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**D2.4- Synthesis, characterization and catalytic performance of Cu/ZnO/Al₂O₃
and MnO_x/Co₃O₄ for the methanol synthesis**

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1 Executive summary

Cu/ZnO/Al₂O₃ (CZA) catalysts with different Al₂O₃ content (hence different Cu loading) either promoted (ZrO₂, Ga, or Pd) or not have been synthesized, characterized and tested for the methanol production from syngas. Syngas with different CO₂/CO ratios (1.9 and 0.5) have been tested. Modules, M= (H₂-CO₂)/(CO+CO₂) of 1 or 2 have been tested. In addition, a catalyst based on CoO_x/MoO_x has also been studied.

CZA catalysts are active for the methanol production from syngas, except for the catalyst with the lowest Cu loading which only displayed activity for the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$). The methanol productivity increases with the Cu loading on the catalyst irrespectively of the reaction conditions. Methanol productivity also depends on reaction conditions, T, P, GHSV and CO₂/CO ratio. For instance, high methanol productivity is reached when CO₂/CO = 0.5 as compared to 1.9. The addition of promoters does not improve methanol productivity except for ZrO₂ at high temperatures.

2 Introduction

Methanol production from syngas at the industry is conducted with Cu/ZnO/Al₂O₃ catalysts. The catalysts are usually synthesized by coprecipitation of nitrate precursors of the metal phases at controlled pH (around 8) and temperature, rendering hydroxycarbonates, which are subsequently calcined to produce oxides. The catalyst should be reduced under controlled conditions to produce Cu⁰/ZnO phases, which are supposed to render the most active moieties for methanol production.

Whereas it has been identified that the presence of small amounts of CO₂ in the syngas are beneficial for the methanol production, the kinetics of the process slow when high amounts of CO₂ are present in the feed, like for instance from biomass derived syngas. Studies dealing with the effect of syngas composition (CO₂/CO ratio) for methanol production are scarce in the literature. In addition, the composition of the catalysts for the transformation of CO₂-rich syngas has not been optimized hitherto.

ZrO₂ has been used in catalysts for methanol production due to its acid properties, which are reported to contribute to CO₂ and CO adsorption and ability to operate with current with high CO₂ content. In addition, Ga- and Pd- have been reported to improve the WGS reaction and methanol production rate, respectively.

In this deliverable, we report the synthesis and characterization of a series of Cu/ZnO/Al₂O₃ catalysts prepared in our labs with different loading of Al₂O₃ (and Cu). The catalytic performance for the methanol production from syngas with different CO₂/CO ratios, and the effect of parameters such as T, P and GHSV have been evaluated. The effect of promoters, ZrO₂, Ga or Pd has been also evaluated. The catalytic performance of the catalysts for the production of methanol has been compared against a benchmark Cu/ZnO/Al₂O₃ catalysts (Katalco 51-8)

3 Methanol synthesis from syngas

The published information about the copper-zinc-alumina (Cu/ZnO/Al₂O₃, CZA) catalysts for the methanol synthesis from syngas is extensive. Despite the interest in methanol production from biomass derived syngas, studies dealing with the effect of CO₂/CO ratio in the catalytic performance of CZA catalysts are scarce. This deliverable reports the results obtained with homemade CZA catalysts with different compositions and the effect of promoters for the synthesis of methanol from syngas with different CO₂/CO ratio under different reaction conditions. In addition, the performance of a commercial catalyst (KATALCCO 51-8) has been also studied.

3.1 Methanol synthesis from syngas with the benchmark catalyst (KATALCO™ 51-8)

Commercial catalyst: KATALCO™ 51-8 (referred to as CZA-comm) is a copper catalyst on a ZnO-Al₂O₃ support with a MgO promoter, used in the synthesis of methanol from H₂, CO and CO₂ mixtures arising from steam reforming of hydrocarbons, coal gasification or POx.

The catalytic bed was prepared by diluting the catalyst (0.2 g, 0.25-0.30 mm) with SiC ($V_{SiC} + V_{catalyst} = 1.65 \text{ cm}^3$) to avoid the formation of temperature gradients during the reaction. The reaction was performed at pressure 50 and 25 bar, varying the GHSV at 2500 and 5000 h⁻¹ and 240 °C and 275°C. The CO₂/CO ratios of 1.9, 1.0, and 0.5 have been studied. In all experiments, the M-module $[M = (H_2 - CO_2)/(CO + CO_2)]$ was 2. In some cases M=1 has been also studied. Each conversion value was obtained by averaging at least 4 points during no less than 4 h under reaction conditions (table X).

Table 1. Experimental matrix, catalytic performance of CZA-comm for the synthesis of methanol under different reaction conditions.

Test no.	Temp. °C	P bar	GHSV m ³ _{syngas} /h/m ³ _{ca}	M	CO ₂ /CO ratio	CO Conversion	CO ₂ Conversion	CO+CO ₂ Conversion
						[%]		
1	240	25	2500	2	1.9	40.2	7.8	19.0
2			5000			26.3	7.4	13.9
3		50	2500			67.6	13.2	31.7
4			5000			54.5	10.9	25.7
5	275	25	2500			15.2	8.6	10.9
6			5000			12.8	8.3	9.9
7		50	2500			47.4	12.0	24.3
8			5000			45.9	11.5	23.5
9	240	25	2500		1	48.1	5.9	26.8
10			5000			38.5	5.5	21.9
11		50	2500			78.7	11.4	44.8
12			5000			68.4	10.8	39.5
13		25	2500			22.7	6.3	14.4
14			5000			20.3	6.2	13.2
15		50	2500			55.2	8.9	31.9
16			5000			53.2	9.3	31.2
17	240	25	2500		0.5	51.7	0.6	34.6
18			5000			48.8	-2.1	31.8

19		50	2500			78.9	5.3	54.3
20			5000			77.1	5.8	53.2
21	275	25	2500			21.9	-1.0	14.2
22			5000			25.6	1.6	17.5
23		50	2500			58.8	-1.9	38.4
24			5000			56.7	1.1	38.0

The benchmark catalyst was also performed for the methanol production with M=1 in order to study the flexibility in the feed composition. In figure 1 the syngas conversion to methanol with M=1 and M=2 is shown.

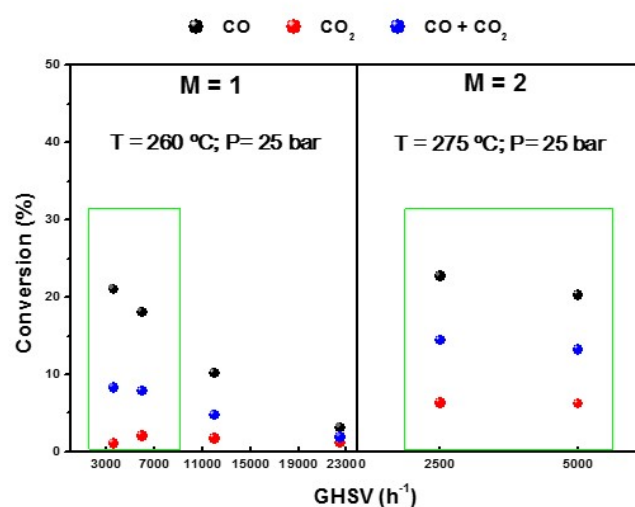


Figure 1. Effect of M in the catalytic activity of CZA_comm. CO₂/CO= 1, 260 – 275 °C and 25 bar.

As observed in Table 1, the conversion values with CO₂/CO=1 at 25 bar decrease with the increasing the temperature from 240 to 275 °C. With this results in mind, Figure 1 shows that feeding the stoichiometric H₂ (M=2) at 275 °C results in higher conversion than with M=1 at 260 °C.

The external diffusivity of CZA-comm was evaluated, see Figure 2. The methanol production from syngas was performed at 240 °C and 50 bar, varying the GHSV from 2500 to 12500 cm³_{syngas}·cm³_{cat}⁻¹·h⁻¹ with syngas CO₂/CO= 1.9.

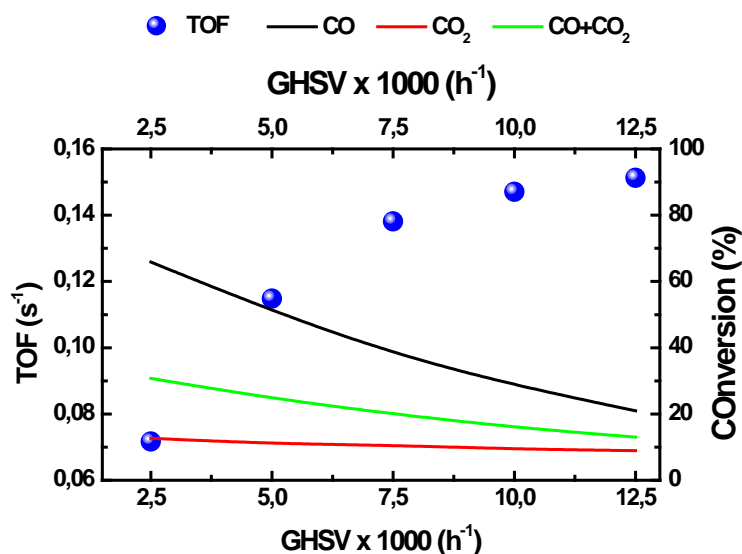


Figure 2. Turn over frequency (left Y-axis) blue dots and syngas conversion (right Y-axis) straight lines obtained with Cu/ZnO/Al₂O₃ commercial catalyst for the methanol production at different GHSV

The methanol productivity rate was also calculated at higher gas hourly space velocities (Fig. 3) at 240 °C, 50 bar and syngas composition CO₂/CO= 1.9.

