doi:10.20944/preprints202106.0308.v1

Article

Modifications in the composition of $CuO/ZnO/Al_2O_3$ catalyst for the synthesis of methanol by CO_2 hydrogenation

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Abstract: Renewable methanol, obtained from CO_2 and hydrogen provided from renewable energy, has been proposed as a way to close the CO_2 loop. In industry, methanol synthesis using the catalyst $CuO/ZnO/Al_2O_3$ occurs at a high pressure. We intend to make certain modification on the traditional catalyst in order to work at lower pressure, maintaining high selectivity. Therefore, three heterogeneous catalysts have been synthesized by co-precipitation in order to improve the activity and the selectivity to methanol under mild conditions of temperature and pressure. Certain modifications on the traditional catalyst $Cu/Zn/Al_2O_3$ were employed such as the modification of the synthesis time and the addition of Pd as a dopant agent. The most efficient catalyst among those tested was a palladium-doped catalyst, 5% $Pd/Cu/Zn/Al_2O_3$. This had a selectivity of 64% at 210°C and 5 bar.

Keywords: CO_2 hydrogenation, Methanol synthesis, Cu/ZnO catalyst; Pd catalyst; Energy storage

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1. Introduction

The scientific community widely considers global warming as a major challenge to our society. The main cause of this critical issue is the increase in the CO_2 concentration in the atmosphere due to the massive use of fossil fuels [1], which has growth in the last years [2]. One of the ways to address this problem is to use the CO_2 as resource in the synthesis of valuable products [3]. Renewable methanol, i.e. methanol obtained from CO_2 and hydrogen provided from renewable energy (solar or wind power), has been proposed by the Nobel Price G. Olah as a way to close the CO_2 loop [4, 5].

Methanol is already one of the key basic chemicals, being the second most manufactured compound from synthesis gas, after ammonia [6]. It is very soluble in water and also easily biodegradable, becoming a viable alternative for large scale efficient energy storage [7]. It stores both carbon and hydrogen in liquid form and may be converted into light olefins, gasoline and hydrocarbons [8]. In industry, methanol is produced using synthesis gas and the traditional catalyst $CuO/ZnO/Al_2O_3$ [9-11]. In order to optimize the process of methanol synthesis and obtain high selectivity values, it is essential to be aware of the reactions that take place in this synthesis.

$$CO_2 + 3\,H_2 \rightleftarrows CH_3OH + H_2O \qquad \Delta H_{298K} = -49.5\ kJ/mol\ CO_2 \tag{1}$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad \Delta H_{298K} = 41.2\ kJ/mol\ CO_2 \tag{2}$$

$$CO + 2\,H_2 \rightleftarrows CH_3OH \qquad \Delta H_{298K} = -90.7\ kJ/mol\ CO \tag{3}$$

Methanol formation is exothermic and therefore the thermodynamic equilibrium is favored at low temperatures, while kinetics is favored by high temperature. In addition, the difference between the number of moles of starting materials and products requires operation at high pressure in order to obtain a high yield to methanol. Although CO_2 hydrogenation is the main reaction in this process, it competes with reverse water-gas-shift (reaction 2) which drops the selectivity to methanol. Reverse water-gas shift is endothermic, and thus its equilibrium is favored at high temperatures [12].

Hence, a compromise between the thermodynamics and kinetics should be pursued to favor the desired product. Although industrial practice favors high pressure (50-100 bar) to increase the yield, the small scale of operation using renewable hydrogen would require lower pressure, to decrease the capital cost. It is possible to increase methanol yield, according to Le Châtelier principle, by removing water or/and methanol in order to shift the equilibrium to the formation of desired product and obtaining a higher conversion. This can be achieved by a membrane reactor, where the membrane removes selectively water or methanol. Struis et al [13] proposed the use of a membrane reactor using Nafion membranes. However, the maximum temperature achievable with such material was 200°C, which is too low. Menéndez et al. [14] proved through a simulation that a membrane reactor with a zeolite membrane could provide higher methanol yield than a conventional one. Gallucci et al. [15] have experimentally proved that the CO_2 conversion in a zeolite membrane reactor was higher than in a traditional one. Preliminary experiments in a zeolite membrane reactor have shown that at low pressure the effect of reverse water-gas-shift dominates, in such way that the removal of water increases more the formation of CO than the methanol synthesis [16]. This implies that there is a need for more selective catalysts at low pressure, in order to achieve the full advantages of a membrane reactor.

The purpose of this work is to prepare, characterize and test a series of different catalysts by modification of the traditional catalyst $CuO/ZnO/Al_2O_3$ and to determine which one exhibits higher selectivity to methanol at low pressure (maximum 5 bar). Moreover, it will be studied if the proposed changes improve the activity of the catalyst at these experimental conditions that could give even better result with the use of a membrane reactor.

2. Experimental

2.1. Reaction system

Gases are fed to the reactor using gas flow controllers (Alicat Scientific). The reactor was a quartz tube with an internal diameter of 10 mm and 40 mm length. For each reaction test, 1 g of catalyst was placed inside the reactor, having on top and bottom quartz wool to support it. A thermocouple is placed in the middle of the catalyst bed and the reactor sits inside a bath filled with silicone oil (Fluke Corporation) which allows working at a maximum temperature of 300℃. The reaction products (composed by light vapors and also condensable gases at room temperature), are carried out through a heat-insulated metal pipe to reach the condensation system, placed into a flask with crushed ice, ethanol and salt. In the analysis zone, after passing the condensation system, the non-condensable gases (H_2, CO_2, water and methanol that did not condense) can be leaded either to a bubble meter to measure the flow or to a gas chromatograph (Agilent Technologies 490 Micro GC). The liquid, a mixture of water and methanol, is analyzed off-line by GC-MS (Shimadzu QP-2010).

