

# Hydrogenolysis of Glycerol in Gas Phase on Cu-Cr Mixed Oxide Catalyst Doped with Ni

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*Hydrogenolysis of glycerol was conducted on catalyst of the type mixed oxide of Cu-Cr doped with NiO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The prepared catalyst was analyzed by XRD, IR and TPR. Catalytic tests were carried out on a laboratory plant in continuous flow system on a reactor equipped with heating mantle, at molar ratio of glycerol / hydrogen of 1/300, glycerol volume hourly space velocities 1000 s<sup>-1</sup>, temperatures 200-220°C and pressures 3-5 bar. The main reaction products identified were propylene glycol and hydroxyacetone. Glycerol conversion increases with temperature and pressure on ranges of parameters studied. Selectivity to propylene glycol increases with increasing of temperature and pressure and the selectivity to hydroxyacetone decreases with increasing of temperature and pressure on the variation range of the parameters studied.*

*Keywords: catalyst, hydrogenolysis, glycerol, propylene glycol, selectivity*

Glycerol is the most important byproduct obtained in the manufacture of biodiesel, alternative biofuel, obtained by using renewable resources respectively by chemical conversion of vegetable and animal fats. Glycerol is obtained in a proportion of 10% compared to biodiesel and thus constitute an important reason that it would not be considered a waste but rather a by-product with real possibilities of superior recovery.

The literature provides various alternatives for converting glycerol into important commercially products. One of the possibilities to exploit the glycerol is the conversion to propylene glycol through catalytic hydrogenation.

The catalytic hydrogenation of glycerol is usually achieved by heterogeneous catalysis both in the liquid phase as well as in the gas phase, stationary regime. If reaction is performed in liquid phase, in order to obtain a good contact between the molecules of glycerol and hydrogen, the gas is continuously bubbled into the liquid. High values of hydrogen pressure favors its solubilization and implicitly the conversion increase of hydrogenated product [1-3]. The necessity of pressure increase (50-60 bar) and the exothermic character of the hydrogenation reaction of glycerol can cause overheating of the catalyst and implicitly his deactivation.

Catalytic hydrogenation in the gas phase of the glycerol can be achieved in conditions much milder of pressure (5-6 bar) on the same catalysts types in continuously flux, with higher selectivity and yields [4,5]. The process unfolds in adiabatic regime although the reaction is exothermic. Low concentration of glycerol in the reaction mixture leads to avoid the risk of overheating and damaging of the catalyst.

Regarding the mechanism for obtaining propylene glycol by hydrogenation of glycerol it was proposed several variants. Montassier and collaborators [6] consider that in the first step occurs dehydrogenation of glycerol to form glyceraldehyde. Then, by nucleophilic attack of water, glyceraldehyde undergoes a dehydration reaction and the unsaturated aldehyde obtained is subsequently hydrogenated to propylene glycol. According the mechanism proposed by Chiu [7] the glycerol molecules

is dehydrated and it form hydroxyacetone (acetol) which subsequently reacting with hydrogen, leading the formation of propylene glycol.

The catalysts used in this process are of great diversity: transition metals deposited on an inorganic oxide [1-3], simple or mixed oxides of transition metals [6-10], Raney nickel [11], Ni-Re /charcoal [12], Ni/Al<sub>2</sub>O<sub>3</sub> [13], Ni, Ru [14], as well as the platinum metals [15-22].

In this paper we intend to achieve propylene glycol by hydrogenolysis in the gas phase of glycerol using a mixed oxide catalyst type of Cu- Cr doped with Ni and deposited on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.

