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# Influence of the Zn/Zr ratio in the support of a copper-based catalyst for the synthesis of methanol from CO<sub>2</sub>

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## ABSTRACT

CuO-ZnO-ZrO<sub>2</sub> catalysts were synthesized by co-precipitation synthesis. Copper content in catalysts was kept constant (30 wt% of Cu<sup>o</sup>) and ZnO was gradually substituted by ZrO<sub>2</sub> in the support to have a greater understanding of the support's effect and to find the optimal ZnO/ZrO<sub>2</sub> ratio. These catalysts were fully characterized and then tested in the methanol synthesis via CO<sub>2</sub> hydrogenation. The effects of reaction temperature and GHSV on the catalytic behavior were investigated. The mix of the characterization results predicted the optimum support that is composed of 50 wt% of ZnO and 50 wt% of ZrO<sub>2</sub> with higher metallic copper surface area and higher copper dispersion. Surprisingly the optimum catalytic results were obtained for the 30Cu-ZZ<sub>66/34</sub> catalyst, whose support was composed of 66 wt% of ZnO and 34 wt% of ZrO<sub>2</sub>. This catalyst presented good CO<sub>2</sub> conversion (19.6%) and methanol selectivity (50%), leading to a methanol productivity of 725 g<sub>MeOH</sub> kg<sub>Cata</sub><sup>-1</sup> h<sup>-1</sup> at 280 °C, 50 bar and a GHSV of 25,000 h<sup>-1</sup> (STP). Finally, the determining factor for the best catalytic activity is not the Zn/Zr ratio. To have the optimal catalytic activity in CO<sub>2</sub> hydrogenation to methanol other parameters should be considered as well. They are: the nature and the state of copper species over the composite support; the homogeneity of the final composite sample, the ZnO particles size, and the number of ZnO-ZrO<sub>2</sub> interactions. The perfect combination of them all plays an important role in the determination of the best copper-based catalyst for the synthesis of methanol from CO<sub>2</sub>.

## 1. Introduction

Since the mid-nineteenth century, anthropogenic Green House Gases (GHGs) emissions, especially CO<sub>2</sub>, have risen sharply due to the industrial age and in particular to the growth in the use of fossil fuels such as coal, oil and natural gas, which are strong emitters of GHGs by combustion.

Several techniques already exist to reduce CO<sub>2</sub> emissions such as capture or storage. However the most promising technique is the CO<sub>2</sub> recovery in chemical, such as urea [1-2], salicylic acid [3], or polycarbonates [4]. Other solutions must be developed in order to further increase the proportion of anthropogenic CO<sub>2</sub> recovered, such as energy vectors, like methanol [5-7]. It is a very important chemical intermediate up to 80 Mt in 2016 [8]. From methanol, it is possible to produce formaldehyde [9], dimethyl ether [10-12], polymer precursors such as ethylene and propylene [13-14] as well as the MTBE [15].

Methanol is industrially synthesized from the catalytic reaction between CO and H<sub>2</sub> on a metal catalyst [16]. In the 1960s, a new type of catalyst was developed with copper oxide on zinc oxide, operating at temperatures of 250-350 °C and reaction pressures of 50-100 bar [17]. Then, catalysts were further optimized with alumina (Al<sub>2</sub>O<sub>3</sub>), this type of catalyst is still used to convert mixtures of H<sub>2</sub>/CO/CO<sub>2</sub> (syngas) to methanol [18-24]. In the 1980s, kinetic and mechanistic studies only considered CO in hydrogenation, without taking CO<sub>2</sub> into account in the formation of methanol

[25-27]. Afterwards, complex kinetic models were developed that showed that methanol was mainly formed from CO<sub>2</sub> [28-30] and that this route is faster than that from CO [31]. Most copper-based catalysts for the CO<sub>2</sub> hydrogenation to methanol contain zinc oxide and the interaction between these two species is paramount. Metallic copper enables adsorption and dissociation of H<sub>2</sub> and the presence of ZnO increases the dispersion of metallic copper and thus the number of active sites in the catalyst [32-33]. It has also been shown that the addition of ZnO in a copper-based catalyst can induce the formation of such active species as Cu<sup>+</sup>-O-Zn partially dissolved in copper particles, thereby forming a Cu-Zn alloy [34]. These sites can considerably increase the activity of the catalyst. Behrens *et al* [35] have recently shown this beneficial effect of a Cu-Zn alloy in the catalyst. The interaction between copper and zinc is therefore important, as shown in the work of Fujitani *et al* [36]. They demonstrated that it is not only metallic copper alone which is the active species in the mechanism, but also Cu-Zn sites, working together for the formation of methanol. The addition of zirconia (ZrO<sub>2</sub>) in the support of the CuO-ZnO catalyst increases even more the dispersion of copper and zinc oxide by decreasing the crystallite size and increasing the specific surface area [37-38]. Zirconia, unlike Al<sub>2</sub>O<sub>3</sub> also plays an important role in the reaction mechanism by participating in the adsorption of CO<sub>2</sub> due to its high basicity [32,39,40]. Sintering of copper and ZnO one of the deactivation reasons could be decreased in the presence of ZrO<sub>2</sub> [37]. Koepfel *et al* [41] have described the Cu-ZrO<sub>2</sub> interface, allowing an improvement in the formation of methanol, as microcrystalline copper particles stabilized by an amorphous matrix of ZrO<sub>2</sub>. It is therefore necessary to have a close interaction between the three species to allow the hydrogenation reaction. This synergy was confirmed recently by DFT calculation in the work of Wang *et al* [42].

Other types of catalysts as platinum-based have been studied [43], supported by various oxides, in particular supported on CeO<sub>2</sub> which allows to obtain very good selectivities in methanol, but low conversions of CO<sub>2</sub> and low durability [44]. Gold supported on ZnO has also been studied in the catalysis of CO<sub>2</sub> hydrogenation [45]. The Au/ZnO-TiO<sub>2</sub> system has similar performance to conventional catalysts of CuO-ZnO-Al<sub>2</sub>O<sub>3</sub> type, but appeared to be much more expensive [46]. The use of silver as an active metal surface has also been studied [47]. Considering all others metals, the preferred one for the synthesis of methanol by the hydrogenation of CO<sub>2</sub> stays mainly copper [22,32,45-49] because of its abundance, low cost and high activity in the synthesis of methanol by CO<sub>2</sub> hydrogenation.

The most used and simplest method of catalysts' production is the co-precipitation method. The purpose of this method is to precipitate one or more metallic cations in the form of carbonates, using a precipitating agent, usually Na<sub>2</sub>CO<sub>3</sub> [50-52]. The co-precipitation allows obtaining of the intimate mixture of cations at atomic level in the precipitate and thus allows a good interaction between them in the final catalyst [19], in particular between copper and zinc which have a similar atomic size. The constant and controlled pH is essential in this synthesis in order to respect the composition of the final catalyst and to favor its homogeneity.

