Influence of reduction time of copper based catalysts: Cu/Al$_2$O$_3$ and CuCr$_2$O$_4$ on hydrogenolysis of glycerol

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High activity of copper based catalysts for C-O bond hydro-dehydrogenation and their poor activity for C-C bond cleavage1 have prompted an attempt to apply such catalysts in the hydrogenolysis of glycerol to 1,2- and 1,3-propanediol. In the present study the influence of hydrogen reduction time of the Cu/Al$_2$O$_3$ and CuCr$_2$O$_4$ copper catalysts on glycerol conversion and selectivity of transformation to propanediols and by-products was studied. At first a general comparison was made between the commercial catalysts and those prepared by the co-precipitation method. As better results were obtained in the presence of catalysts prepared by co-precipitation, they were selected for further detailed studies of the influence of reduction time. For both prepared catalysts Cu/Al$_2$O$_3$ and CuCr$_2$O$_4$ the reduction time of 8 h was optimal. In the presence of Cu/Al$_2$O$_3$ catalyst the conversion of glycerol was 59.0%, selectivity of transformation to 1,2-propanediol 77.4% and selectivity to 1,3-propanediol 1.9%. In the presence of CuCr$_2$O$_4$ the glycerol conversion was 30.3% and selectivity to 1,2-propanediol 67.3%.

Keywords: hydrogenolysis, 1,2-propanediol, 1,3-propanediol, glycerol.

INTRODUCTION

As a result of increased biodiesel production by transestrification of vegetable oils, large amounts of crude glycerol byproduct are produced. In 2010 global production of glycerol was approximately 21 000 Mt and it is estimated that before 2015 it will rise to about 32 000 Mt[2]. As for 9 kg of biodiesel about 1 kg of glycerol is produced[3], it is estimated that by 2015 approximately 3 200 Mt of waste glycerol will be formed. There is a large interest in developing processes that would enable conversion of glycerol to high value chemical compounds. One of the promising approaches is the reaction of hydrogenolysis of glycerol to 1,2- and 1,3-propanediol. Both diols have a wide range of applications. They are used as biodegradable functional fluids e.g. antifreeze and precursors for the synthesis of unsaturated polyester resins and pharmaceuticals[4]. The main uses of 1,2-propanediol are listed in Table 1[5].

1,3-propanediol is used for the production of poly(trimethylene terephthalate) known for its good resilience and dyeability6[−7]. 1,3-Propanediol can also be applied in the production of polyethers, polyurethanes[8], polyesters, plasticizers, paints, copolymers[9], laminates, resins, detergents and cosmetics[10].

Hydrogenolysis of glycerol proceeds by dehydration of glycerol to the intermediates: acetol and 3-hydroxypropanal and their subsequent hydrogenation to 1,2- and 1,3-propanediol respectively. The dehydration of glycerol is catalyzed by acid sites of a catalyst and the hydrogenation occurs on the metal sites[12]. The most probable products of dehydration of glycerol are 2-propene-1,2-diol and 1-propene-1,3-diol, because they are the compounds whose rearrangement leads to acetol and 3-hydroxypropionaldehyde[13] (Fig. 1).

In hydrogenolysis of glycerol, the by-products including ethylene glycol, ethanol, methanol, ethane and methane, are formed as a result of C-C bond cleavage in glycerol and propanediols molecules. By-products may also be formed in the hydrogenolysis of 1,2- and 1,3-propanediol (Fig. 2). In the dehydration of 1,3-propanediol propanal is formed; 1-propanol is a product of its subsequent hydrogenation. In the dehydration of 1,2-propanediol propanal or propanone may be formed whose hydrogenation leads to 1-propanol and 2-propanol, respectively. Propane and propene can be products of hydrogenation of 1- and 2-propanol[14].

Under certain reaction conditions, e.g. at high glycerol concentration, polymerization reactions may occur[3]. As a result of those reactions polypropylene glycols, polyethylene glycols and polyglycerols can be formed.