2.2. Catalyst synthesis

Two $CuO/ZnO/Al_2O_3$ catalysts were prepared using as basis a co-precipitation method described in literature [17]. Changes in the precipitation time from 30 (CZA-30′) to 150 minutes (CZA-150′) and the addition of palladium as a dopant agent (PdCZA-30′) were studied.

Two aqueous solutions of concentration 1 M were prepared, the first one using copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$, Panreac, 98%) and zinc nitrate ($Zn(NO_3)2{\cdot}6H_2O$, Sigma-Aldrich, 98%) and the second one with aluminium nitrate ($Al(NO_3)3{\cdot}9H_2O$, Sigma-Aldrich,

doi:10.20944/preprints202106.0308.v1

≥98%) and sodium carbonate (Na_2CO_3, Sigma-Aldrich, 99.5%). The ratio (mass basis) of copper to zinc and to aluminium was 45:45:10. The two mixtures were slowly added into a 600 mL beaker containing distilled water over a period of 30 or 150 minutes, with vigorous stirring. The addition of the two aqueous solutions was performed at a temperature of 70 ℃ and the pH was maintained constant at a value of 8. The blue formed precipitate was allowed to mature for further 30 minutes at the same temperature. The solution was filtered and the precipitates were then thoroughly washed with hot deionized water. The solid was dried overnight at 110 ℃ and calcined in a muffle oven at 150 ℃ for 1 h, 200 ℃ for 1 h, 250 ℃ for 1 h, 300 ℃ for 1 h and 350 ℃ for 4 h. The catalyst slightly changed its color into a darker green upon calcination and it was then sieved in order to collect the desired particle size for the reactor (200-315 μm).

The addition of palladium was carried out by the incipient wetness technique. Therefore, the catalyst with precipitation time of 30 minutes with the chosen particle size of 200-315 μm was used to synthetize the Pd doped catalyst. In order to obtain 5% $Pd/CuO/ZnO/Al_2O_3$, palladium nitrate (Pd(NO3)2, Sigma-Aldrich, 100%) in water was added to the catalyst. The catalyst impregnated with Pd was dried at 110 ℃ for 12 h and then sieved again to assure the particle size stayed the same upon the addition of palladium [18].

2.3. Catalyst characterisation

BET surface analysis was carried out by nitrogen physisorption using a Micrometrics Tristar 3000 V6.08 analyzer. The samples were degassed at 200 ℃ for 10 h (VacPrep 061 of Micromeritics). Electron microscopy was made with a Field Emission Scanning Electron Microscope from Carl Zeiss MERLINTM, which has an X-ray spectrometer with dispersive energy that also allows determining the semi-quantitative analysis with EDS (INCA 350, Oxford Instruments–X-Max). X-ray diffraction technique was carried out using a D-Max Rigaku diffractometer which has a rotary anode and uses a graphite monochromator to pick the CuKα radiations. This equipment works at voltage of 40 kV and intensity of current of 80 mA which has a Cu anode.

2.4. Reaction tests

Reaction experiments were performed using a conventional fixed-bed catalytic reactor. First, the catalyst CZA-30′ was tested at different temperatures (180, 200, 210, 220 and 240 ℃) and pressures (1, 2.5 and 5 bar) in order to choose the optimal conditions for a high methanol selectivity. Once these parameters were decided, taking into account the results of the experiments with the conventional catalyst, the other two catalysts were tested under the same experimental conditions. Therefore, a screening of catalysts was performed for the direct hydrogenation of CO_2 into methanol. For each catalyst, experiments were carried out using 1 g of sample and at a flow rate of 100 mL(STP)/min ($H_2/CO_2 = 3/1$), being the total time on stream 7 h.

3. Results and discussion

3.1. Catalyst characterization

The obtained results from the nitrogen adsorption technique are shown in Table 1. The specific surface area decreases when the synthesis time is larger. Therefore, CZA-30′ has a significantly bigger area than CZA-150′. This suggests that at a slower co-precipitation the formed crystals are bigger as they keep forming on top of precipitated crystals, while in a quick synthesis, when a higher oversaturation is reached, it causes the formation of more and smaller crystals. This makes CZA-150′ to have a smaller specific surface area. The catalyst CZA-150′ shows an area similar to the catalyst synthesized by Hong et al. [17], but the CZA-30′ shows a higher value. When palladium is added on the traditional catalyst, the area slightly increases, but compared to CZA-30′ it shows no micropores. This is probably because palladium blocks the micropores of the original catalyst.

Table 1. EDS analysis results (%wt).

Sample	O	Pd	Al	Cu	Zn
CZA-30′	34.4	-	6.3	34.7	24.6
PdCZA-30′	21.3	3.9	2.9	30.8	37.4
CZA-150′	21.9	-	4.2	30.5	38.7

The morphology of the synthesized catalysts is presented in Figure 1 as comparison to CZA-30′ to show the changes produced by the different time of synthesis or supports used. Furthermore, a study between the fresh and used CZA-30′was carried out in order to observe the impact of methanol synthesis process upon the catalyst. Therefore, the appearance and the size of these samples are going to be discussed for each of the three catalysts.

