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D2.6 - Catalytic performance of novel catalyst mixtures for the direct synthesis of DME.

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1 Executive summary

This deliverable reports the results of obtained in our study to identify the optimum catalysts mixture for the direct synthesis of DME (dimethyl ether) from syngas. Two kind of acid catalysts for the DME production from methanol were tested, the commercial catalyst $\gamma\text{-Al}_2\text{O}_3$ and the supported heteropolyacid HWSi/TiO₂ (HPA). For the methanol synthesis from syngas we used a Cu-based commercial KATALCO™51-8 (referred to as CZA_com). Both catalysts were mixed in m:a (metallic:acid) ratios of 10:90, 50:50 ad 90:10. The DME production from syngas was tested in a fixed bed reactor at 270 °C, 25-50 bar, 5000-7500 h⁻¹ for the mix with $\gamma\text{-Al}_2\text{O}_3$ and 7500-15000 h⁻¹ for the mix with HPA. The mixture containing HPA was also tested at 240 °C. Syngas CO₂/CO-ratio= 1.9 with M=2 was used.

The results obtained show that mixtures containing HPA are not selective to DME, and products such as olefins are formed. The catalysts mixtures with $\gamma\text{-Al}_2\text{O}_3$ are selective to DME and methanol, and the highest productivity to DME was obtained with the m:a= 50:50 at 270 °C, 50 bar and 5000 h⁻¹. Nevertheless, the highest DME/methanol productivity-ratio was obtained with the m:a= 10:90, at the same reaction conditions.

The catalyst mixture 50:50 was selected to study the stability with the time on stream (TOS), at the optimum reaction conditions. It was observed that after 140 h under study, CO conversion drops by 50 %, while the CO₂ conversion remains constant. It was also observed that the methanol productivity decreases very significantly during the TOS, while the DME one increases slightly within the same time.

2 Introduction

Methanol production from syngas at the industry is conducted with Cu/ZnO/Al₂O₃ catalysts; the commercial catalyst used was the KATALCO™51-8. On the other hand, the methanol dehydration to produce DME is performed with acid catalysts either commercial γ -Al₂O₃ or the homemade TiO₂ supported tungstosilicic acid (HSiW) referred to as HPA.

In order to study the direct synthesis of DME from syngas, we have proposed three mixtures with different metallic:acid (m:a) ratio catalysts.

In this deliverable, we report the results of obtained in our study to identify the optimum catalysts mixture for the direct synthesis of DME from syngas.

3 Identifying the optimum composition of catalyst mixtures for the production of DME from syngas

This deliverable reports the results obtained in our study aimed to identify the optimum catalysts mixture for the direct synthesis of DME from CO₂-rich syngas. In this context, we report the syngas (CO₂+CO) conversion, referred to as C conversion and the DME productivity with different catalytic mixtures compositions and reaction conditions.

For the study we have used the two best acid catalysts already identified in D2.3, namely the benchmark commercial catalyst γ -Al₂O₃ and a heteropolyacid (tungstosilicic acid) supported on TiO₂ HSiW/TiO₂. These catalysts are very active for the methanol dehydration reaction $2 \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$

As catalyst for the production of methanol from syngas ($\text{CO}_x + \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$) we have chosen only the commercial catalysts based on Cu dispersed on ZnO/Al₂O₃ KATALCO™51-8 (referred to as CZA_com).

3.1 Catalysts mixtures preparation

The commercial catalyst: KATALCO™ 51-8 is a copper catalyst dispersed on a ZnO-Al₂O₃ support with a MgO promoter. This catalyst is used in the synthesis of methanol from syngas (H₂, CO and CO₂) in different compositions. The γ -Al₂O₃ catalyst is a bimodal 70-5000 Å, 255 m²/g and 1.60 cm³/g.

In this study for the direct production of DME from CO₂-rich syngas, we have used catalytic bed comprising two catalytic functions. The catalytic bed consists on a physical mixture of CZA_com denoted as *m*, and the acid catalyst, either γ -Al₂O₃ or HWSi/TiO₂, denoted as *a*_(γ -Al₂O₃) or *a*_(HPA), respectively, in different ratios. The following m:a ratios: 10:90, 50:50 and 90:10 have been studied.

In order to prepare the catalytic bed, both catalysts were sieved to a particle size of 0.25-0.30 mm and physically mixed in the selected ratios. The catalytic bed was prepared by diluting 0.2 g of the m:a catalyst with SiC ($V_{\text{SiC}} + V_{\text{catalyst}} = 1.65 \text{ cm}^3$) to avoid the formation of temperature gradients during the reaction. The reaction was performed at pressures of 25 and 50 bar, using GHSV of 2500 and 5000 h⁻¹ at 240 °C and 270°C. The composition of the syngas was CO₂/CO-ratio of 1.9, M-module= 2.

