

Influence of the Calcination Atmosphere on Copper-Aluminum Catalysts for the Selective Dehydration of Glycerol

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Abstract

The present work studied the influence of two atmospheres (air or N₂) in the calcination step at 500 °C on catalysts based on copper and aluminum with a 28 mol% of Cu. The catalysts were characterized and tested in gas-phase reactions for the selective dehydration of glycerol into acetol.

Introduction

The rising biodiesel production has led to an abundance of glycerol as a by-product, driving down its cost [1]. This biomass-derived molecule possesses immense potential, capturing the attention of industry and researchers who are eager to explore its valorization. Among all the possible products, acetol is used for aldol condensation with furans as an intermediate step to obtain aviation biofuel through the Sugar to Jet Fuels (STJ) route. Since acetol is typically derived from fossil fuels, producing it from glycerol would make the process renewable and carbon-free. Acetol can be produced by dehydrating glycerol on weak to moderate acidic sites, with transition metals like Ni or Cu on acidic supports such as Al₂O₃ or Fe₂O₃. Ni facilitates the breaking of C-C bonds, promoting the formation of by-products. In contrast, Cu is active in the breaking of C-O bonds with higher selectivity towards acetol, reducing the production of by-products [2]. In this context, the current study aims to investigate the influence of the calcination atmosphere (air or N₂) in the properties and catalytic activity of CuAl catalysts in the production of acetol from glycerol.

Experimental

Catalysts were synthesized by the coprecipitation method by dissolving copper and aluminum nitrates in mili-Q water at 40 °C under constant stirring. The molar ratio of copper was defined as Cu/(Cu+Al) at 28 mol%. An ammonium hydroxide solution was added to the mixture until reaching a pH of 6. After that, the hydrated catalytic precursor was dried overnight at 105 °C and separated into two equal

portions. The calcination was done in a furnace at 500 °C for 3 hours over two different atmospheres: air and N₂. The resulting catalysts were tested in a small-scale laboratory plant using a fixed bed quartz reactor containing 0.3 g of catalyst on which 1.6 g of inert sand was placed to preheat the feed. Before each experiment, the catalysts were activated at 300 °C for 1 hour with a 100 cm³ STP min⁻¹ H₂ flow. Once the catalyst was activated, the temperature was set at 250 °C, and a 10 wt.% aqueous glycerol solution was introduced in the reactor at 0.1 mL min⁻¹ for 2 hours. The reactor outlet stream was conducted to a condenser where the liquids were collected, and the gas products were analyzed online with a gas chromatograph. The analysis of liquid products was carried out offline with a GC-FID. The fresh and spent catalysts were subjected to different characterization techniques (XRD, N₂ adsorption-desorption, and H₂-TPR) to study their physicochemical properties.

Results and discussion

The textural properties of the fresh and spent catalysts are shown in Table 1. The results revealed fresh mesoporous catalysts with a similar BET surface area (S_{BET}) of around 225 m² g⁻¹. The N₂ atmosphere generated higher pore volumes (V_{P}) with lower pore diameters (d_{P}). After the reactions, the catalyst calcined in the air atmosphere maintained the textural properties better, conserving the S_{BET} and V_{P} unaltered and slightly decreasing the d_{P} . However, the N₂ atmosphere catalyst after reaction produced significant decreases in S_{BET} of 27% and in V_{P} , conversely, the d_{P} increased concerning the fresh catalyst.

The H₂-TPR results (Figure 1) exposed that the N₂ atmosphere decreased the activation temperature from 280 °C in the air atmosphere to 250 °C. The presence of two peaks in the reduction profile indicates the possible reduction in two stages due to the presence of two types of particles: highly dispersed and bulk [3].

Table 1. Textural properties of fresh and spent (in brackets) CuAl catalysts by N₂ adsorption-desorption analysis.