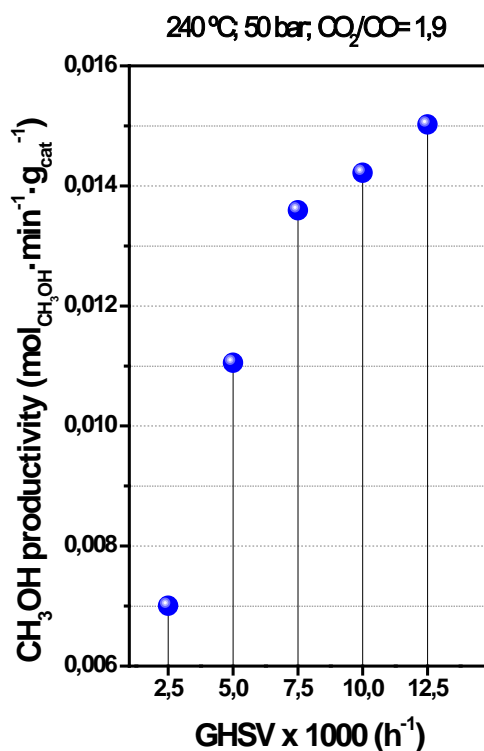


Figure 3. Methanol productivity vs GHSV with CZA-comm

Figure 2 reveals the range at which diffusivity phenomena are present. At low GHSV, changes in the system are not controlled by the chemical reaction rate but by external diffusivity, as shows the increasing productivity per gram of copper with the GHSV at these low values. When the productivity reaches a plateau in its maximum value, the controlling process switches to the catalysis phenomena, and is observed for GHSV values between 7500-10000 h⁻¹.

In view of these results, GHSVs of 7500 and 15000 h⁻¹ were selected to study the performance of the CZA catalysts prepared in our lab.

3.2 Methanol synthesis from syngas with Cu/ZnO/Al₂O₃ catalysts

3.2.1 Synthesis of Cu/ZnO/Al₂O₃ catalysts for methanol synthesis

A series of Cu/ZnO/Al₂O₃ catalysts with Al₂O₃ loadings of 5, 20, 30 and 40 wt.%, maintaining the Cu/ZnO ratio equal to 2.4 mol have been prepared by co-precipitation of the salt precursors; Cu(NO₃)₂; Zn(NO₃)₂ and Al(NO₃)₃. Na₂CO₃ was used as the precipitating agent and the pH was controlled using a pH-stat around a value of 8. The catalysts obtained are labelled as CZA_X where X is the wt.% fraction of Al₂O₃ in the catalyst.

Table 2. Catalyst nomenclature and nominal composition and actual composition determined from ICP (in parenthesis) (wt.%)

Catalyst	Cu	ZnO	Al ₂ O ₃
CZA_5	62 (67)	33 (29)	5 (5)
CZA_11	57.7	30.7	11.6
CZA_20	52.2 (59)	27.8 (24)	20 (18)
CZA_30	45.7	24.3	30
CZA_40	39.2	20.8	40
CZA_50	32.6 (33)	17.4 (13)	50 (54)

3.2.2 Characterization of CZA-X catalysts for methanol synthesis

The elemental composition of the catalysts CZA_X (X: 5, 20 and 50) catalysts was obtained by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Results are shown in Table 2. As observed, the values obtained agree well with the nominal values.

The Cu/ZnO/Al₂O₃ catalysts prepared have been characterised by a combination of several techniques. *In situ* XRD were recorded under H₂ flow at increasing temperatures from r.t. until 300°C. The data were used to determine the temperature at which CuO is fully reduced. In addition, the diffractograms recorded at 250°C were used to determine the size of Cu⁰ crystallites. Figure 1 shows the diffractograms for the samples reduced at 250 °C, the size of Cu particles as determined from the Scherrer equation is shown in the Figure. Cu crystallite size ranges between 4 and 15 nm.

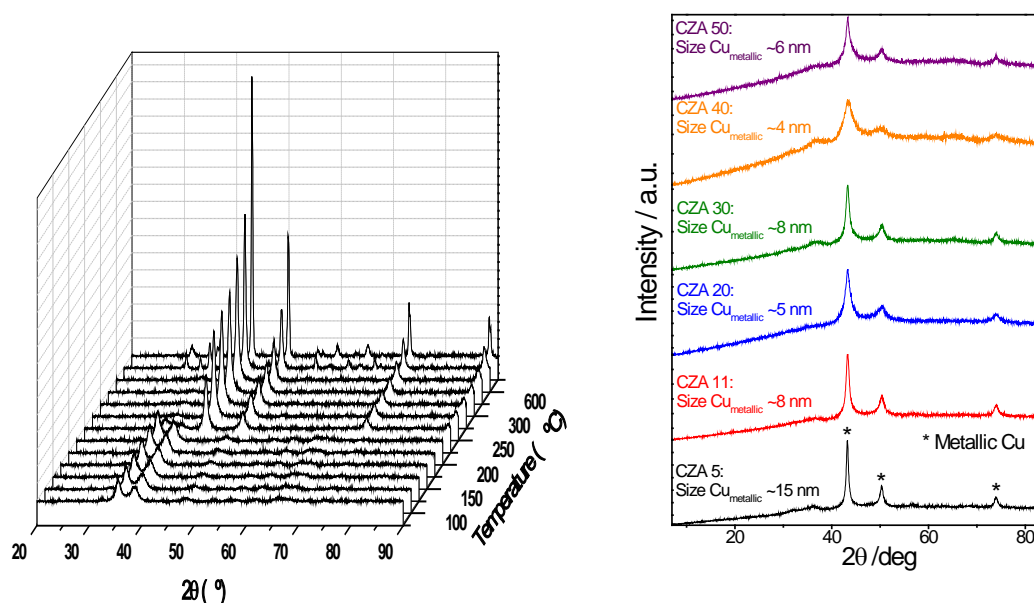


Figure 4. Left: Diffractograms for CZA-11 recorded at increasing temperatures under H₂. Red diffractograms are for CuO (01-080-0076), blue ones for metallic Cu (01-085-1326) and green ones for the spinel (01-078-0556). Right: Diffractograms of CZA_X catalysts reduced at 250°C, and Cu⁰ particle size as obtained from the Scherrer equation

Diffraction lines for ZnO or Al₂O₃ phases are not observed in the diffractograms at 250°C (diffraction lines for ZnO can be observed at T above 600°C, at higher temperatures the formation of the spinel is also detected). The lack of such diffraction lines indicates that these phases are either amorphous or highly dispersed in the catalysts.

The morphology of the CZA_X catalysts has been analysed by electron microscopy combining HR-TEM, STEM, HAADF and SAED techniques. Figure 5 shows a representative image of CZA_11 illustrating how particles are composed of Cu and ZnO domains (see FFT patterns in the inset to the figure) coexisting in one single particle. The composition of the particle has been analyzed in the STEM mode across the particle. As observed in Figure 5, Cu is distributed along the particle whereas Zn is preferentially located at the edges of the particle.

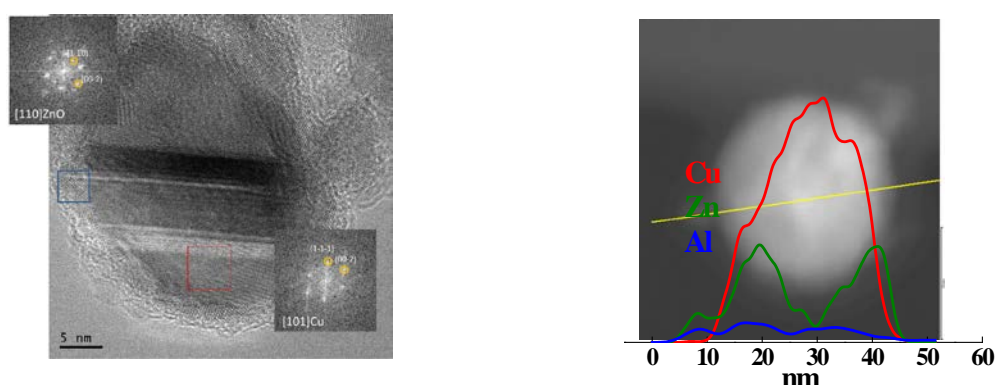


Figure 5. Left: HRTEM image of CZA_11. The FFT diagrams (inset figures) of selected regions indicate the presence of crystalline domains of Cu (red square) and ZnO (blue square). Right: Z-contrast compositional profile of CZA_11.

The same conclusions can be drawn for the rest of the CZA_X series. Particles are composed of Cu and ZnO particles.

