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NEW CATALYSTS USED IN THE HYDROGENOLYSIS REACTION OF GLYCEROL

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Abstract

The catalytic hydrogenolysis of glycerol, a by-product of the biodiesel manufacturing process was studied on copper chromite catalysts with different chemical composition. The obtaining of propylene glycol was studied under mild reaction conditions (180-240ºC temperature range, 8 hours reaction time and moderate pressures). These important parameters have significant effects on the glycerol conversion and that is way the actual study was concerned to the obtaining of a superior selectivity to propylene glycol by optimizing the reaction conditions. The water content in the raw material seems to damage the process development, coming out the requirement to use small amounts of water in order to achieve an increased reactor productivity.

Keywords: biodiesel, copper chromite catalysts, glycerol, propylene glycol

1. Introduction

In recent decades a particular attention has been paid to the processing of the regenerative raw materials due to the alarming consumption rate of the global resources of conventional fuels by the continuously growing and developing of mankind. The biodiesel was found to be one of the most promising alternative to the conventional fuels due to its advantageous features, namely: it is less polluting, is bio-degradable and can be obtained from a great variety of plant raw materials (Agarwal, 2007; Ahmad et al., 2011; Atabani et al., 2013; Demirbas, 2009; Lapuerta et al., 2008; No, 2011; Singh and Singh, 2010). Apart from this, according to the European Union directives the member countries are obliged to substitute gradually the traditional transport fuel with the bio-fuel so that the biodiesel fuel will attain 20% in the overall consumption till 2020 (Official Journal of the European Union, 2013).

The biodiesel manufacturing process leads to glycerol as valuable by-product. Taking into account the biodiesel industry, large amounts of obtained glycerol cannot be regarded as a residue and its processing is nowadays a subject of a great concern (Shinmi et al., 2010).

Furthermore, the glycerol processing as a by-product is estimated to bring a significant contribution to lower the price of biodiesel. On the other hand, the synthetic glycerol with a higher purity will lead to its increase price due to the purification difficulties. Various glycerol processing ways are found in the studies reported in literature (Abhari, 2009; Bagheri et al., 2015; Cardona et al., 2007; Castelló et al., 2014; Cheng et al., 2013; Corma et al., 2007; Díaz-Álvarez et al., 2014; Nanda et al., 2014; Schultz et al., 2014). Thus, a quite interesting alternative of processing the crude glycerol stands out, namely the hydrogenolysis to propylene glycol as a particularly important market product. Since the price of crude glycerol resulting

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from the biodiesel manufacturing is much lower than the synthetic glycerol price, its processing by conversion to propylene glycol is expected to be a quite economically and efficient process.

Due to the high efficiency of hydro-dehydrogenation of C-O bonds and poor activity for C-C bonds cleavage the most interesting seems to be copper base catalyst, such as copper-chromite. Chromium promotes dehydrogenation and confers a geometric promoting effect and also affects the metal-support interactions (Kim et al., 2010; Wolosiak et al., 2012). The hydrogenolysis is a catalytic process and the cooper chromite is the most applied catalyst mentioned in literature (Adkins et al., 1950; Lazier and Arnold, 1943). Although the cooper chromite ($CuCr_2O_4$) is less active than the nickel catalysts and requires a much longer hydrogenation time even at high reaction temperatures it was noticed that the presence of an alkaline-earth metal oxide in the composition promotes its stability (Manda, 2009). The oxide catalysts are known to contain often mixed oxides along with simple oxides. Consequently, during the catalytic reactions, after preliminary treatments and depending on the reaction conditions one or several oxides of the catalyst can be reduced. A particular attention has been paid in recent years to the $CuO-CuCr_2O_4$ catalytic system in the catalytic hydrogenolysis of glycerol and in this respect the reduction of the cooper chromite in the presence of the CuO or Cr_2O_3 phases with a wide composition domains was approached (Casale and Gomez, 1994; Casale and Gubitosa, 1994a, 1994b, 1996, 1997). Detailed studies on reduction by hydrogen were also carried out on various catalytic oxide systems such as: $NiO-Cr_2O_3$, CuO-ZnO and $CuO-Al_2O_3$, $CuO-Fe_2O_3$, $CuO-Cr_2O_3$. These catalytic systems show a major interest in terms of their application also as hydrogenation-dehydrogenation, oxidation or cracking catalysts (Sasca et al., 1995).

These considerations justify the opportunity of the present study devoted to the testing of two commercial copper chromite catalysts with different chemical composition in the hydrogenolysis reaction of glycerol.

2. Experimental

The glycerol 99.8%wt. was supplied by Oleo Chemicals Germany and the hydrogen of 99.98% purity was manufactured by the Linde Gaz Company, Romania. Two copper chromite catalysts were supplied by ChimComplex Borzesti (CC1) and Merck (CC2), respectively. The characteristics and chemical compositions are given in Table 1.

The catalysts were submitted to grinding and screening operations to obtain particle size of 0.2-0.4 mm, then were submitted to some physico-chemical analyses. The X-ray diffraction data (DRX) were performed with a Brucker diffractometer using the CuKα radiation. The adsorption-desorption isotherms of nitrogen were recorded at 77 K, on a Micromeritics ASAP 2010 equipment. Prior to the adsorption

measurements the samples were degased at 323 K for 12 hours. The specific area was evaluated by the BET method. The measuring equipment used to study the thermal behaviour of the catalysts is a complex thermo gravimetric analyzer TA Instruments SDT Q 600. It allows simultaneous TGA (thermo gravimetric analysis) and DSC (differential scanning calorimetric) and monitories the heat flow and variation of sample mass when the temperature varies according to method.