3.2 CZA_com/HWSi catalytic activity

As reported previously (see deliverable 2.3) HPA based catalysts are very active for the production of DME from methanol. In fact, they show very high activity at lower temperatures than γ -Al₂O₃, being active at temperatures below 200°C. In principle, this is an advantage since it avoids catalyst deactivation by coke, which is produced at high temperatures over γ -Al₂O₃ during methanol dehydration. As a consequence, we evaluated the direct transformation of syngas to DME over a catalyst bed containing different mixture of CZA_com and HSiW/TiO₂ under different reaction conditions, 240 and 270 °C, 40 bar, 7500 and 15000 h⁻¹ with two m:a mixtures of 90:10 and 50:50. Although not shown in this report, we also evaluated the production of DME from syngas over a mixture of CZA_com and HPA at 200°C. However, at such low temperatures we found no catalytic activity, probably because at such low temperature the kinetics of the syngas to methanol reaction are very slow. The minimum operating temperature at which we could observe DME production from syngas is 240°C.

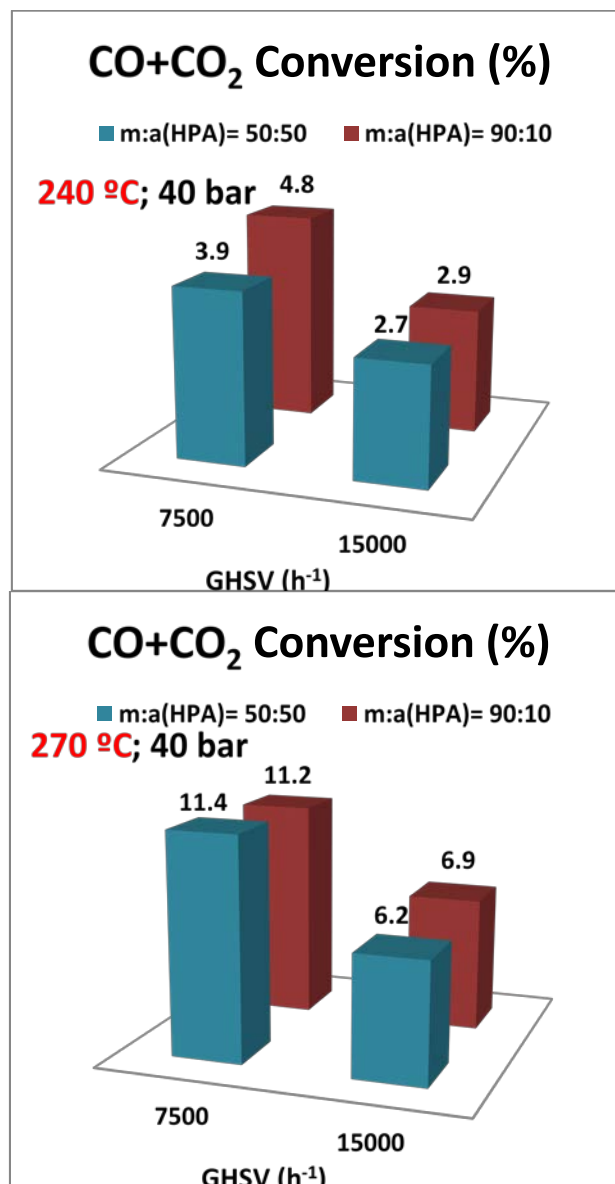


Figure 1. C Conversion with the catalysts mixtures: KATALCO and HSiW/TiO₂ with different ratios (m:a: 50:50 and 90:10) at 40 bar, 240-270 °C, 7500-15000 h⁻¹ and syngas CO₂/CO= 1.9 and m= 2.

As shown in Figure 1, the C (CO₂ + CO) conversion increases with the reaction temperature and decreases with the increasing GHSV for both catalytic mixtures. It can also be observed that C conversions are higher over the mixture containing the highest ratio of CZA_{com} (m:a 90:10). This effect is more relevant at 240 °C than at 270 °C.

In all cases, methanol and DME were observed as the reaction products. In fact, methanol and DME, particularly the former, were the only products observed with the m:a_(HPA) = 90:10 mixture. Remarkably, a major selectivity shift is observed when a higher fraction of acid catalyst is present in the catalyst bed, i.e. with the m:a_(HPA) = 50:50 mixture. As observed in the chromatogram shown in Figure

2, along with DME and methanol (note that in this case the DME/methanol ratio is higher than with the m:a = 90:10) a series of products are also observed.

We have not analyzed in detail the nature of these products but, in view of their position (retention times) and shape (symmetric and sharp), they probably account for hydrocarbons of different molecular weight.

It appears, that under the studied reaction conditions, the acid catalyst (HPA) is capable to convert methanol into hydrocarbons, in a process akin to the methanol-to-olefins (MTO) or methanol-to-gasolines (MTG) processes usually conducted over acid catalysts, typically HZSM5 and SAPOs. In view of these results, we tested the dehydration of methanol to DME with HPA conducted at 270°C but lower pressures up to 20 bar (note that methanol cannot be gasified at high pressure) also reveal the formation of undesired products along with DME.