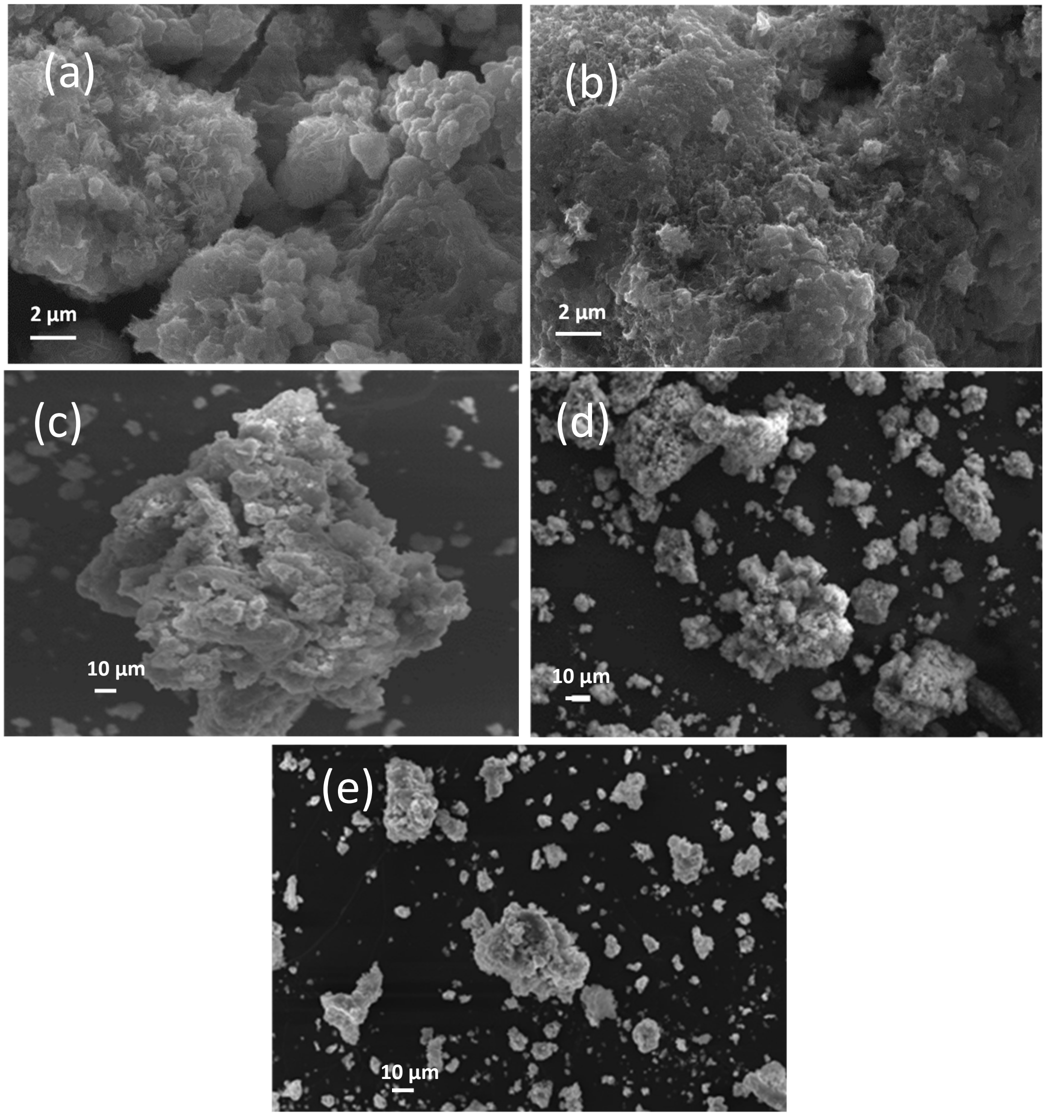

Figure 1. FESEM images: a) CZA-30′, b) PdCZA-30′, c) CZA-30′, d) CZA-150′ and e) CZA-30′ used.

doi:10.20944/preprints202106.0308.v1

Upon adding the palladium, the crystal size remains similar to the original CZA-30′ catalyst (Figures 1a and 1b). This was expected, since the small amount (5%) of palladium was not enough to greatly change the catalyst morphology. The only modification seen is that the particles are much smaller than in the original one. The brighter spots present in the PdCZA-30′ sample are palladium coatings on the catalyst. Upon reactions, it can be stated that the aggregates are broken and hence they become smaller. Although the catalyst crushes a bit upon reaction as it can be noticed in Figure 1e, later on in the results of the experimental tests carried out it is proved that the catalyst gives the same results, having a high reproducibility.

In Figure 2, XRD of CZA-30′ is shown in comparison with CZA-150′. It can be observed a structural change that is affected by the precipitation time. The catalyst co-precipitated in 150 minutes forms larger crystals which are expected to give less reactivity. The calculation of the crystallite size for ZnO with the Scherrer equation, from the peak at 2θ=31.8°, shows that the ZnO platelets have a thickness of 8.8 nm in the case of CZA-30′, and 12.7 nm in the case of CZA-150′. The crystal size of the CZA-30′ is smaller but these small crystals form larger aggregates and this is caused by the shorter synthesis time that forms smaller particles. XRD of PdCZA-30′ is similar to the XRD of CZA-30′.