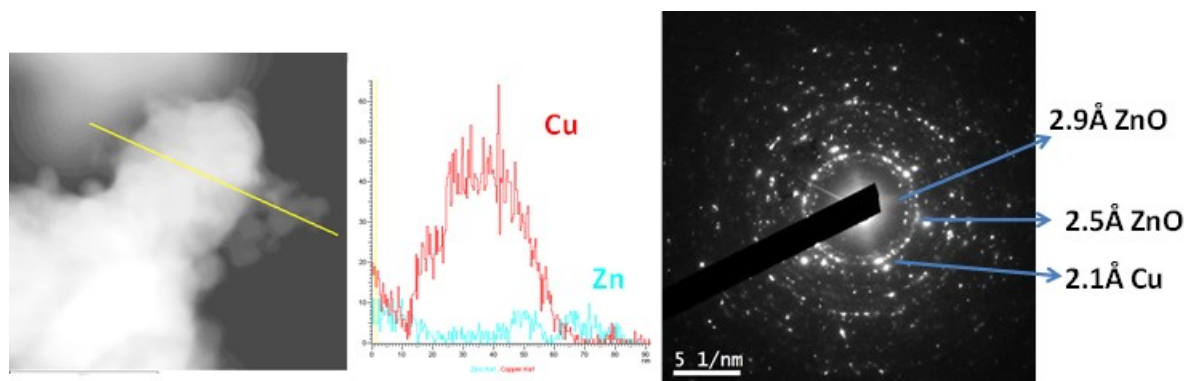


Figure 6. From left to right, STEM, line scan composition and SAED pattern of CZA_5 catalyst.

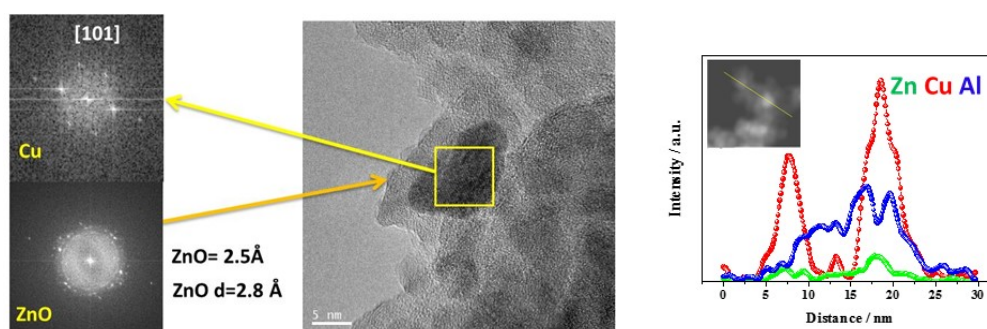


Figure 7. Left: HR-TEM and FFT diagrams indicating the presence of Cu and ZnO phases and Right: compositional analysis across a CZA_50 particle

In general, microscopy results reveal the presence of Cu and ZnO phases that coexist in all particles. In most cases, Cu and ZnO particles are vicinal and present a large interphase. A preferential orientation towards the Cu [110] planes is observed. Al₂O₃ is distributed homogeneously in the particles. For the samples with high Al₂O₃ content (*e.g.* CZA_50) it can be observed that Al₂O₃ is located at the surface of the particles, probably covering Cu particles.

Particle size and specific surface areas of CZA_X has been determined from TEM images by counting more than 100 particles. The average size ($d_{v/a}$) has been calculated as follows ($d_{v/a} = \Sigma d^3 / \Sigma d^2$). The values has been used to estimate specific surface areas (A_s). The values obtained are CZA_10: $d_{v/a}$ = 26 nm and A_s =26 m²/g. CZA_20: $d_{v/a}$ = 25.6 nm and A_s =26 m²/g. CZA_30: $d_{v/a}$ = 6 nm and A_s =110 m²/g and CZA_50: $d_{v/a}$ = 7.1 nm and A_s =94 m²/g.

Thermogravimetric analyses under controlled atmosphere have been also carried out. Figure 8 shows the differential H₂-DTA analyses for all samples.

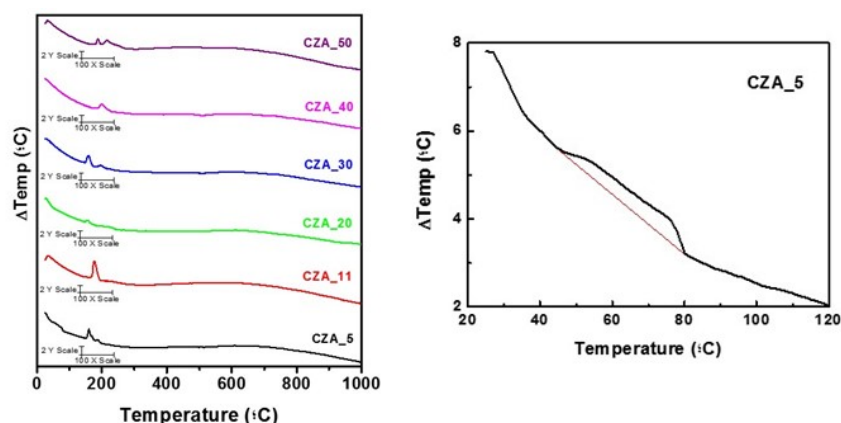


Figure 8. Left: H₂-differential thermal analysis (H₂-DTA) profiles of the CZA-series recorded in H₂/N₂ (20/80 v/v flow at 2°C/min). Right: Magnification of the TGA profile of CZA_5 at low temperature

As observed in Figure 8, a reduction process is observed at ca. 200°C for all samples. In addition, a further reduction process at low temperature is observed for CZA_5 (the sample with the highest content of Cu) suggesting that Cu particles are reduced (partially) at low temperatures. These results are in good agreement with the XRD data shown above, and with the reducibility analysis conducted by thermal programmed reduction (TPR) in H₂ (data not shown).

The textural properties of the catalysts have been determined from the N₂ adsorption-desorption isotherms. The samples display similar isotherms with a hysteresis loop, more visible in the samples with higher Al₂O₃ loading. The specific surface areas (BET method) lay around 40 m²/g for CZA_5, 11 and 20. The samples with higher Al₂O₃ loading (CZA_30, 40 and 50) display BET areas around 110 m²/g. Results are shown in Figure 9.

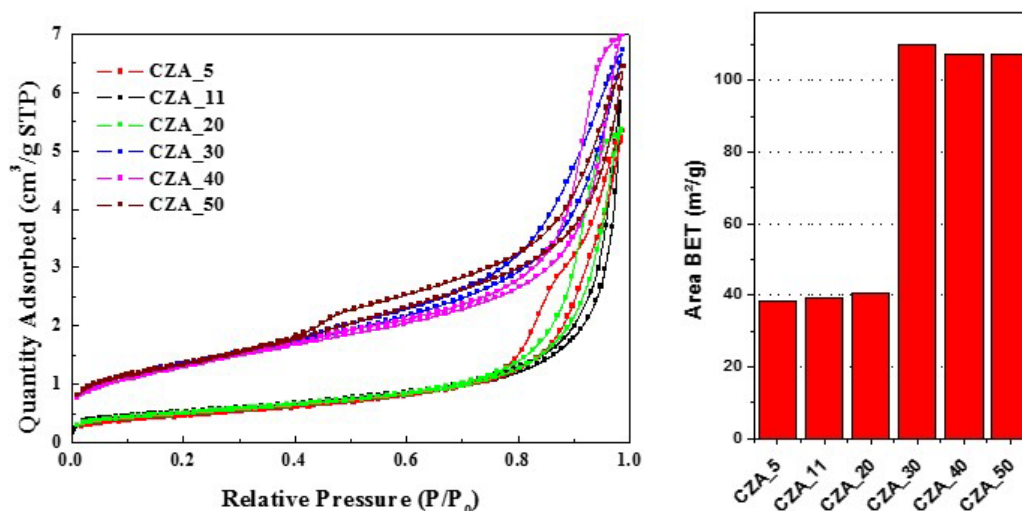


Figure 9. Left: N₂ adsorption-desorption isotherms. Right: Specific surface areas of CZA_X catalysts

The surface composition of the CZA_X catalysts has been analyzed by X-ray photoelectron spectroscopy (XPS). The spectra of the samples treated at 250°C in H₂ were recorded. The spectra of all samples show a peak at ca. 932.7 eV corresponding to the Cu 2p_{3/2} and assigned to metallic Cu. In addition peaks at ca. 74.5 eV (for Al 2p), 1021.6 (for Zn 2p_{3/2}) were observed and ascribed to Al in Al₂O₃ and Zn²⁺ species, respectively. The surface atomic composition was evaluated for the area of the XPS peaks. The values obtained are collated in Table 3.

Table 3. Surface atomic composition of CZA-X catalysts

	%at. Cu	%at. Zn	%at. Al
CZA_20	11	15	75
CZA_30	9	13	77
CZA_40	9	9	81
CZA_50	6	9	85

As observed, the amount of surface Cu and Zn increases for the samples with the lower concentration of Al₂O₃, *i.e.*, with the increasing content of Cu. This trend, which may be in apparent conflict with the observation of the decreasing Cu particle size in the samples with higher Cu loadings indicates that Al₂O₃ phases could be deposited on the surface of Cu particles for the samples with high Al₂O₃ loadings.

The hydrophobicity of the catalysts was assessed by placing a drop of H₂O on the surface of the catalyst and observing the contact angle. As deduced from the images in Figure X, CZA_5 is a more hydrophobic catalyst than CZA_20-30 and 50. This observation clearly indicates that hydrophobic/hydrophilic properties are dominated by the Al₂O₃ loading on the samples, as depicted in Figure 10.

