

# CO<sub>2</sub> hydrogenation into methanol over Cu/Zn/Zr catalysts prepared by a surfactant-assisted co-precipitation followed reflux in one-step method

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## Abstract:

Cu/Zn/Zr catalysts were synthesized by a surfactant-assisted co-precipitation followed reflux in one-step method with different ratios of surfactant and characterized by XRD, BET, RTP, XRF, CO<sub>2</sub>-TPD and N<sub>2</sub>O-TPD techniques. The materials prepared were tested in the CO<sub>2</sub> hydrogenation reaction to methanol. Cu/Zn/Zr-c catalyst was the most active for CO<sub>2</sub> conversion. In the relation of methanol yield was observed that the crystallization of zinc phase not increase the yield for methanol. The Cu/Zn/Zr-a catalyst showed the best yield for methanol and the Cu/Zn/Zr-c catalyst displayed the higher CO<sub>2</sub> conversion.

**Keywords:** CO<sub>2</sub>, Methanol, Cu/Zn/Zr Catalyst.

## 1. Introduction

The carbon capture and utilization (CCU) into methanol can represent a new economy for CO<sub>2</sub> and also help the environment [1]. Therefore, the development of a new catalyst has been a key research to optimize the CO<sub>2</sub> conversion.

In this context, Cu-Zn-Zr catalysts have gained an increasing interest due to synergistic effects between the compounds that favor a high catalytic activity for methanol production [2].

A large number of approaches for preparing supported Cu-based catalysts (e.g., deposition-precipitation, incipient wetness impregnation, and colloidal deposition methods) have been intensively explored. However, in most cases, especially for high metal loadings, it is difficult to obtain well-dispersed phases between the metallic and oxide domains. Then, an alternative route, such as one-pot method, involves higher dispersion and interaction between copper and the other elements can be important for a good catalytic performance that requires bifunctional catalysts [3].

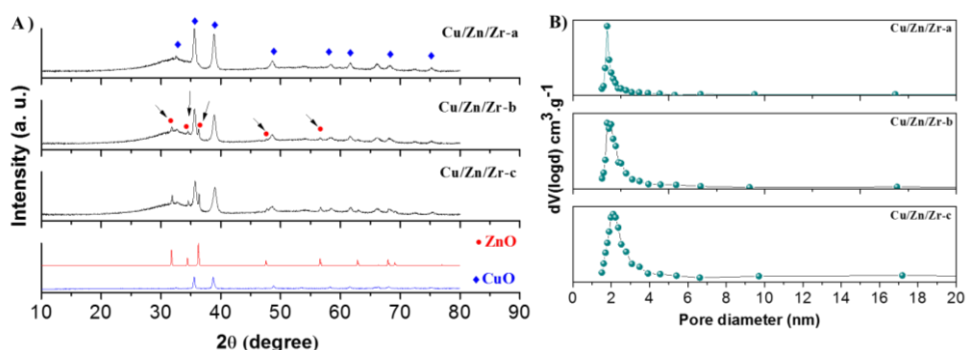
The purpose of this study is to evaluate the structure-activity relationships by different ratios of surfactant in the synthesis of Cu/Zn/Zr catalysts for CO<sub>2</sub> hydrogenation to methanol.

## 2. Experimental

Cu/Zn/Zr catalysts were prepared by one-pot co-precipitation followed reflux method with 30 wt.% Cu, 15 wt.% Zn and 55 wt.% Zr. In this procedure, a solution of ZrO(NO<sub>3</sub>)<sub>2</sub>.xH<sub>2</sub>O, and two other solutions of copper and zinc nitrates were prepared and then Pluronic P-123 was added (molar ratio surfactant/Cu-Zn-Zr = 0.015, 0.03 and 0.06). After that, aqueous NaOH (0.5M) was added drop-wise at room temperature to an aqueous solution containing the elements and P-123 under stirring by careful pH = 11. The slurry formed was refluxed for 24 h at 110 °C. After that, the materials were washed 2 times with water and 1 time with acetone, dried in the oven at 100 °C/24 h. Then, the resulting precursors were calcined in air at 500 °C/2 h with a heating rate of 3 °C.min<sup>-1</sup>. The catalysts were designated as Cu/Zn/Zr-a, Cu/Zn/Zr-b and Cu/Zn/Zr-c, where (a), (b) and (c) correspond the different molar ratio surfactant/Cu-Zn-Zr. The physicochemical properties of catalysts were investigated by XRD, BET, TPR, XRF, CO<sub>2</sub>-TPD and N<sub>2</sub>O-TPD techniques. CO<sub>2</sub> hydrogenation tests were carried out using a stainless steel reactor, which contained 0.4 g of catalyst diluted with 0.2 g of SiC. Firstly, all catalysts were reduced in H<sub>2</sub> flow (30 mL.min<sup>-1</sup>) at 300 °C for 1 h. The reaction was conducted at 250 °C and 20 bar with a mixture of CO<sub>2</sub> and H<sub>2</sub> (molar ratio 1:3 and GHSV = 6 L. h<sup>-1</sup>.g<sup>-1</sup>).