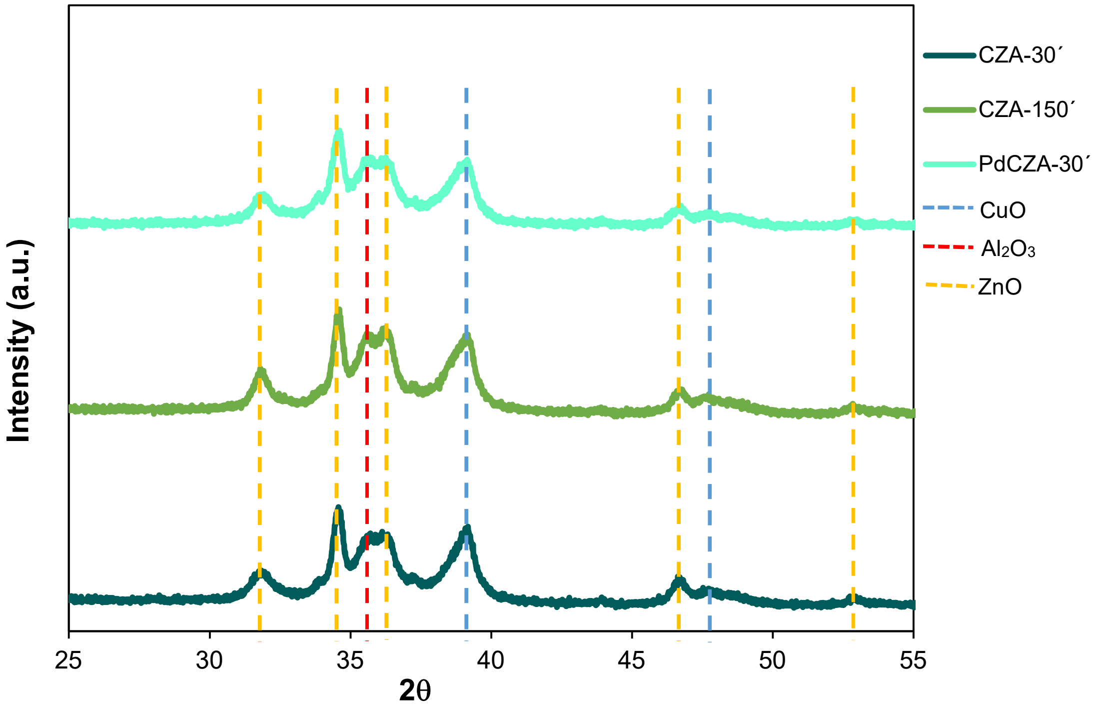

Figure 2. XRD diffractogram for CZA-30´, CZA-150´ and PdCZA-30´.

All the metal oxides, CuO, ZnO and Al_2O_3 are present in the structure of the three catalysts and these have been identified on the graph. These results correspond to the analysis carried out by Hong et al. [17]. As for the palladium-based catalyst, peaks for the dopant agent were not detected in the diffractogram. This is probably caused by the small percentage of palladium. Figure 3 shows the EDS mapping of Cu, Zn and Al in the CZA-30′ catalyst. It shows that that the distribution of all metals in the prepared catalyst was highly homogeneous.

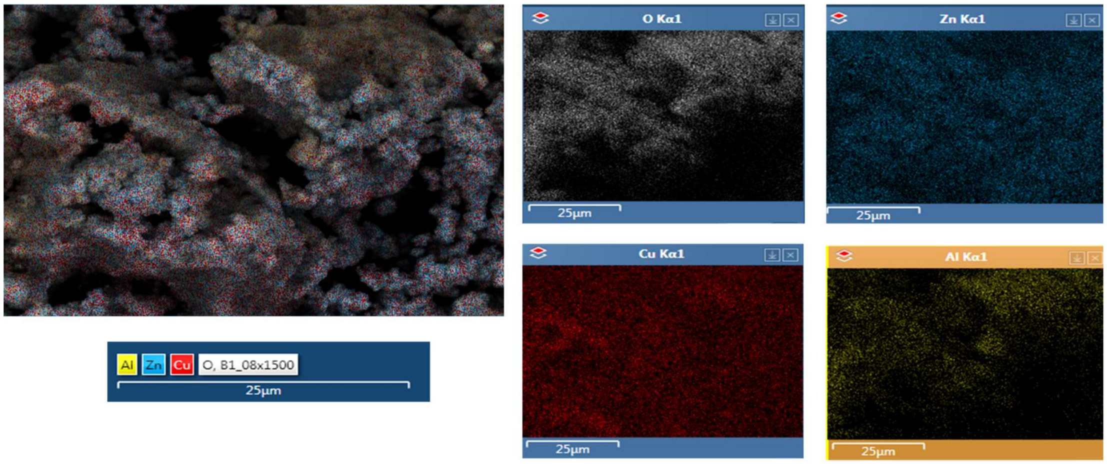

Figure 3. EDS mapping of CZA-30′.

The contents of these species observed for the catalysts (Table 2) were close to the nominal ratios used for preparing the starting solutions.

Table 1. Specific surface area, pore volume and diameter calculated after BET analysis.

