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TWO-STAGE CONVERSION OF GLYCEROL INTO PROPYLENE GLYCOL OVER Cu/Al₂O₃ CATALYST

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Abstract. The conversion of 30 % glycerol mixture in ethanol over Cu/Al₂O₃ catalyst at 493 K/0.1MPa was studied under Ar-H₂ flow with different H₂ content. It was shown, that 84 % selectivity towards hydroxyacetone is achieved at using 2.5 % H₂ concentration in a carrier gas. Then the product obtained at 493 K has been hydrogenated into a propylene glycol at 448 K in pure H₂ flow under 1.2 MPa. 89 % selectivity towards propylene glycol was achieved at moderate consumption of hydrogen H₂/C₃H₈O₂ = 4 (mol). Two-stage conversion of glycerol into the propylene glycol at different pressure is proposed.

Keywords: glycerol dehydration, Cu/Al₂O₃ catalyst, hydroxyacetone, propylene glycol.

1. Introduction

Currently, the propylene glycol (PG) is a large-scale product (0.9·10⁶ tons per year [1]), obtained *via* hydration of propylene oxide at 453–493 K and 1.5–2.5 MPa [2]. Recently, many investigators have attended to perspective ways of propylene glycol obtaining *via* hydrogenation of accessible and low-cost glycerol (GL-PG process) [3–14]. Usually the mixed metal-oxide (predominantly Cu/oxide) catalysts were utilized. The two-stage mechanism of PG obtaining with intermediate acetol formation is considered [3–14]. M. Akiyama *et al.* [5] have proposed to use a temperature-gradient reactor for hydrogenation of glycerol. According to this important proposition, the dehydration of glycerol to acetol should be performed at 473–493 K, but hydrogenation of acetol into PG has to be realized at 433–393 K, as it follows from the thermodynamic equilibrium. The usage of a two-reactor scheme has allowed obtaining high selectivity (80–90 %) towards PG at 100 % glycerol conversion [5, 10]. However, the large excess of hydrogen (molar ratio of H₂/C₃H₈O₃ = 10–140)

is required for selective PG formation [5, 10]. This circumstance can hamper realization of GL-PG process in industry. Thus, for processing of 1 ton/h of glycerol it is necessary to feed more than 30000 m³/h of hydrogen in a reactor, that will demand large energy expenses.

In this work the results on realization of proposed two-stage GL-PG process are presented. The data on selective obtaining hydroxyacetone from glycerol are given in this communication as well. This reactive α -hydroxyketone is used as a feed stock for synthesis of different oxygenates [15], in particular, acetyl acetate [16].

2. Experimental

30 wt % solution of glycerol in anhydrous ethanol was used as a reagent. The Cu/Al₂O₃ and CuO-Cr₂O₃/Al₂O₃ catalysts (atomic ratio of Cu:Al = 3:4; $S = 165$ m²/g; $V_p = 0.31$ cm³; $D_p = 7.5$ nm) were prepared using a co-precipitated method as described in [10].

The experiments were performed using a stainless steel down flow reactor with a fixed bed of a catalyst (6 cm³). Before the experiment, the catalyst was reduced in H₂ flow at 453–493 K for 5 h. During the first 6 h the load aging of catalyst was observed. For this reason all data presented here were taken after 6 h training of the catalyst.

At the first stage of the experiment (493 K, 0.1 MPa), the content of hydrogen in gas phase (Ar+H₂) varied from 0 to 100 %. A pump Waters 590 was used for feeding 30 % glycerol solution in the reactor under LHSV = 2 h⁻¹, that corresponds to the load on the catalyst of 7 mmol C₃H₈O₃/g_{cat}/h.

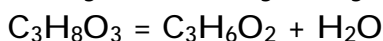
At the second stage of the experiment (448–493 K, 1.2 MPa), the product obtained at the first stage was fed in a reactor (LHSV = 3 h⁻¹) under hydrogen flow of 90 cm³/min.