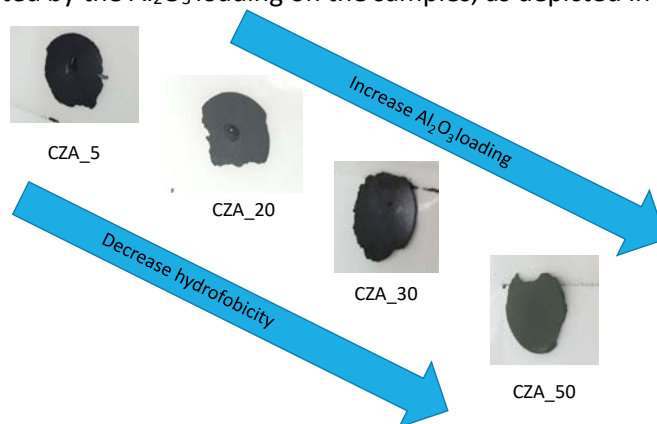


Figure 10. From left to right pictures of H₂O drop on CZA_X : X= 5, 20, 30 and 50 catalysts

The oxidation state and environment of Cu in CZA_11 and CZA_50 has been studied by x-ray absorption (XAS) in the the SpLine at the ESRF synchrotron facilities in Grenoble (France). X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) spectra were collected on the Cu K-edge. Figure 11 (left) shows the XAS spectra. Cu foil and CuCl₂ are used as Cu⁰ and Cu²⁺ standards. XANES Cu K-edge of CZA_11 and CZA_50 lies close to Cu⁰ but with a slightly displacement to higher energy (inset figure), indicating the presence of a small amount of oxidized Cu, more evident for CZA_50. The EXAFS region, at higher energies, show a less defined spectra compared to Cu foil, indicating a smaller particle size in our samples. Fourier-transformation of the EXAFS for CZA_11 and CZA_50. For the sake of comparison, the spectra for a metallic Cu foil is also shown. As observed, the main peak appears at ca. 2.5 Å and is ascribed to Cu-Cu distances (*i.e.*, metallic Cu). In addition, a peak

indicative of a distance a ca. 1.8 Å ascribed to Cu-O bonds in CuO is also observed. Both CZA samples are mainly composed of metallic Cu, but a small fraction of partially oxidized Cu is also observed. The content of such oxidized phases is higher in CZA_50 than in CZA_10 probably due to the smaller size (higher oxophilicity) of the Cu particles in the former. Similar conclusions can be drawn from the XANES spectra, Figure 11 (right).

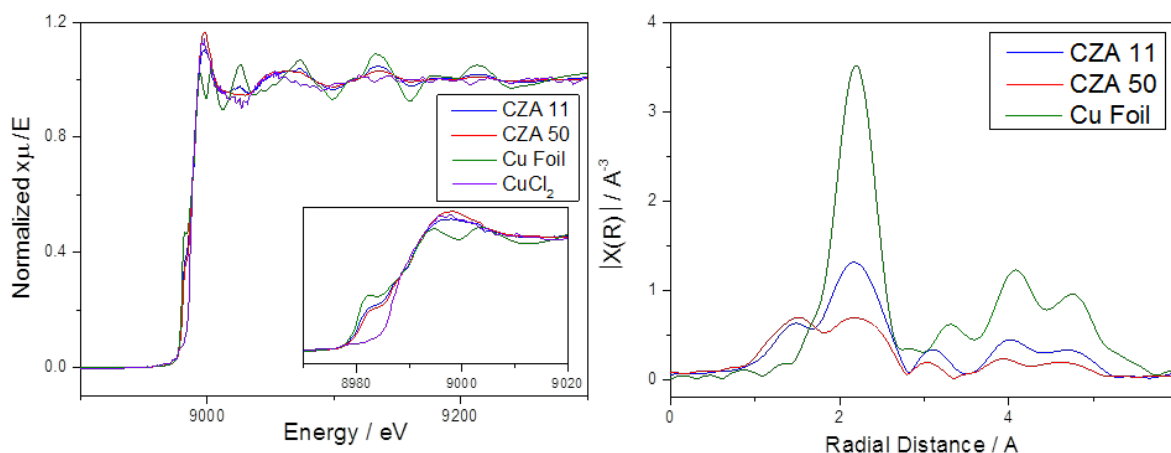


Figure 11. Left: Cu K-edge XAS spectra of CZA_11, CZA_50, CuCl₂ and Cu foil. Right: Fourier Transformation from Cu K-edge EXAFS signal for CZA_11, CZA_50 and Cu foil.

In summary, we have synthesized a series of Cu/ZnO/Al₂O₃ catalysts with different loadings of Cu, ZnO and Al₂O₃ phases by co-precipitation of the metallic precursors at controlled pH (8). The composition of the catalysts is close to the targeted one. After reduction at 250°C metallic Cu and ZnO phases are detected, in most cases forming interphases between both phases. XAS results indicate the presence of partially oxidized Cu in all samples, especially in the ones with the lowest Cu loading. Al₂O₃ is homogeneously in the catalysts. The samples with the higher amount of Al₂O₃ display some Al₂O₃ covering Cu and ZnO particles.

3.2.3 Catalytic performance of CZA_X catalysts for methanol synthesis

The catalytic performance of CZA_5, 20 and 50 catalysts has been evaluated in a fixed bed micro reactor under different reaction conditions (240-275 °C; 25-50 bar; 7500-15000 h⁻¹ and CO₂/CO-ratios of 0.5 and 1.9). Additionally, CZA_5 was evaluated at 40 bar / 260 °C and CO₂/CO-ratio 0.5. Unless otherwise stated M=2.

Previous to the catalytic tests, the catalysts under study were pre-treated at 250 °C under a H₂/N₂ flow (20/80 vol.) for 2.5 hours. Methanol was the only product detected (along with CO₂ and CO) in all cases except for CZA_50 catalyst, which is not active for the production of methanol under the reaction conditions studied in this project, being active only for the water gas shift reaction.

CO + CO₂ conversion and CH₃OH production were calculated from Eq. 1 and Eq. 2, respectively

$$X_{CO+CO_2}(\%) = \frac{(CO_{in}+CO_{2in})/N_{2in} - (CO_{out}+CO_{2out})/N_{2out}}{(CO_{in}+CO_{2in})/N_{2in}} * 100 \quad \text{Eq.1}$$

$$\eta_{MeOH} \left(\frac{mol}{h} \right) = \eta_{CO} \cdot X_{CO} + \eta_{CO_2} \cdot X_{CO_2} \quad \text{Eq.2}$$

Where η_{CO} and η_{CO_2} are the molar rate of the corresponding compounds in the feed. They are obtained taking into account the gas rate and the reaction conditions.

Figure 12 compares CH₃OH productivity for CZA_5 and CZA_20 obtained at different reaction conditions as indicated in the Figure (25 and 50 bar, 240°C and 270 °C, 7500 and 15000 h⁻¹ and CO/CO₂ = 1.9 or 0.5)

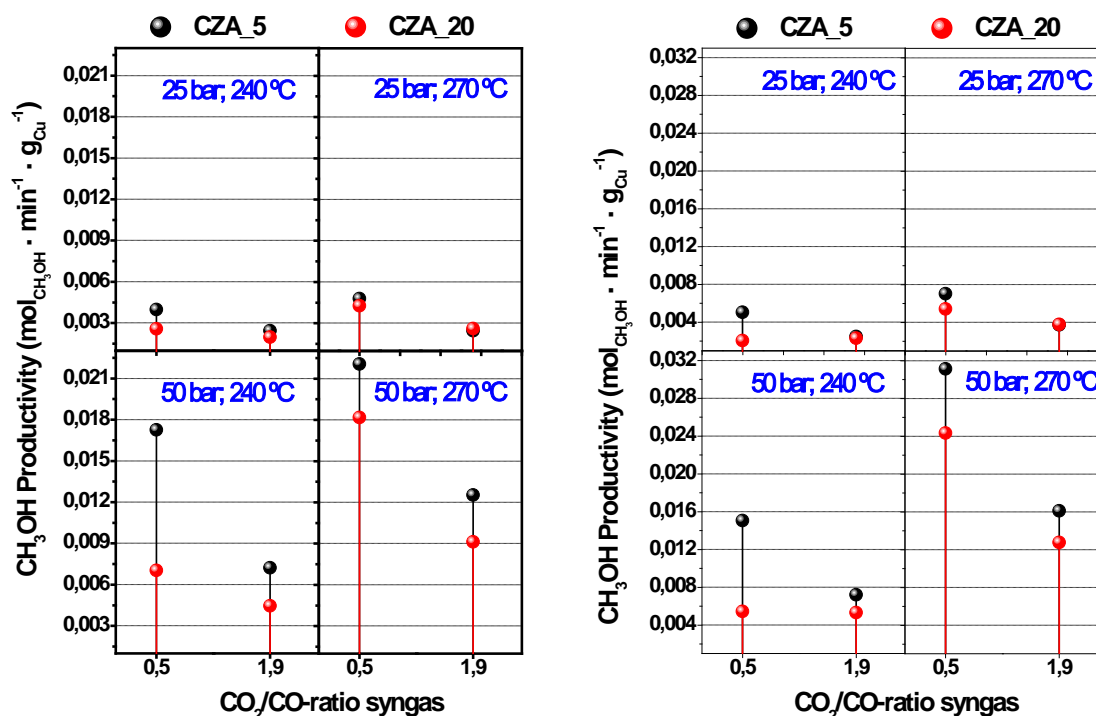


Figure 12. Methanol productivity with CZA_5 and CZA_20 at 7500 h⁻¹ (left) and 15000 h⁻¹ (right) under different reaction conditions

In all cases, the only products detected were CO, CO₂ and CH₃OH indicating that only the (R)WGS (reverse water gas shift reaction) and the methanol production were the only reactions taking place. This observation indicates that the Al₂O₃ in the support lacks of acidity and it only serves as support for the Cu and ZnO phases. The lack of acidity accounts to the preparation method, which as described above is based on the precipitation of the metallic oxides at high pH (=8) followed by calcination. Under this high pH the acid sites of the Al₂O₃ are blocked irreversibly.