Sample	Specific surface Area (m²/g)		Pore volume (cm³/g)		Pore diameter (nm)	
	S_{BET}	$S_{micropore}$	V_{pore}	$V_{micropore}$	d_{pore}	$d_{micropore}$
CZA-30′	111.9	12.3	0.5	0.005	18.2	1.6
PdCZA-30′	123.7	-	0.3	-	10.7	-
CZA-150′	65.9	4.7	0.2	0.002	14.6	1.7

3.2. Reaction tests

Reaction tests with the synthesized catalysts were carried out in order to find which one gives the highest selectivity to methanol. Prior to the comparison between the catalysts, the experimental conditions (temperature and pressure) that worked the best for CZA-30′ were determined. The rest of the catalysts were tested using the same experimental conditions, this way allowing them to be comparable. In addition, diagnostic tests performed by changing the catalyst particle size and flowrate allowed to exclude mass transfer limitations when working with 200-315 µm and 100 ml (STP) / min, respectively. Reaction tests were performed using CZA-30′ at 5 bar and 180, 200, 220 and 240°C. A greater conversion of CO_2 with temperature is observed (Figure 4a). However, this increase in conversion is solely a consequence of CO production due to the endothermic nature of the reverse water-gas shift reaction. As it observed in Figure 4b the selectivity at 240 °C was very poor and therefore these conditions are not useful for further tests. The highest selectivity was achieved at 180 °C, but the conversion was very low (1.1%). Therefore, in order to have a slightly better conversion and to maintain the highest selectivity possible, the choice remains between 200 and 220 °C. At 200 °C selectivity had a good value of 78.3 %, but the conversion was only 1.8 %, while at 220 °C there was a better conversion of 4.5 %, but the selectivity dropped to 25.7 %. Hence, an intermediate temperature was studied.

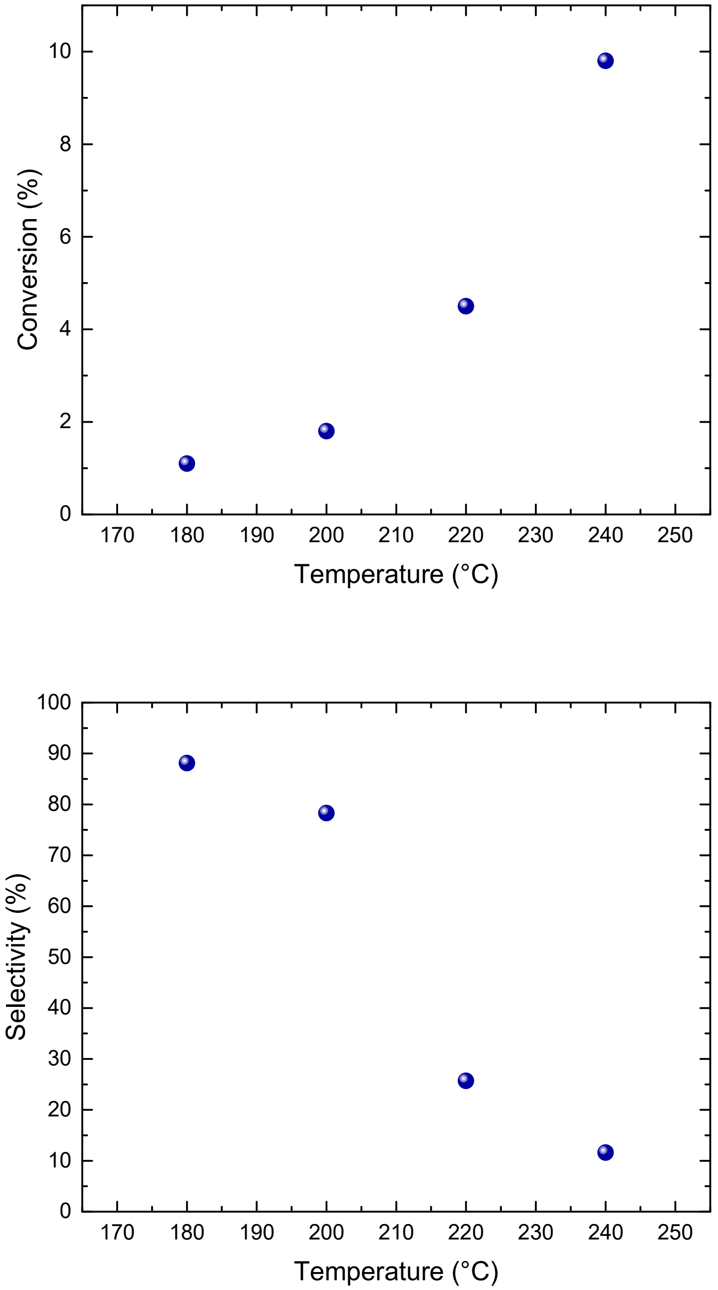

Figure 4. a) Conversion and b) selectivity for CZZ-30′ at 5 bar, T=180, 200, 220 and 240°C.

The evolution of conversion and selectivity along the time-on-stream at 5 bar and 200, 210 and 220°C is shown in Figure 5. As expected, the middle temperature (210°C) gives the best results, in terms of yield to methanol (i.e., the product of conversion and selectivity), among the temperatures assessed. The objective was maintaining a high selectivity as well a high conversion. Hence, the water-gas-shift is indeed less favored at this temperature and it is more selective to methanol. Therefore, this temperature is chosen to be used for further reaction tests to analyze the effect of pressure for the CZA-30′ catalyst and for the further screening of catalysts.