Many studies have been carried out to find catalysts

Table 1. Applications of 1,2-propanediol[5]

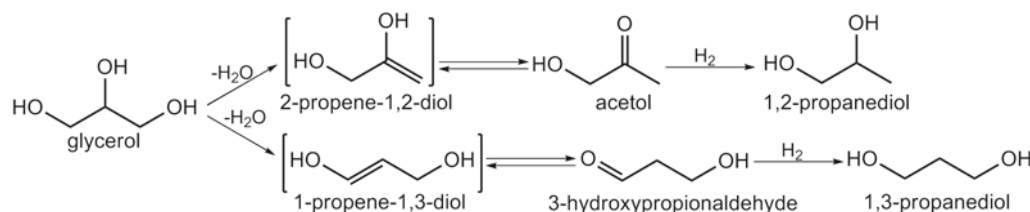| 1,2-propanediol (pharmaceutical grade)	1,2-propanediol (industrial)
Cosmetics and toiletries	Plastics and resins
Food industry	Aircraft deicers
Animal feed	Heat transfer fluids
Pharmaceuticals	Liquid detergents
	Paints and coatings

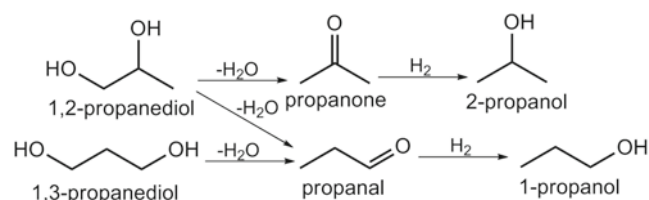**Figure 1.** Reaction routes to 1,2- and 1,3-propanediol in hydrogenolysis of glycerol[12−13]

Figure 2. Byproducts formed in hydrogenolysis of 1,2- and 1,3-propanediol[14]

ensuring high conversion of glycerol and selectivity of transformation to 1,2- and 1,3-propanediol in the hydrogenolysis of glycerol under relatively mild reaction conditions. Cu based catalysts are promising as they exhibit high efficiency for C-O bond hydro-dehydrogenation and poor activity for C-C bond cleavage. It is assumed that the Cu^0 particles are the active sites for hydrogenolysis of glycerol, and the Cu^+ particles help inhibit sintering of the active phase. Therefore, it is beneficial to reduce those catalyst before hydrogenolysis. As a result of the reduction of copper catalysts by hydrogen, copper crystallites become smaller and the dispersion of copper species is higher[1], which improves conversion of glycerol and selectivity of transformation to 1,2-propanediol. For CuO/SiO_2[1] catalyst reduced by hydrogen the conversion of glycerol increased from 52.7% to 73.4% and selectivity of transformation to 1,2-propanediol increased from 93.1% to 94.3%. For CuO/ZnO catalyst reduced by hydrogen, the conversion of glycerol increased from 21.1% to 22.5%, but the selectivity of transformation to 1,2-propanediol increased from 29.4 to 83.6%[11]. The activity of copper catalysts was highly influenced by the conditions under which the reduction of catalyst by hydrogen was carried out. Until now the effect of reduction temperature on hydrogenolysis of glycerol has been studied for commercial $CuCr_2O_4$[3] and Cu/Al_2O_3 prepared by the catalysts impregnation method[4]. For both catalysts the highest yield of 1,2-propanediol was obtained after reduction by hydrogen at 300°C. For $CuCr_2O_4$ catalyst the reduction time was 4 h, while for Cu/Al_2O_3 it was 3 h.

In the present study the effect of reduction time of a catalyst on hydrogenolysis of glycerol in the presence of these catalysts is presented. The hydrogenolysis process was evaluated by calculating the conversion of glycerol and the selectivity of transformation to 1,2- and 1,3-propanediol in relation to glycerol consumed. In addition, selectivities of transformation to liquid by-products: ethylene glycol, 2-propanol, 1-propanol, methanol, ethanol and by-products in the gas phase: 2-propanol, 1-propanol, methanol, ethanol, propane, ethane and methane were calculated. The $CuCr_2O_4$ and Cu/Al_2O_3 catalysts were prepared by the co-precipitation method.

EXPERIMENTAL

Reagents

The studies were performed using glycerol, 99 wt% from Chempur. The catalysts: $CuCr_2O_4$ (30% $CuCr_2O_4$, 70% CuO), 31% Cu/Al_2O_3 were purchased from Alfa Aesar GmbH & Co. KG. The catalysts: Cu/Al_2O_3 and $CuCr_2O_4$ were reduced by hydrogen at 300°C.

Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, analytically pure), chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$, analytically pure) and

aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, analytically pure), used in the preparation of Cu/Al_2O_3 and $CuCr_2O_4$ catalysts as well as potassium carbonate (K_2CO_3, analytically pure) and sodium hydroxide (NaOH, analytically pure) were purchased from POCh S.A.