In this study the composite CuO-ZnO-ZrO<sub>2</sub> materials were chosen as catalysts for CO<sub>2</sub> hydrogenation to methanol. In order to understand the influence of ZrO<sub>2</sub> presence in the support on the materials properties and their catalytic performance, the progressive substitution of ZnO by ZrO<sub>2</sub> in the support was performed. Several researchers have already worked on this kind of catalyst [56-59] but the optimized Zn/Zr ratio in a copper-based catalyst hasn't been studied. In our previous work the kinetic parameters of this reaction using CuO-ZnO-ZrO<sub>2</sub> and CuO-ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts were studied, showing that the activation energies are higher for alumina supported material and thus affect the selectivity to methanol [30,60]. The novelty of the present manuscript is precisely in the study of the most selective CuO-ZnO-ZrO<sub>2</sub> catalyst in order to understand the influence of the composition and quantity of ZrO<sub>2</sub> needed for the optimal composition. The materials are synthesized by conventional batch co-precipitation method with different Zn/Zr ratio keeping the same content of copper. These

catalysts were fully characterized and their catalytic performances were evaluated. The optimal chemical composition of this type of catalysts for the methanol synthesis from the CO<sub>2</sub> hydrogenation was presented.

## 2. Experimental

### 2.1 Preparation of catalytic materials

The CuO-ZnO-ZrO<sub>2</sub> (30-CuZZ) catalysts were all synthesized by the classical co-precipitation method at constant pH in batch mode [55,61]. The amount of copper was kept constant for all samples (30 wt% of Cu<sup>0</sup> in the final catalyst), the ZnO:ZrO<sub>2</sub> ratio was varied.

For the preparation of 4.00 g of fresh catalyst with ZnO:ZrO<sub>2</sub> mass ratio equal to 66:34, a solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (19.3 mmol, 4.71 g), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (20.4 mmol, 6.28 g) and ZrO(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (7.1 mmol, 2.38 g) was prepared by dissolving these salts in 47 mL of distilled water, then heated to 60-65 °C, to obtain a solution with 1.0 M concentration of metallic cations (pH = -0.4). The second 1.6 M solution of Na<sub>2</sub>CO<sub>3</sub> (pH = 12.4, adjusted) was prepared and used as the precipitating agent. The carbonates/nitrates molar ratio of 1.1 was chosen to have a slight excess of carbonates to ensure the complete precipitation of all the metallic cations. These solutions were added dropwise into 100 mL of water at adjusted and constant pH = 6.3 and heated at 60-65 °C. The pH and temperature were monitored during the co-precipitation step using a HI-207 HANNA pH-tester. After the reaction, the precipitate was aged with gentle stirring in the mother liquor during three hours at 60-65 °C, then filtered and washed with hot distilled water. The washing was finished when the conductivity of the filtrate was close to the distilled water, approximately 15 μS cm<sup>-1</sup>, measured with a VWR CO 3100L conductimeter, meaning no ions (especially Na<sup>+</sup>) are washed out anymore. The precipitate was then dried at 95 °C for 48 h. Afterwards the obtained solid was calcined at 400 °C for four hours with a temperature ramp of 2 °C min<sup>-1</sup>. The powder obtained was sieved to reserve the particle size of 100-125 μm for catalytic tests.

The five samples with different ZnO:ZrO<sub>2</sub> mass ratio were prepared and abbreviated as Cu-ZZ<sub>100/0</sub>, Cu-ZZ<sub>66/34</sub>, Cu-ZZ<sub>50/50</sub>, Cu-ZZ<sub>34/66</sub>, Cu-ZZ<sub>0/100</sub>.

### 2.2 Catalytic materials characterization

Specific surface area measurements were performed by nitrogen adsorption-desorption at -196 °C using the Brunauer-Emmet-Teller (BET) method on a Micromeritics ASAP 2420 apparatus. Samples were previously outgassed at 250 °C overnight to remove the adsorbed moisture.

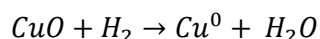
The crystalline structure of the catalysts was determined by X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer equipped with a LYNXEYE detector and a Ni filter for CuKα radiations over a 2θ range between 10 and 95 ° and a step of 0.016 ° every 0.5 s. The crystallite size was calculated using the Debye-Scherrer equation. The crystallite size of CuO is calculated from the CuO (111) plane at 2θ = 38.9 ° (JCPDS 48-1548). The crystallite size of ZnO is calculated from the ZnO (100) and (110) planes at 2θ = 31.9 ° and 56.8 ° respectively (JCPDS 36-1451).

The morphology of the catalysts was studied with a ZEISS GEMINI SEM 500 scanning electron microscope with a resolution of 1.2 nm at 500 V and 1.1 nm at 1 kV, equipped with an Inlens secondary electron (SE) detector and a SE2 detector.

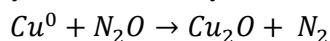
The elemental analysis was performed by inductively coupled plasma atomic emission spectroscopy ICP-AES. The quantitative determination of metal content in the catalysts was made based on the analysis of certificated standard solution. The sample preparation was made by dissolving 10 mg of dried and ground samples catalyst in concentrated aqua regia solution.

The X-ray photoelectron spectroscopy (XPS) measurements were performed in an ultrahigh vacuum (UHV) spectrometer equipped with a RESOLVE 120 MCD5 hemispherical electron analyzer. The Al K $\alpha$  hv=1486.6 eV dual anode X-ray source was used as incident radiation. The constant pass energy mode was used to record both survey and high resolution spectra, with pass energies 100 and 20 eV respectively. The C1s peak of the adventitious carbon at 285 eV is set as reference.

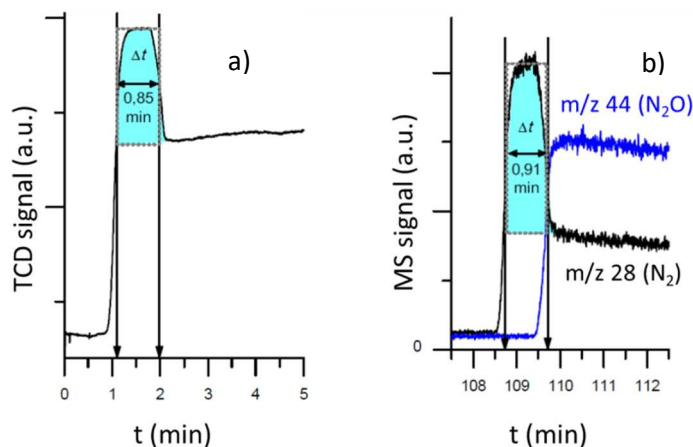
Reducibility studies were performed by temperature-programmed reduction method (TPR-H<sub>2</sub>) on a Micromeritics AutoChem II 2920 apparatus with 50 mg of fresh CuO-ZnO-ZrO<sub>2</sub> catalyst loading. The total gas flow rate of 10% H<sub>2</sub> in Ar was kept constant 50 mL min<sup>-1</sup> with a heating ramp of 10 °C min<sup>-1</sup> until final temperature 500 °C. The CuO reducibility was calculated in percentage from the theoretical H<sub>2</sub> consumption that is needed to reduce the amount of CuO in the catalyst that is determined by ICP-AES. The reaction of CuO reduction included in the calculations is following:



The copper metallic surface area was determined by N<sub>2</sub>O surface reaction on a Micromeritics AutoChem II 2920 apparatus. Firstly, approximately 500 mg of fresh CuO-ZnO-ZrO<sub>2</sub> catalyst were reduced at 300 °C, heating rate 1°C min<sup>-1</sup>, hold time 12 h, under a constant flow 50 mL min<sup>-1</sup> of 10 % H<sub>2</sub> in Ar keeping the conditions as close to the reactional conditions as possible. Then the reduced catalyst was purged with Ar and cooled down to 50 °C. Secondly, the reduced catalyst was treated under the flow of 50 mL min<sup>-1</sup> of 2 % N<sub>2</sub>O in Ar for 15 min oxidising thus only the surficial layer of the reduced copper by N<sub>2</sub>O to Cu<sub>2</sub>O by following equation:



The N<sub>2</sub>O consumption was registered with a TCD detector, according to a procedure close to those of Evans *et al.* [62] and Chinchén *et al.* [63]. The study was reported in more details in the PhD thesis of Kobl [64]. It was experimentally shown that a minimum catalyst loading is needed to get a sort of flat plateau in the TCD signal, that indicates the presence of pure N<sub>2</sub> in the flow, N<sub>2</sub>O being fully consumed. This was confirmed by following simultaneously the effluent gas by both TCD and mass spectrometer (MS) for one experiment. This plateau was considered for the calculations of the N<sub>2</sub>O consumption (see *Figure 1*).