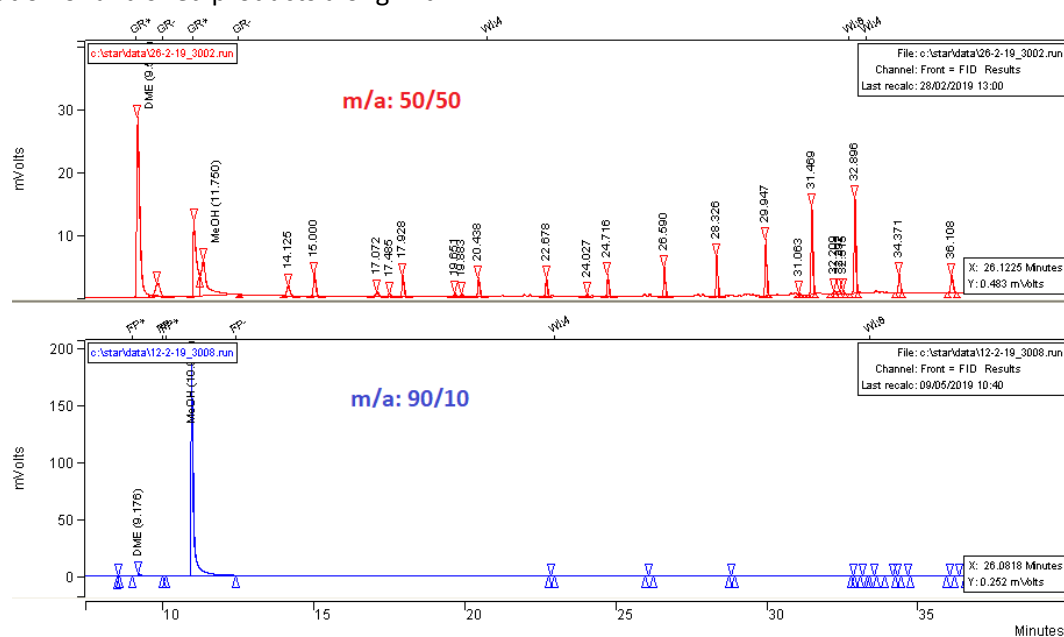


Figure 2. FID chromatogram of both mixtures: 50:50 (red color) and 90:10 (blue color) at 40 bar, 270 °C, 7500 h⁻¹ and syngas CO₂/CO= 1.9 and m= 2.

In view of these results, i.e., the lack of syngas transformation to and poor selectivity to DME, and production of non-desired by products (hydrocarbons) with the mixtures containing HPAs we decided to focus on γ -Al₂O₃ as the acid catalyst for DME production from syngas.

3.3 CZA_{com}/ γ -Al₂O₃ mixtures catalytic activity

In this section, we report the results obtained for the direct synthesis of DME from CO₂-rich syngas over catalytic mixtures of CZA_{com} and γ -Al₂O₃. Previous studies indicate that DME production from syngas (with H₂/CO= 1.5) is optimized by using a catalytic mixture containing a high loading of the Cu-catalyst, typically 90 < CZA < 92.5. In this context, we decided to study the catalysts ratio m:a= 90:10 and compare it with a mixture containing m:a= 50:50. However, our results indicated that DME productivity increases for this latter composition, so we also studied a mixture with higher amount of acid catalysts, namely m:a of 10:90. C-conversions obtained over the different mixtures studies have been compared to that obtained over CZA_{com} under the same reaction conditions.

To compare the results with the γ -Al₂O₃ (the reaction from methanol to DME) is not relevant since the methanol content or its space velocity during the reaction with the catalysts mixtures is unknown.

Syngas conversion over the different catalytic mixtures were tested at 270 °C (lower temperatures were not studied since $\gamma\text{-Al}_2\text{O}_3$ is not active), pressure of 25 and 50 bar and using GHSV of 5000 and 7500 h^{-1} and keeping the syngas composition $\text{CO}_2/\text{CO}=1.9$ with $M=2$. The activity results are expressed in terms of CO, CO_2 and $\text{CO}+\text{CO}_2$ conversion, DME productivity per $\gamma\text{-Al}_2\text{O}_3$ or DME per mixture of catalysts, and the DME/MeOH productivity ratio.