Catalyst preparation

The Cu/Al_2O_3 catalyst was prepared by the modification of the coprecipitation method, described by Mane et al.[15]. 0.05 M aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were mixed under vigorous stirring. An aqueous solution of 0.02 M K_2CO_3 was then added to the solution obtained. The precipitate was aged overnight and filtered off. Subsequently, the precipitate was washed with deionized water, dried at 90°C for 8 h, calcined at 400°C for 4 h and reduced by hydrogen at 300°C.

The $CuCr_2O_4$ catalyst was prepared by our own method, based on the method described by Kim et al.[16]. 0.35 M aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ were mixed upon vigorous stirring. Then the aqueous solution of 0.5 M NaOH was added. The precipitate was aged overnight and filtered off. The precipitate obtained was washed with deionized water, dried at 90°C for 6 h, calcined at 300°C for 6 h and reduced by hydrogen at 300°C.

The SEM analyses and X-ray microanalyses were performed in order to examine the particle morphology.

Hydrogenolysis of glycerol

The hydrogenolysis of glycerol was carried out in a Berghoff autoclave with a capacity of 150 cm³. The autoclave made of stainless steel was equipped with a Teflon insert of 140 cm³ capacity and a magnetic stirrer. The reactor was charged with 20 cm³ of glycerol solution with a 80 wt% concentration and with the catalyst in the amount of 6 wt% in relation to glycerol. After the reactor was filled, its contents were purged with hydrogen. The reactor was filled five times with hydrogen up to a pressure of 5.0 MPa and each time the pressure was reduced to atmospheric value. The syntheses were carried out at the following parameters: temperature 200°C, pressure 3.0 MPa, 80 wt% glycerol aqueous solution, reaction time 24 h, stirring speed 100 rpm. After the reaction, the autoclave was cooled to the ambient temperature, and the amount of the gas phase was measured using a counter Elster-Amco. The samples for the analyses of the gas phase composition were collected in the gaseous pipettes. The catalyst was separated from the liquid phase by centrifugation and the mass balance was performed.

The parameters characterizing the catalyst activity were glycerol conversion and the selectivity of transformation to 1,2-propanediol in relation to glycerol consumed. They were calculated in the following way:

Conversion

$$C = \frac{\text{Amount of glycerol consumed [mol]}}{\text{Amount of glycerol introduced to the reactor [mol]}} \times 100\%$$

(1)

Selectivity

$$S_{1,2-PD} = \frac{\text{Amount of 1,2-propanediol obtained [mol]}}{\text{Amount of consumed glycerol [mol]}} \times 100\%$$

(2)

The selectivities of transformation to the following compounds: 1,3-propanediol, acetol, ethylene glycol, methanol, ethanol, 1- and 2-propanol, methane, ethane and propane were calculated in the same way. A small amount of di- and tripropylene glycols occurred in certain products.

Analytical methods

The composition of liquid phase was determined by the method of internal standard (phenol) using gas chromatography. The determinations were carried out on a GC 8000 SERIES gas chromatograph with computer aided data collection and handling using the Chrom-Card Trace GC software. The gas chromatograph was equipped with a flame ionization detector (FID) and a DB-WAX glass capillary column 30m×0.25mm×0.5µm.

The detector temperature was 240°C, sample chamber 100°C. The flow of air amounted to 350 cm³/min, hydrogen 30 cm³/min, carrier gas (helium) 2 cm³/min. The analyses were performed according to the following temperature programme: 5 min isothermally at temperature 100°C, temperature increase to 240°C at the rate 10°C/min, 6 min isothermally at 240°C.

The gas phase composition was determined on a Chrom 5 chromatograph with a steel column (3m×4mm) packed with Porapak Q. The analyses were performed with a FID detector, according to the following temperature programme: 4 min isothermally at 200°C, temperature increase at the rate 15°C/min to 190°C. The detector temperature was 200°C, while that of the sample chamber was 90°C. The flow of carrier gases was fixed as follows: nitrogen 23 cm³/min, air 400 cm³/min, hydrogen 40 cm³/min.

After performing the mass balance, the conversion of glycerol and selectivity of transformation to 1,2- and 1,3-propanediol as well as to by-products were calculated.

