**Comparison of CuO-ZnO-X catalysts (X = Al2O3, MnO, ZrO2) for the reverse water gas shift reaction at low pressure**

A. Portillo\*, A. Ateka, J. Ereña, A.T. Aguayo, J. Bilbao

*Dep. Chemical Engineering, Univ. of the Basque Country UPV/EHU, P.O. Box 644, 48080 Bilbao, Spain;*

 *tel. +34 946015361, e-mail: \*Corresponding author: ander.portillo@ehu.eus*

**Highlights**

* The r-WGS reaction at low pressure allows obtaining high CO yields from CO2.
* r-WGS is interesting as a preliminary stage of the synthesis of hydrocarbons from CO2.
* The CuO-ZnO-ZrO2 catalyst is the most suitable for the r-WGS reaction.

**1. Introduction**

CO2 valorization to fuels and chemicals plays a key role in the current commitment for reducing the consequences of global warming. In this regard, the direct synthesis of hydrocarbons (Fischer Tropsch, FTS) and the indirect synthesis through methanol (MeOH) as intermediate receive great attention. In both routes the r-WGS reaction plays a relevant role, since CO is more reactive than CO2 [1]. Nowadays, the indirect synthesis is receiving more attention, since in this process catalyst deactivation and methane formation are lower.

Therefore, the aim of this work is to compare the activity of different CuO-ZnO based catalyst, doped with Al2O3, MnO or ZrO2 (named CZA, CZMn and CZZr, respectively) for the r-WGS reaction at low pressure. The activity and stability of these catalysts for the synthesis of MeOH has already been established [2] and the low pressure study conducted here will allow to: i) identify CO yield avoiding its conversion to MeOH, and, ii) evaluate future prospects of these catalysts for the r‑WGS reaction at low pressure as a previous stage in the hydrocarbons synthesis processes, given the advantages over CO2 valorization, thus, greater reactivity of CO and lower water concentration in the medium (which attenuates reaction and favors catalyst deactivation)

**2. Methods**

CuO-ZnO-XO (CZX) metallic functions have been prepared by precipitation of the aqueous nitrate solution (1M) with the desired Cu/Zn/X ratio of 2/1/1.5 (being X= Al, Mn, Zr) with Na2CO3 (1M) at pH=7 and 70°C. The following stages consist of aging the precipitate at 70°C for 1 h, filtering and washing the precipitate to remove the remaining Na+ ions, drying and calcination (300°C, 10h).

The runs have been conducted in a fixed bed reactor (Microactivity‑Reference, PID Eng. Tech.) connected on-line to a Varian CP4900 micro gas-chromatograph for the continuous analysis of the products. Reaction conditions are as follows: H2/CO2 molar ratio in the feed, 3; temperature, 200‑300 ℃; pressure, 1.6-6 bar; space time, 5‑13.5 gcath(molC)-1; time on stream, up to 24 h.

**3. Results and discussion**

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| As an example, Figure 1a and 1b show the effect of pressure and temperature on the yield of the CO2 hydrogenation reaction products (CO and MeOH) and CO/MeOH molar ratio, with CZMn catalyst and 13.5 gcath(molC)-1. In light of the results in Fig. 1a, as predicted thermodynamically, higher pressures lead to higher MeOH production, while CO yield is lightly affected. However, increasing temperature (Fig. 1b) gives way to higher CO yield, as WGS equilibrium is highly dependent on temperature. Furthermore, MeOH production shows a maximum at 225℃, justified both by the improvement of the kinetics at higher temperature, and to the thermodynamic limitations of exothermic reactions, as it is the case.Fig 1c shows the catalytic behavior of the three studied catalysts. For CZZr catalyst, a remarkably higher CO yield is achieved at 3 bar and 350 ºC, which is the pursued goal for the selection of the most suitable catalyst to be used in the CO2 valorization processes. |  |
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| **Figure 1.** CO and MeOH yields and CO/MeOH ratio for CZMn at 13.5 gcat h molC-1 and 250 ºC; 3 bar (b); and at 250 ºC and 3 bar for CZA, CZZr and CZMn. |

**4. Conclusions**

Figure 1. CO and MeOH yields and CO/MeOH ratio a 13.5 gcath (molC)-1, at 250℃ for CZMn (a), at 3 bar for CZMn (b) and at 250℃ and 3 bar (c).

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Low pressure experiments have allowed ascertaining the activity for the r-WGS reaction of catalysts commonly used for the synthesis of MeOH, among which the activity of CZZr stands out. These results are interesting to contemplate the installation of a low pressure r-WGS unit (of moderate costs) as a previous stage to the synthesis hydrocarbons (at high pressure), with the advantages of the higher reactivity of CO and the presence of water in the feed, which would be separated at the outlet of the r-WGS unit).

**Acknowledgements**

Figure 1. CO and MeOH yields and CO/MeOH ratio a 13.5 gcath (molC)-1, at 250℃ for CZMn (a), at 3 bar for CZMn (b) and at 250℃ and 3 bar (c).

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