	Air atmosphere	N ₂ atmosphere
S _{BET} (m ² g ⁻¹)	224.5 (219.5)	226.7 (165.8)
V _P (cm ³ g ⁻¹)	0.40 (0.36)	0.48 (0.34)
d _p (nm)	6.73 (5.79)	6.26 (6.76)
Crystallite CuO or Cu size (nm)	13.4 (14.7)	14.5 (18.5)

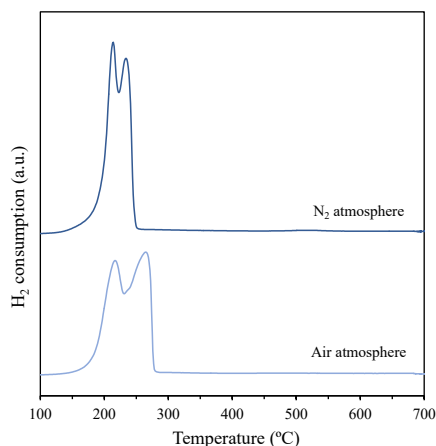


Figure 1. H₂-TPR of fresh catalysts calcined at 500 °C

Concerning the metallic phases the XRD analysis (Figure 2) revealed the presence of CuO (JCPDS 01-072-0629) in the fresh catalysts and metallic copper (Cu) (JCPDS 01-085-1326) in the spent catalysts. The presence of Cu indicated that the reduction step was successful and that after reactions the active metal did not re-oxidize demonstrating good stability. The crystallite sizes of CuO and Cu were smaller in the fresh and spent catalyst calcined in the air atmosphere, demonstrating higher copper dispersion.

Regarding the catalytic activity, glycerol primarily generated liquid products, including acetol, 1,2-propanediol, and ethylene glycol. The reaction conditions minimized gas production, resulting in a stream containing only H₂ and CO₂ due to the high activity of Cu in the WGS reaction. The glycerol conversion was 97 % in both cases, with acetol yields of 71.0 % and 60.5 % for the catalysts calcined in air and N₂ atmosphere, respectively.

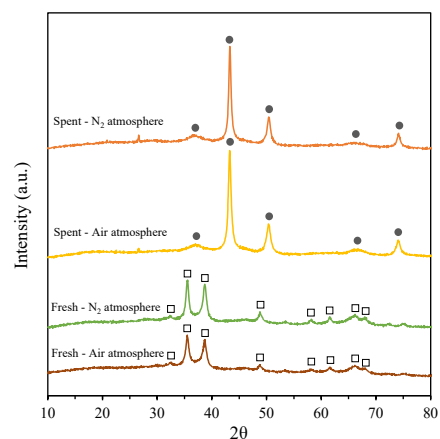


Figure 2. XRD patterns of fresh and spent catalysts. (●) Cu; (□) CuO.

Conclusions

The calcination atmosphere influenced the physicochemical and textural properties of the CuAl catalysts. Calcination in a N₂ atmosphere lowered the reduction temperature of copper and increased the crystallite size of metallic copper in the spent catalyst, reducing its dispersion. The catalyst calcined in an air atmosphere exhibited better textural properties after reactions and showed a slight improvement in catalytic activity for acetol production, achieving an acetol yield of 63.0 %.

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References

- [1]. LETE, A., RASO, R., GARCÍA, L., RUÍZ, J. and ARAUZO, J. Synthesis of ketones from glycerol and 1,2-propanediol using copper and nickel catalysts: Unraveling the impact of reaction phase and active metal. *Fuel*. 2024, 371(A), 132001.
- [2]. CHECA, M., NOGALES-DELGADO, S., MONTES, V., and ENCINAR, J. Recent advances in glycerol catalytic valorization: a review. *Catalysts*. 2020, 10.
- [3]. MANE, R., YAMAGUCHI, A., MALAWADKAR, A., SHIRAI, M. and RODE, C. Active sites in modified copper catalysts for selective liquid phase dehydration of aqueous glycerol to acetol. *RSC Advances*. 2013, 3, 16499-16508.