RESULTS AND DISCUSSION

The first stage of research was to compare conversions of glycerol and selectivities of transformation to 1,2- and 1,3-propanediol obtained in the presence of: unreduced and reduced catalysts Cu/Al_2O_3 and $CuCr_2O_4$ both commercially available and prepared by the co-precipitation method (Table 2). The reduction was conducted by hydrogen. The catalysts prepared by co-precipitation were labeled as $Cu/Al_2O_3^P$, $CuCr_2O_4^P$. The commercial catalysts were labeled as $Cu/Al_2O_3^C$, $CuCr_2O_4^C$. The conditions of reduction: 300°C and 4 h were selected on the basis of reports by Dasari[3] and Guo[4].

For both the commercial and coprecipitated copper catalysts the reduction by hydrogen had higher impact on selectivity of transformation to 1,2-propanediol than on conversion of glycerol. It is interpreted as a result of formation of Cu^0 particles during the reduction, as they are active sites for hydrogenation of acetol. Reduction of the catalyst by hydrogen did not have, however a significant influence on the selectivity of transformation to 1,3-propanediol. The latter compound was obtained only in hydrogenolyses carried out with the commercial $CuCr_2O_4^C$ and co-precipitated $Cu/Al_2O_3^P$ catalysts. Reduction of the commercial $CuCr_2O_4^C$ had no effect on the selectivity of transformation to 1,3-propanediol, while for $Cu/Al_2O_3^P$ it was slightly increased.

As far as Cu/Al_2O_3 catalyst is concerned, higher conversions of glycerol and selectivities of transformation to 1,2-propanediol were achieved in the presence of the catalyst prepared by co-precipitation. Higher copper content and more homogeneous structure are supposed to be responsible for better results obtained in the presence of $Cu/Al_2O_3^P$ than the commercial catalyst. The SEM images revealed that the commercial $Cu/Al_2O_3^C$ catalyst contained aggregates and irregular-shaped clusters of 200–450 µm in size (Fig. 3). The $Cu/Al_2O_3^P$ catalyst prepared in our laboratory by the co-precipitation method was composed of agglomerates with different shape and smaller size in the range of 100–300 µm. X-ray analysis revealed that the commercial $Cu/Al_2O_3^C$ catalyst was composed of 26.95% Cu and 73.04% Al, whereas the catalyst prepared by co-precipitation had 66.14% Cu and 33.86% Al.

In hydrogenolysis of glycerol in the presence of the commercial unreduced $CuCr_2O_4^C$ catalyst the conversion of glycerol was insignificantly lower compared to that in the presence of $CuCr_2O_4^P$ but the selectivity of transformation to 1,2-propanediol was almost twice higher. After reduction by hydrogen, the conversion of glycerol increased in the presence of the commercial $CuCr_2O_4^C$ catalyst and decreased in the presence of $CuCr_2O_4^P$. For both catalysts the selectivity of transformation to 1,2-propanediol increased to a large extent. Moreover, the increase was much higher for $CuCr_2O_4^P$, which was interpreted as a result of too low temperature and too short time of calcination of this catalyst (300°C, 6 h). During the reduction of $CuCr_2O_4^P$, large amounts of water were formed. The presence of water in the unreduced $CuCr_2O_4^P$ could therefore decrease its activity and consequently result in obtaining low selectivity of transformation to 1,2-propanediol. During the commercial catalyst reduction almost no water was formed. However, on the basis of the difference in selectivities to 1,2-propanediol after reduction it is possible that the commercial catalyst was purchased as already reduced.

As can be observed in SEM images (Fig. 3), the structure of $CuCr_2O_4^P$ was more homogeneous than that of the commercial catalyst. $CuCr_2O_4^P$ was composed of spherical-shaped agglomerates with size of 1 µm. The SEM of $CuCr_2O_4^C$ revealed the presence of different shape agglomerates of sizes smaller than 10 µm. Regular structure and smaller size of agglomerates can be the

Table 2. Comparison of glycerol conversion and selectivities of transformation to 1,2- and 1,3-propanediol in the presence of commercial and prepared by co-precipitation catalysts: Cu/Al_2O_3 and $CuCr_2O_4$

