst mixture}. As shown in Table 1, these values are lower than the highest CO₂+CO conversions and DME productivities reported in the literature. However, establishing a proper comparison between the results reported in this work and previous works is difficult due to the wide range of reaction conditions reported in the literature. In particular, studies using CO₂-rich syngas are lacking in the literature. Palgunadi et al. reported a total carbon conversion of 85 % and a DME selectivity of 66% using a mixture with equal amounts of a CZA catalyst and γ-Al₂O₃ working at 41.3 bar, 270 °C and 6000 h⁻¹; however, these results were obtained with a CO₂-free syngas [23]. Under similar reaction conditions, 50:50 CZA:γ-Al₂O₃, 50 bar, 270 °C and 5000 h⁻¹, we obtained a carbon conversion of 15 % (ca. 5 times lower) and a DME selectivity of ca. 22%. The lower performance obtained in our work accounts the higher content of CO₂ in the syngas used in our experiments, and it clearly illustrates the deleterious effect of the presence CO₂ for the direct production of DME.

Similarly, Peláez et al. using a catalytic bed with a high content of CZA and CO₂-free syngas obtained carbon conversions four times higher than the one obtained in our work under similar reaction conditions, only we used CO₂-rich syngas. They also reported a selectivity to DME of 64 %, corresponding to a DME productivity of ca. 25 mmol DME/h/g_{catalyst mixture} [31], while under similar reaction conditions we obtained DME productivities ca. 10 times lower.

The comparison between the catalytic performances reported in Table 1 (obtained using CO₂-free or CO₂-poor syngas) and the results obtained in this work clearly demonstrate that the production of DME from syngas is strongly affected by the presence of CO₂ in the syngas. As observed, carbon conversion, and especially DME productivity are affected by the presence of CO₂ and it accounts to the formation of a high amount of H₂O during the process that results in the poisoning of γ-Al₂O₃.

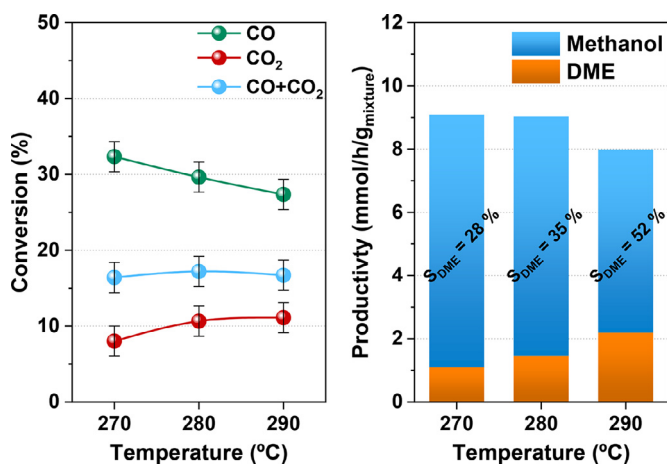


Fig. 3. Conversions and productivities obtained with the CZA:γ-Al₂O₃ 50:50 mixture at 50 bar and 5000 h⁻¹ at different temperatures. Syngas composition: CO/CO₂/H₂=1/1.9/7.7 vol.

3.2. Effect of reaction temperature

Once the optimum composition (in terms of DME productivity) of the catalysts mixture for the synthesis of DME is identified, the selectivity towards DME was optimized. Experiments at higher temperatures (280 and 290 °C) were performed at 50 bar and 5000 h⁻¹, as these conditions demonstrated to be the best ones in terms of total carbon conversion and DME productivity. A comparison of the results obtained at the three temperatures is shown in Fig. 3.

As observed, the total carbon conversion is not affected by the reaction temperature. This is because CO and CO₂ conversions are affected in opposite ways; whereas CO conversion decreases with the increasing temperature, CO₂ conversion increases with temperature. It should be noted though, that even if the CO+CO₂ conversion remained similar at all temperatures, the increase in CO₂ conversion with temperature, via r-WGSR and/or CO₂ hydrogenation, results in a higher partial pressure of water in the system. On the other hand, the results in Fig. 3 show that DME productivity and selectivity increases with temperature, from 28 % at 270 °C to 52 % at 290 °C. Noticeably, DME productivity doubles by increasing reaction temperature from 270 to 290 °C. It seems like by working at higher reaction temperature it is possible to reduce the inhibition of γ-Al₂O₃ by H₂O. This effect is due to the higher kinetics of the methanol dehydration process with temperature [14] and possibly to a faster desorption of water or methanol-water clusters [56] from the active centres of γ-Al₂O₃. Water desorption from the surface of γ-Al₂O₃ is progressively favoured at temperatures above 250 °C [57,58].

As shown in Table 1, working at similar reaction conditions of P and T (50 bar and 295 °C) Jiang et al. reported a carbon conversion of 65 % and DME selectivity of 72 % [52]. These values are higher than the ones reached in our work, but again they were obtained using a CO₂-free syngas and lower GHSV.