Table 1. Characteristics and chemical composition of the catalysts

Catalyst	*CC1*	*CC2*
Form	extruded	powder
Particle size (Å)	189.7	188.0
CuO(%)	39.83	43.89
Cr_2O_3 (%)	32.22	42.09
BaO (%)	1.84	10.36
Fe_2O_3 (%)	0.37	0.03
Na_2O (%)	0.14	0.01

The analysis method consisted in a linear increase of temperature with 10°C/min up to 1500°C, the sample being in this time under argon flow of 100 ml/min (inert atmosphere). The TPR determinations were performed using a multifunction device type CHEMBET manufactured by Quantachrome. The catalysts were firstly activated with hydrogen at 10 bar by heating at 280°C for 4 h and then tested in the hydrogenolysis process of glycerol in liquid phase. The tests were carried out in a steel autoclave type reactor of 200 mL equipped with stirrer and electric heating. The temperature was controlled using a Pt-100 sensor located in the autoclave and connected to a thermosetting system. The desired d amount of glycerol was introduced in the reactor containing the activated catalysts under continuous stirring. Repeated purgings were then performed 5 times with hydrogen for air removing. The hydrogenolysis reactions were conducted in the following conditions: catalyst/glycerol ratio wt.=5%, reaction temperature of 180-240˚C, pressure in the range of 10-20 bar, and a reaction time of 8 hours.

After the reaction time has ended the autoclave was brought to the atmospheric pressure and cooled at the room temperature. The catalyst was then separated by centrifugation and the reaction mass was submitted to physico-chemical analyses. The composition of the liquid phase was determined by gas-liquid chromatography on a Hewlett-Packard 6890 Plus apparatus equipped with a flame ionization detector (FID).

Quantitative analysis of liquid phase products, namely propylene glycol, acetol and unreacted glycerol was carried out by the method of internal standard. With every experiment the total conversion of glycerol, (ζ_G) selectivity to propylene glycol (Φ_{PG}) and propylene glycol yield (η_{PG}) were calculated. Every data set for the calculated performance criteria represents the arithmetic average of no less than 3 experimental determinations.

The formulas that were used for yield, conversion and selectivity are mentioned. Propylene glycol selectivity is defined as the ratio of the number of moles of the propylene glycol product formation to that of the glycerol consumed in the reaction, taking into account the stoichiometric coefficient. The conversion of glycerol is defined as the ratio of number of moles of glycerol consumed in the reaction to the total moles of glycerol initially present. The yield of propylene glycol is defined as the ratio of the number of moles of propylene glycol produced to the theoretical number of moles of the propylene glycol.

3. Results and discussion

The structural properties of the samples were firstly estimated by X-ray diffraction measurements (XRD). In Fig. 1 the diffraction X-ray patterns for both cooper chromite catalysts are given. The diffraction peak at $43.3°$, $50.5°$, $74.1°$ indicate the presence of metallic copper in both catalysts. The delafossite $CuCrO_2$ peaks are $31.4°$, $36.4°$, $40.8°$, $55.8°$, $62.4°$, $65.4°$, $65.3°$, $71.5°$.