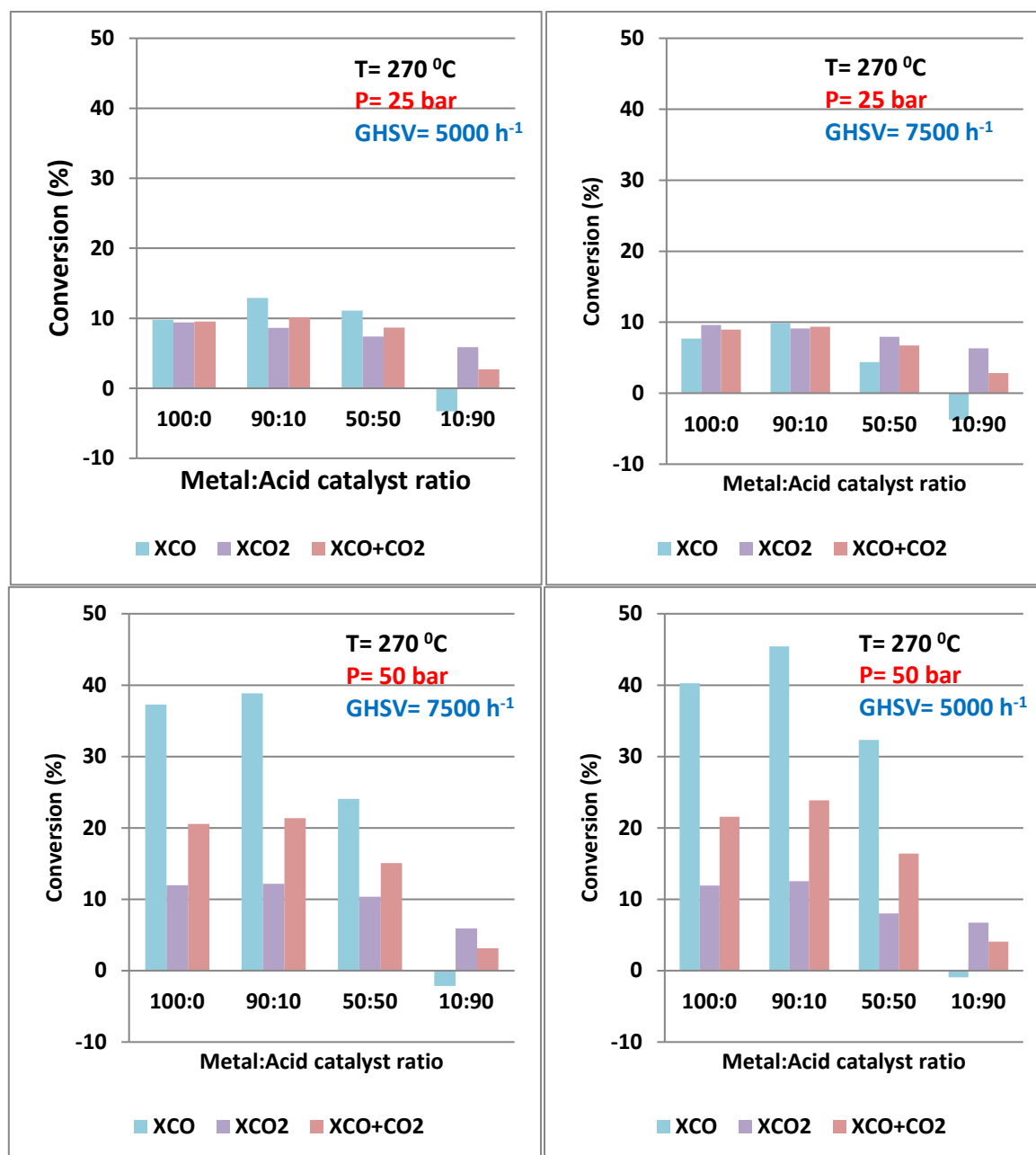


Figure 3. CO, CO₂ and CO+CO₂ conversion of different ratio catalysts at 270 °C, 25-50 bar, 5000-7500 h^{-1} , $\text{CO}_2/\text{CO}=1.9$ and $M=2$.

As observed in Figure 3, reaction pressure is the single variable that has the greatest impact in C conversion, higher than T and GHSV. This effect is more pronounced with the increasing fraction of CZA_{com} in the catalyst. The CO conversion in the mixture 90:10 was higher than that obtained over pure CZA_{com} (m:a= 100:0) at all the reaction conditions studied. The CO₂ conversion with the m:a ratio 90:10 is higher than the 100:0 only at 50 bar.

The mixtures with a lower content of CZA_com (m:a = 50:50 and 10:90) result in lower C conversions than CZA_com. C conversions are slightly higher at 5000 h⁻¹ than at 7500 h⁻¹, when the other reaction parameters remain constant.

The productivities of methanol and DME are shown in Figures 4 and 5 under different reaction conditions (GHSV).