The reaction products were analyzed using a gas chromatography (Chrom 5 with 50 m capillary column) and ^{13}C NMR spectroscopy (Bruker Avance 400) methods.

3. Results and Discussion

3.1. Conversion

of Glycerol to Hydroxyacetone:



In our experiments the $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst was stable in the ethanol-glycerol feedstock up to 50 h whereas deactivation of the catalyst in a water-glycerol mixture after 15 h was observed (Fig. 1). The same effect was observed in our previous work [10]. Thus ethanol as the glycerol diluent has the pronounced advantage in comparison with water. The $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst also demonstrated better selectivity towards acetol than $\text{CuO-Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$. Therefore we used ethanol-glycerol mixture and $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst for the further investigation.

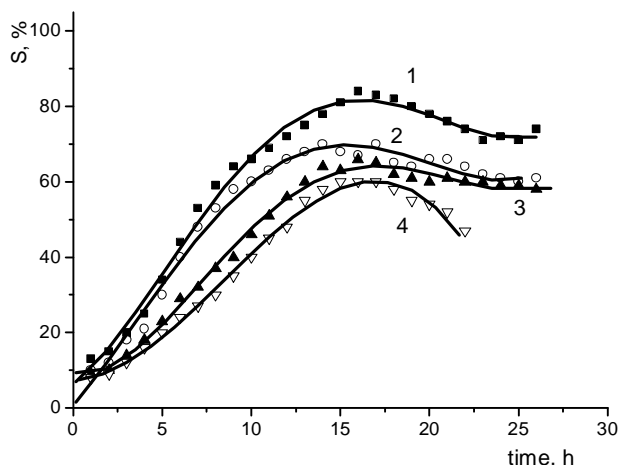


Fig. 1. Selectivity towards acetol as the function of time (493 K, 0.1 MPa, 7 mmol $\text{C}_3\text{H}_8\text{O}_3/\text{g}_{\text{cat}}/\text{h}$): glycerol-ethanol mixture over $\text{CuO}/\text{Al}_2\text{O}_3$ (1) and $\text{CuO-Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ (2); glycerol-water mixture over $\text{CuO}/\text{Al}_2\text{O}_3$ (3) and $\text{CuO-Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ (4)

To check possibility of ethanol dehydrogenation under reaction conditions we have passed pure ethanol and ethanol with elevated glycerol content through the catalyst. Pure ethanol resulted in formation up to 16 wt % of acetaldehyde depending on H_2 concentration in the carrier gas. Further aldol condensation of the aldehyde was observed as well. However glycerol depresses acetaldehyde formation due to the stronger adsorption of glycerol than ethanol on the catalyst surface. At glycerol

content of 6 % acetaldehyde formation was only 8 wt %. When the feedstock of 30 wt % glycerol was used the acetaldehyde content after the first stage of the experiment does not exceed 1 %. At the second stage acetaldehyde is reduced to ethanol.

Glycerol conversion of 100 % was observed at 493 K over $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst under 7 mmol $\text{C}_3\text{H}_8\text{O}_3/\text{g}_{\text{cat}}/\text{h}$. The main products at the conversion of 30 wt % glycerol solution in ethanol are acetol ($\delta = 209$; 68; 25 ppm) and propylene glycol 68; 67; 21 ppm). By-products are represented by a wide range of hemi-ketals ($\delta = 99$; 73; 72; 66; 64; 21 ppm., $\delta = 94$; 75; 73; 62; 21 ppm) and cycle ketals ($\delta = 110$; 77; 66; 26; 25 ppm; $\delta = 109$; 72; 71; 26; 18 ppm) derived from interaction of acetol with glycerol or propylene glycol. Also ethyl lactate ($\delta = 176$; 66.4; 62; 20; 14 ppm), 2-ethoxy-1,3-propanediol ($\delta = 97$; 72.5; 56; 21; 15 ppm) as well as unidentified products were observed.

The composition of glycerol dehydration product appears to be quite sensitive to H_2 /glycerol ratio. At diminishing H_2 flow the yield of PG and acetol was decreased, but the content of by-products was strongly raised (Table 1).