A smooth basic line is noticed together with a sharp shape of the peaks which indicates a good crystalline structure. For a comparison with the modified structure of the solid, the copper chromite from Borzesti was selected and submitted to the diffraction analyses of initial and used form (Fig.1(a), (b)- b). Some differences can be observed in the diffraction X-ray patterns. The basic lines of the two samples seem to be the same, but the position and number of peaks are not accordingly. Other differences consist in different intensities of the peaks with same indexes and in disappearance of other such as those of very low intensity. Besides, the number of phases in the diffraction X-ray pattern of the used catalyst is much higher. Therefore, the presence or absence of certain peaks could be an indicative that the sample under study may contain also other crystalline phases or has a rather distorted structure. These features could be attributed to the reduction of one or more oxides in the catalyst during the catalytic reaction depending on the reaction conditions or due to preliminary treatments. Based on the literature data on the diffraction analysis of the initial and reduced samples, the reduction process can be described by the Eqs. (1-2) (Sasca et al., 1995):
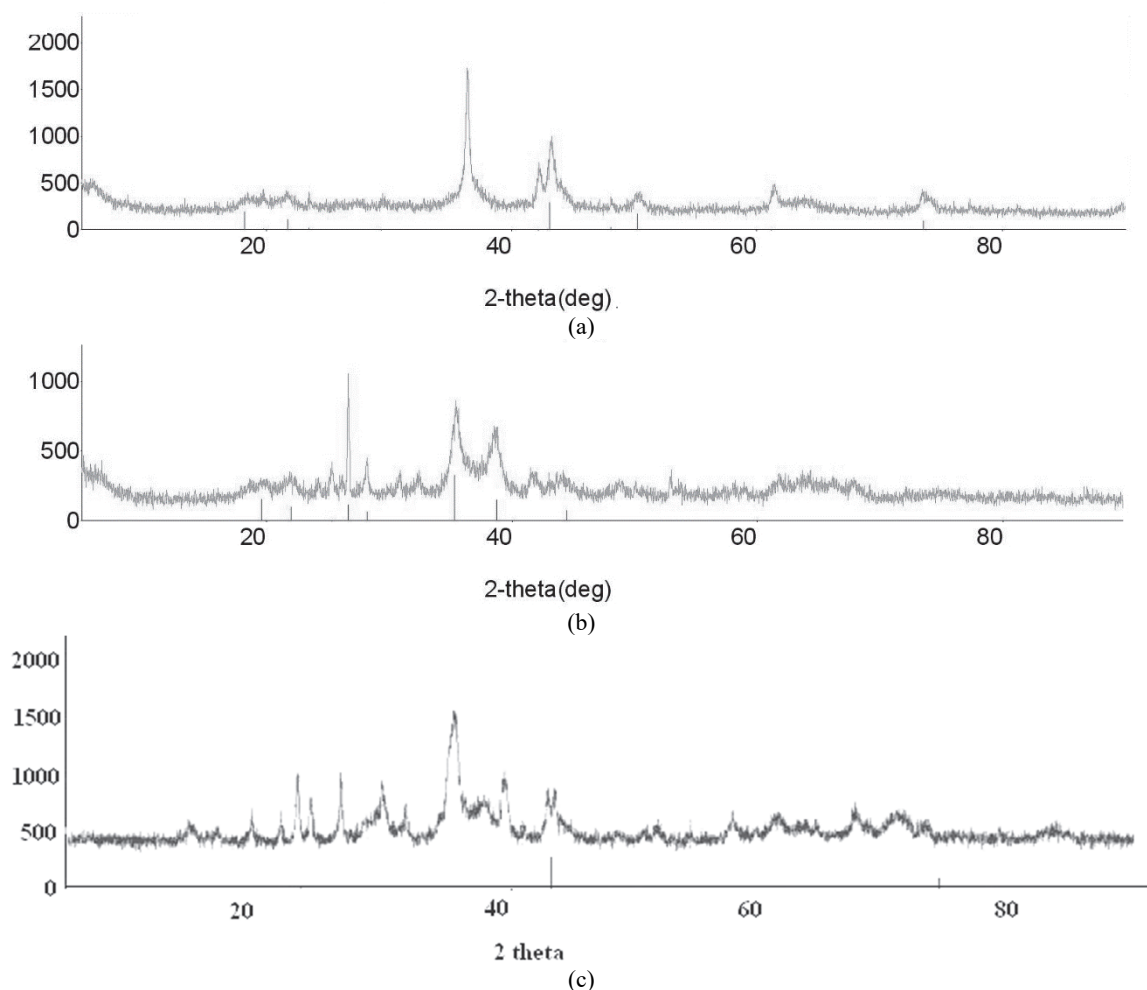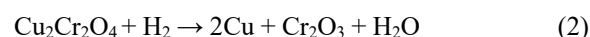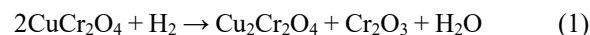
$$2CuCr_2O_4 + H_2 \rightarrow Cu_2Cr_2O_4 + Cr_2O_3 + H_2O \qquad (1)$$

$$Cu_2Cr_2O_4 + H_2 \rightarrow 2Cu + Cr_2O_3 + H_2O \qquad (2)$$

(a)

(b)

(c)

Fig. 1. X-ray patterns of copper chromite: (a) CC1-initial form; (b) CC1-used form; (c) CC2-initial form
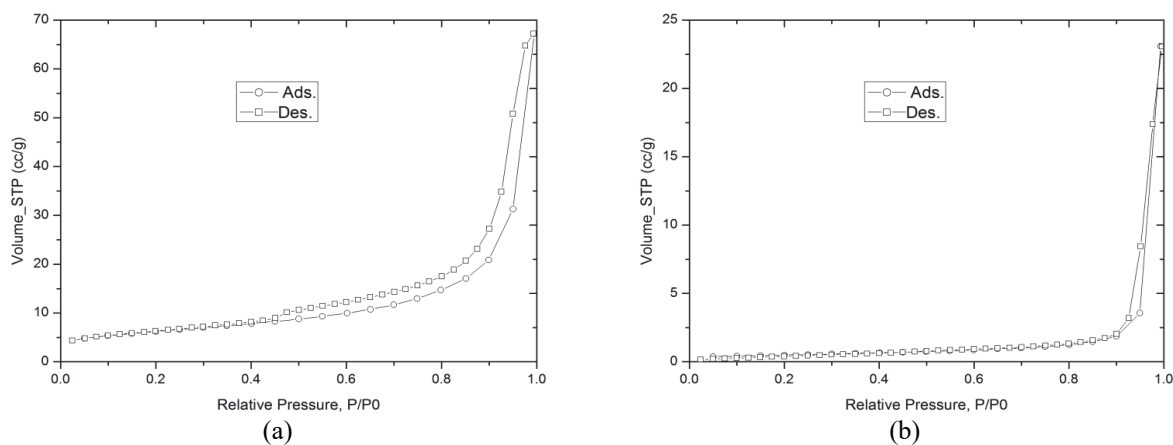
Fig. 2. Adsorption-desorption isotherm of nitrogen of the copper chromite catalysts: a) CC1; b) CC2

The mechanism of the $CuCr_2O_4$ reduction involves a stage of Cu^{2+} reduction leading to formation of crystalline $Cu_2Cr_2O_4$. This reduction stage is developed on the contact surface of the crystalline grains or contact planes. Since the oxide catalysts often contain both mixed and simple oxides, the glycerol hydrogenolysis to propylene glycol could be assumed to lead to new oxide phases such as the Cr oxides (e.g. Cr_5O_{12}).

