

## Selective hydrogenolysis of glycerol to 1,2-propanediol on the catalysts containing Cu-Ag phase deposited on oxide supports ( $\text{Al}_2\text{O}_3$ , $\text{TiO}_2$ )

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### Introduction

In the recent years the worldwide production and consumption of biodiesel has rapidly increased. The biodiesel production process co-generates glycerol at a rate of 1 mole for every 3 moles of alkyl-fatty esters synthesized, approximately 10 wt% of the total product. Due to decreasing fossil fuels resources and increasing air pollution, the effective utilization of renewable resources such as glycerol by conversion into useful chemicals is essential. For that reason, intensive research aiming to convert glycerol to value-added chemicals has started.

Among the value-added chemicals, propylene glycol (PG) is a major commodity that is widely used as biodegradable functional fluids such as de-icing reagents, antifreezes and coolants, and as precursors in the syntheses of unsaturated polyesters resins.

The hydrogenolysis of glycerol to 1,2-propanediol, is considered as two-step reaction: dehydration of glycerol to acetol and hydrogenation of intermediate to glycol. Hydrogenolysis of glycerol is a catalytic conversion that allows obtaining PG in a way, which is environmentally and economically attractive compared to its production from petroleum derivatives. [1]

### Materials and Methods

Two series of catalysts with copper active phase modified by silver, with different Cu and Ag content were synthesized.  $\text{TiO}_2$  and acidic  $\text{Al}_2\text{O}_3$  were used as supports. The catalysts were obtained by wet impregnation method, using water solutions of copper and silver nitrates, followed by drying (120°C, 10 h) and calcination in the air flow (350°C, 5 h).

The phase composition of the obtained catalysts was determined by X-ray powder diffraction (XRD). Thermo-programmed reduction ( $\text{H}_2$ -TPR) was conducted in order to examine the reducibility of the catalysts. The specific surface area and the pore distribution were measured by  $\text{N}_2$  adsorption with a Quantachrome Autosorb-1 device. Catalytic tests were carried out in a batch reactor (100 ml) with mechanical stirring in 200°C under 15 atm of  $\text{H}_2$ , 400 rpm, for 5h. The catalytic reactions were preceded by reduction of the catalysts at 150°C, under 2 atm of  $\text{H}_2$ , 100 rpm for 2 h. The obtained catalysts were tested in such conditions and the most active catalyst was chosen. In the next step, optimization of reduction and reaction parameters was conducted in order to find the most efficient conditions. Additionally, influence of an addition of heteropolyacid and hydroxide was checked.

### Results and Discussion

Phase composition of the catalysts was determined by X-ray diffraction method. It is found that copper is present as CuO, irrespective of the type of the support. On  $\text{Al}_2\text{O}_3$ , silver is present as metallic particles and as  $\text{Ag}_2\text{O}$ . In the case of catalysts supported on  $\text{TiO}_2$ , there is no metallic form of silver.  $\text{H}_2$ TPR profiles are in line with XRD analysis and the

catalysts reduction temperature depends on their chemical composition. For catalysts containing copper, two CuO forms are present: CuO weakly bonded to the support, which is reducible at lower temperatures (200°C-260°C); and copper strongly bound to the support, which is reducible at higher temperatures (300°C-500°C). The increase of Ag content results in the lowering of the surface area.

Figure 1 shows comparison of impact of: modification of the reduction (200°C, 5 atm  $\text{H}_2$ ) and reaction (24 h, 40 atm  $\text{H}_2$ ) conditions, influence of the addition of heteropolyacid, or sodium hydroxide on catalytic activity. Longer reaction time, higher  $\text{H}_2$  pressure during both reduction and reaction, higher temperature of reduction and NaOH addition resulted in increased conversion and selectivity toward 1,2-propanediol. The addition of heteropolyacid resulted in increased conversion but decrease in selectivity to 1,2-propanediol.

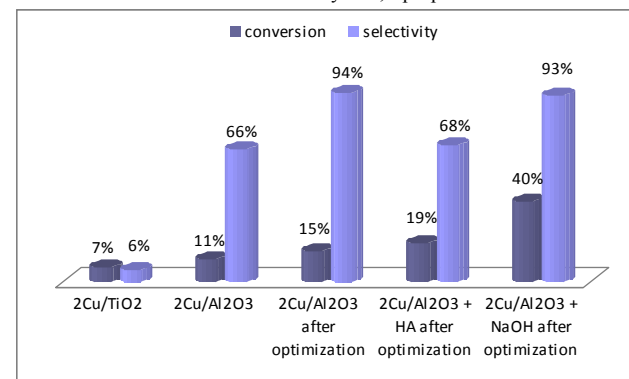


Figure 1. Influence of reduction and reaction conditions optimization, addition of heteropolyacid and hydroxide

### Significance

Based on physicochemical characterization of the obtained catalysts it is found that addition of Ag modify CuO properties and influences the surface area of the samples. Catalysts containing  $\text{Al}_2\text{O}_3$  are much more active and selective toward 1,2-propanediol in examined reaction than catalysts containing  $\text{TiO}_2$ . Reaction time and  $\text{H}_2$  pressure are the crucial parameters for hydrogenolysis reaction. Optimization of reaction conditions allowed increasing conversion of glycerol and selectivity toward 1,2-propanediol. Catalytic test with addition of sodium hydroxide performed the highest efficiency.

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### References

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