**Figure 1.** Simultaneous follow-up of the reactive frontal chromatography analysis: (a) by TCD, (b) by MS. The arrows indicate the start and the end of the N<sub>2</sub>O consumption.

The metallic copper surface area was calculated by quantifying the amount of consumed N<sub>2</sub>O and assumption of 1.46 10<sup>19</sup> copper atoms per square meter [65]. The copper metallic dispersion was calculated according to the following formula (2-1):

$$D_{\text{Cu}^0}(\%) = S_{\text{Cu}^0} \times \frac{N_S}{\omega_{\text{Cu}^0}} \times \frac{M_{\text{Cu}}}{N_A} \quad (2-1)$$

With  $D_{Cu^\circ}$ (%), the metallic copper dispersion,  $S_{Cu^\circ}$ , the metallic copper surface area,  $N_S$ , the copper surface density ( $1.46 \cdot 10^{19}$  atom  $m^{-2}$ ),  $\omega_{Cu^\circ}$ , the copper mass fraction in the catalyst,  $M_{Cu}$ , the copper molar mass and  $N_A$ , the Avogadro constant.

The TEM analyzes were made with a transmission electron microscope JEOL 2100, equipped with a LaB<sub>6</sub> filament and a High Resolution (HR) polar part allowing a point-to-point resolution of 0.2 nm to 200 kV (voltage) maximum equipped with an X-ray detector (EDX energy dispersive X-ray spectrometry) of the SDD (Silicon drift detector) type. The analysis was performed using a copper grid revealing a high copper content, thus only Zn and Zr content will be shown.

### 2.3 Catalytic activity

The catalytic tests for the methanol synthesis via CO<sub>2</sub> hydrogenation were carried out in a constant flow stainless-steel fixed-bed reactor. For a conventional catalytic test, the powder catalyst with 100-125  $\mu m$  particle size was placed in the reactor between two beds of quartz wool held by a quartz rod, that was placed on a stainless-steel grid to prevent any movement of the catalytic bed during pressure variations. The reaction was carried out at 50 bar, between 240 and 300 °C with a gas hourly space velocity (GHSV) of 10,000 or 25,000  $h^{-1}$  (STP).

For easier comparison of the materials' catalytic properties the total gas flow ( $Q_{total}$ ) maintained constant 40.0  $mL \cdot min^{-1}$  (STP) as well as the GHSV. The mass of different catalysts ( $m_{cat}$ ) was adjusted depending on the apparent density ( $d_{app}$ ) of the materials according to equation (2-2). The gas molar composition is following  $H_2/CO_2/N_2 = 3.9/1.0/0.7$ , nitrogen is added as internal standard, hydrogen content is kept in excess in order to compare with previously reported results [55][66].

$$GHSV = \frac{Q_{total} \times d_{app}}{m_{cata}} \quad (2-2)$$

Catalysts were reduced beforehand under a flow of H<sub>2</sub> of 6.2  $mL \cdot min^{-1}$  (STP, 50 bar) with a heating ramp of 1 °C  $min^{-1}$  up to 300 °C followed by a 12 hour hold. After the reduction, the temperature was decreased to 100 °C and the reactor was then purged, still under pressure, with the reaction gases. The initial gas content was analysed and then the temperature of the reactor was increased with a heating ramp 1 °C  $min^{-1}$  up to the desired reaction temperature.

The gaseous products were analysed by online gas microchromatograph Inficon 3000, equipped with two modules: an MS5A module for the separation of H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO, a PPQ module for separation of light gases (N<sub>2</sub>, O<sub>2</sub>, CO, CH<sub>4</sub>, Ar), CO<sub>2</sub> and MeOH. The both modules were equipped with thermal conductivity detectors (TCD). The liquid products, water and methanol, were condensed at ambient temperature in a trap and analysed after each reaction temperature (48 h of reaction time of collection the condensate) using offline Agilent gas chromatograph 6890N, equipped with the Solgelwax column from SGE Analyticals and a flame ionization detector (FID).

The stability of the catalysts in time on stream experiments was evidenced by analyzing the gas products with online gas microchromatograph. Live monitoring of the CO formation and its ratio to the internal standard (N<sub>2</sub>) was realized. The CO/N<sub>2</sub> ratio during each temperature was stable all along the catalytic test.

The conversions (CO<sub>2</sub> and H<sub>2</sub>) and selectivities (MeOH and CO) were determined by the total carbon balance of the combined gas and liquid phases. The methanol productivity was calculated and expressed in two different ways: methanol productivity per catalyst mass ( $g_{MeOH} \cdot kg_{cat}^{-1} \cdot h^{-1}$ ) and methanol productivity per copper surface area ( $mg_{MeOH} \cdot m_{Cu^\circ}^{-2} \cdot h^{-1}$ ). The calculation of TOF was done according to equation (2-3).

$$TOF = \frac{Methanol \ productivity}{M_{methanol}} \times \frac{N_A}{N_S \times S_{Cu^\circ}} \quad (2-3)$$

The thermodynamic calculations were made using the ProSimPlus3 software with a Soave-Redlich-Kwong thermodynamic model. A Gibbs reactor was used, based on the minimization of the Gibbs energy of the defined thermodynamic system (CO<sub>2</sub>, H<sub>2</sub>, CH<sub>3</sub>OH, H<sub>2</sub>O and CO).

### 3. Results and discussion

#### 3.1 Characterization results

The list of the prepared catalytic materials is given in *Table 1*, where the results of all main characteristics are presented. Apparent density of the copper-based catalysts varies between 0.32 and 1.15. The increase in apparent density is linear: higher is the ZrO<sub>2</sub> content in the support, higher is the apparent density of the catalyst. The same phenomenon is observed for the specific surface areas. This could be explained by initially bigger specific surface area of the pure zirconium oxide comparing to pure ZnO, 46 vs 16 m<sup>2</sup> g<sup>-1</sup> respectively (*Table 1*). The smallest surface area, 41 m<sup>2</sup> g<sup>-1</sup>, was observed for 30Cu-ZZ<sub>100/0</sub> and the highest surface area, 156 m<sup>2</sup> g<sup>-1</sup>, is determined for 30Cu-ZZ<sub>0/100</sub>. The same observations were reported by Liu *et al* [67]. With the increased ZrO<sub>2</sub> content in the catalyst support, the pore morphology is modified. *Fig. 2* displays the nitrogen adsorption-desorption isotherms and the pore size distribution. All isotherms (*Fig. 2a*) are of type IV with a small hysteresis loop which is increased with increasing ZrO<sub>2</sub> content in the support, indicating the progressive formation of mesopores in Zr-containing samples. Without zirconia, the 30Cu-ZZ<sub>100/0</sub> catalyst's isotherms are quite flat indicating that it obviously does not possess high porosity. Having only zirconia in the support the hysteresis loop on the isotherms is more visible and some mesopores (4 nm) appear as shown on the pore size distribution graph (*Fig. 2b*).