The nitrogen adsorption-desorption isotherms were taking into account (Fig. 2). In Fig. 2, a low amount of accessible micro-pores is noticed (for the $p/p_0 < 0.05$ ratio the adsorbed nitrogen amount is quite low). Consequently, the obtained isotherm is an intermediate form between the isotherms of the II and III types, caused by the non-uniform pores. Thus, the first part is of the IInd type and the last of the IIIrd type. The weak adsorber-adsorbate interactions would explain the absence of the abrupt slopes probably to appear on certain portion (of the IVth type, for instance). Similar characteristics of the isotherm shape were noticed on both investigated copper chromite catalysts. The specific area estimated by the BET method was of $53m^2g^{-1}$ for the copper chromite Merck (CC2) catalyst and of 26 m^2g^{-1} for the copper catalyst coming from Borzesti (CC1). The physical and chemical treatments are expected to result in structural changes or mass losses as was confirmed by the thermal analysis (Fig. 3).

The thermo-gravimetric curve (TG) reveals four temperature ranges between 50-1500°C where the mass losses are brought about at different rates with an overall mass decrease less than 10% till 1500°C, similar characteristics being observed on both copper chromite catalysts.. The first mass loss noticed at temperatures till 152°C of about 2.7% of the sample total mass comes from the loss of the adsorbed water. The water evaporation is also noticed on the DSC curve as a wide peak within the same temperature range. The second interval between 150-500°C would be attributable to the loss of bound water and to some small molecular compounds resulting by splitting of certain covalent bonds. The losses within this range are less than 2% of the entire sample mass. On the DSC curve of the sample the peak noticed around the

temperature of 300°C could be attributed to some phase transformations. According to literature the catalyst sintering occurs at a temperature value, attaining 40% of the melting temperature meaning 325°C for the copper chromite (Huges, 1984). That is why the working temperatures with the copper chromite catalysts should be rather low (below 300°C) to avoid the catalyst sintering.

The third temperature interval ranges between 500-850°C and the mass losses attaining 4% of the sample mass proceed at a higher rate. Apart from this a wide peak is noticed between 500-1500°C attributable to the melting endothermic process (the heat absorption exceeding 17 Kcal/mol) while the peak at 1063°C would be indicative of a solid phase arising in the melt. Above 1400°C the mass loss of the fourth stage begins. The variation in the basic line of the DSC curve could be attributed to modification of the thermal conductivity of the material during thermal treatment.

The TPR Analysis makes evident the oxide species reduced to metal by hydrogen. The thermoreduction spectra are plotted as hydrogen consumption (on the ordinate) versus temperature (on the abscissa). The hydrogen consumption does not strictly refers to the hydrogen involved in the reduction reactions because other phenomena could also happen during the experimental procedure, namely:

- The reduced metal is able to adsorb hydrogen from the gas mixture at certain temperatures being subsequently desorbed.
- Sometimes the hydrogen diffuses through the catalyst surface when the so-called "spillover" phenomenon happens on the support surface. The spillover hydrogen can be subsequently desorbed at higher temperatures.
- Some support materials are reducible and can contribute to the formation of the TPR profiles.

For this reason the consumed hydrogen, expressed as arbitrary units can be calculated as follows (Eq. 3):

$$H_{2\ consumed} = H_{2\ consumed\ to\ the\ metal\ reduction} + H_{2\ consumed\ to\ the\ support\ reduction} + H_{2\ adsorbed} + H_{2\ spilover} \quad (3)$$
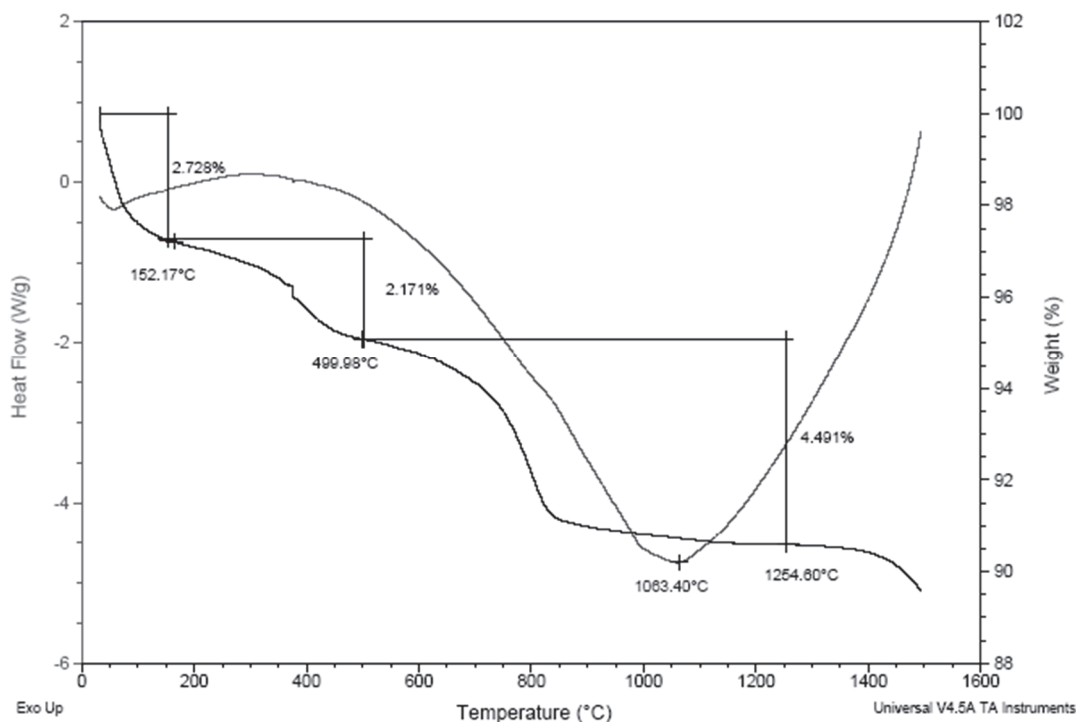
Fig. 3. TG and DSC curves for the copper chromite sample from Borzesti (CC1)
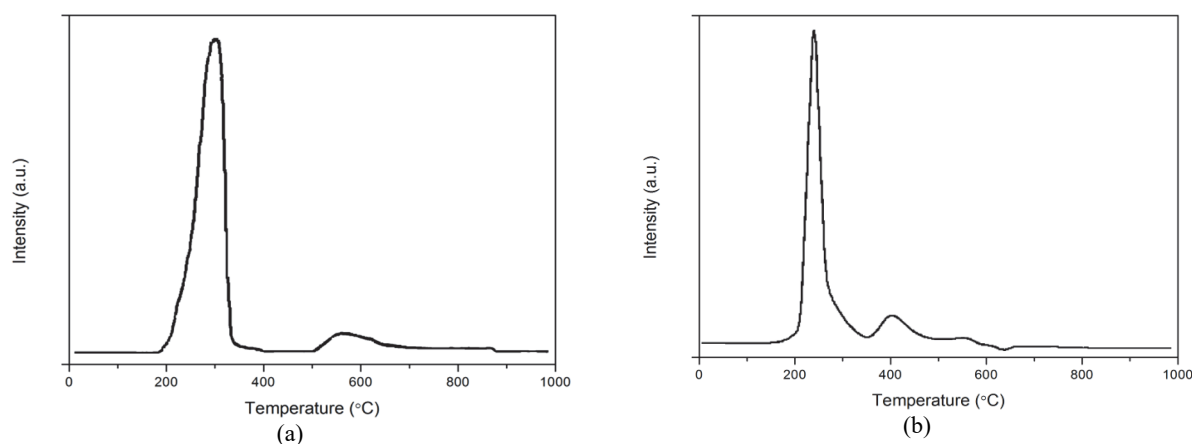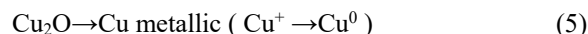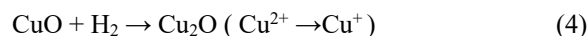