Catalyst	Conversion [%]	Selectivity [%]	
		1,2-PD	1,3-PD
$CuCr_2O_4^C$	30.2	35.3	3.0
$CuCr_2O_4^C$ reduced	33.5	55.8	3.0
$CuCr_2O_4^P$	31.1	18.2	0.0
$CuCr_2O_4^P$ reduced	30.6	58.8	0.0
$Cu/Al_2O_3^C$	34.0	36.5	0.0
$Cu/Al_2O_3^C$ reduced	35.4	41.1	0.0
$Cu/Al_2O_3^P$	50.3	36.8	1.2
$Cu/Al_2O_3^P$ reduced	55.4	61.1	1.6

P- prepared by co-precipitation

Figure 3. SEM images of commercial catalysts reduced by hydrogen: $Cu/Al_2O_3{}^C$ (a); $CuCr_2O_4{}^C$ (c) and prepared by co-precipitation method: $Cu/Al_2O_3{}^P$ (b); $CuCr_2O_4{}^P$ (d)

reason for the higher activity of $CuCr_2O_4{}^P$ catalyst in hydrogenolysis. Moreover $CuCr_2O_4{}^P$ was composed of 55.75% Cu and 44.25% Cr, whereas in the commercial catalyst the X-ray analysis revealed the presence of Si. The quantitative composition of this catalyst was as follows: 45.55% Cu, 44.45% Cr and 10.00% Si. The reason for the formation of 1,3-propanediol in the presence of the commercial catalyst and not in the presence of that prepared by co-precipitation is still difficult to explain.

Because better results were obtained in the presence of the catalysts prepared by co-precipitation and reduced by hydrogen, these catalysts were selected for further studies of the impact of the reduction time.

Extension of the reduction time of $Cu/Al_2O_3{}^P$ reduction from 4 h to 8 h enhances the glycerol conversion from 50.3% to 59.0% and the selectivity of transformation to 1,2-propanediol from 36.8% to 77.4%. The 1,3-propanediol selectivity also slightly increased (from 1.2 to 1.9%) (Fig. 4). Thus, the most beneficial reduction time of $Cu/Al_2O_3{}^P$ ensuring the highest conversion of glycerol and selectivity of transformation to 1,2-propanediol was 8 h. After that time, particles of metallic copper Cu^0 and Cu^+ occur in the largest amounts in this catalyst. The Cu^0 copper comprises of the active phase of glycerol hydrogenolysis and the Cu^+ particles prevent sintering of the catalyst[1]. A lower activity of the catalyst reduced for a time shorter than 8 h is a result of the presence of the Cu^{2+} particles as well as a result of the smaller
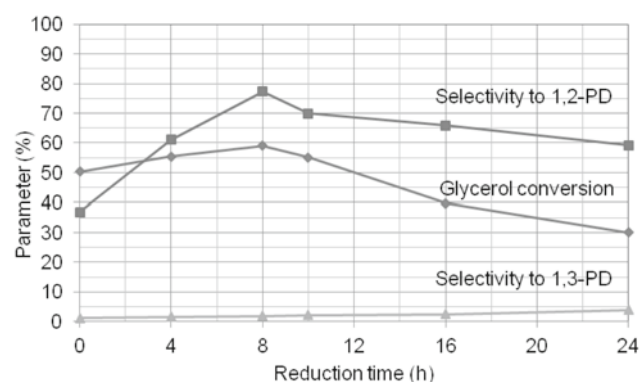

Figure 4. The influence of reduction time by hydrogen of the Cu/Al_2O_3 catalyst on the glycerol conversion and selectivity of transformation to 1,2- and 1,3-propanediol

amount of Cu^0 particles. Decrease in glycerol conversion and selectivity of transformation to 1,2-propanediol after extension of the reduction time from 8 h to 24 h results from sintering of the Cu^0 copper particles on the support surface. The catalyst contains too small amount of Cu^+ particles in relation to Cu^0 particles.

Extension of the reduction time of Cu/Al_2O_3P to 8 h decreases the selectivity of transformation to the compounds derived from the degradation of glycerol and propanediols, particularly methane, methanol, and ethanol (Table 3). Over the time period of 24 h the growth of selectivity of transformation to acetol proceeds. The

Table 3. The effect of reduction time by hydrogen of the CuAl$_2$O$_3$P catalyst on the selectivity of transformation to by-products