## 3. Results and discussion

As seen in Fig. 1A), only diffraction peaks corresponding to the monoclinic CuO structure (JCPDS 89-2530) are visible for Cu/Zn/Zr-a catalyst, while the diffraction peaks of ZnO and ZrO<sub>2</sub> cannot be observed. With the increase surfactant ratio, Cu/Zn/Zr-b and Cu/Zn/Zr-c catalysts, both diffraction peaks of CuO and ZnO structures (JCPDS 89-1397) appeared. However, the diffraction peaks of ZrO<sub>2</sub> cannot be observed again. This indicates that the amount of surfactant and the calcination temperature were not enough to get crystallites of ZrO<sub>2</sub>. Besides that, both specific surface ( $S_{BET}$ ) area and copper metallic area ( $MSA$ ) increase for higher ratios of surfactant (Table 1). The presence of mesoporous was evaluated by pore size distribution (Fig. 1B). All samples showed a uniform mesoporous pore size distribution, which mainly centered at 2.5 nm.



**Figure 1.** A) XRD patterns and B) pore size distributions of catalysts.

The products obtained by CO<sub>2</sub> hydrogenation were methanol, CO and lower amounts of methane. Two competing reactions can occur during CO<sub>2</sub> hydrogenation over metallic sites, methanol synthesis and reverse water-gas-shift. Methanation also occurs and is thermodynamically favored. The CO<sub>2</sub> conversion was more favored by Cu/Zn/Zr-c catalyst due to the higher specific surface area ( $S_{BET}$ ), copper metallic area ( $MSA$ ), metallic dispersion ( $D_{Cu}$ ) and lower crystallite size of copper oxide. However, this catalyst was more active for CO production. In the relationship of methanol yield was observed that the amorphous zinc oxide and the higher density of basis sites at the conditions of reaction favored the yield for methanol. Then, Cu/Zn/Zr-a catalyst showed the best yield for methanol.

**Table 1.** Textural, structural properties and catalytic performance of the different Cu/Zn/Zr catalysts.

Catalysts	$S_{BET}$ (m <sup>2</sup> /g)	Crystallite size CuO (nm)*	$MSA$ (m <sup>2</sup> Cu/g <sub>cat</sub> )**	$D_{Cu}$ (%) **	CO <sub>2</sub> -TPD (mmol g <sup>-1</sup> )***	X(CO <sub>2</sub> ) %	Yield (%) Methanol
Cu/Zn/Zr-a	72	19.8	7.3	4.8	1305	14.6	16.0
Cu/Zn/Zr-b	84	17.5	8.0	5.6	1176	15.5	14.4
Cu/Zn/Zr-c	111	15.6	11.3	7.5	989	18.4	9.1

\*Determined from full width at half maxima of CuO (111) XRD peak; \*\* N<sub>2</sub>O chemisorption method; \*\*\* at 250°C

#### 4. Conclusions

The present study demonstrates that all catalysts show significant activity for CO<sub>2</sub> conversion. The activity of catalysts was directly linked to basic, metallic sites and crystallite size of copper. The crystallization of zinc phase not favored the yield for methanol. The catalyst Cu/Zn/Zr-c displayed the higher CO<sub>2</sub> conversion due to the smaller crystallite size and higher copper metallic area. The Cu/Zn/Zr-a catalyst showed the best yield for methanol due to higher density of basic sites.

#### References

1. M. Porosoff, B. Yan, J. Chen, Energy. Environ. Sci. 9 (2016) 62.
2. L. Li, D. Mao, J. Yu, X. Guo, Journal of Power Sources 279 (2015) 394.
3. Q. Hu, G. Fan, L. Yang, F. Li, ChemCatChem 6 (2014) 3501.