3.3. Effect of in situ water removal

The results obtained in our work clearly show using a CO₂-rich syngas results in lower total carbon conversion and DME productivity. This feature has been ascribed to a higher production of H₂O due to the presence of CO₂ and to thermodynamic effects [59]. Recently, the *in situ* removal of H₂O to enhance DME productivity from syngas has been proposed [60]. In order to assess this approach, the direct synthesis of DME from CO₂-rich syngas has been studied by adding 800 mg of zeolite 3A (as H₂O-sorbent) in the 50:50 CZA:γ-Al₂O₃ catalytic bed at 50 bar, 290 °C and 5000 h⁻¹. Fig. 4 shows the total carbon conversion and DME and methanol obtained using the catalytic bed with zeolite 3A.

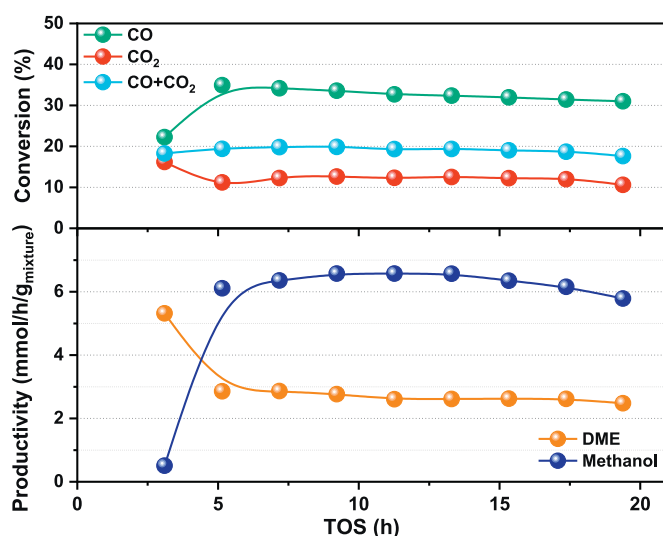


Fig. 4. Evolution of conversions and productivities obtained with the mixture 50:50 CZA:γ-Al₂O₃ combined with the zeolite 3A at 290 °C, 50 bar and 5000 h⁻¹.

A strong positive effect in terms of DME productivity due to the *in situ* removal of water can be clearly observed at low times on stream (TOS < 5 h). DME productivity obtained in the presence of 3A zeolite is two times higher than that obtained under similar reaction conditions without the 3A zeolite in the reaction mixture (see Fig. 3). Moreover, the results obtained in terms of CO₂ conversion (16 %) and DME/methanol ratio (10.4) at the outlet of the reactor are higher than the equilibrium values of 13 % and 2.6, respectively. This observation validates the idea that the sorption enhanced DEM synthesis (SEDMES) is a suitable approach to increase DME production from CO₂ rich syngas. It should be noted though, that the enhancement in the productivity (and selectivity) of DME declines with time on stream. After ca. 5 h on stream, DME productivity values are in line with those obtained without 3A. Probably, this behaviour accounts to the saturation of the 3A zeolite. For an industrial application of the SEDMES process, the regeneration of the zeolite is required. Previous studies show that the sorption capacity of zeolite 3A can be regenerated by PSA [61].

3.4. Deactivation of the CZA:γ-Al₂O₃

The production of DME from CO₂ rich syngas over the 50:50 mixture was monitored during 260 h. Fig. 5 shows the evolution of CO, CO₂, CO+CO₂ conversions and methanol and DME productivities during 260 h at 270 °C, 50 bar and 5000 h⁻¹.

A strong decline of the CO conversion (from 39 % to 16 %) and methanol productivity (from 11 to 5.5 mmol of methanol per gram of catalyst mixture per hour) during the first ca. 100 h on stream can be observed in Fig. 5. This decline became less steep at increasing TOS. In particular, the rate of the CO conversion loss was 0.28 per hour during the first 25 h, but only 0.14 per hour between the 25 and 50 h on stream. Eventually, this decrease in CO conversion became much lower, with a rate of only 0.02 percent points of conversion per hour in the last 50 hours of reaction. On the other hand, both CO₂ conversion and DME productivity per gram of catalytic mixture remained constant during time on stream. This is because the CO₂ conversion is close to the equilibrium value and therefore a moderate catalyst deactivation may not be reflected in the conversion achieved. The stability of the DME productivity indicates that the change at increasing times on stream should be occurring in the CZA phase of the mixture.

The fresh and used catalysts mixtures were characterized by Raman and XRD. The Raman spectra of the used catalytic bed lack features indicative of the formation of carbon deposits, suggesting that the ob-