Reduction time [h]	Glycerol conversion [%]	Selectivity to by-products												
		Liquid phase						Gas phase						
		Acetol	EG	2-PO	1-PO	CH$_3$OH	C$_2$H$_5$OH	CH$_4$	C$_2$H$_6$	C$_3$H$_8$	CH$_3$OH	C$_2$H$_5$OH	2-PO	1-PO
0	50.3	6.3	0.9	6.9	6.8	12.6	1.3	10.9	0.1	0.1	8.7	0.6	1.9	1.2
4	55.4	6.5	0.9	4.9	5.8	5.3	0.8	6.5	0.0	0.5	3.5	0.3	0.6	0.6
8	59.0	7.2	1.0	1.4	1.9	2.3	0.7	2.2	0.0	0.6	0.9	0.3	0.4	0.5
10	55.2	9.6	0.5	3.5	3.3	2.6	0.7	3.6	0.1	0.5	1.1	0.2	0.5	0.5
16	39.7	10.6	0.7	3.8	4.5	3.6	0.5	3.1	0.1	0.4	2.2	0.1	0.6	0.7
24	30.1	12.0	0.9	5.1	5.9	4.1	1.3	2.3	0.1	0.3	2.2	0.1	0.8	0.9

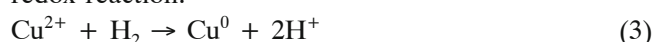EG – ethylene glycol. 2-PO – 2-propanol. 1-PO – 1-propanol

predominant by-product is methanol regardless of the reduction time of the catalyst. The other compounds such as methane, 1- and 2-propanol, ethanol and those mentioned in Table 3 were obtained in smaller amounts. At a concentration level below 0.2 wt%, the presence of compounds such as glycidol, acrolein, glyceraldehyde, glycolaldehyde, propanal, paraldehyde, lactic acid and diethylene glycol was detected by GC-MS.

The effect of reduction time observed for CuCr$_2$O$_4$P catalyst was slightly different (Fig. 5). After the reduction of CuCr$_2$O$_4$P by hydrogen for 4 h the glycerol conversion slightly decreased, but the selectivity of transformation to 1,2-propanediol increased significantly. Extension of the reduction time to 8 h enhances the selectivity of transformation to 1,2-propanediol from the initial 18.2% obtained over the unreduced catalyst to 67.3%. Further extension of reduction time to 24 h leads to only 2.3% increase in the selectivity of transformation to 1,2-propanediol.

1,3-Propanediol was obtained only in the presence of the catalyst reduced for 10, 16 and 24 h. The selectivity of transformation to 1,3-propanediol was: 1.1%, 2.3% and 2.4%. The glycerol conversion reaches the maximum value in the presence of unreduced catalyst. The greatest decrease occurs over the time period of 16-24 h. The highest selectivities of transformation to 1,2-propanediol (70.2%) and 1,3-propanediol (2.4%) were obtained in the presence of CuCr$_2$O$_4$P reduced by hydrogen for 24 h, whereas the conversion of glycerol was lower and amounted to 25.4%. Decreased glycerol conversion was mostly associated with sintering of copper particles on

Figure 5. The effect of reduction time by hydrogen of the Cu-Cr$_2$O$_4$P catalyst on glycerol conversion and selectivity of transformation to 1,2- and 1,3-propanediol

the support surface, however, it could also have resulted from destruction of epitaxial bond between the metallic copper and oxide.

The copper chromite catalyst possesses the structure of a spinel in which 8 copper atoms are located in the tetrahedral coordination, whereas 16 chromium atoms in the octahedral coordination. The studies of Khasin et al.[17] demonstrated that the reduction of copper chromite catalyst by hydrogen leads to the adsorption of hydrogen by the oxygen structure with simultaneous formation of metallic copper in the form of flat particles which are epitaxially combined with oxide. These authors also claimed that the reduced catalyst contains absorbed hydrogen atoms and the particles of metallic copper, epitaxially combined with the structure of copper oxide phase. They exhibit the catalytic activity in the hydrogenation reactions. The reduction of Cu^{2+} particles in the copper chromite catalyst can be presented by the redox reaction:

$$Cu^{2+} + H_2 \rightarrow Cu^0 + 2H^+ \qquad (3)$$

After the reduction of copper to the metallic form (Cu^0) the absorption of hydrogen proceeds.

As a consequence of this process, the dissociative activation and absorption of hydrogen on the surface of metallic copper takes place.

$$H_2 + Cu^0_s \rightarrow 2H_{ads} \qquad (4)$$

When the epitaxial bond occurs between the metallic copper and the chromite phases, the possibility of further absorption of hydrogen appears and the redox reaction takes place.