Formation of by-products may be depressed at using high GHSV values because of high H_2 excess of hydrogen or shorter contact time as well. To clarify if the contact time or excess of H_2 is responsible for byproduct formation we have varied the hydrogen content in Ar-H_2 carrier gas from 0 to 100 vol %. The carrier gas flow (30 cm^3/min) and $\text{GHSV} = 2690 \text{ h}^{-1}$ remain constant. The results are presented in Table 2. At decreasing H_2 concentration in the gas flow the content of acetol increases and PG regularly impinges (Table 2). The content of by-products decreases as well. Maximal content of the by-products of 40.8 % is observed at 100 % H_2 flow that corresponds to H_2 /glycerol molar ratio of 2 (Tables 1 and 2). It became clear that only very high excess of H_2 or, alternatively, very low H_2 content could depress the by-product formation.

According to generally adopted scheme of glycerol transformation over the Cu-containing catalysts intermediate products are glyceraldehyde and pivaldehyde [3-14]. Obviously, high H_2 excess retards glycerol dehydrogenation and accelerates hydrogenation of pivaldehyde to hydroxyacetone. The very high H_2 excess depresses the formation of byproducts derived from acetol and propylene glycol formation as well.

The maximal 83 % selectivity towards acetol is observed at 2.5 % H_2 concentration. In pure Ar flow acetol selectivity reduces up to 71 % (Table 2).

The catalyst quickly becomes deactivated in the absence of hydrogen in the carrier-gas (Fig. 2). Obviously hydrogen provides more stable work of the catalyst.

Table 1

Effect of H₂ flow on the conversion products content*

H ₂ flow, cm ³ /min	GHSV, h ⁻¹	H ₂ /C ₃ H ₈ O ₃ , mol	HA, wt %	PG, wt %	Other
30	2690	2	36	23	41
44	3230	3	39	28	33
74	5650	5	53	30	17
222	16680	16	46	39	15

Note: * 493 K; 0.1 MPa; 7 mmol C₃H₈O₃/g_{cat}/h; HA – hydroxyacetone; PG – propylene glycol; other – ethyl lactate and ketals.

Table 2

Effect of H₂ content in Ar-H₂ flow on products selectivity*

H ₂ content, vol %	H ₂ /C ₃ H ₈ O ₃ , mol	HA, %	PG, %	Other
100	2	36	23	41
50	1	48	21	31
30	0.7	69	18	13
6	0.13	72	16	12
2.5	0.05	84	11	5
2.5**	0.05	85	10	5
0	0	71	14	15

Notes: * 493 K, 0.1 MPa, 7 mmol C₃H₈O₃/g_{cat}/h, GHSV=2690 h⁻¹; ** 493 K, 0.1 MPa, 11 mmol C₃H₈O₃/g_{cat}/h, GHSV = 2690 h⁻¹

Table 3

Effect of temperature on the hydrogenated products content*

T, K	PG, %	HA, %	EL, %	NS, %
493	29	33	12	26
468	58	25	7	10
448	89	7	2	2
448**	81	12	3	4

Notes: * 1.2 MPa; H₂/C₃H₆O₂ = 4; LHSV = 3 h⁻¹; EL – ethyl lactate; NS – non specified products; ** 0.1 MPa H₂/C₃H₈O₃ = 46; LHSV = 3h⁻¹ [10]