*Fig. 3* shows the X-ray diffractograms of calcined materials. Zirconia is supposed to be in an amorphous or nanocrystallite state and was not observable. The size of CuO crystallites is between 9 and 13 nm and without obvious dependence on the ZnO/ZrO<sub>2</sub> ratio for ZnO-containing samples.

**Table 1.** Characterization results of the fresh 30Cu-ZnZr catalysts

Catalyst	d <sub>app</sub> <sup>a</sup> (g cm <sup>-3</sup> )	BET S <sub>BET</sub> <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	D (nm) <sup>c</sup>		CuO reducibility (%) <sup>d</sup>	S <sub>Cu</sub> <sup>e</sup> (m <sup>2</sup> Cu <sup>o</sup> g <sub>cata</sub> <sup>-1</sup> )	D <sub>Cu</sub> <sup>e</sup> (%)	Content (wt%) <sup>f</sup>	
			CuO	ZnO				Cu	Na
30Cu-ZZ <sub>100/0</sub>	0.32	41	12	13	91.2	6.4	3.3	31	0.01
30Cu-ZZ <sub>66/34</sub>	0.51	79	10	10	95.1	10.5	5.4	30	-*
30Cu-ZZ <sub>50/50</sub>	0.84	97	12	9	94.3	12.4	6.4	30	0.07
30Cu-ZZ <sub>34/66</sub>	0.97	109	13	11	93.4	11.1	5.7	30	0.09
30Cu-ZZ <sub>0/100</sub>	1.15	156	11	-	96.1	4.4	2.3	29	0.11
CuO		16							
ZnO		29							
ZrO <sub>2</sub>		46							

<sup>a</sup> Apparent density

<sup>b</sup> Specific surface area

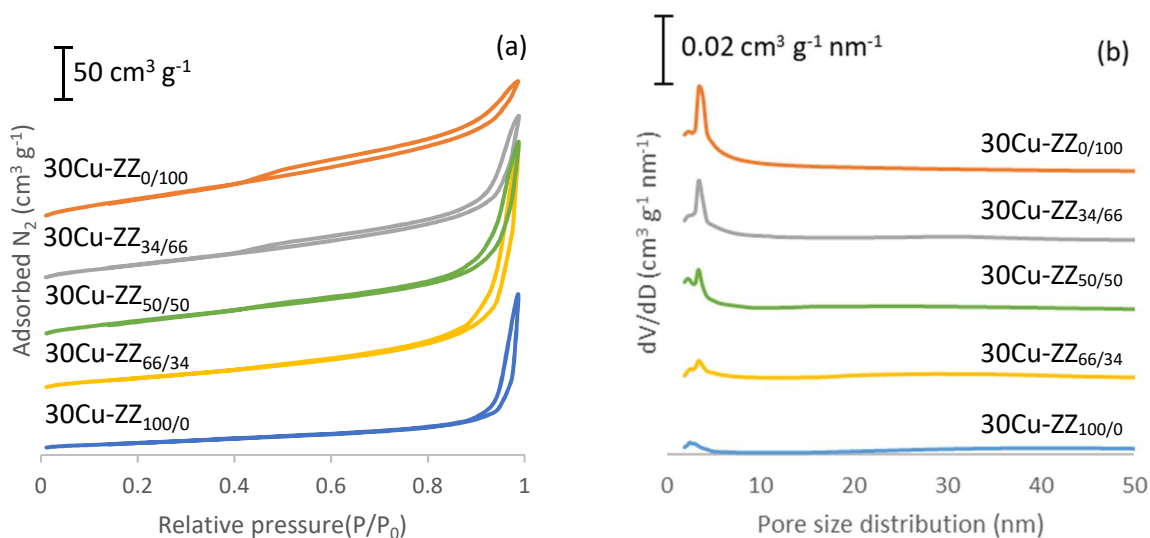
<sup>c</sup> Crystallite size determined by XRD using the Debye-Scherrer equation

<sup>d</sup> CuO reducibility calculate from the amount of consumed H<sub>2</sub>

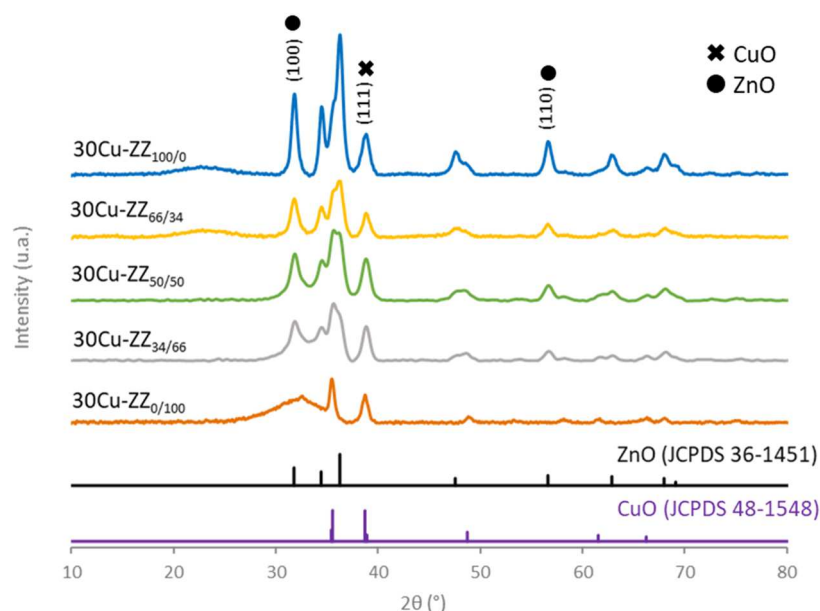
<sup>e</sup> Copper metallic surface area obtained by N<sub>2</sub>O surface reaction

<sup>f</sup> Content of each element determined by ICP-AES, the oxygen content wt% is not presented