## Experimental part

The catalyst of the type mixed oxide of Cu-Cr was prepared from a precursor complex. This precursor complex has been obtained by co-precipitation of a mixture of nitrates of Cu and Cr in the ratio of 4: 1 in the presence of tartaric acid (Ta). The precipitate was extracted in a solution containing 10% ethanol and an aqueous solution of ammonium hydroxide in the ratio of 1: 1. The precipitate was dried in vacuum at 90°C for 4 h to stabilize the complex formed [Cr Cu<sub>4</sub> Ta<sub>6</sub>] × 5H<sub>2</sub>O. Then the precipitate was solubilized in water and it was added Ni nitrate at a metal ratio of Cu-Cr: Ni of 10: 1. The solution obtained was impregnated on a support of alumina shaped in the form of balls with 2-3mm diameter. Calcination temperature was established by studying the decomposition of complexes combination [Cr Cu<sub>4</sub> Ta<sub>6</sub>] × 5H<sub>2</sub>O and the stabilization of crystalline phases by TGA -DSC determinations on TA Instruments SDT Q600. Thus the catalyst was dried in vacuum at 110°C for 4 h and calcined under an inert atmosphere at 850°C for 6 h.

The prepared catalyst was analyzed by XRD on TUR-M62 with HZG3 diffractometer, by IR on Specord 75 IR Spectrofotometer and TPR was determined on CHEMBET 3000 apparatus. Catalytic tests were carried out on a laboratory plant in continuous flow system equipped with a reactor with heating mantle. The parameters were: ratio of glycerol / H<sub>2</sub> 1/300, glycerol volume hourly space velocities 1000 s<sup>-1</sup>, temperatures between 200-220°C and

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pressure of 3-5 bar. The reaction products were analyzed by Mass Spectrometer -Gas Chromatograph GC-MS (7820GC / DS Agilent 5975C MSD).

## Results and discussions

From TGA curve study (fig.1) is observed mass losses in three steps. The first step is in the range of 50-150 °C and occurs with the mass decreasing by 1% because of hydration water loss by the complex  $[\text{Cr Cu}_4 \text{Ta}_6] 5\text{H}_2\text{O}$ . Between 150 - 750°C it is observed a decrease of approximately 2% of the sample mass, but with a much lower velocity which is due to thermal decomposition of the complex. Between 750 - 850°C it is observed a mass loss with high speed; the decrease is up to 2.5% from the initial mass of the sample. This mass loss is due to phase transformations that take place.

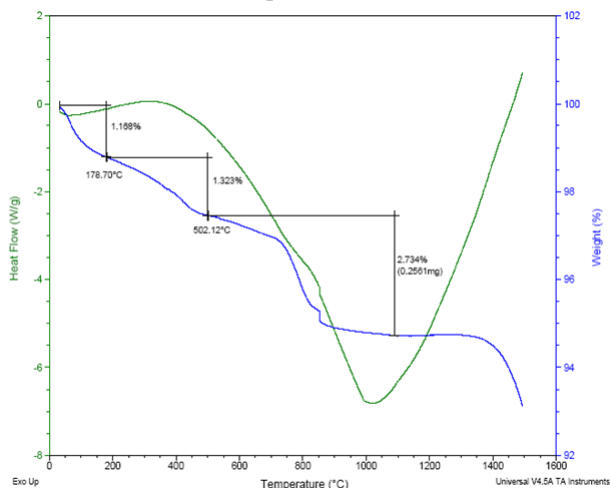


Fig.1. The spectra TGA / DSC for catalyst Cu-Cr doped with NiO

In DSC graph can notice a slight decrease of the heat flow in 50 -150°C range, corresponding to water evaporation. Between 400 - 1500°C is viewed an endothermic effect extended which includes phenomena of evaporation, sintering and melting, whose value is 22 kcal / mol.

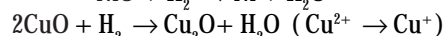
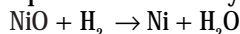
In X-ray diffraction spectra of undoped catalyst, calcined at 850°C are highlighted spectral lines characteristic of a  $\text{CuCr}_2\text{O}_4 + \text{Cu}_2\text{Cr}_2\text{O}_4 + \text{CuO}$  mixture in the ratio 2: 4: 1 (fig. 2a). By introducing NiO like dopant are observed changes in terms of intensity and of their width (fig.2.b). This might be due either to overlap of the initial signals with those of Ni oxide, or to penetration of Ni atoms in the networks spinel of Cu and Cr producing deformations thereof by changing the length of atomic bonds.