Comparing the two catalysts with the highest Cu content (CZA_5 and CZA_20) (Figure 12, left) reveals that CZA_5 produces methanol in a higher rate than CZA_20 at both GHSV (7500 and 15000 h⁻¹). Moreover, CO₂ conversion values near to the equilibrium are reached with both CZA_5 and CZA_20 at almost all conditions of pressure, temperature, GHSV and gas composition. This observation suggests that the difference between the activities of both catalysts accounts to a higher CO conversion on CZA_5. This better performance of the CZA_5 linked to the better CO conversion explains the fact that the difference between the productivities of both catalysts is more evident when the syngas is richer in CO, i. e., when CO₂/CO is equal to 0.5. It can be concluded that both catalysts are similarly active for the CO₂ hydrogenation reaction, but a better conversion of CO is achieved with the CZA_5 (the one with more copper content). Nonetheless, when compared to the CZA_comm, no improvement has been achieved with the CZA_5 or CZA_20, neither in terms of conversion nor in terms of productivity.

Table 4 compiles the activity values obtained for these three catalysts at 50 bars, 240 °C, 7500 h⁻¹ and CO₂/CO=1.9

Table 1. Comparison of the catalytic activities of the CZA_comm, CZA_5 and CZA_20 at 50 bars, 240 °C, 7500 h⁻¹ and CO₂/CO=1.9.

	Conversion (%)		Productivity
	CO	CO ₂	mol _{CH₃OH} /min ⁻¹ / g _{Cu} ⁻¹
CZA_comm	37.1	12.6	0.015
CZA_5	16.8	7.5	0.007
CZA_20	4.4	7.9	0.004

It is also observed that the CH₃OH production is higher when CO₂-poor syngas (CO₂/CO=0.5) is fed irrespective of the other reaction conditions studied. This may be due, in part, to catalytic limitations given that the CO+CO₂ conversion is more restricted as the CO₂ content increases in the syngas, at least within the studied range.

As expected, due to the high molar interchange in the methanol production reaction from CO₂, the reaction pressure plays a key role in the catalytic performance. Thus, at 270 °C and CO₂/CO = 0.5, the increment in CH₃OH production rate is 323% with CZA_20 and 357 % with CZA_5 when the reaction pressure is incremented from 25 to 50 bars. The rate is incremented from 0.007 to 0.031 mol/min/g_{Cu} when the pressure rises to 50 from 25 bars with CZA_5 catalyst. This behaviour is also observed at higher space velocity. The highest CH₃OH production rates (not conversion) are obtained at GHSV= 15000 h⁻¹ and 270 °C.

We aimed to prepare catalysts in which the Al₂O₃ serves not only as support to Cu and ZnO phases, but it also catalysed the dehydration of methanol to dimethyl ether (DME). We prepared a catalyst by incipient wetness impregnation of Cu and ZnO onto γ-Al₂O₃. The catalyst obtained was a Cu/ZnO/γ-Al₂O₃ with 60 wt% of γ-Al₂O₃, referred to as CZA_60I. We could not prepare catalysts with higher Cu (and ZnO) loading due to the low solubility of the salt precursors. The performance of CZA_60I for the methanol production was tested at 240-270 °C, 25-50 bar, 7500-15000 h⁻¹ with the syngas CO₂/CO = 0.5. The results were compared with the CZA_50 because they have similar composition, see Figure 13.

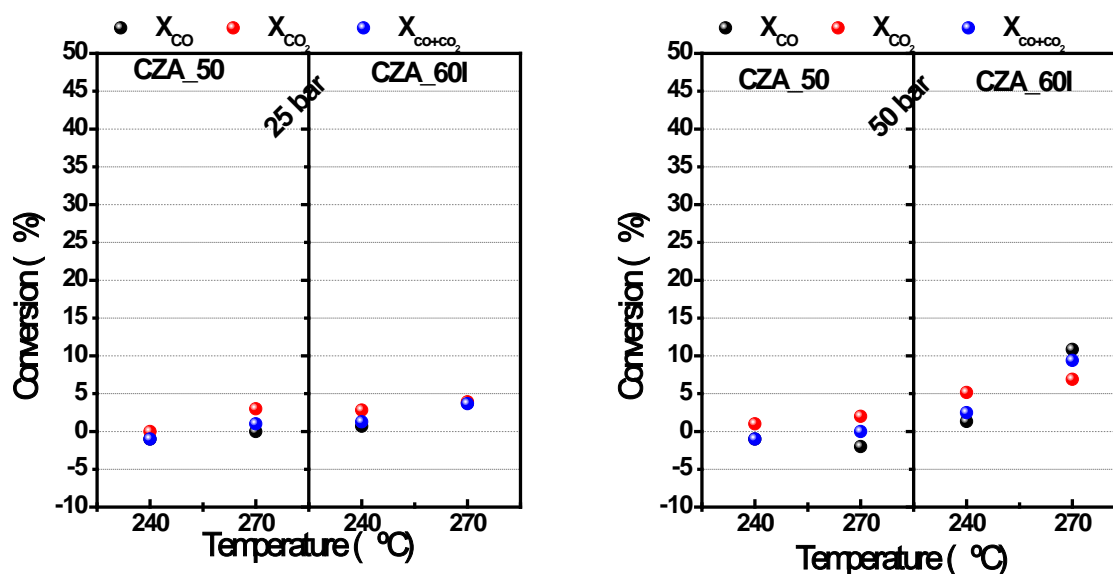


Figure 13. CO, CO₂ and (CO+CO₂) conversion of CZA_50 and CZA_60I at GHSV= 7500 h⁻¹.

As observed in Figure 13, CZA_50 lacks of activity for the methanol production reaction, and it shows moderate activity for the reverse water gas shift reaction. This feature has been ascribed to the low Cu loading on this catalyst. On the other hand, CZA_60I shows moderate activity for methanol production, especially at 270°C and 50 bar reaching a combined CO + CO₂ conversion of ca. 9.5 %. The GHSV has a marked effect in this process, and the conversion decreases below 2 % when GHSV increases to 15000 h⁻¹, as observed in Figure 14.

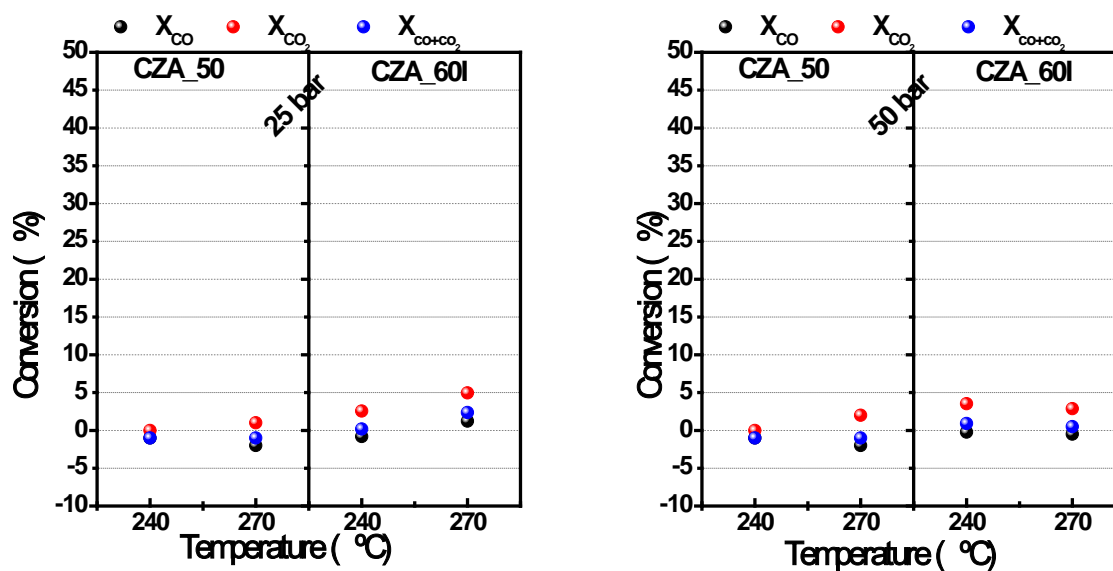


Figure 14. CO, CO₂ and (CO+CO₂) conversion of CZA_50 and CZA_60I at GHSV= 7500 h⁻¹.