The reduction of copper-chromite catalysts through the substitution of copper cations by the protons in the spinel structure does not destroy this structure[17].

Extension of the reduction time of CuCr$_2$O$_4$P catalyst over the time period 0–24 h decreases the selectivity of transformation to: methane, methanol, ethylene glycol, 1- and 2-propanol (Table 4). Additionally, the selectivities of transformation to acetol, ethane and propane increase.

The use of Cu/Al$_2$O$_3$P catalyst leads to higher selectivities of transformation to acetol in comparison with those over the CuCr$_2$O$_4$P catalyst. As a result, in the concentration range 1.9–2.7 wt% of acetol, corresponding to the reduction times 0–8 h of Cu/Al$_2$O$_3$P catalyst an increase in the selectivity of transformation to 1,2-propanediol is observed. The acetol formed was further hydrogenated to 1,2-propanediol. After longer reduction times of the
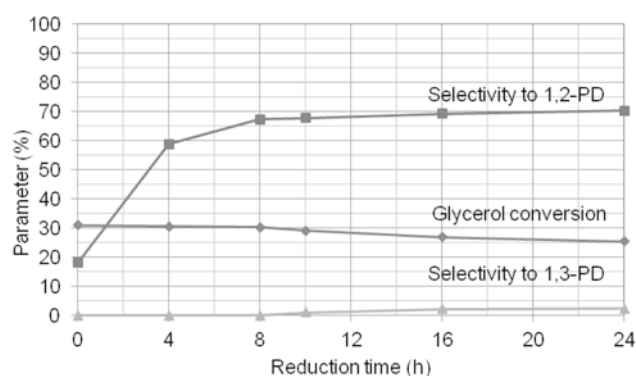
Table 4. The effect of reduction time by hydrogen of the $CuCr_2O_4{}^P$ catalyst on the selectivity of transformation to by-products

Reduction time [h]	Glycerol conversion [%]	Selectivity to by-products												
		Liquid phase						Gas phase						
		Acetol	EG	2-PO	1-PO	CH_3OH	C_2H_5OH	CH_4	C_2H_6	C_3H_8	CH_3OH	C_2H_5OH	2-PO	1-PO
0	31.1	1.7	4.3	17.6	11.7	15.6	1.6	6.6	0.0	0.1	10.9	1.0	2.8	1.8
4	30.6	2.9	1.1	8.1	4.9	7.3	0.8	5.4	0.0	0.1	5.4	0.3	1.7	0.5
8	30.3	3.3	0.5	7.7	4.3	5.2	0.4	3.2	0.0	0.1	2.3	0.0	1.6	0.4
10	29.2	3.7	0.4	6.4	3.2	5.1	0.4	3.1	0.1	0.4	2.2	0.0	1.2	0.3
16	26.9	4.0	0.3	5.2	2.6	4.7	0.2	2.8	0.2	0.5	2.2	0.0	0.7	0.2
24	25.4	4.3	0.2	4.9	2.3	3.8	0.2	2.6	0.4	0.9	2.1	0.0	0.6	0.2

EG – ethylene glycol. 2-PO – 2-propanol. 1-PO – 1-propanol

catalyst (10–24 h), the selectivity of transformation to 1,2-propanediol decreases in spite of further increase in the concentration and selectivity of transformation to acetol. This is confirmed by the fact that the acetol hydrogenation to 1,2-propanediol proceeds slower than its formation as a result of glycerol dehydration. The extension of the reduction time of $CuCr_2O_4{}^P$ catalyst results in an increased selectivity of transformation to acetol, but the selectivity to 1,2-propanediol was increasing during overall reduction period 0–24 h.

CONCLUSIONS

For both Cu/Al_2O_3 and $CuCr_2O_4$ catalysts the best results were obtained after 8 h reduction by hydrogen at 300°C. It is assumed that after 8 h reduction by hydrogen the Cu^0 and Cu^+ particles were formed in both catalysts. Extension of the reduction time from 8 to 24 h may cause the sintering of copper particles, which decreases the activity of these catalysts in hydrogenolysis of glycerol. Moreover, the Cu/Al_2O_3 catalyst gave better results than $CuCr_2O_4$. In the presence of Cu/Al_2O_3 almost twice higher conversion of glycerol and about 10% higher selectivity of transformation to 1,2-propanediol were obtained than in the presence of $CuCr_2O_4$.

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