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# Continuous Glycerol Dehydration to Acetol over CuO/ZrO2: Catalyst Design and Active Sites Understanding

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## PURPOSE OF THE ABSTRACT

### 1. Introduction

Among all the catalytic routes to valorize the biodiesel synthesis co-product glycerol, selective dehydration to acetol (hydroxyacetone) is believed to become a crucial reaction. Acetol is a non-toxic compound used as a flavor, an additive in dyes and cosmetics, and a skin tanning agent. Moreover, it is a valuable intermediate to produce olefins, acetone, furan derivatives, acetic and lactic acids, or 1,2?propanedio. Our group recently illustrated how acetol could even be used to produce 2-methylpiperazine via reductive cycloamination[1].
Therefore, continuous catalytic processes to produce acetol are ripe for substantial improvements resulting in better acetol productivities and an increase in the yield of other chemicals obtained from it, being usually Cu-based materials the preferred choice. In that line, an appealing support for CuO to be assessed is ZrO2, whose different polymorphs, i.e., tetragonal and monoclinic, are known to have distinct acid-base properties [2,3].

### 2. Experimental

The materials were prepared by incipient wetness impregnation, using aqueous solutions of $Cu(NO_3)\cdot 2.5H_2O$ with adequate concentrations to achieve 5 wt.% Cu in the final solid, in the following supports: i) monoclinic ZrO2 from Chempur, ii) tetragonal ZrO2 from Chempur, and iii) a physical mixture of them (60 monoclinic : 40 tetragonal, in wt.%). The resulting catalysts were named CuO/m-ZrO2, CuO/t-ZrO2 and CuO/mxt-ZrO2, respectively. They were characterized by ICP, N2 adsorption, XRD, HR-TEM and temperature-programmed techniques (NH3,CO2-TPD, and H2-TPR). Additionally, in-situ FTIR and XPS studies were carried out impregnating CuO/m-ZrO2 with glycerol. Catalytic tests were performed in a fixed-bed reactor by feeding a liquid mixture of glycerol and MeOH (50:50 in weight), at 240 ºC for at least 8 h.

### 3. Results

The characterization data in Table 1 show similar results regarding the Cu loading (between 5.7 and 5.9 wt.%) of CuO/ZrO2 materials, while the tetragonal zirconia based sample offers a slightly higher surface area, also exposing the higher acid site density compared to their analogous materials.

Table 1. Main textural and physicochemical properties of different CuO/ZrO2 materials.

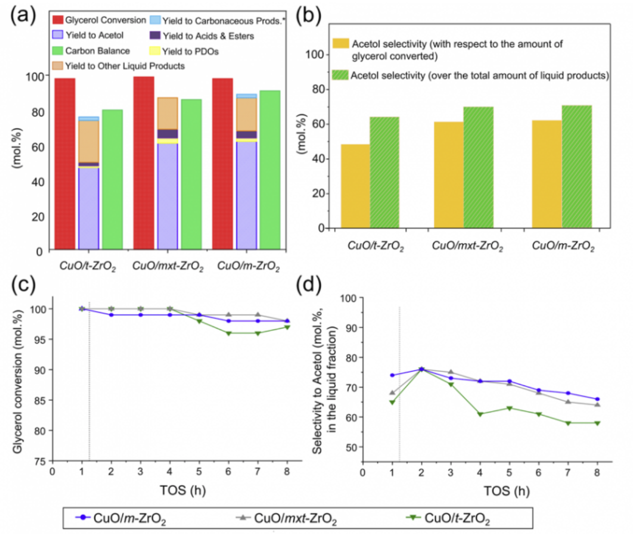
| Catalyst | Cu(wt.%) | Surf. area[BET](m2/g) | Nº acid sites(µmolNH3/g) | Acid site density(µmolNH3/m2) |
|---|---|---|---|---|
| CuO/t-ZrO2 | 5.7 | 123 | 311 | 2.53 |
| CuO/mxt-ZrO2 | 5.9 | 105 | 177 | 1.69 |
| CuO/m-ZrO2 | 5.7 | 75 | 115 | 1.53 |