3.3 Methanol synthesis from syngas with Pd-promoted Cu/ZnO/Al₂O₃ catalysts

Previous studies have shown that CO conversion to methanol can be enhanced by using Pd-based catalysts. We have explored the effect of doping CZA_5 with a small amount of Pd for the synthesis of methanol from syngas

3.3.1 Synthesis of Pd-Cu/ZnO/Al₂O₃ catalysts for methanol synthesis

The Pd-CZA catalysts were synthesized by the impregnation at incipient wetness method. The appropriate amount of a solution containing acetone and the Pd precursor, (C₅H₈O₂)₂Pd to obtain a Pd loading of 0.1, 0.05 and 0.01 wt.% Pd in the final catalyst was added dropwise to the catalyst under study (Katalco™ 51-8 and CZA_5). The catalysts obtained were identified by adding the prefix Pd-.

3.3.2 Characterization of Pd-Cu/ZnO/Al₂O₃ catalysts for methanol synthesis

The crystalline structures were studied by *in-situ* XRD under H₂, rising the temperature up to 600°C (Figure 15).

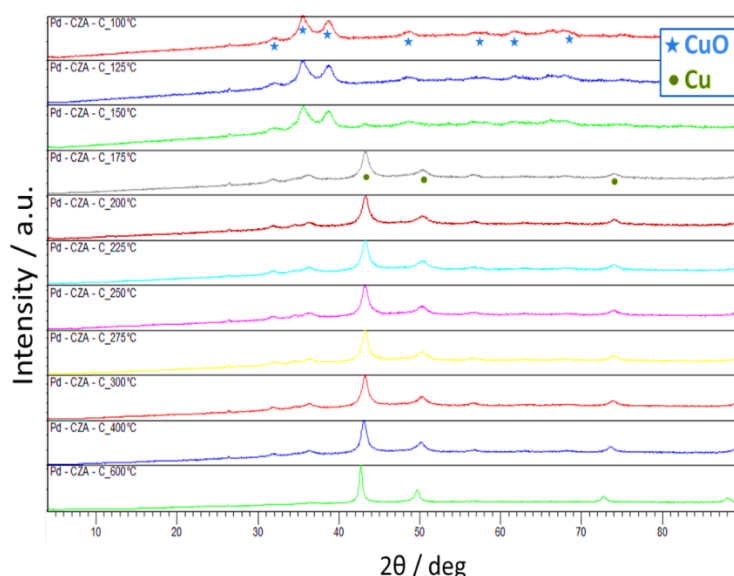


Figure 15. X-ray diffractograms of the Pd-CZA catalysts recorded at increasing the temperature in H₂ atmosphere

As observed in Figure 15 diffraction lines corresponding to metallic Cu are observed in the diffractograms recorded at T ≥ 175 °C; i.e., the presence of Pd shifts the reduction of CuO to Cu⁰ at lower temperatures. This is an expected result since the Pd is known to favor the reducibility of the oxides due to its high H₂ spillover property.

3.3.3 Catalytic performance of Pd-CZA catalyst for methanol synthesis

Catalytic tests have been conducted as described above (see section 3.2.3). Figure 16, compares the methanol productivity obtained for Pd-CZA_5 and Pd-CZA-commercial

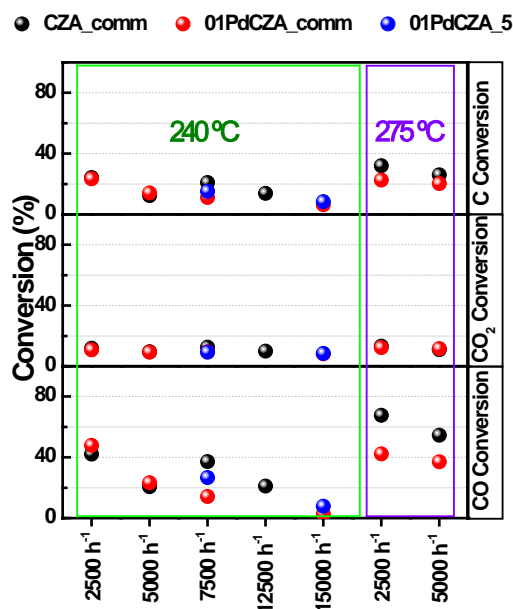


Figure 16. Conversion of CZA-comm, Pd-CZA-comm and 0.1Pd-CZA_5 measured at 50 bar.

As shown in Figure 16, the conversions of CO, CO₂ and CO+CO₂ are not affected by the addition of Pd, neither for the commercial catalyst nor for CZA_5, under the studied conditions. Figure 17 compares the effect of GHSV, pressure and temperature of Pd-CZA_5 vs the non-promoted CZA_5. To confirm the lack of promotion that Pd loading presents on the CZA_5 catalyst, a comparison between the activities of the CZA_5 and the 01PdCZA_5 was made at the same conditions of pressure, temperature, GHSV and gas composition. The result of this comparative study is displayed in Figure 17.

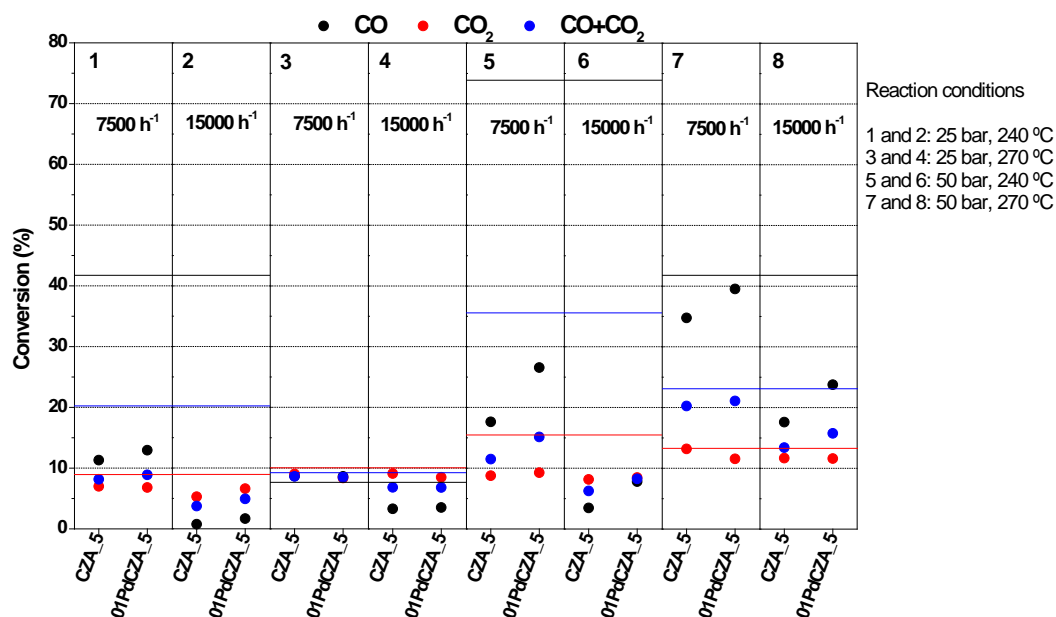


Figure 17. Comparison of the catalytic activity of the CZA_5 catalyst and 01PdCZA_5 catalyst at different conditions of P, T and GHSV. Gas composition: CO₂/CO=1.9, M module=2. Lines represent the equilibrium conversion for the compound(s) of the corresponding color.

At low pressure (25 bars) no significant improvement is achieved by means of the Pd adding to the CZA_5. At high pressure (50 bars), an increase in the CO conversion is clearly observed with the 01PdCZA_5, especially at low temperature, where this improvement rises the CO conversion 50 % compared to that obtained with the CZA_5. This effect has a lower impact at 270 °C and 7500 h⁻¹ because of thermodynamics limitations. Pd loading has no relevant effect on the CO₂ conversion under these conditions and with this gas composition

Considering these results, we decided not testing the catalyst with lower loadings of Pd: 0.01Pd-CZA_5 and 0.05Pd-CZA_5.

3.4 Cu/ZnO/ZrO₂/Al₂O₃ catalysts for methanol synthesis

3.4.1 Synthesis and characterization

ZrO₂ has been used in Zr-Cr catalysts for methanol production. ZrO₂ has been used as a promoter of Cu-based catalysts for the synthesis of methanol from pure CO₂. In addition, it is reported that ZrO₂ containing Cu catalysts are more tolerant to impurities such as S-compounds than ZnO ones. A series of Cu/ZnO/ZrO₂/Al₂O₃ (CZZA) catalysts have been prepared by co-precipitation at controlled pH with Na₂CO₃. Their nomenclature, expected composition and actual composition are shown in Table 5. The actual composition of the catalysts was obtained by the Inductively Coupled Plasm-Optic Emission Spectroscopy (ICP-OES) technique.

Table 5. Nomenclature and composition of the CZZA catalysts

	Composition (wt. %)							
	CuO		ZnO		ZrO ₂		Al ₂ O ₃	
	Expected	Actual	Expected	Actual	Expected	Actual	Expected	Actual
CZZA_1	45	--	20	--	20	--	15	--
CZZA_2	60	56	15	20	15	6	10	18
CZZA_3	60	62	20	23	10	4	10	10
CZZA_4	60	60	10	10	20	23	10	7
CZZA_Ga*	58.2	67.5	14.6	13.6	14.6	5.2	9.7	11.3

*Ga₂O₃ composition (wt%): 3 % (expected), 2.4% (actual).