\* could not be determined due to technical limitations – very small quantity



**Figure 2.** (a) Adsorption/desorption isotherms and (b) pore size distribution of 30Cu-ZZ fresh catalysts

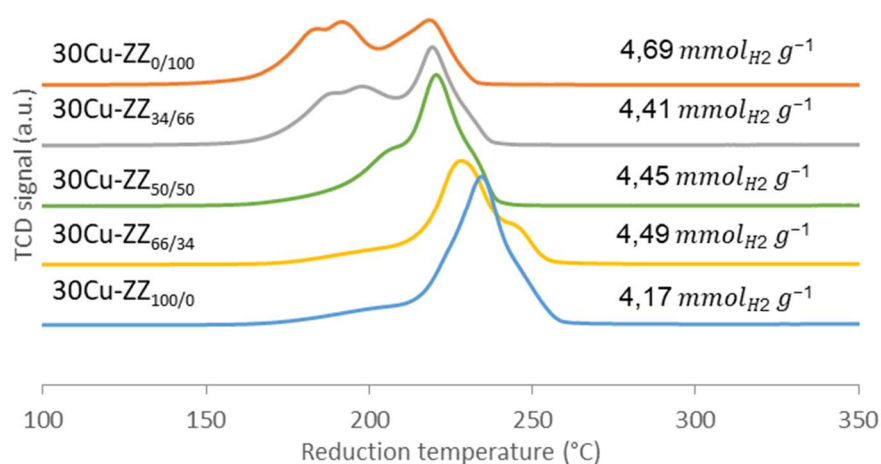


**Figure 3.** X-ray diffractograms of 30Cu-ZZ fresh catalysts.

Prior to the analysis of composite catalysts, the H<sub>2</sub>-TPR experiments were carried out in the same conditions for the single oxides ZnO and ZrO<sub>2</sub>. No reduction was observed in both cases. H<sub>2</sub>-TPR profiles of the Cu-containing materials are shown in *Figure 4*. The reduction of the copper oxide for the catalyst free of zirconia 30Cu-ZZ<sub>100/0</sub> occurs around 235 °C, in the form of a single large peak with little foregoing and behind shoulders with total H<sub>2</sub> consumption equal to 4.17 mmol<sub>H<sub>2</sub></sub> g<sup>-1</sup>. The peak is more defined than those of other reduction profiles and indicates a more homogeneous size distribution of reducible copper oxide species. When the ZrO<sub>2</sub> content is increased to 34 % in the catalyst support, the reduction temperature of CuO decreases and the H<sub>2</sub> consumption increases (4.49 mmol<sub>H<sub>2</sub></sub> g<sup>-1</sup> for 30Cu-ZZ<sub>66/34</sub>). The behind shoulder peak becomes visible, indicating some heterogeneity in the copper oxide species formed. In this case it is likely that there are two possible types of interaction of CuO with the ZnO/ZrO<sub>2</sub> support: CuO may interact with ZnO and with ZrO<sub>2</sub> separately. The further increase of Zr content in the samples brings the enlargement of the reduction



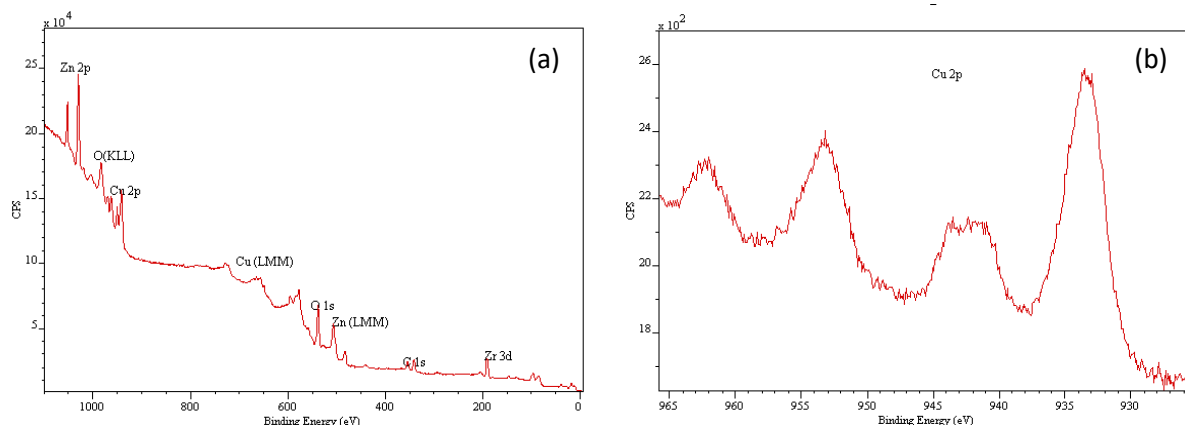
peaks and more visible separation of the foregoing shoulder, the behind shoulder is observable only for the 30Cu-ZZ<sub>66/34</sub> sample. As the ZrO<sub>2</sub> content increases from 34 to 50 %, a peak shoulder is progressively transformed into a second reduction zone when the ZrO<sub>2</sub> content increases from 50 to 66 % in the support until splitting completely with a content of 100 % ZrO<sub>2</sub> in the support. The highest H<sub>2</sub> consumption is reached at 100 % ZrO<sub>2</sub> in the catalyst support: 4.69 mmol<sub>H<sub>2</sub></sub> g<sup>-1</sup> for 30Cu-ZZ<sub>0/100</sub> and indicates the highest reducibility among all the samples (*Table 1*). The decrease in the CuO reduction temperature and the increase in H<sub>2</sub> consumption, when the ZrO<sub>2</sub> amount increases, probably indicates smaller particle size of CuO and thus weaker interaction between CuO species and the support [67][68]. This fact confirms that the presence of Zn is still necessary for the interaction and stabilization of CuO with the support. The H<sub>2</sub> consumption was used for the calculation of the reducibility of CuO species in the catalysts, the chemical composition of the catalysts was determined beforehand (*Table 1*). In the sample 30Cu-ZZ<sub>100/0</sub> with only ZnO present in the support the reducibility is the smallest indicating quite strong interactions between CuO and ZnO. The presence of ZrO<sub>2</sub> increases slightly the reducibility and thus accessibility of copper species for catalysis. When there is no ZnO, but only ZrO<sub>2</sub> present in the support, the reduction is clearly carried out in two stages: the first zone of consumption of H<sub>2</sub> before 200 °C and the second around 220 °C. This splitting can be explained by different insertions or interactions between the copper and the support [69] or by a heterogeneous distribution of CuO particles by their size [70].



**Figure 4.** H<sub>2</sub> consumption during TPR for 30Cu-ZZ fresh catalysts.

Additional XPS studies were performed for some samples in order to observe the elemental composition over the surface and combine the results with H<sub>2</sub>-TPR experiments. *Figure 5* displays the total survey scan for the 30Cu-ZZ<sub>34/66</sub> sample as well as the high resolution spectrum for Cu2p region. The XPS peaks of all elements that exist in the samples surface are detected in the survey scans. High resolution XPS spectra of all elements were also acquired. The shape and position of the Zn2p, Cu2p and Zr3d peaks are characteristic of previously reported data on ZnO, ZrO<sub>2</sub> and CuO respectively [68]. The shape of the high resolution spectrum for Cu2p region was the same for all tested samples indicating the presence of only Cu<sup>2+</sup> species (*Fig. 5b*). Two possible copper species could be present over the materials surface: CuO and Cu(OH)<sub>2</sub> [71]. The presence of hydroxyl species is very likely due to the moderate calcination temperature of the materials and due to the formation of malachite-like hydroxo-carbonates during the co-precipitation synthesis. The presence of these species could confirm the heterogeneous reduction profiles obtained during the H<sub>2</sub>-TPR experiments where different types of copper-support interactions were observed. The surface composition of all elements was calculated by using the area of the core level peaks, normalized to the photoemission cross section by assuming a homogeneous distribution arrangement model. The surface atomic ratios of all elements of all tested samples are summarized in *Table 2*. It was evidenced once again that the presence of Zr in the

materials support make the copper more accessible and present on the surface – the weight content of copper is similar in all samples (*Table 1*) but the atomic content on the surface (*Table 2*) is much smaller for the 30Cu-ZZ<sub>0/100</sub> sample, without Zn. The traces of sodium that were found in the samples (*Table 1*) were not considered as significant and thus their presence was not discussed in terms of affection the characterization and catalytic results.