Figure 1 shows that the yield to liquid products, yield to acetol, and the acetol selectivity decrease for CuO/t-ZrO2. In good agreement with what has been previously reported for other materials, it seems that, although acid centers are needed for first glycerol adsorption, an excess of them starts to impair selectivity[4]. Thus, the CuO/m-ZrO2 catalyst offers a good compromise between glycerol conversion and acetol selectivity (yield ?60%) and little variation in the selectivity to acetol during reaction (?75%). On the catalyst operation at the molecular level, the combination of in-situ XPS and FTIR studies (Fig. 2) allowed us to conclude that Cu2+ evolve towards Cu1+, believed to be the active Cu species in this reaction[5]. In addition, glycerol reacts over these Cu1+ species forming an intermediate containing a C=O double bond.

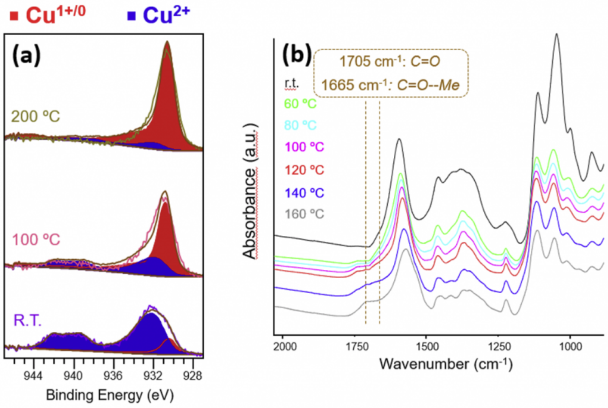
## 4. Conclusion

Glycerol can be transformed to acetol with high yields (?60%) by using an environmentally friendly CuO/ZrO2 catalyst and high glycerol concentrations in the feed. The acidity has been found a key factor determining acetol selectivity. Moreover, the role of active species could be unraveled through in-situ characterization studies, finding Cu1+ to be the actual Cu species in the working catalyst and the reaction proceeding through a C=O double bond intermediate. Further information will be presented in the congress evaluating reusability, explaining the distinct reaction pathways by working at low conversions, and the of water.

## FIGURES



Cumulative (a) glycerol conversion, yield to liquids and carbon balance, (b) acetol selectivities, (c) glycerol conversion *vs* time on stream, and (d) acetol selectivity vs time on stream for the dehydration of glycerol over different CuO supported on $ZrO_2$ catalysts. Reaction conditions: feed = methanol/glycerol (50/50 in weight), flow = 2 mL/h, with 0.5 g catalyst, at 240 ºC, TOS = 8 h. a Calculations for CuO/mxt-$ZrO_2$ based only on the liquid fraction. *Other liquid products: acetoin, acetoin methyl ether, 3-methoxybutanol, hydroxyacetone dimethyl acetal, solketal and other unidentified by-products.



(a) Cu2$p_{3/2}$ XPS region studied at different temperatures and (b) FTIR spectra acquired at different temperature steps under static vacuum conditions for CuO/*m*-$ZrO_2$ impregnated with a mixture MeOH/Glycerol (a: 50:50, b: 90:10 wt.%).

### FIGURE 1

Figure 1

Catalytic results

### FIGURE 2

Figure 2

In situ characterization results

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## KEYWORDS

Glycerol | Selective dehydration | Copper catalyst | Cu species

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## BIBLIOGRAPHY

[1] J. Mazarío, Z. Raad, P. Concepción, C. Cerdá-Moreno, M.E. Domine, Catal. Sci. Technol., 10 (2020), 8049-8063.
[2] W. Hertl, Langmuir, 5 (1989) 96-100.
[3] K.-H. Jacob, E. Knözinger, S. Benier, J. Mater. Chem., 3 (1993) 651-657.
[4] T.P. Braga, N. Essayem, A. Valentini, RSC Adv., 5 (2015), 93394-93402.
[5] J. Mazarío, P. Concepción, M. Ventura, M.E. Domine, J. Catal., 385 (2020), 160-175.