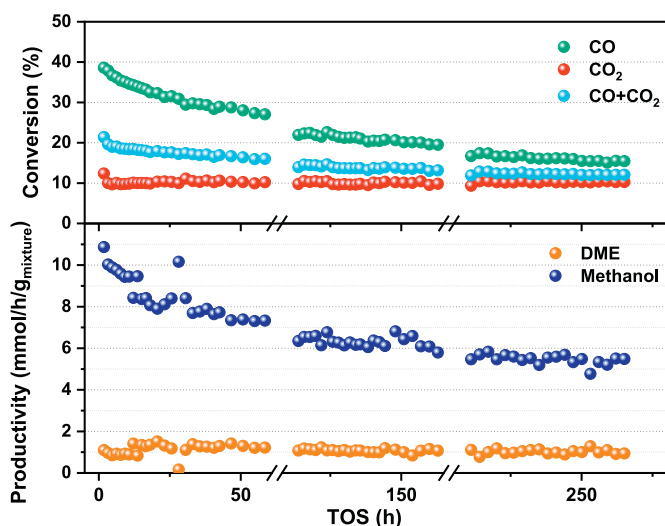


Fig. 5. Evolution of conversions and productivities at 270 °C, 50 bar and 5000 h⁻¹ with CZA:γ-Al₂O₃ 50:50 mixture

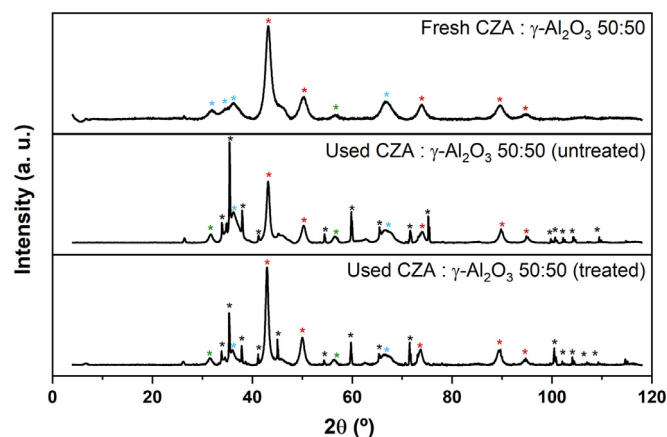


Fig. 6. X ray diffractograms for fresh CZA:γ-Al₂O₃ 50:50 after reduction under H₂/N₂ 20/80 at 250 °C (top panel), and for the used catalyst mixture (CZA:γ-Al₂O₃ 50:50) as obtained after 260 h on stream, used (central panel) and for the used catalytic mixture subjected to a reduction process (bottom panel). Cu⁰ (red), γ-Al₂O₃ (blue), ZnO (green), and SiC (black).

served catalyst deactivation is not caused by coke deposits on any of the catalytic phases.

Fig. 6 shows the diffractograms of the fresh catalytic mixture (after reduction under H₂/N₂ 20/80 at 250 °C with a heating rate of 2 °C/min), and those of the used mixture as recovered from the reactor (used) and after the same reduction process (used-reduced). Although not shown, the diffractograms of the individual CZA and γ-Al₂O₃ phases were also recorded and used for the identification of the individual phases.

The diffractograms shown in Fig. 6 reveal the presence of metallic Cu, ZnO and γ-Al₂O₃ phases (the latter one is responsible for the peak at 46°). In addition, the diffractograms for the used catalyst mixture display a set of sharp, intense peaks ascribed to a small fraction of SiC that could not be removed from the used sample before the analysis. The mean crystallite size of the Cu phases of the fresh and used samples has been calculated using the Scherrer equation. The average size of the Cu particles in the fresh sample is 5.5 nm, increasing to 8.4 nm for the used catalyst. According to Eq. 6, these particle sizes correspond to Cu surface areas of 123 and 76 m²/g_{Cu} in the fresh and used samples, respectively. This result clearly indicates that Cu particles tend to agglomerate during time on stream, likely due to the high partial pres-

sure of water [44,62], being responsible for the observed decreasing in total carbon conversion during reaction, in good agreement with previous reports [63]. As observed in Fig. 6, CO and CO₂ conversion are not affected similarly during time on stream. As discussed above, this is because, contrary to CO, CO₂ conversions are close to the equilibrium value. Therefore, the loss in catalytic activity due to the agglomeration of Cu particles is strongly reflected in the CO conversion reactions.

4. Conclusions

The direct synthesis of DME from a CO₂-rich syngas over three mixtures with different proportions of commercial catalysts for methanol (CZA) and DME (γ-Al₂O₃) synthesis has been studied. The mixture with equal amounts of both catalysts provided the highest DME productivity, while the mixture with the highest CZA:γ-Al₂O₃ mass ratio of 9 recorded the highest selectivity towards DME. A comparison between the results presented in this work and the literature, clearly show that the presence of a large fraction of CO₂ in the syngas strongly affects catalytic performance, leading to lower total carbon conversions and DME productivities. This is because the presence of CO₂ in the syngas results in a high productivity of H₂O in the catalytic bed, leading to both the agglomeration of the Cu particles, therefore resulting in lower CO conversions, and to the deactivation of the γ-Al₂O₃ catalyst, therefore decreasing methanol conversion to DME. The removal of water by an adsorbent material, namely zeolite 3A, in the catalytic bed results in a high productivity of DME; however, this is a transient effect, and once the zeolite is saturated, total carbon conversion and DME productivity decline again. Nevertheless, the results presented in this work demonstrate the positive effect of *in situ* water removal for the direct synthesis of DME from CO₂-rich syngas, opening the way for developing strategies to maintain H₂O removal operational during the synthesis of DME.

Declaration of Competing Interest

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

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