IR spectra (fig. 3a, b) it is observed that doping the catalyst with NiO does not influence the width bands but small increases in transmission occurs in wavelengths areas of 36-32, 16-12 and 8-4  $\text{cm}^{-1}$ .

From spectrum obtained by thermal programmed reduction (fig. 4) it can be seen that the reduction process begins at 200°C, between 300-500°C this process achieve maximum hydrogen consumption and it becomes insignificant after 700°C.

Hydrogen consumption can be attributed to:

- reduction of NiO and CuO oxide in the presence of hydrogen (oxide species detected by XRD):



- reduction of oxygen released from the network of catalyst and moved on thereof surface, thereby creating oxygen vacancies;

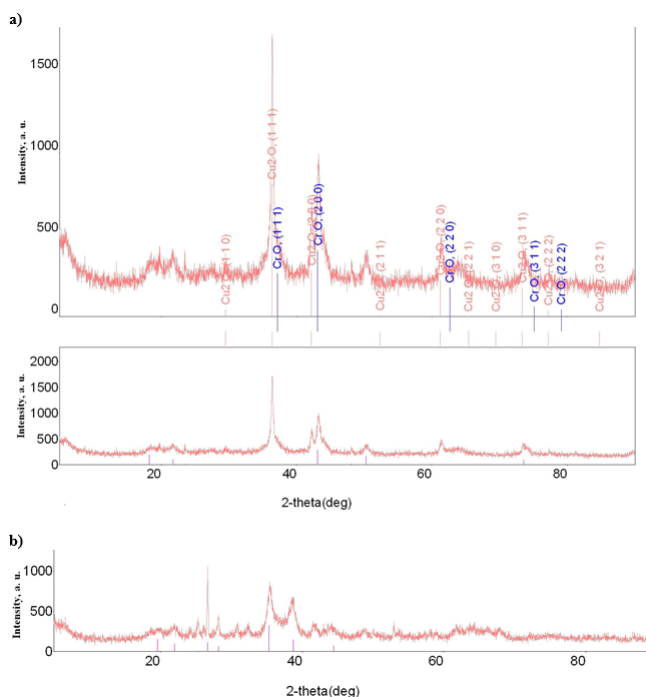


Fig.2. XRD spectra: a) mixed oxide catalyst type Cu-Cr undoped with NiO; b) mixed oxide catalyst type Cu-Cr doped with NiO

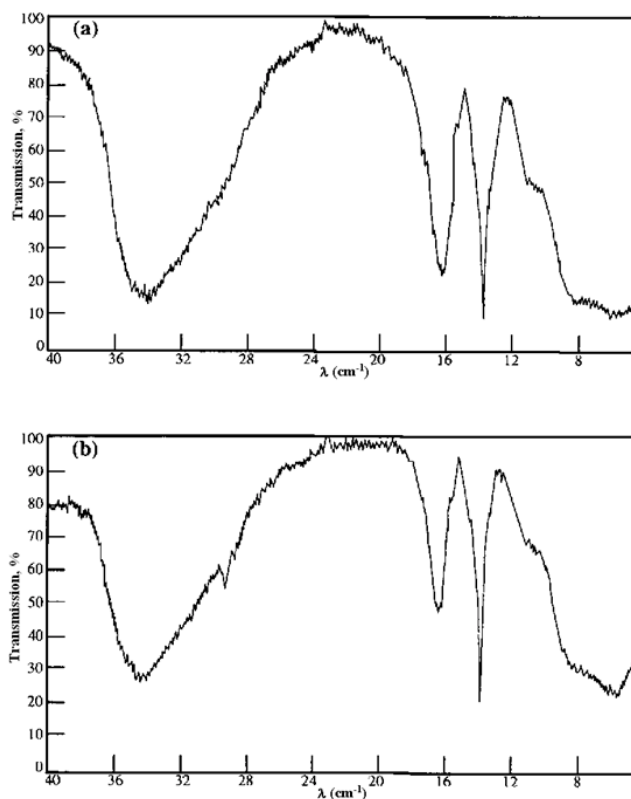


Fig.3. IR spectra for: a) mixed oxide catalyst type Cu-Cr undoped with NiO; b) mixed oxide catalyst type Cu-Cr doped with NiO

- physical adsorption (by weak links) of hydrogen on the catalyst surface that subsequently, at higher temperatures is desorbes;

- activated hydrogen adsorption on metal species.