Fig. 4. Thermo programmed reduction profiles of the copper chromite catalysts: (a) CC1; (b) CC2

The profiles of the thermo-programmed reduction of copper chromite catalysts are presented in Fig. 4. It can be seen in Fig. 4(a) that the hydrogen consumption starts at 200°C and is over at 330°C with a maximum at 300°C attributable to:

- reduction of the oxygen, reached on the catalyst surface after releasing from the copper chromite network which would result in occurrence of vacancies that could be occupied in their turn by oxygen coming from the chromite bulk.
- physical adsorption of hydrogen on the chromite surface (by weak bonds) and its subsequent desorption at higher temperatures.
- since a phase of copper oxide was identified by X-ray diffraction, the following reduction in the presence of hydrogen would develop (Eqs. 4-5):

$$CuO + H_2 \rightarrow Cu_2O \ (\ Cu^{2+} \rightarrow Cu^+) \tag{4}$$

$$Cu_2O \rightarrow Cu \ metallic \ (\ Cu^+ \rightarrow Cu^0 \ ) \tag{5}$$

Furthermore, the Cr_2O_3 separated from chromite by reduction remains as amorphous state since the crystalline phase of chromic oxide does not appear in the initial sample. As for the weakly intense peak at 580°C it could be attributed to a hydrogen adsorption on the chromite surface.

As regards TPR profile of CC2 catalyst (Fig. 4b), the first reduction peak in the low temperature range (245°C) is due to the stepwise reduction of surface Cu^{2+} and Cu^+ species in different local coordination environment to Cu^0, whereas those in the high temperature region (400°C) with a shoulder at 550°C were due to the reduction of bulk $CuCr_2O_4$.

Catalytic tests were made in order to establish total conversion of glycerol (ζ_G), selectivity to propylene glycol (Φ_{PG}) and propylene glycol yield (η_{PG}). The influence of reaction temperature was studied in 180-240°C range, under 20 bar reaction pressure, 8 hours reaction time and catalyst/glycerol ratio wt.=5%. The obtained experimental results over copper chromite catalysts are given in Figs. 5 (a), (b).

As made evident by the data from Fig. 5 (a) over copper chromite from Borzesti (CC1) the conversion increases steadily from 28.83 to 89.47% over the entire investigated temperature range. Although the increase in the reaction temperature is apparently accompanied by the increasing glycerol conversion the calculated selectivity values over 200°C begin to decrease constantly simultaneously with the increase in the concentration of the by-products.

The experimental data obtained with the Merck copper chromite catalyst (CC2) are given in Fig. 5 (b) (Marinoiu et al., 2013). The data from Fig. 5 (b) reveal that the glycerol conversion in the presence of Merck copper chromite (CC2) increases significantly with increasing of temperature in 180-240°C domain. A quite low conversion (<2%, too slowly for being practically useful) was obtained when glycerol was heated at temperatures below 180°C. At higher reaction temperatures, the conversion increased constantly within the 180-220°C range from 8.00 to 70.62%. However, over 220°C the conversion decreased slowly and constantly. It is an unexpected result, which requires supplementary investigation studies. A possible explanation could be connected with the deactivation of catalyst at higher temperatures. Bienholz et al. (2010) reported an decrease of conversion with temperature increasing, caused by catalyst deactivation, due to heavy by-products, such as polyglycerols, polyglycols.The experimental data indicate an increase of selectivity with increasing of temperature (74% at 200°C) followed by a decrease. The reaction yield also increases within the 180-220°C range till 38.75% and

decreases after the attaining of this value. Therefore, the temperature's increase till 200°C has a positive influence on the conversion, yield and selectivity, then the mentioned performance criteria decrease excepting being the conversion that increases further in case of the copper chromite from Borzesti (CC1). The decrease of selectivity is caused especially by the increasing of balance for secondary reactions (Σx=18-24%).