**Figure 5.** XPS spectra of the 30Cu-ZZ<sub>34/66</sub> sample: survey scan spectrum (a) and high resolution spectrum for Cu2p (b).

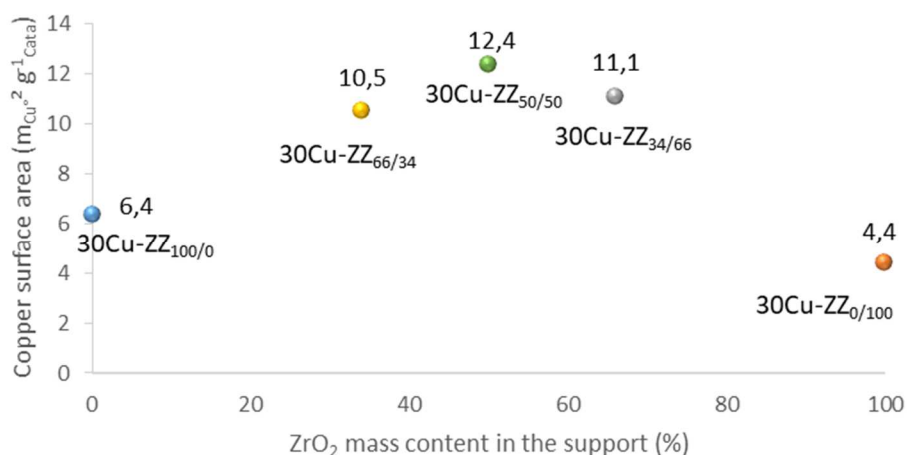
**Table 2.** Surface atomic composition of the fresh 30Cu-ZnZr catalysts

Catalyst	Content (%) <sup>a</sup>			
	Cu	Zn	Zr	O
30Cu-ZZ <sub>100/0</sub>	13.3	32.4	0	54.3
30Cu-ZZ <sub>66/34</sub>	- <sup>b</sup>	-	-	-
30Cu-ZZ <sub>50/50</sub>	15.4	22.5	5.8	56.4
30Cu-ZZ <sub>34/66</sub>	17.6	14.6	9.8	58.0
30Cu-ZZ <sub>0/100</sub>	17.8	0	17.7	64.5

<sup>a</sup> determined by XPS analysis

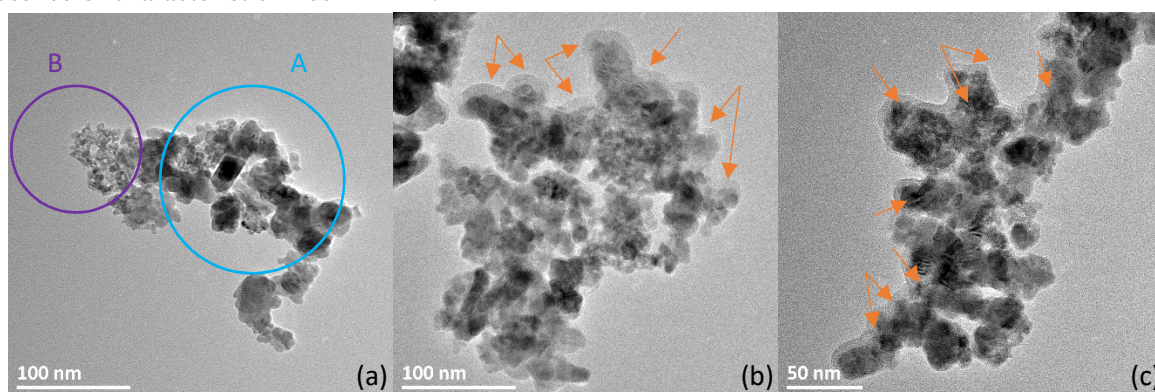
<sup>b</sup> could not be determined due to technical limitations

*Figure 6* illustrates the variation of the copper metallic surface area as a function of the mass content of ZrO<sub>2</sub> in the support. Here the copper defects that could be present according to the work of Fichtl *et al* [72] were not considered. All the copper surface area measurements of the present catalytic materials family, that were prepared by the same synthesis method, were performed in the same conditions. The results are shown on the *Fig.6*. When the catalyst support is composed only of ZnO or ZrO<sub>2</sub> oxide, the copper metallic surface area is the lowest (6.4 and 4.4 m<sub>Cu</sub><sup>2</sup> g<sub>Cata</sub><sup>-1</sup> for 30Cu-ZZ<sub>100/0</sub> and for 30Cu-ZZ<sub>0/100</sub>, respectively) despite their great difference in specific surface area measured by BET method and quite high atomic copper presence on the surface for 30Cu-ZZ<sub>0/100</sub> sample. This shows that the metallic copper surface area is not necessarily related to the specific surface area of the material but depends on the interactions between metallic Cu and the support. Indeed, when the two oxides (ZrO<sub>2</sub> and ZnO) are simultaneously present in the support, the metallic copper is more efficiently dispersed and reaches the highest metallic copper surface area 12.4 m<sub>Cu</sub><sup>2</sup> g<sub>Cata</sub><sup>-1</sup> for the mass ZnO/ZrO<sub>2</sub> ratio of 50/50. The simultaneous presence of ZnO and ZrO<sub>2</sub> in the support allows the increase of the metallic copper surface area of the catalyst. The metallic copper dispersion follows the same trend; the results are displayed in *Table 1*. The lowest dispersion when the support is composed of only one oxide (3.3 % and 2.3 %, for 30Cu-ZZ<sub>100/0</sub> and 30Cu-ZZ<sub>0/100</sub>, respectively). When the support of the catalyst is composed of the same amount of Zn and Zr (by mass of oxides) the metallic copper dispersion is the highest, 6.4 % for 30Cu-ZZ<sub>50/50</sub>.



**Figure 6.** Metallic copper surface area as a function of the ZrO<sub>2</sub> mass content in the support.

The 30Cu-ZZ<sub>66/34</sub> catalyst only was analyzed by TEM, the images are shown in *Figure 7*. Two distinct types of crystals of different sizes were observed. Zone A (*Fig. 7a*) is composed of large crystals, in the range of 20-30 nm, which is larger than the size of the crystallites determined by XRD (*Table 1*). Zone B (*Fig. 7a*) seems rather granular with small crystals (about 4 to 7 nm). The heterogeneity of the crystal sizes was confirmed by visualizing different particles (*Fig. 7b* and *7c*). A zone of fine grains, similar to an amorphous phase on the edge of the crystals, is observed (orange arrows, *Fig. 7b* and *7c*). This amorphous phase could be attributed to ZrO<sub>2</sub> thus, explaining the absence of characteristic lines in XRD.



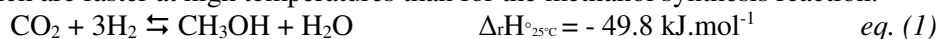
**Figure 7.** TEM images in light field for the 30Cu-ZZ<sub>66/34</sub> fresh catalyst.