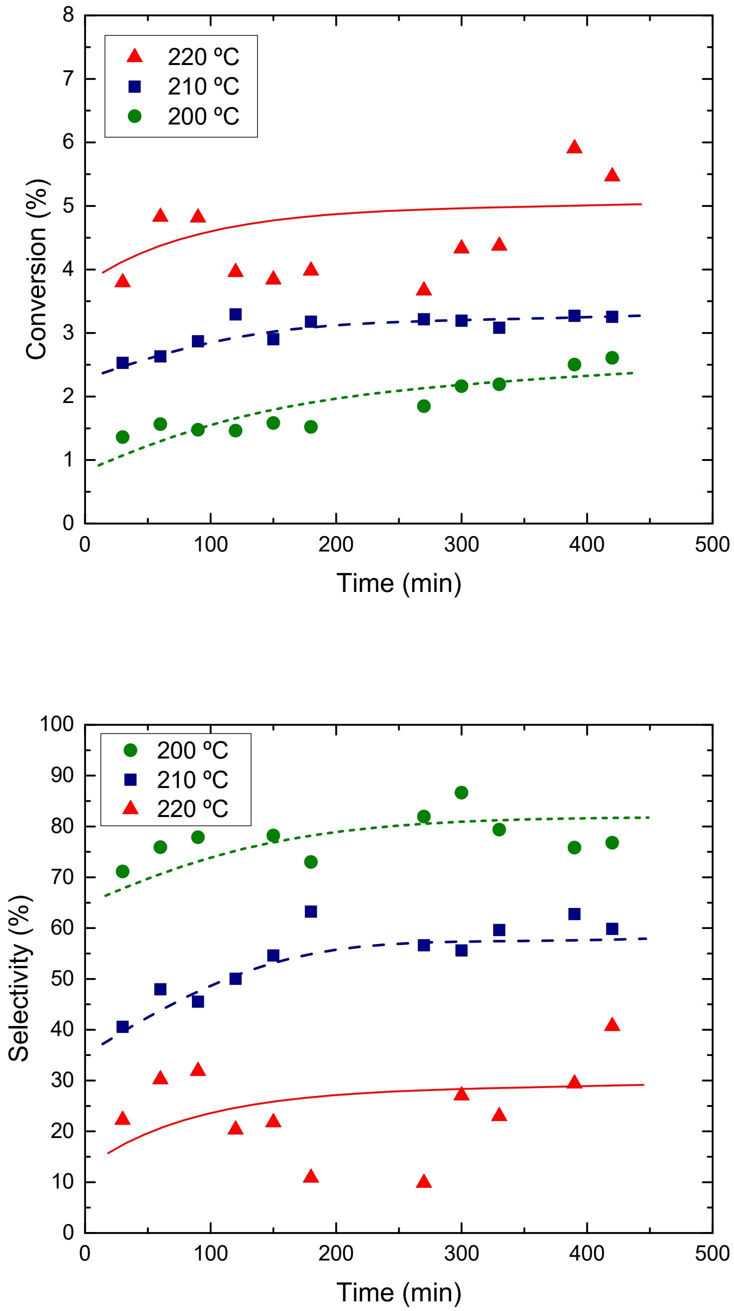

Figure 5. a) Conversion and b) selectivity for CZZ-30′ at 5 bar.

In order to observe the effect of pressure for the synthesis of methanol by direct dehydrogenation of carbon dioxide, reaction tests for CZA-30′ were carried out at 210°C. This temperature favours methanol selectivity and CO_2 conversion, so by assessing different pressure values it should be able to be observed which one works the best. The

doi:10.20944/preprints202106.0308.v1

experimental set-up reaches a maximum pressure of 5 bar. Therefore, apart from the highest value of 5 bar which was already tested at 210 °C giving a conversion of 3.1 % and a selectivity of 52.7 %, another two pressures were tested: 1 and 2.5 bar.

Pressure has a determining effect (Figure 6) because a decrease in the number of moles occurs in the formation of methanol, whereas the RWGS reaction does not produce any variation in this aspect. That is, according to Le Chatelier's principle, a pressure increase shifts the equilibrium of reaction towards the formation of MeOH, while the equilibrium in reaction (2) is not affected. At lower pressure, the water-gas shift reaction is more favored; hence, more carbon monoxide and water will be formed, decreasing the selectivity to methanol. According to the previous results, the experimental conditions for further comparison of catalysts were chosen as 5 bar and 210°C.