According to the experimental results it has been found that the optimum reaction temperature depends on the initial pressure of the hydrogen, due to its low solubility in aqueous solutions. For this reason, an optimum temperature for each reaction pressure can be determined, maximizing the yield of PG result. Certainly, the optimum operating pressures will be chosen taking into account two scenarios: high yields coupled with high costs of industrial equipment working at high pressure versus lower yields under mild reaction.

Experimental results presented in Fig. 6 revealed a different behaviour of the two copper chromite catalysts. The total conversion on CC2 catalyst increases with the increase of pressure up to 20 bar, after which remains quasi-constant. A drop in the conversion was evidenced on CC1 catalyst at continuous increase of the operating pressure. This behavior which is inconsistent with the literature data (Dasari et al., 2005) is probably due to the significant differences between the two tested catalysts in connection to the chemical composition and especially in respect to the content of Ba (1.84 % wt. in CC1, 10.36 wt.% respectively for CC2, expressed as BaO) and the molar ratio Cu: Cr (1.182 for CC1, respectively 0.996 for CC2).

For both catalysts, the selectivity to propylene increases continuously with increasing of operating pressure, and the results are accordingly to literature data. With the operating pressure increasing, the selectivity increased up to 83%, which is interpreted as a result of a greater accessibility of the catalyst active sites to hydrogen.

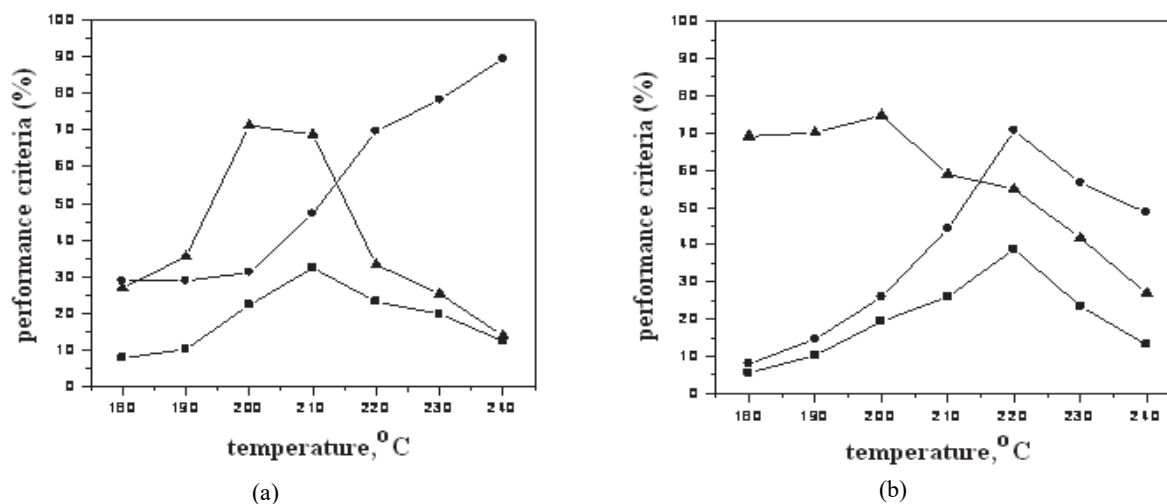| (a) | (b) |

Fig. 5. Variation of the PG yield (■), glycerol conversion(●) and PG selectivity (▲) with reaction temperature for glycerol hydrogenolysis in the presence of the CC1 (a) and CC2 (b) catalyst
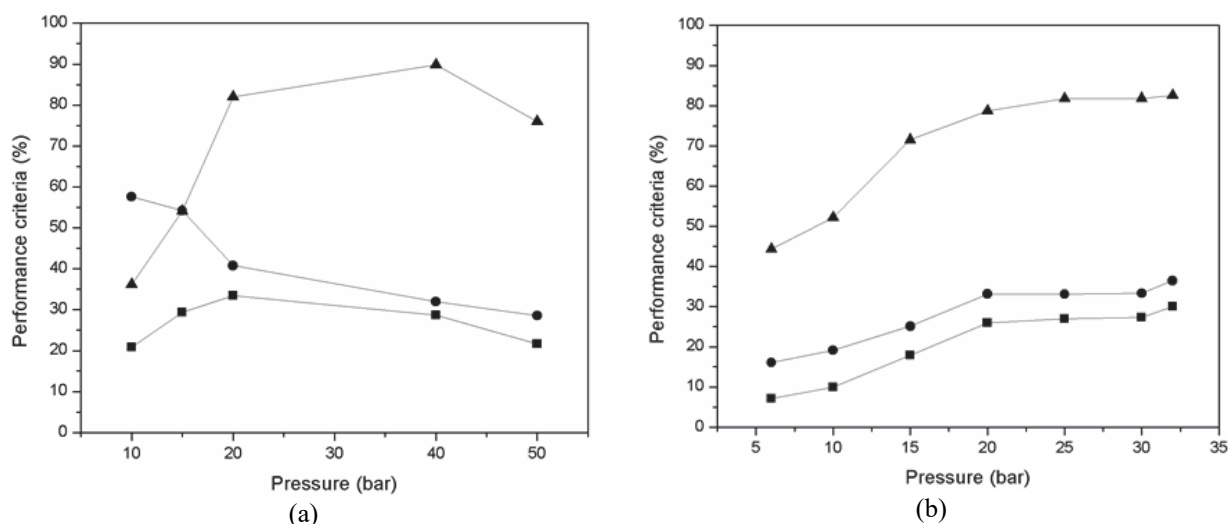
(a)