We also studied the addition of Ga to the CZZA catalyst. Some authors have demonstrated that Ga has a promoter effect, both in the activity of copper catalysts towards methanol synthesis, as well as in their stability. The high activity of these materials in the hydrogenation of CO₂ would be related to the presence of the Ga₂O₃ species on the surface of the catalyst, which would cause an increase in the Cu⁺/Cu⁰ ratio on the surface of the catalyst during the reaction. We prepared a catalyst with almost the same composition than CZZA_2 with Ga (3 wt%) by the co-precipitation technique. The catalyst was labelled as CZZA_Ga (shown in Table 5).

Specific surface areas and pore size distribution of the CZZA catalysts were obtained from the N₂ adsorption-desorption isotherms. The obtained results are summarized in Table X.

Table 6. BET area and pore size of the CZZA catalysts

CATALYST	BET AREA (M ² /G)	AVERAGE PORE SIZE (NM)
CZZA_1	97	20
CZZA_2	62	35
CZZA_3	88	54
CZZA_4	42	40
CZZA_Ga	28	32

Figure 18 displays the XRD of CZZA_1, CZZA_2 and CZZA_3, the only peaks detected are for the CuO phase. In the diffractogram of CZZA_Ga, a further low intensity peak at ca. 30° is observed and ascribed to ZrO₂ phases.

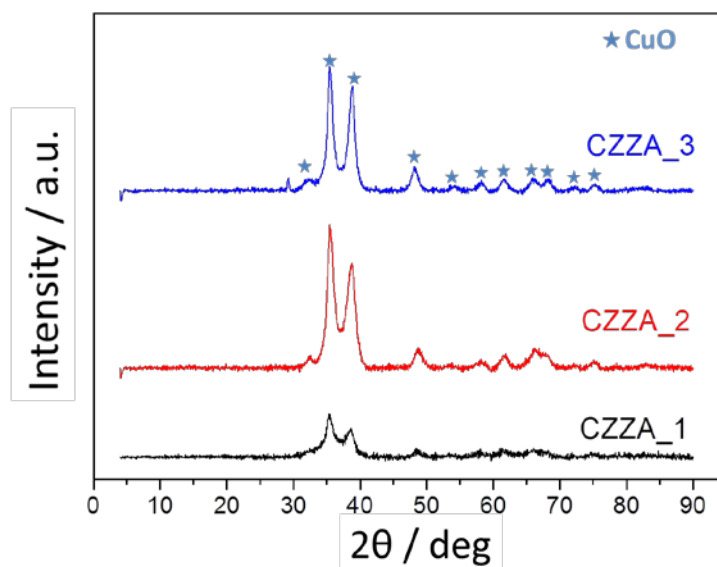


Figure 18. X-ray diffractograms of the CZZA catalysts.

3.4.2 Catalytic activity

The catalytic activity of the CZZA catalysts for the methanol synthesis reaction was tested using a syngas with a CO₂/CO molar ratio of 1.9 (M module of 2). The catalysts have been tested under different reaction conditions, T 240 and 270 °C; P 25 and 50 bar; GHSV 7500, 8000, 15000 h⁻¹. CZZA_1 and CZZA_2 were the only catalysts that produced methanol under the conditions explored in this work CZZA_3 and CZZA_4 only showed activity for the water-gas-shift reaction.

Figure 19 shows the results obtained for the CZZA_1, CZZA_2 at 50 bar. The activity of CZA-comm are shown for comparison. This activity is expressed as methanol productivity per gram of copper in the catalyst.

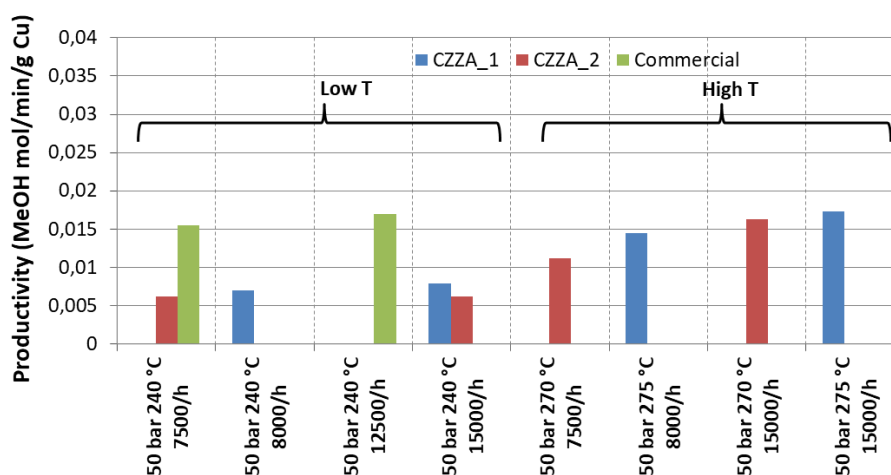


Figure 19. Methanol productivity with CZZA_1, CZZA_2 and CZA-comm. Reaction conditions: 50 bar, CO₂/CO=1.9, M =2

At low temperature (240 °C), the commercial catalyst shows higher methanol productivity than CZZA_1 and CZZA_2, which display similar activities. As shown in Table 1, the activity of CZA-comm decreases with the increasing temperature (when compared at the same GHSV and P). By contrary, the activity of CZZA_1 and CZZA_2 increases with temperature. In fact, when the temperature rises from 240 to 275 °C, CZZA_1 and CZZA_2 double their productivity. The different performance can be explained by the higher CO₂ conversions shown by the CZZA catalysts as compared to CZA-comm, see Table 7.

Table 7. Comparison of the CO₂ conversion relative to the equilibrium conversion of the CZZA_1, CZZA_2 and the commercial CZA.

Reaction conditions	% of the CO ₂ equilibrium conversion achieved		
	CZA-comm	CZZA_1	CZZA_2
50 bar, 240 °C, 7500 h ⁻¹	68	--	--
50 bar, 240 °C, 12500 h ⁻¹	58	--	--
50 bar, 270°C, 7500 h ⁻¹	--	--	86
50 bar, 270°C, 15000 h ⁻¹	--	--	82
50 bar, 275°C, 8000 h ⁻¹	--	89	--
50 bar, 275°C, 15000 h ⁻¹	--	85	--

Although a more extensive investigation should be conducted to further clarify this observation, the fact is that very high CO₂ conversions (compared to the equilibrium) have been achieved with the CZZA_1 and CZZA_2 catalysts at high spatial velocities. Note that at high GHSV, CZA-comm records lower CO₂ conversions. High activities for the CO₂ dehydration are desirable when the content in this compound is elevated in the syngas.

3.5 Copper-zinc oxide-zirconium (CZZ) catalysts

3.5.1 Synthesis

Cu/ZnO/ZrO₂ catalysts with ZrO₂ loadings of 5, 10, and 30 wt.%, maintaining the Cu/Zn 2/1 w/w have been prepared by co-precipitation with Na₂CO₃ (henceforward denoted as CZZ_X where X is the wt.% fraction of ZrO₂ in the catalyst).

3.5.2 Characterization

Specific surface areas of the CZZ catalysts were calculated from the N₂ adsorption-desorption isotherms. The composition of the catalysts was determined by EDX spectroscopy. The results are shown in Table 8.

Table 8. Composition obtained from ICP-OES and BET area of the CZZ catalysts

	Composition by EDX (wt.%)			BET area
	Cu	Zn	Zr	m ² /g
CZZ_10	39	25	36	81
CZZ_30	24	24	52	45
CZZ_50	14	13	73	100

The CZZ catalysts prepared have been characterised by several techniques. XRD was used to determine their crystalline structures. Figure 21 shows the collected diffractograms of the three catalysts.

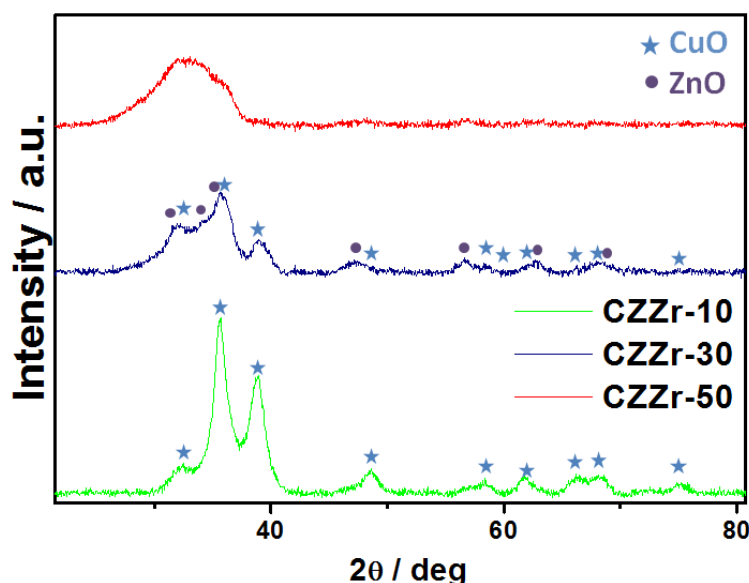


Figure 2. X-ray diffractogram of the CZZ catalysts.

In the CZZ_10, the crystalline structure of the CuO can be observed clearly, but as the amorphous ZrO₂ loading increases, the characteristic peaks of the CuO are less visible. Thus, in the CZZA_30 it is still possible to identify the CuO pattern, but in the catalysts with the maximum ZrO₂ loading, these peaks are no more visible.