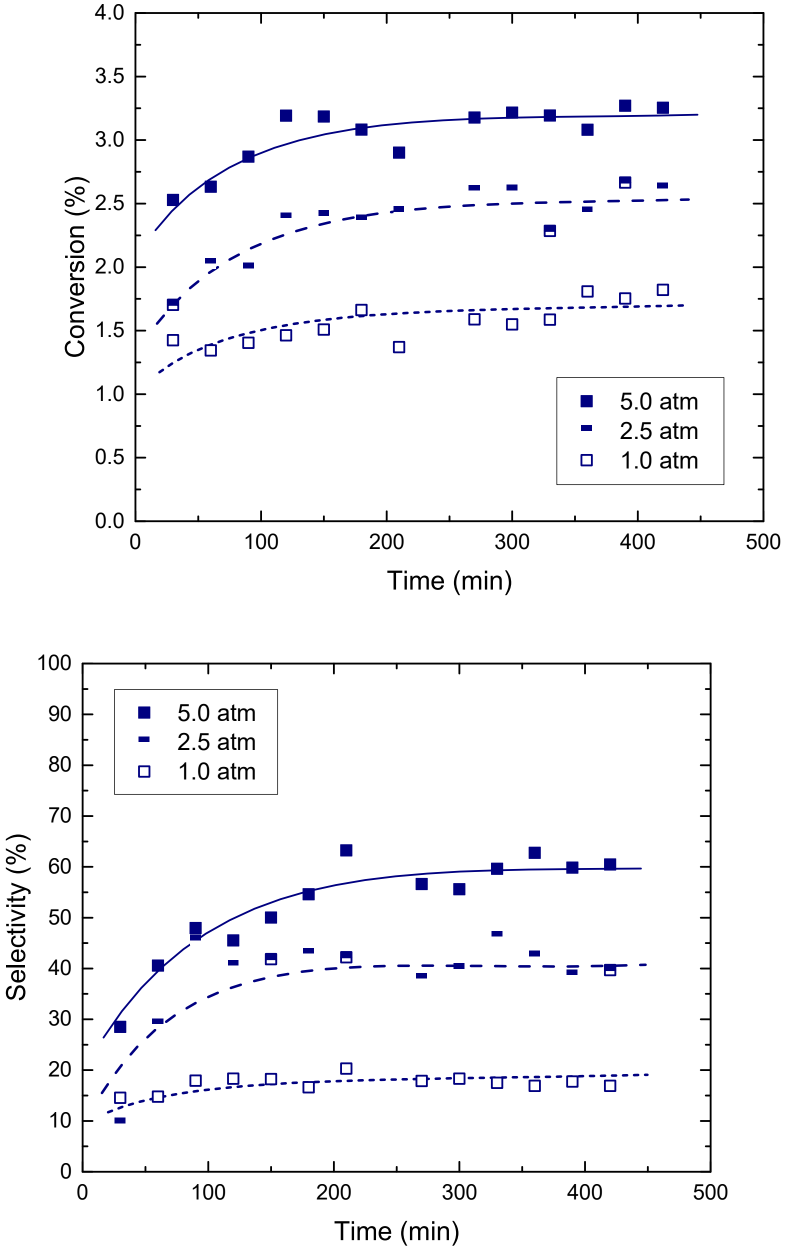

Figure 6. a) Conversion and b) selectivity for CZA-30´ at 210°C.

doi:10.20944/preprints202106.0308.v1

Figure 7 shows the comparison of the carbon dioxide conversion with CZA-30′ and CZA-150′. As the precipitation time increases, the conversion becomes poorer, which is probably related with the lower surface area of the latter. Although the selectivity is greater when the synthesis time is larger, as the conversion has such a small value, the better yield was given by CZA-30′ (1.63% vs 1.45%).

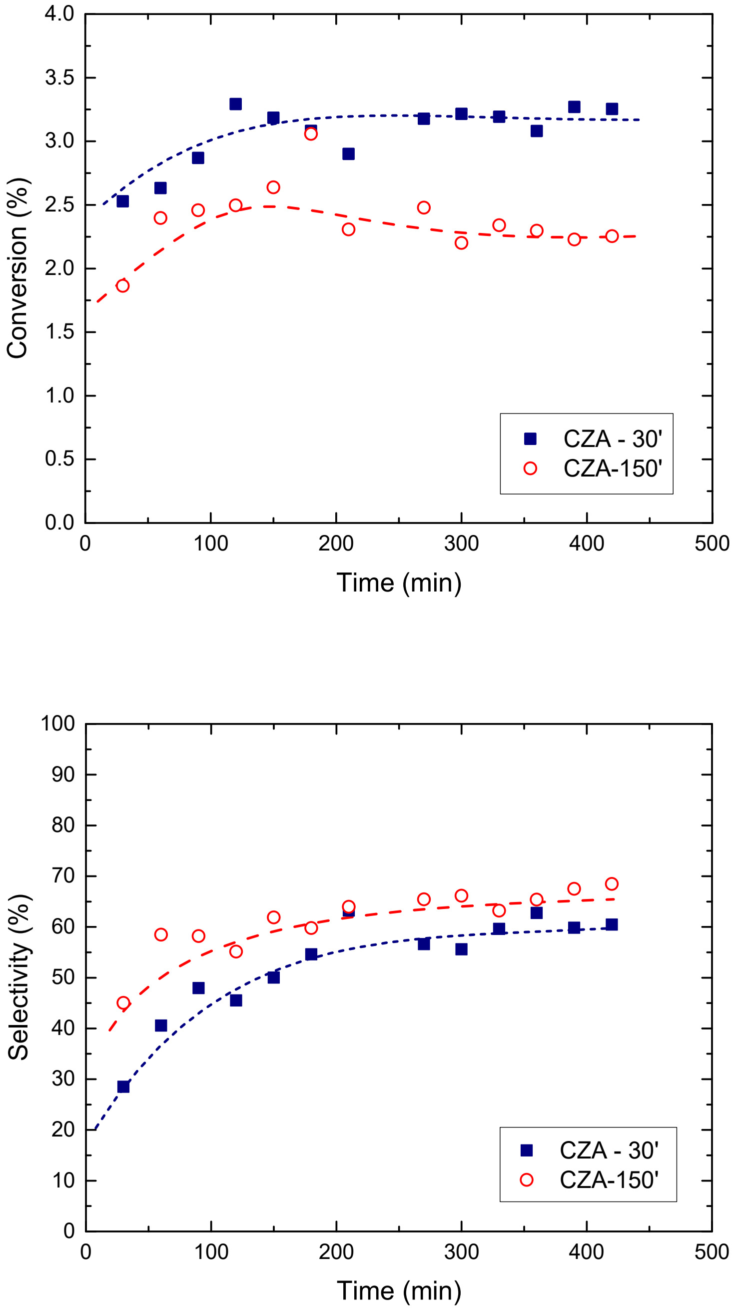

Figure 7. a) Conversion and b) selectivity for CZA-30′ and CZA-150′ at 210°C.