(b)

Fig. 6. Variation of PG yield (■), glycerol conversion (●) and PG selectivity (▲) with pressure in glycerol hydrogenolysis process over the CC1 catalyst (a) and CC2 catalyst (b)

The results also show that, under the same operating conditions, the CC2 catalyst is more selective than CC1 catalyst, this difference for selectivity is even greater as the pressure is higher. This significant difference for selectivity could be related to the presence of a respectable amount (about 18% wt.) of an alumino-silicate (molar ratio $SiO_2:Al_2O_3 = 7$), added as a binder.

Considering these aspects, it is not surprising that the yield of propylene glycol for CC1 catalyst increases by around 33% over the investigated range of 10 to 20 bars then begins to decrease. For CC2 catalyst the yield is increasing continuously with increasing the operating pressure of approx. 7.1% at 6 bar up to 30.02 % at 32 bar, the increase being more pronounced and almost linear in the range 6-20 bar, after which it becomes almost constantly.

In view of the entire experimental results the CC2 catalyst could be selected on the basis of the discussed performance criteria, as appropriate to achieve the hydrogenolysis of glycerol to propylene glycol. Since around 20 bars, depending on the variation of pressure for a complete conversion of glycerol, appears a plateau, this value can be considered to be an optimum for carrying out the reaction, and the use of pressures over 20-25 bar, is no justified from the economic point of view.

The water is not only a solvent but also a product from glycerol hydrogenolysis process, so the effect of its content on the glycerol total conversion, selectivity to propylene glycol and yield of propylene glycol was further studied. The experiments were carried out at the temperature of 200°C, pressure of 20-22 bar, reaction time 8 h and catalyst/glycerol ratio wt.=5% in the reaction mixture. The obtained experimental data are given in Table 2. The data from the Table 2 suggest that the water from the reaction mixture has a negative effect and could promotes the phenomenon of thermal sintering. The copper chromite used for too long time in hydrogenolysis process could be deactivated. The increase in the energy cost caused by the water heating was found to

be avoided by using a raw material as concentrated as possible. Moreover, the water content must be as low as possible for obtaining a high reactor productivity and efficient performance criteria since the glycerol hydrogenolysis develops with formation of water as a by-product as shown by the experimental results in Table 2. This statement is supported by the literature studies that confirm the above conclusion and even recommend the water removal as far as it is formed (Dasari et al., 2005).

Table 2. Effect of water content from the raw material on the performance criteria on the glycerol hydrogenolysis process

No.	Glycerol, %	Performance criteria		
		$\eta_{PG}(\%)$	$\zeta_G(\%)$	$\Phi_{PG}(\%)$
1	99.80	19.36	25.90	74.73
2	89.90	15.38	37.52	40.98
3	79.86	5.82	38.95	14.95

4. Conclusions

In the present paper the optimization of some reaction conditions for the glycerol hydrogenolysis to propylene glycol in the presence of two commercial copper chromite catalysts was studied under mild reaction conditions (180-240°C temperature range, 8 hours reaction time and moderate pressures). The conversion increased up 89.47% over the entire investigated temperature range. However, the temperatures over 200°C affect significantly the selectivity to propylene glycol.

Under the studied technological parameters, the hydrogen pressure increasing in the range caused a significant improvement in the selectivity to propylene glycol up to 83%. The CC2 catalyst could be selected on the basis of the discussed performance criteria, as appropriate to achieve the hydrogenolysis of glycerol to propylene glycol. Since around 20 bar appears a plateau, this value can be considered to be an optimum for carrying out the reaction, and the use of pressures over 20-25 bar, is no justified from the economic point of view. In order to increase the

hydrogenolysis reactor productivity the water must be used in as low as possible amounts since it results also as a by-product.

References

Abhari R., (2009), Flexible glycerol conversion process. USA Patent, No. *20090054701-A1*.

Adkins H., Burgoyne E.E., Schneider H.J., (1950), The copper-chromium oxide catalyst for hydrogenation, *Journal American Chemistry Society*, **72**, 2626-2629.

Ahmad A.L., Yasin N.H., Derek C.J.C., Lim J.K., (2011), Microalgae as a sustainable energy source for biodiesel production: A review, *Renewable and Sustainable Energy Reviews*, **15**, 584-593.

Agarwal A.K., (2007), Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines, *Progress in Energy and Combustion Science*, **33**, 233-271.

Atabani A.E., Silitonga A.S., Ong H.C., Mahlia T.M.I., Masjuki H.H., Badruddin I.A., Fayaz H., (2013), Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production, *Renewable and Sustainable Energy Reviews*, **18**, 211-245.

Bagheri S., Julkapli N.M., Yehye W.A., (2015), Catalytic conversion of biodiesel derived raw glycerol to value added products, *Renewable and Sustainable Energy Reviews*, **41**, 113-127.

Bienholz A., Schwab F., Claus P., (2010), Hydrogenolysis of glycerol over a highly active CuO/ZnO catalyst prepared by an oxalate gel method: influence of solvent and reaction temperature on catalyst deactivation, *Green Chemistry*, **12**, 290-295.