Energy dispersive X-ray spectroscopy (EDX) was used to analyse the composition of different zones. The results are presented in *Figure 8*. They have to be compared with the theoretical mass contents of the individual oxides in the catalyst: 41.5 wt% of ZnO and 21.0 wt% of ZrO<sub>2</sub> for 30Cu-ZZ<sub>66/34</sub>. Zone C (*Fig. 8a* and *8b*), similar to zone A of *Fig. 7a*, appears rather dark and compact and contains 42 wt% of ZnO and only 3 wt% of ZrO<sub>2</sub>. Zone D (*Fig. 8a* and *8c*), rather granular, similar to zone B of *Fig. 7a*, contains 25 wt% of ZnO and 35 wt% of ZrO<sub>2</sub>. The zone D, composed of small crystals is a great deal richer in ZrO<sub>2</sub> than the zone C, poor in ZrO<sub>2</sub>, composed of larger crystals. The values of the mass compositions obtained for zone C are very far from the theoretical composition, unlike zone D which approaches it, but which still contains more zirconium and less zinc. These results could explain the splitting of the H<sub>2</sub>-TPR profile in to peaks. It is suggested that smaller particles are reduced at lower temperature and the bigger particles having higher content of Zr and thus stronger copper-support interaction are reduced at higher temperature. The EDX analysis clearly



<b>30Cu-ZZ<sub>0/100</sub></b>	276.0	240	13.2	7.0	53	47	7.0	145	33.0	11.8
		260	18.6	9.0	43	57	8.0	167	38.0	13.6
		280	23.2	9.6	29	71	6.7	139	31.6	11.3
		300	25.7	10.1	22	78	5.7	115	26.1	9.4
<b>Thermo</b>	/	240	33.4	22.4	80	20	26.8	/	/	/
		260	30.5	17.8	64	36	19.4	/	/	/
		280	29.5	14.3	44	56	13.0	/	/	/
		300	30.1	11.9	27	73	8.1	/	/	/
<b>State of the art</b>										
<b>30CuZn-Z</b> [55]	/	280	23.2	9.8	33	67	/	331	26.0	9.3
<b>CuZnZr</b> [73]	/	240	22.4	/	64	/	/	620	8.5	3.0
<b>CZAZ-0Al</b> [48]	/	250	25.9	/	62	/	/	219	7.3	2.6
<b>M-CZZ(16)</b> [42]	/	220	18.2	/	80	/	/	297	/	20
<b>C6Z3Z1-OX</b> [39]	/	240	18.0	/	51	/	/	305	10.9	3.9

For all the catalysts, the CO<sub>2</sub> and H<sub>2</sub> conversions increase with the reaction temperature and tend towards the thermodynamic values. During the CO<sub>2</sub> hydrogenation in these conditions apart from the methanol synthesis (*eq. 1*) the reverse water gas shift reaction (RWGS) (*eq. 2*) takes place in the same time. As the temperature increases, the methanol selectivity decreases. The CO selectivity increases simultaneously and CO becomes predominant in the reaction products due to the kinetics of RWGS which are faster at high temperatures than for the methanol synthesis reaction.



When the temperature increases, the catalyst 30Cu-ZZ<sub>100/0</sub> presents the lowest CO<sub>2</sub> conversion (9.4 % at 240 °C). The addition of ZrO<sub>2</sub> in the support allows increasing the conversion to approximately 14 % for the catalysts 30Cu-ZZ<sub>66/34</sub> and 30Cu-ZZ<sub>34/66</sub> at the same temperature. Catalysts 30Cu-ZZ<sub>66/34</sub> and 30Cu-ZZ<sub>34/66</sub> also show the most appropriate conversions of H<sub>2</sub> at 240 °C with 7.2 and 7.3 %, respectively. The conversions of H<sub>2</sub> and CO<sub>2</sub> increase with temperature and approach thermodynamic values at high temperature (300 °C): approximately 25 % for CO<sub>2</sub> and 10 % for H<sub>2</sub> (Table 3).

MeOH selectivity drops rapidly from 240 to 300 °C in all cases, to the benefit of the formation of CO. However, the increase of ZrO<sub>2</sub> content in the support plays a positive role for MeOH selectivity: growth from 33 % for 30Cu-ZZ<sub>100/0</sub> (at 260 °C) to 50 % for the catalysts 30Cu-ZZ<sub>66/34</sub> (at 240 °C) at the same CO<sub>2</sub> conversion (14-15 %). By comparing methanol selectivities at the same CO<sub>2</sub> conversion for all the catalysts, the 30Cu-ZZ<sub>66/34</sub> catalyst leads to the highest methanol selectivity: 50 % at 14 % CO<sub>2</sub> conversion (240 °C).

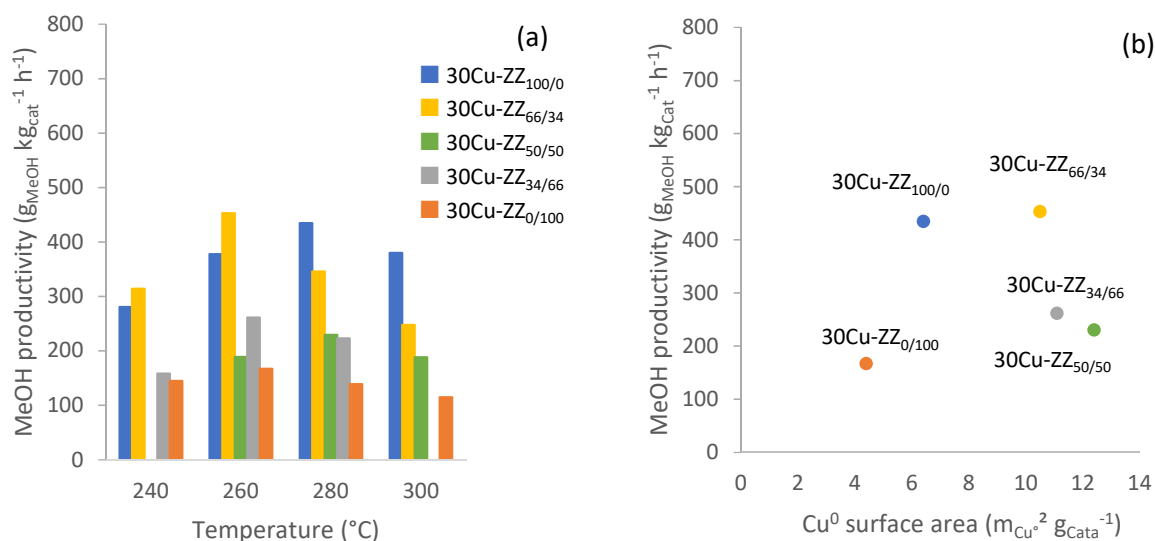
When ZnO is progressively substituted by ZrO<sub>2</sub> in the catalyst support, methanol yield can reach the maximum of 10.7 % for the catalyst 30Cu-CZZ<sub>34/66</sub> at 260 °C. However, when all ZnO is substituted with ZrO<sub>2</sub>, the methanol yield decreases for the catalyst 30CuZZ<sub>0/100</sub>. This indicates that the presence of both oxides in the catalyst support, ZnO and ZrO<sub>2</sub>, is necessary to improve catalytic performance, the matter is to find their optimal content.