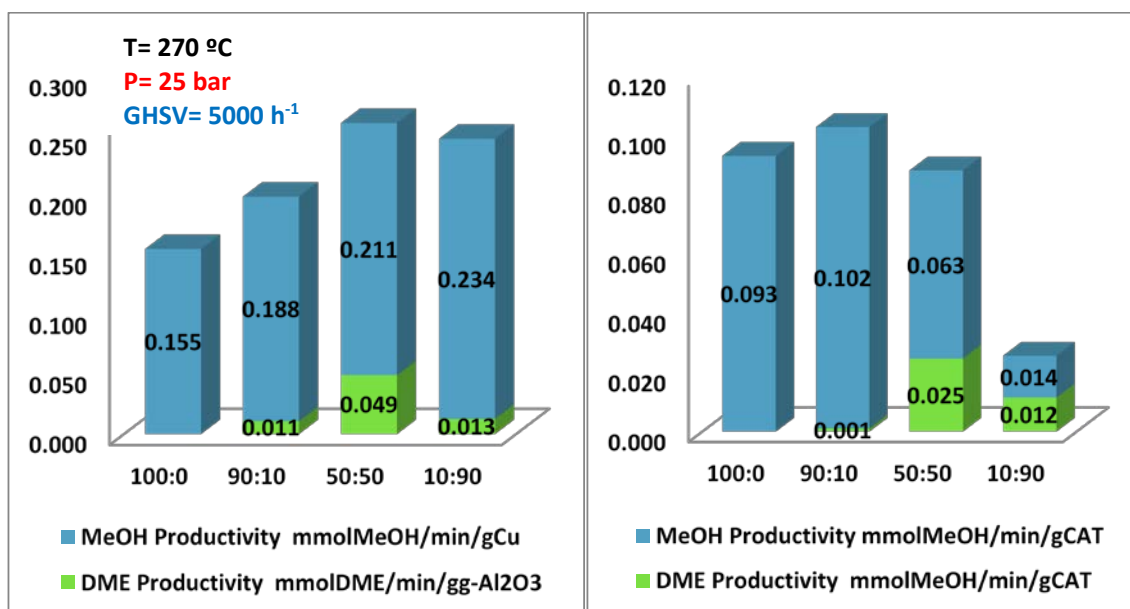


Figure 4. Methanol and DME productivity at 270 °C, 25 bar, 5000 h⁻¹, CO₂/CO= 1.9 and M= 2 (left: expressed as mmol_{MeOH}/min/g_{Cu} and mmol_{DME}/min/g_{γ-Al₂O₃}; right: mmol_{MeOH}/min/g_{Cat} and mmol_{DME}/min/g_{Cat}).

As shown in figure 4, the highest productivity of DME was achieved for the mixture containing equal amounts of CZA_com and γ-Al₂O₃, *i.e.*, m:a = 50:50. However, the catalytic mixture m:a = 10:90 is the one displaying the highest DME/Methanol ratios under all conditions studied.

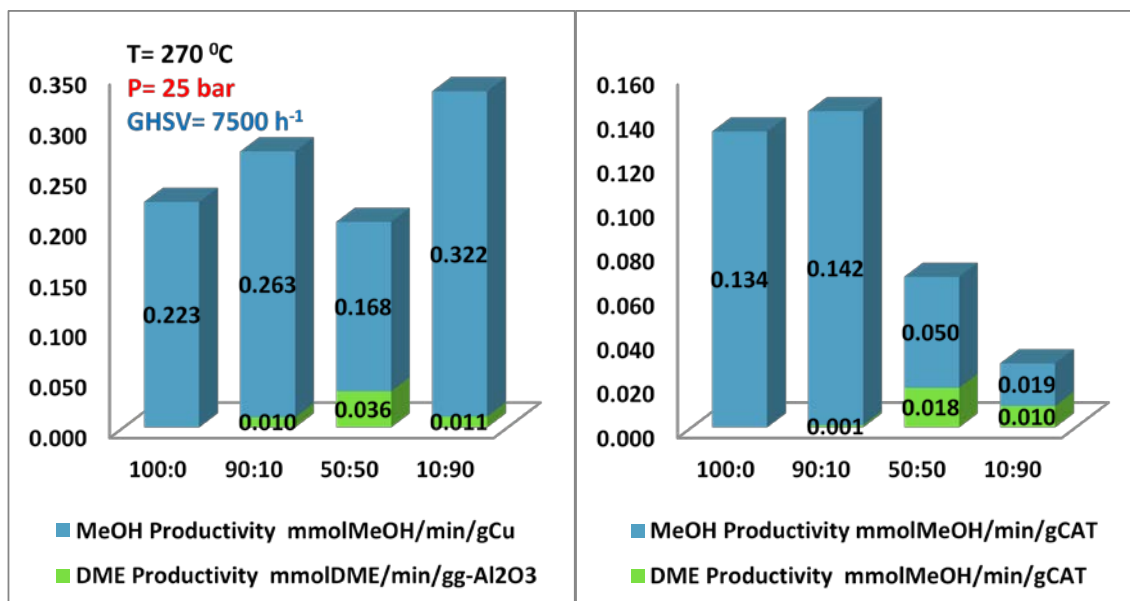


Figure 5. Methanol and DME productivity at 270 °C, 25 bar, 7500 h⁻¹, CO₂/CO= 1.9 and M= 2 (left: expressed as mmol_{MeOH}/min/g_{Cu} and mmol_{DME}/min/g_{γ-Al₂O₃}; right: mmol_{MeOH}/min/g_{Cat} and mmol_{DME}/min/g_{Cat}).

