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Effect of copper loading and CO2/CO ratio for the production of methanol over Cu/ZnO/Al2O3 catalysts from biomass-derived syngas

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PURPOSE OF THE ABSTRACT

Intro

There is a consensus in that methanol production depends on the actual surface of the metallic copper particles in Cu/ZnO/ Al2O3 (CZA) catalysts [1, 2]. It seems well-established that the optimal composition of these catalysts is ca. 60/30/10 Cu/ZnO/Al2O3 [3]. Whereas it is widely accepted that the molecule which is mainly hydrogenated is CO2 [3], the kinetics of the reaction with pure CO2/H2 or CO2-rich CO2/CO/H2 mixtures are significantly slower [4, 5]. This feature is particularly relevant when syngas is obtained from biomass, usually containing large amounts of CO2. The effect of the feed composition (CO2/CO/H2) on the performance of CZA catalysts during methanol production has not been studied so far. In this work, a series of CZA catalysts with different Cu loadings have been synthesized, characterized and tested for the methanol synthesis reaction, using CO2/CO/H2 mixtures with different CO2/CO ratios. The results helped to evaluate the effects of the copper content and the CO2/CO ratio in this process.

Experimental

The CZA_X catalysts, where X denotes the copper loading (% wt.), were synthesized by the co-precipitation method at 65 °C and pH=8, using a 2 M solution of the corresponding nitrates and a NaCO3 1.6 M solution. After aging, the precipitates were dried at 65 °C and calcined at 325 °C during 2.5 h.
Catalyst composition was analyzed by ICP-OES. Specific surface areas were evaluated form the N2 adsorption-desorption isotherms. The reducibility of the catalysts was studied by H2-ATG. In situ DRX was used to follow the evolution of the crystalline structure of the CZAs with temperature under H2. Catalytic tests were carried out under different conditions: 25 and 50 bar, 240 and 270 °C, 7500 and 15000 h-1 and feed compositions of 1.9/1/7.7 and 0.5/1/3.5 CO2/CO/H2.

Results and discussion

The Table 1 shows that the composition of the catalysts is near to the expected. CZA_60 and CZA_50 have specific areas around 40 m2/g, whereas CZA_30 has higher area, due to its higher Al2O3 content. According to H2-ATG and in situ XRD analyses, catalysts are reduced at 250 °C.
In the catalytic tests, only the CZA_60 and CZA_50 proved to be active towards the methanol production, irrespectively of the CO2/CO/H2 composition. On the other hand, CZA_30 fails to show methanol production activity, but it shows moderate activity for the reverse water gas shift reaction (RWGS; CO2+H2 --> CO+H2O). Comparing the two catalysts with higher copper contents at 7500 h-1 (Fig. 1), it can be observed that CZA_60 produces methanol in a higher rate than CZA_50. It is also observed that the CH3OH production is higher when

CO_2-poor syngas is fed at all the reaction conditions studied. As expected, due to the high molar interchange in the methanol production reaction from CO_2, the reaction pressure plays the most important role.
Thus, at 270 ºC and CO_2/CO-ratio 0.5, the increment in CH_3OH production rate is 323% with CZA-50 and 357 % with CZA-60 when the reaction pressure is incremented from 25 to 50 bars. This behavior is also observed at higher space velocity (results not shown). The highest CH_3OH production rates are obtained at GHSV= 15000 h^{-1} and 270 ºC. The rate is incremented from 0.007 to 0.031 mol/min/gCu when the pressure rises to 50 from 25 bars with CZA_60 catalyst.

Conclusions

We have shown that both the Cu loading and the actual CO_2/CO/H_2 ratio have a strong influence in the methanol production rate over CZA catalysts. Increasing the Cu loading from 50 to 60 wt.% and decreasing the CO_2/CO-ratio from 1.9 to 0.5 in the syngas lead to an improvement of the methanol production rate.

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FIGURES

Catalyst	Cu	ZnO	Al_2O_3	BET area
		%		m^2/g
CZA_60	66.6	28.6	4.8	38
CZA_50	58.6	23.7	17.7	41
CZA_30	33.0	13.1	53.9	107

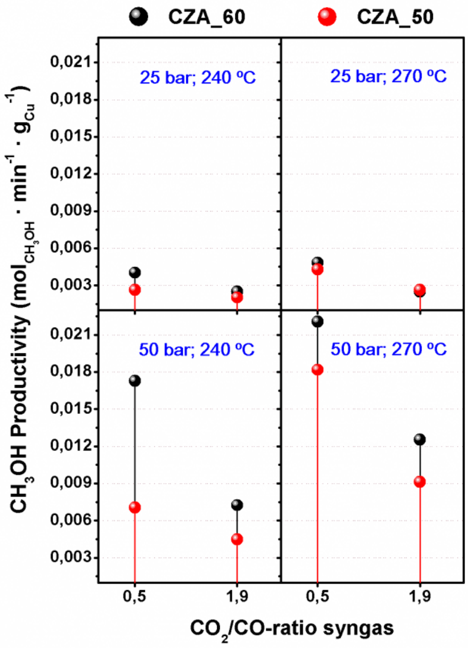

FIGURE 1
Table 1. Catalyst composition and BET areas
Composition in %, BET area in m2/g

FIGURE 2
Figure 1. CH3OH productivity of CZA_50 and CZA_60 at different reaction conditions and 7500 h-1.
Black dots: CZA_60
Red dots: CZA_50

KEYWORDS
Biomass-derived syngas | Syngas composition | Copper-zinc-alumina composition | Methanol production

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