The main reaction products identified were propylene glycol and hydroxyacetone (acetol). The results of catalytic tests are shown in figures 5-10. In figures 5 and 6 is seen an increase in glycerol conversion with temperature and respectively pressure. Thus, the slope of glycerol conversion increases with the temperature on 200-220°C range. The conversion of glycerol increases with the pressure after an almost constant slope on 3 - 5 atm range.

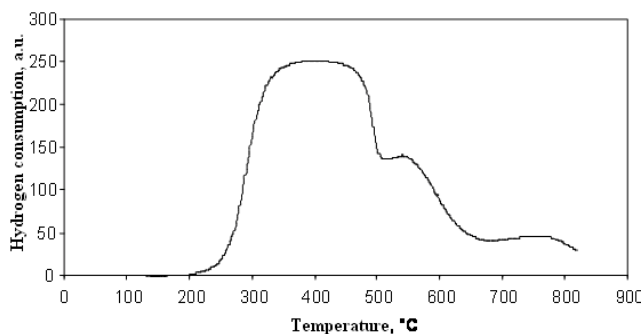


Fig. 4. Thermal programmed reduction spectrum for mixed oxide catalyst type Cu-Cr doped with NiO

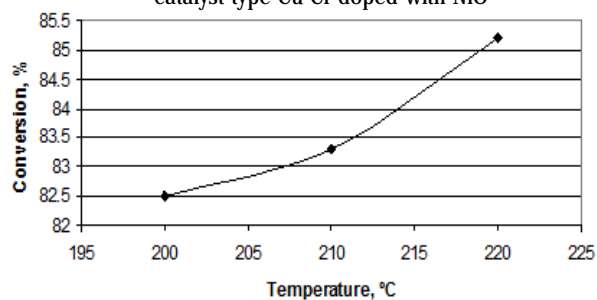


Fig.5. Variation of glycerol conversion with temperature at 3atm

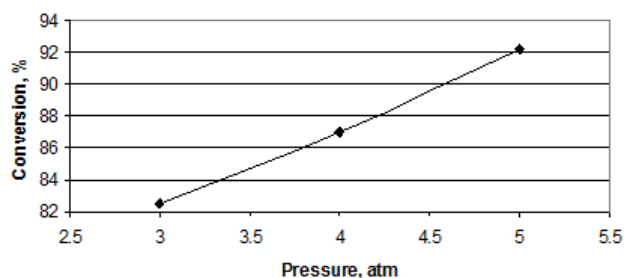


Fig.6. Variation of glycerol conversion with pressure at 200°C

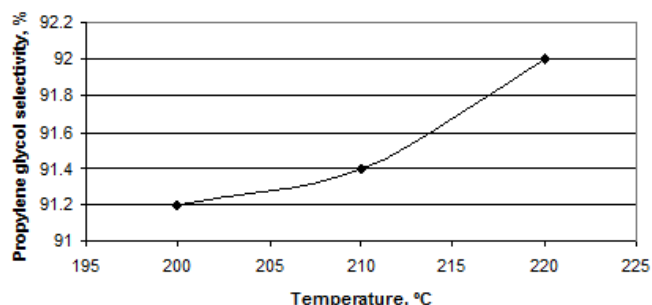


Fig.7. Variation of propylene glycol selectivity with temperature at 3atm

The variation of propylene glycol selectivity with temperature and respectively pressure are shown in figures 7 and 8. Selectivity to propylene glycol increases with temperature on the temperature range 200-220°C, after a slope that increases with temperature. Selectivity to