The reducibility of the samples has been analyzed by H₂-TPR (not shown: All catalysts display a single reduction peak from ca. 180 to 250 °C with peak maxima at ca. 210 °C. In view of these results, the catalysts will be reduced at 250 °C previous to the catalytic tests.

3.5.3 Catalytic activity

The catalytic activity of the CZZ catalysts was tested at different temperatures (250, 275 and 300 °C), pressures (25, 40 and 50 bar) and GHSV (9000, 12000 and 15000 h⁻¹). The composition of the used feed mixture was CO₂/CO=1. Methanol is not formed with CZZ_30 catalyst, which only showed activity for the WGS reaction. On the other hand, CZZ_10 and CZZ_50 showed catalytic activity for the synthesis of methanol. Their performance has been compared with that of CZZ_50 and CZA_50, since they have similar Cu loading.

Although a clear improvement is achieved with the CZZ_50 when compared to the CZA_50, given that the former produced methanol while the latter did not, very low CO+CO₂ conversions were obtained, as shows Figure X. The results varied in a very narrow range in the chosen reaction conditions, but the fact is that the CO+CO₂ conversion was always below 5 %. No further experimentation was made on this type of catalysts.

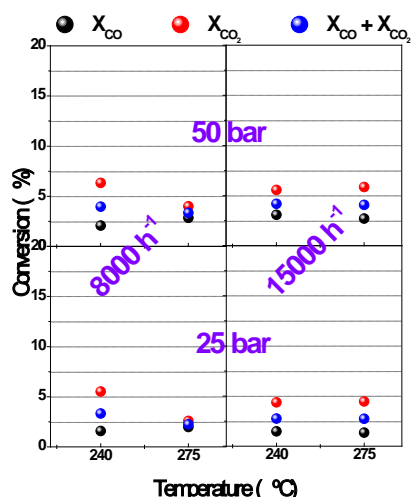


Figure 3. CO, CO₂ and CO+CO₂ conversions results for CZZ_50. CO₂/CO=0.5, M=2. Catalyst pre-treated at 250 °C for 2.5 h in a current of H₂/N₂ 20/80 vol.

3.6 Synthesis of MnO_x-Co₃O₄ catalysts for methanol synthesis

3.6.1 Synthesis

A Mn-Co hybrid oxide catalyst (wt. Mn/Co ratio equal to 1) was synthesized by the capillary inclusion method. For that, a template (Pluronic P123, HCl, TEOS, n-butanol) has been prepared via autothermal synthesis in an autoclave reactor. This type of catalyst is reported to be active for the methanol synthesis reaction at low pressures.

3.6.2 Characterization

The textural and structural properties of Mn-Co catalyst were studied by N₂ adsorption-desorption isotherms and X-ray diffraction, respectively. The calculated value of the BET area parting from the isotherm data is 114 m²/g. The X-ray diffractogram is shown in Figure X. The Co₃O₄ pattern is the most identifiable, to which corresponds all the visible peaks, but could be hindering the characteristic peaks of the MnO_x, which are located at 2θ values of 36, 42 and 57 °.

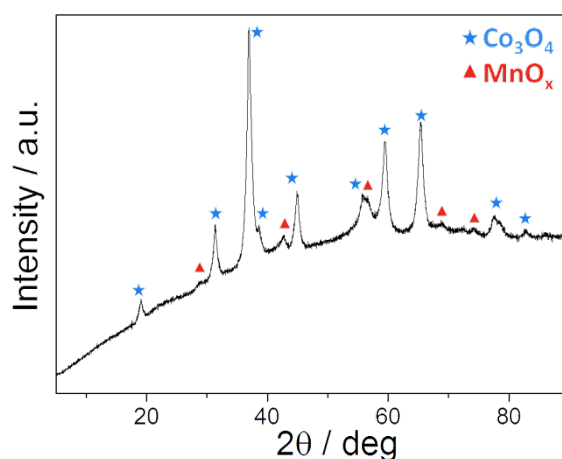


Figure 24. X-ray diffractogram of the Mn-Co catalyst.

The reduction profile (H₂-TPR) of the Mn-Co catalyst (not shown) reveal that different reduction processes take place. At 350 °C, where the first reduction ends, the cobalt is reduced to CoO. The active sites of this catalyst are thought to be located in the interphase MnO/CoO, so the activation protocol was performed at 350 °C to ensure the proper oxidation state of the Co.

For Co-Mn nanoparticles we also characterized by XAS (XANES and EXAFS) at the ESRF synchrotron in Grenoble. We studied Mn and Co K-edges to get the oxidation states and environment; we compared them with several reference compounds and with Co and Mn precursors. Figure 25 (left) shows the Mn XANES region. The position of the Mn K-edge of Mn-Co catalyst is very similar to MnO precursor, indicating Mn²⁺ oxidation state. The EXAFS region, Figure 25 (right) is also very similar to MnO indicating a similar environment and coordination.

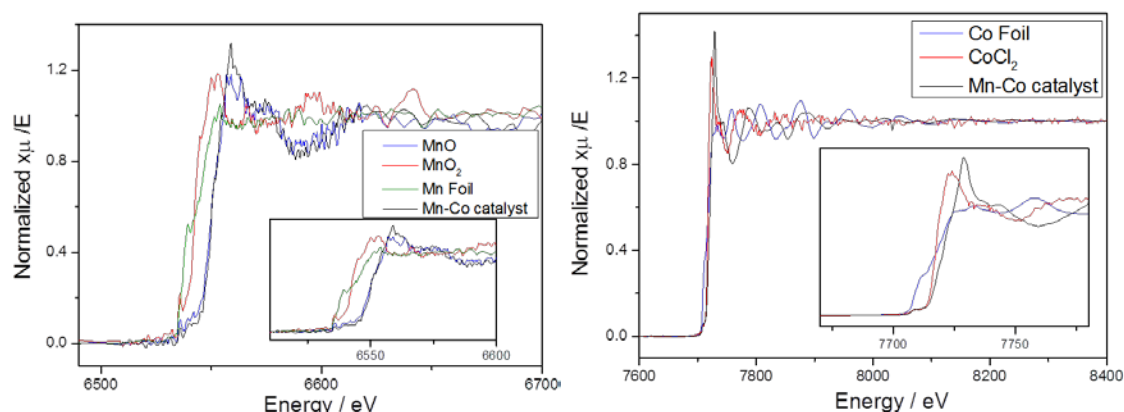


Figure 25: Left: XANES Mn K-edge of Mn-Co catalyst compared with several standards. Right: XAS Co K-edge of Mn-Co catalyst compared with several standards

Co K-edge is illustrated in Figure 25 (right) together with Co foil and CoCl₂ as standards of Co⁰ and Co²⁺. The inset of the figure shows a displacement to higher energies of Co K-edge on Mn-Co catalyst compared to Co⁰ and Co²⁺ standards, indicating that the oxidation state of Co is higher than Co²⁺ in our catalyst.

3.6.3 Catalytic activity

The Mn-Co catalyst was tested for the methanol synthesis reaction at different pressures (1, 6 10, 20 and 50 bar) at 240 °C and different GHSV (7500, 10000 and 12500 h⁻¹), using a CO₂/CO molar ratio of 1.9 in the syngas composition, with an M module of 2. The results of the experiments at GHSV=12500 h⁻¹ in terms of conversion are shown in Table 9.

Table 9. Catalytic activity of the Mn-Co catalyst at 240 °C, 12500 h⁻¹ and different pressures. Syngas composition: CO₂/CO=1.9 (mole), M module=2

Pressure bar	Conversion (%)		
	CO	CO ₂	CO+CO ₂
1	1.3	-0.2	0.3
6	3.2	2.6	2.8
10	1.6	1.9	1.8
20	3.9	0.8	1.8
50	11.8	0.1	4.0

The expected high activity at low pressures was not seen, in fact, barely any activity was observed until 50 bars. The results obtained in the preliminary tests did not show any improvement in comparison to the commercial CZA or the CZA_X catalysts at similar pressures (25 and 50 bar), in which the CO+CO₂ conversion achieved was considerably higher, e. g. 13 % for the commercial CZA in the same conditions. Moreover, at 20 and 50 bars the CO₂ conversion is practically zero. Considering these results, no more investigation on the Mn-Co catalyst was carried out.

4 Conclusion

Cu/ZnO/Al₂O₃ (CZA) catalysts with different compositions have been prepared by coprecipitation of metallic precursors under controlled pH. The catalysts have been studied for the methanol production from syngas with different CO₂/CO ratios under different reaction conditions (P, T, GHSV). The partial substitution of ZnO by ZrO₂ has been explored. The effect of the addition of Pd- or Ga- has been studied. The activity has been compared to that of a commercial catalysts also based on Cu/ZnO/Al₂O₃. The CZA catalysts showed activity for methanol production, however, the catalysts with the lowest Cu loading only show activity for the water gas shift reaction. Under most studied conditions, the productivity of methanol with the commercial catalyst is higher than that with the CZA catalyst prepared in this project. However, this feature should be studied carefully since catalytic performance strongly depends on reaction conditions. Thus, ZrO₂-containing catalyst display higher methanol productivity at high temperature than the commercial one, which activity decreases with the increasing temperature. Also, it is important to remark that the methanol productivity depends strongly on the CO₂/CO ratio (and M module). Higher methanol productivities are recorded with CO₂-poor feeds.

5 Acknowledgment

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