When the space velocity is increased from 5000 to 7500 h⁻¹ (at 270 °C and 25 bar), the DME productivity decreases in all the mixtures studied, as shown in figure 5. There's also an optimum DME productivity at m:a= 50:50.

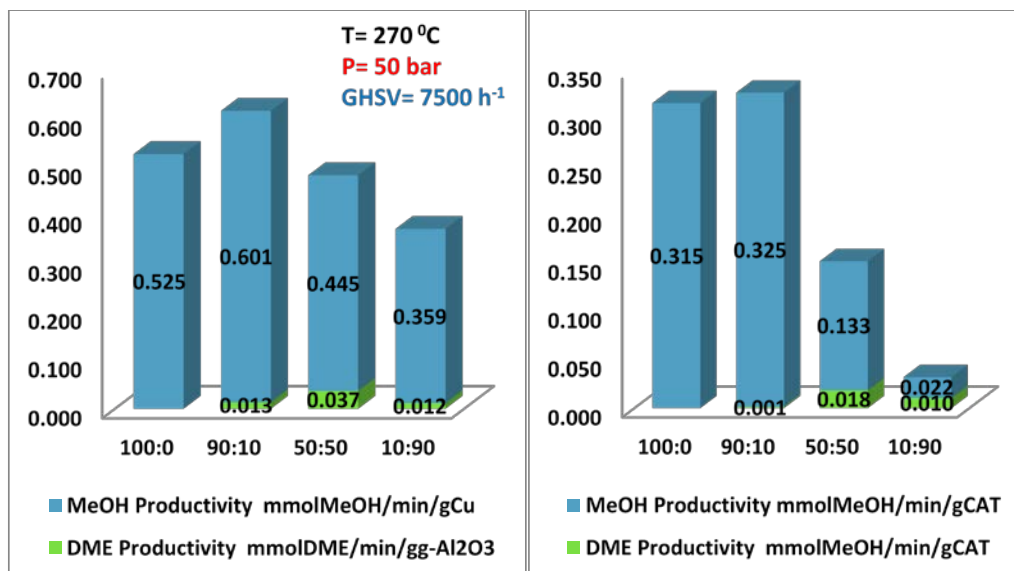


Figure 6. Methanol and DME productivity at 270 °C, 50 bar, 7500 h⁻¹, CO₂/CO= 1.9 and M= 2 (left: expressed as mmol_{MeOH}/min/g_{Cu} and mmol_{DME}/min/g_{γ-Al₂O₃}; right: mmol_{MeOH}/min/g_{Cat} and mmol_{DME}/min/g_{Cat}).

A similar trend is observed when the reaction pressure is raised to 50 bar. Thus, as shown in Figure 7, DME productivity is also higher with the catalysts mixture 50:50 irrespectively of the GHSV. This trend account to a higher C conversion rather than to a higher selectivity to DME, since methanol production (per gram of Cu) is also the highest for this particular catalyst mixture.