Selectivity and conversion with PdCZA-30′ are compared with those of CZA-30´ catalyst in Figure 8. The catalyst with Pd gave a similar conversion as the undoped one, it only exhibited higher conversion in the first 200 min, and then it slightly dropped reaching the same values as CZA-30´. As for the selectivity PdCZA-30´ displayed a more irregular development in time, but overall it has a better selectivity than CZA-30′. In order to check its reproducibility, the PdCZA-30′ experiment at 210 ºC and 5 bar was repeated and we found that the catalyst activity and selectivity followed (not shown) the same patterns.

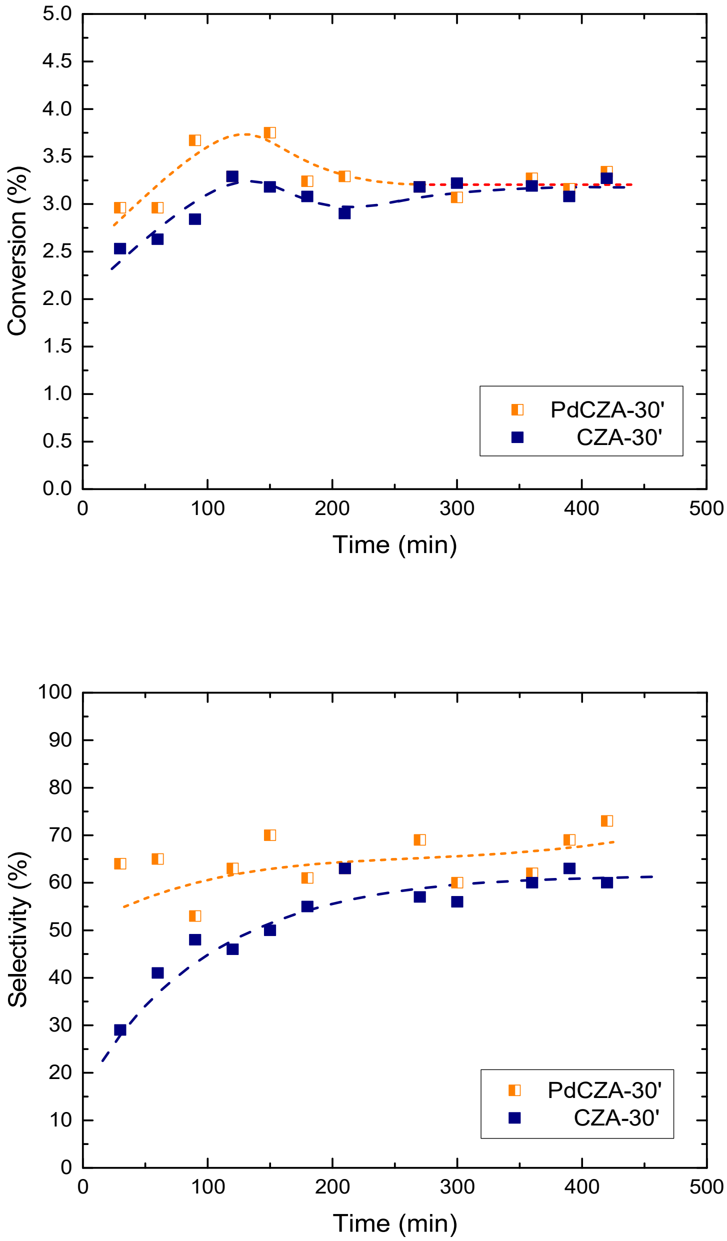

Figure 8. a) Conversion and b) selectivity for PdCZA-30´ and CZA-30´ at 5 bar and 210°C.

4. Conclusions

The effect of temperature and pressure in the formation of methanol by CO_2 hydrogenation was studied. As expected, the selectivity to methanol increased at high pressures and low temperatures. The most favorable conditions for the synthesized catalyst, working in the low pressure range (1-5 bar), were the pressure of 5 bar and a temperature of 210 °C. Furthermore, it was established that the change in the precipitation time from 30 minutes to 150 gave a smaller specific surface area than the conventional one, providing also a lower activity and yield to methanol. The best results were achieved for the palladium-based catalyst PdCZA-30′ which exhibit a selectivity to methanol with an average value of 63.4% for a conversion of 3.2%, clearly better than the conventional $CuO/ZnO/Al_2O_3$ catalysts. Therefore, this catalyst constitutes the best option for further studies in membrane reactor.

Author Contributions: Conceptualization, J.S, J.H. and M.M.; methodology, J.S, J.H. and M.M; validation, B.T. and J.L.; writing—original draft preparation, J.S. and J.H.; supervision, M.M. All authors have read and agreed to the published version of the manuscript.

Funding: Ministerio de Ciencia, Innovación y Universidades: CTQ2016-76533-R and PID2019-106196RB-I00

Conflicts of Interest: The authors declare no conflict of interest.

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