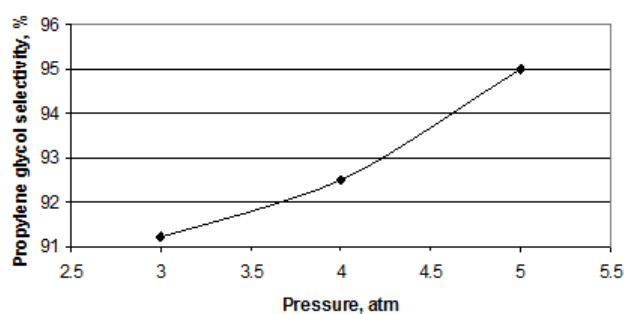


Fig.8. Variation of propylene glycol selectivity with pressure at 200°C

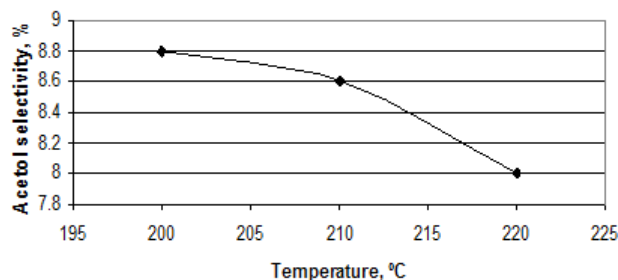


Fig.9. Variation of acetol selectivity with temperature at 3atm

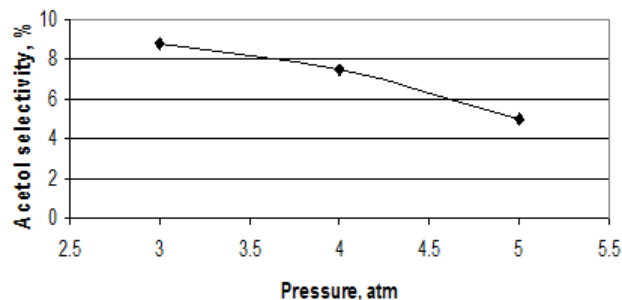
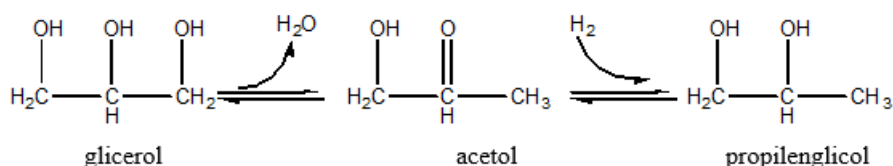


Fig.10. Variation of acetol selectivity with pressure at 200°C

propylene glycol increases with pressure after a slope that grows on the pressure range 3-5 atm.

The variation of hydroxyacetone selectivity with temperature and respectively pressure are shown in figures 9 and 10. Selectivity to acetol decreases with temperature on the temperature range 200-220°C, after a slope that increases with temperature. Selectivity to acetol also decreases with pressure, after a slope that increases with pressure on the pressure range of 3-5 atm.

The presence of acetol as a byproduct of the reaction, leads to the hypothesis that the hydrogenolysis of glycerol in gas-solid system on catalyst selected, takes place pursuant to the mechanism proposed by Chiu et al according to which, by dehydration of the glycerol molecule is formed in a first step hydroxyacetone, which subsequently is reacted with hydrogen resulting in the formation of the propylene glycol and water [7]. This mechanism is supported by a number of studies that deal with getting propanediols in biocatalytic ways [22]:



## Conclusions

Catalyst type mixed oxide of Cu-Cr doped with NiO, on alumina support has been shown to be active in the hydrogenolysis of glycerol in the gas phase. The main reaction products identified were propylene glycol and

hydroxyacetone. Glycerol conversion increases with temperature and pressure on ranges of parameters studied. Selectivity to propylene glycol increases with increasing of temperature and pressure and the selectivity to hydroxyacetone decreases with increasing of temperature

and pressure on the variation range of the parameters studied.

*Dedicated to the 150<sup>th</sup> anniversary of the Romanian Academy*

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