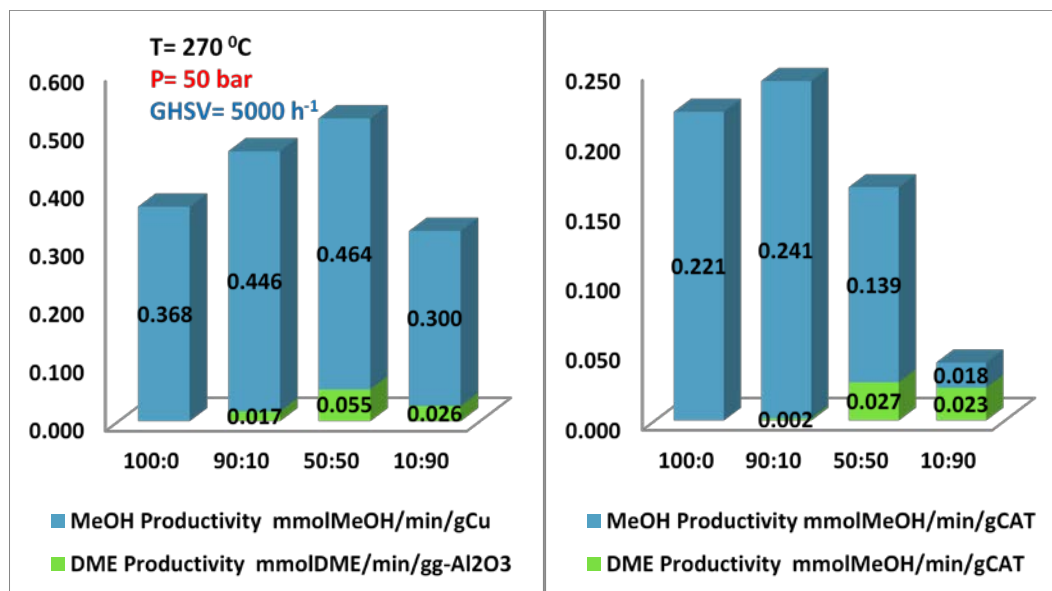


Figure 7. Methanol and DME productivity at 270 °C, 50 bar, 5000 h⁻¹, CO₂/CO= 1.9 and M= 2 (left: expressed as mmol_{MeOH}/min/g_{Cu} and mmol_{DME}/min/g_{γ-Al₂O₃}; right: mmol_{MeOH}/min/g_{Cat} and mmol_{DME}/min/g_{Cat}).

The highest DME productivities have been obtained working at high pressure (50 bar) and low GHSV (5000 h⁻¹) with the CZA_{com} to γ-Al₂O₃ ration of 50:50.

However, due to the relevance of DME separation from the products flow, the absolute productivity of DME may not be the only factor to be considered. Thus, Figure 8 shows the DME/methanol-ratios obtained under all reaction conditions studied in this work. As observed, the DME/methanol ratios obtained increases with the increasing content of γ-Al₂O₃ in the mixtures.

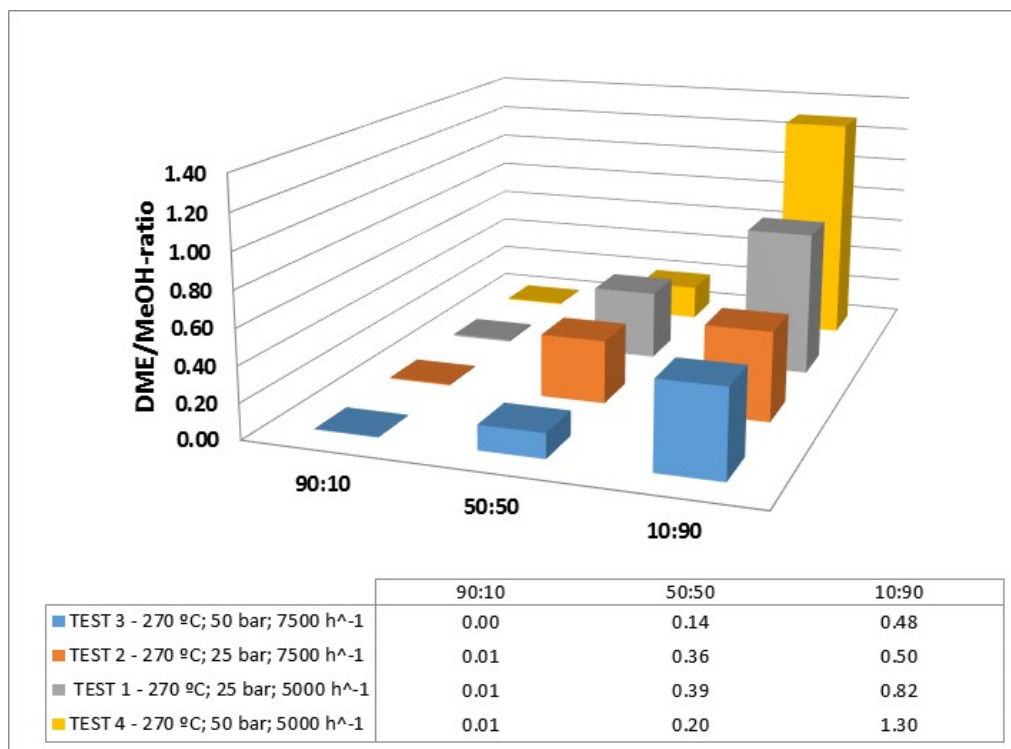


Figure 8. DME-methanol-ratio in the out flow at 270 °C, 25-50 bar, 5000-7500 h⁻¹, CO₂/CO= 1.9 and M= 2.

The higher DME/methanol-ratio was obtained with the mixture m:a mixtures of 10:90 at 270 °C, 50 bar and 5000 h⁻¹. The mixture 50:50, which leads to the highest DME productivities, especially at high pressure, displays higher DME/methanol ratio at 25 bar than at 50 bar. The mixture with the highest CZA loading got the lowest DME selectivity.

Despite the m:a mixture of 10:90 gave the best results in terms of DME selectivity, the highest DME productivity was obtained with the catalysts mixture 50:50 at 270 °C, 50 bar and 5000 h⁻¹. These are the conditions chosen for the durability test.

3.4 Optimum composition of catalyst mixtures for the production of DME from syngas. Durability test.

The catalyst mixture 50:50 was selected to study the stability with the time on stream (TOS), at the optimum reaction conditions.