From the characterization results it could be supposed that the best catalytic activity would be expected for the 30Cu-CZZ<sub>50/50</sub> sample with biggest metallic copper surface area and copper dispersion. It appears that this catalyst does not systematically show the most optimal catalytic performance. This observation agrees with the work of Wang *et al* [42]. When catalytic performance is evaluated as MeOH productivity per mass of catalyst (*Fig. 9a*), the effect of the progressive substitution of ZnO by ZrO<sub>2</sub> is significant. Indeed, when ZrO<sub>2</sub> content increases in the catalyst support, MeOH productivity decreases rapidly. An exception is observed for the catalyst 30Cu-ZZ<sub>66/34</sub>. Thus, this catalyst has the greatest productivity, 453 g<sub>MeOH</sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> at 260 °C. When the ZrO<sub>2</sub> content exceeds 34 wt% in the support, the productivity of methanol per catalyst mass decreases: 167 g<sub>MeOH</sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> at 260 °C for 30Cu-ZZ<sub>0/100</sub>. Our catalysts are still competitive compared to the other catalysts



in the literature (Table 3), even if it is always difficult to compare the catalytic results because of the different catalytic test conditions and some missing information in the papers.

By plotting the methanol productivity as a function of the metallic copper surface area (Fig. 9b), no relationship of proportionality between these two quantities appears. This is consistent with the fact that TOF numbers, based only on  $\text{Cu}^\circ$  as active sites, vary from one Cu-ZZ catalyst to another (see Table 3). It is suggested that the determining factor for the catalytic activity is more complicated than simply the nature and the state of copper species. Other parameters that could play a role are the ZnO particle size or the number of oxygen vacancies generated by the ZnO-ZrO<sub>2</sub> interactions [42].



**Figure 9.** CH<sub>3</sub>OH productivity per catalyst mass at different temperatures under 50 bar and a GHSV (STP) of 10,000 h<sup>-1</sup> (a) and CH<sub>3</sub>OH productivity per metallic copper surface at different temperatures under 50 bar and a GHSV (STP) of 10,000 h<sup>-1</sup> (b).

### 3.3 Effect of GHSV

The influence of GHSV on methanol productivity was studied by varying the catalyst mass under the same flow of reactants. The results obtained with the 30Cu-ZZ<sub>66/34</sub> catalyst at GHSV 10,000 h<sup>-1</sup> and 25,000 h<sup>-1</sup> are presented in Table 4. CO<sub>2</sub> conversion decreases from 22.2 % to 17.9 % and the H<sub>2</sub> conversion decreases from 10.0 % to 7.4 % at the reaction temperature 280 °C, when GHSV increased from 10,000 to 25,000 h<sup>-1</sup>. At the same reaction temperature, methanol selectivity is almost not affected by gas velocity, 34 % and 36 % for 10,000 h<sup>-1</sup> and 25,000 h<sup>-1</sup>, respectively.

According to the work of Arena *et al* [73] when the GHSV increases, the specific CO<sub>2</sub> reaction rate (mol<sub>CO2</sub> g<sub>cat</sub><sup>-1</sup> s<sup>-1</sup>) increases linearly. Here the methanol productivity is increased from 346 to 725 g<sub>MeOH</sub> kg<sub>Cata</sub><sup>-1</sup> h<sup>-1</sup> when GHSV is increased from 10,000 to 25,000 h<sup>-1</sup> (STP). The same observation is made for the other reaction temperatures as shown in Table 4 confirming the absence of diffusional limitations and getting the possibility of higher methanol production per masse of catalyst and per unit of time.

**Table 4.** Catalytic results at different GHSV and 50 bar for the 30Cu-ZZ<sub>66/34</sub> catalyst.

Catalyst 30Cu-ZZ <sub>66/34</sub>	Catalyst mass (mg)	T (°C)	Conversion (%)		Selectivity (%)		MeOH yield (%)	MeOH productivity (g kg <sub>cata</sub> <sup>-1</sup> h <sup>-1</sup> )	TOF (10 <sup>-3</sup> s <sup>-1</sup> )
			CO <sub>2</sub>	H <sub>2</sub>	MeOH	CO			
<b>10,000 h<sup>-1</sup></b>	122.4	240	13.7	7.2	50	50	6.9	314	10.7

		260	19.6	9.4	50	50	9.8	453	15.4
		280	22.2	10.0	34	66	7.5	346	11.8
		300	24.0	9.6	22	78	5.3	248	8.5
<b>25,000 h<sup>-1</sup></b>	48.0	240	6.9	2.6	48	52	3.3	378	12.9
		260	12.5	5.6	45	55	5.7	641	21.8
		280	17.9	7.4	36	64	6.4	725	24.7
		300	22.7	8.6	27	73	6.1	692	23.6

#### 4. Conclusions

The progressive substitution of ZnO by ZrO<sub>2</sub> in the support of copper-based materials has shown the effect of the presence of ZrO<sub>2</sub> on the physicochemical characteristics and on the catalytic performances for the methanol synthesis from CO<sub>2</sub>.

With this progressive substitution, the apparent density of the catalysts, as well as the specific surface area and the reduction temperature of CuO increase with ZrO<sub>2</sub> content. Different CuO-support interactions were formed when ZrO<sub>2</sub> was introduced. Copper surface area is the lowest for catalyst supports composed of a single oxide (6.4 and 4.4 m<sub>Cu</sub><sup>o2</sup> g<sup>-1</sup> for 30Cu-ZZ<sub>0/100</sub> et 30Cu-ZZ<sub>100/0</sub>, respectively) but increases strongly with the combined presence of ZnO and ZrO<sub>2</sub> in the support (up to 12.4 m<sub>Cu</sub><sup>o2</sup> g<sup>-1</sup> for 30CuZZ<sub>50/50</sub>). Pure zirconia as the catalyst support has no interest in terms of the dispersion of metallic copper. The interactions between ZnO and ZrO<sub>2</sub> help to increase both the copper dispersion and metallic surface area.

The catalysts were tested at 10,000 h<sup>-1</sup> (STP) at the CO<sub>2</sub> hydrogenation to methanol. The catalyst 30Cu-ZZ<sub>66/34</sub> showed a maximal methanol productivity by catalyst mass (453 g<sub>MeOH</sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> at 260 °C with a methanol selectivity of 50% and a CO<sub>2</sub> conversion of 19.6%). However, increase of ZrO<sub>2</sub> content in the catalyst support decreases methanol production. By increasing GHSV to 25,000 h<sup>-1</sup> (STP), CO<sub>2</sub> and H<sub>2</sub> conversions decrease, MeOH selectivity increases, resulting in a higher methanol productivity of 725 g<sub>MeOH</sub> kg<sub>Cata</sub><sup>-1</sup> h<sup>-1</sup> at 280 °C and bringing the prepared material on the high level of methanol productivity known in the state-of-the-art. It was proven that the combined presence of both ZnO and ZrO<sub>2</sub> within the copper catalyst support is necessary. Finally, the determining factor for the best catalytic activity is not the Zn/Zr ratio. It is more complicated than a simple nature and the state of copper species over the composite support. Other parameters as the homogeneity of the final composite sample, the ZnO particles size, and the number of ZnO-ZrO<sub>2</sub> interactions could play an important role in the determination of the best copper-based catalyst for the synthesis of methanol from CO<sub>2</sub>.

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Graphical abstract