Cardona C., Posada J., Montoya M., (2007), *Use of Glycerol from Biodiesel Production: Conversion to Added Value Products*, Proc. of European Congress of Chemical Engineering (ECCE-6), Copenhagen, 13-17.

Casale B., Gomez A.M., (1994), To form propanediol and lactic acid, sulfided ruthenium catalyst, by-product glycerol. USA Patent, No. *5276181 A*.

Casale B., Gubitosa G., (1994a), Hydrogenation catalyst, and a method for its preparation and use, in particular for hydrogenation and/or hydrogenolysis of carbohydrates and polyhydric alcohols, USA Patent, No. *5326912 A*.

Casale B., Gubitosa G., (1994b), Method for producing lower polyhydric alcohols by hydrogenolysis of higher polyhydric alcohols, USA Patent, No. *5354914 A*.

Casale B., Gubitosa G., (1996), Hydrogenation to reduce compounds of ruthenium and palladium or platinum or rhodium deposited on activated carbon in suspension, then depositing copper, USA Patent, No. *5543379 A*.

Casale B., Gubitosa G., (1997), Method for producing lower polyhydric alcohols and a new ruthenium-based catalyst used in this method, USA Patent, No. *5600028 A*.

Castelló M.L., Dweck J., Aranda D.A.G., Pereira R.C.L., Guimarães Neto M.J.R., (2014), ZSM5 as a potential catalyst for glycerol pyrolysis, *Journal of Sustainable Bioenergy Systems*, **4**, 61-67.

Cheng L., Keaton L.L., Hong L., (2013), Microbial conversion of waste glycerol from biodiesel production into value-added products, *Energies*, **6**, 4739-4768.

Corma A., Iborra S., Velty A., (2007), Chemical routes for the transformation of biomass into chemicals, *Chemical Reviews*, **107**, 2411-2502.

Dasari M.A., Kiatsimkul P.P., Sutterlin W.R., Suppes G.J., (2005), Low-pressure hydrogenolysis of glycerol to propylene glycol, *Applied Catalysis A: General*, **281**, 225-231.

Demirbas A., (2009), Progress and recent trends in biodiesel fuels, *Energy Conversion and Management*, **50**, 14-34.

Díaz-Álvarez A.E., Francos J., Crochet P., Cadierno V., (2014), Recent advances in the use of glycerol as green solvent for synthetic organic chemistry, *Current Green Chemistry*, **1**, 51-65.

Huges R., (1984), *Deactivation of Catalysts*, Academic Press, San Diego, California.

Kim N.D., Oh S., Joo B.J., Jung S.K., Yi J., (2010), Effect of preparation method on structure and catalytic activity of Cr-promoted Cu catalyst in glycerol hydrogenolysis, *Korean Journal of Chemical Engineering*, **27**, 431-434.

Lapuerta M., Armas O., Rodrıguez-Fernandes J., (2008), Effect of biodiesel fuels on diesel engine emissions, *Progress in Energy and Combustion Science*, **34**, 198-223.

Lazier W.A., Arnold H.R., (1943), Copper chromite catalyst, *Organic Syntheses*, **2**, 142-145.

Marinoiu A., Cobzaru C., Carcadea E., Capris C., Tanislav V., Raceanu M., (2013), Hydrogenolysis of glycerol to propylene glycol using heterogeneous catalysts in basi aqueous solutions, *Reaction Kinetics, Mechanisms and Catalysis*, **109**, 63-73.

Manda T.A., (2009), *Studies on catalytic hydrogenation of glycerol*, PhD Thesis, "Gheorghe Asachi" Technical University of Iasi, Romania.

Nanda M.R., Yuan Z., Qin W., Ghaziaskar H.S., Poirier M.A., Xu C., (2014), Catalytic conversion of glycerol to oxygenated fuel additive in a continuous flow reactor: Process optimization, *Fuel*, **128**, 113-119.

No S.Y., (2011), Inedible vegetable oils and their derivatives for alternative diesel fuels in CI engines: A review, *Renewable and Sustainable Energy Reviews*, **15**, 131-149.

Official Journal of the European Union, (2003), On the promotion of the use of biofuels or other renewable fuels for transport, The Directive 2003/30/EC of the European Parliament and of the Council, On line at: ec.europa.eu/energy/res/.../doc/.../en_final. Htm.

Sasca V., Stefanescu M., Savii G., (1995), A kinetic-study upon the hydrogen reduction of CuO, $CuCr_2O_4$ in oxidic system of the Cr_2O_3 center dot CuO type II copper chromite reduction, *Chemistry Magazine*, **46**, 147-152.

Singh S.P., Singh D., (2010), Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review, *Renewable and Sustainable Energy Reviews*, **14**, 200-216.

Schultz E.L., de Souza D.T., Caramez Triches Damaso M., (2014), The glycerol biorefinery: a purpose for Brazilian biodiesel production, *Chemical and Biological Technologies in Agriculture*, **1**, 1-7.

Shinmi Y., Koso S., Kubota T., Nakagawa Y., Tomishige K., (2010), Modification of Rh/SiO_2 catalyst for the hydrogenolysis of glycerol in water, *Applied Catalysis B: Environmental*, **94**, 318-326.

Wolosiak-Hnat A., Milchert E., Lewandowski G., (2012), The influence of technological parameters on hydrogenolysis of glycerol in the presence of $CuCr_2O_4$ catalyst, *Journal of Advanced Oxidation Technologies*, **15**, 405-417.