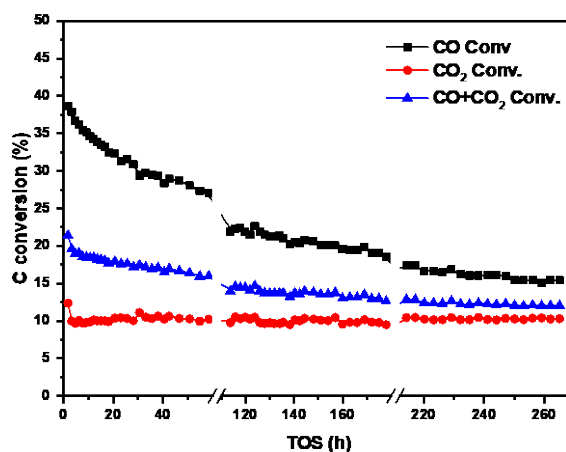


Figure 9. CO, CO₂ and CO+CO₂ conversion with m:a= 50:50 at 270 °C, 50 bar, 5000 h⁻¹, CO₂/CO= 1.9 and M= 2.

Figure 9 shows the evolution of CO, CO₂ and CO₂+CO conversion with time on stream. As observed CO₂+ CO conversion declines with TOS until ca. 120 h when it reaches the stationary state at conversions around 15 %. This deactivation accounts mostly to the declining in CO conversion. On the other hand, CO₂ conversion remains steady during TOS.

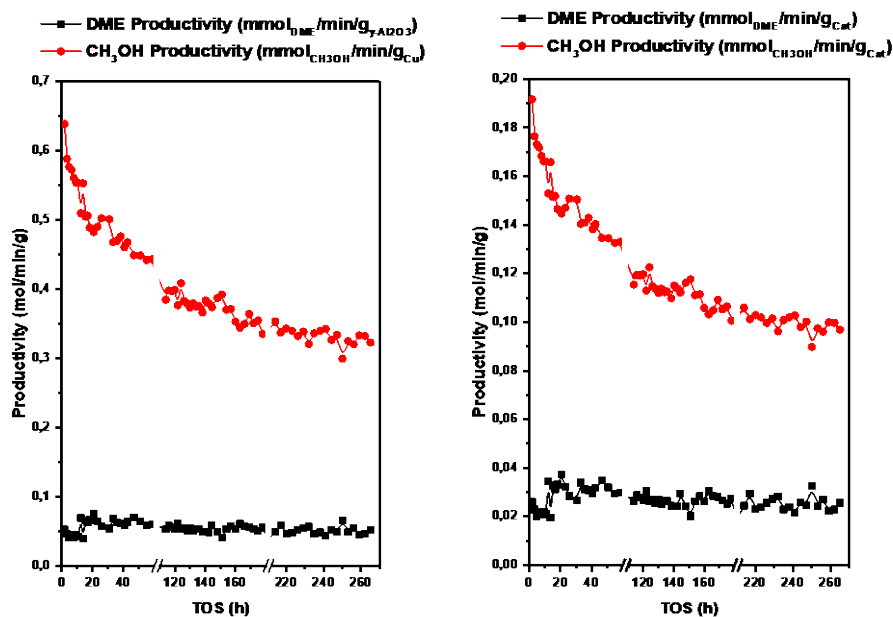


Figure 10. Methanol and DME productivity with m:a= 50:50 at 270 °C, 50 bar, 5000 h⁻¹, CO₂/CO= 1.9 and M= 2 (left: expressed as mmol_{MeOH}/min/g_{Cu} and mmol_{DME}/min/g_{γ-Al₂O₃}; right: mmol_{MeOH}/min/g_{Cat} and mmol_{DME}/min/g_{Cat}).

The evolution of DME and methanol productivities with TOS are shown in Figure 10. As observed, DME productivity remains constant during the study (ca 260 h), but a swift drop of methanol productivity (ca. 50%) is observed. This feature suggests that the catalyst responsible for methanol production, CZA_{com}, is becoming deactivated during operation.

4 Conclusion

- Syngas can be directly transformed to DME using catalytic beds containing a mixture of CZA_com and an acid catalyst. DME productivity depends on the actual ratio of each catalyst.
- In all cases, either pure methanol or DME / methanol mixtures are obtained
- The catalytic mixture using heteropolyacids (HPA) as acid catalyst is not 100 % selective to DME and methanol and by products (most likely hydrocarbons) are also obtained.
- The catalysts mixtures with CZA_com and γ -Al₂O₃ yielded the best results in terms of DME productivity. The catalysts mixture m:a= 50:50 led to the highest DME productivities, especially at 270 °C, 50 bar and 5000 h⁻¹.
- The highest DME/methanol productivity-ratio was obtained with the mixture m:a= 10:90 at 270 °C, 50 bar and 5000 h⁻¹.
- The durability study (265 h on stream with the m:a 50:50 mixture) reveals that methanol production drops by ca. 50 % during TOS but DME production remains roughly constant.

5 Acknowledgment

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