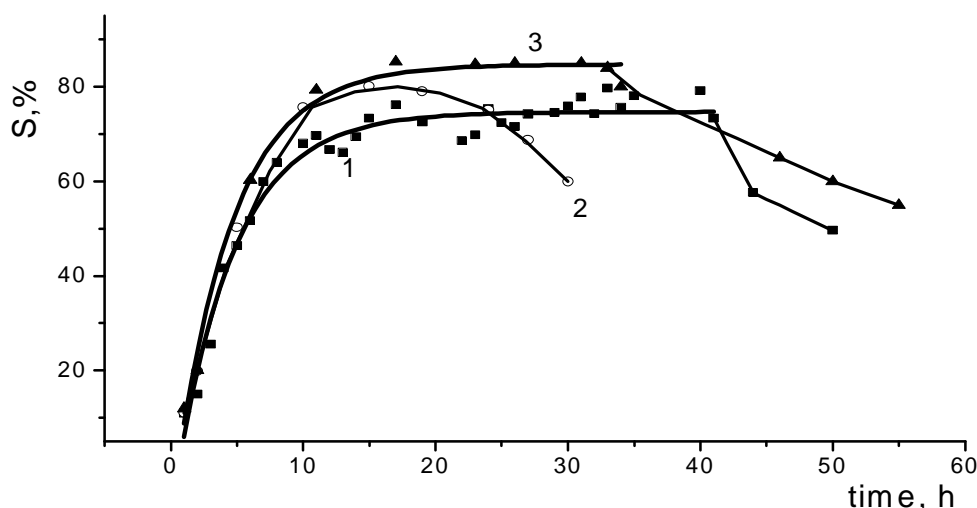
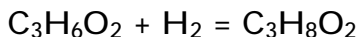


Fig. 2. Changes in acetol selectivity with time at 493 K under 7 mmol C₃H₈O₃/g_{cat}/h: 6 vol % H₂ (1); 0 vol % H₂ (2) and 2.5 vol % H₂ (3)

3.2. Hydrogenation of Hydroxyacetone into Propylene Glycol:



At the second stage the product of glycerol transformation into acetol obtained at the first stage at 2.5 % H_2 content in a gas flow (Table 2) was hydrogenated in pure H_2 flow under 1.2 MPa. The same $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst was used. The hydrogenation is performed under H_2 flow of $90 \text{ cm}^3/\text{min}$ that corresponds to $\text{H}_2/\text{acetol} = 4$ molar ratio. The content of products obtained at different temperatures of hydrogenation is presented in Table 3.

At 493 K the composition of hydrogenation product is close to that of glycerol dehydration under similar conditions (see Table 1). Obviously equilibrium of dehydrogenation-hydrogenation process is achieved at 493 K and $\text{H}_2/\text{glycerol}$ molar ratio close to 4. Formation of by-products especially ethyl lactate under these conditions is strongly increased.

Conversion of acetol and selectivity towards propylene glycol rise at decreasing temperature whereas the formation of by-products decreases. The highest propylene glycol content of 89 % was gained at 448 K. It is important to note that not only acetol but also by-products are hydrogenated under these conditions.

The comparison of present data with previous result on hydrogenation of glycerol [10] (448 K, 0.1 MPa $\text{H}_2/\text{C}_3\text{H}_8\text{O}_3 = 46$; $\text{LHSV} = 3 \text{ h}^{-1}$) shows that the hydrogenation reaction at 448 K proceeds more effectively under the increased pressure: 12 times increase in pressure requires 12 times smaller H_2 excess. The hydrogenation at 1.2 MPa results in increasing selectivity towards propylene glycol up to 89 %.

4. Conclusions

The conversion of 30 % glycerol solution in ethanol over $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst at 493 K was studied under $\text{Ar}-\text{H}_2$ flow with different H_2 content.

The selectivity of 84 % towards hydroxyacetone is achieved at 2.5 % H_2 concentration in the carrier gas.

The hydrogenation of this product at 448 K/1.2 MPa H_2 over $\text{Cu}/\text{Al}_2\text{O}_3$ allows achieving 89 % PG selectivity. Consumption of hydrogen is 12 times lower

than the one with 0.1 MPa two-reactor scheme of GL-PG conversion.

Thus, two-stage scheme of GL-PG conversion with intermediate formation of hydroxyacetone as co-product is proposed.

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ДВОСТАДІЙНЕ ПЕРЕТВОРЕННЯ ГЛІЦЕРИНУ В ПРОПІЛЕНГЛІКОЛЬ НА $\text{Cu}/\text{Al}_2\text{O}_3$ КАТАЛІЗАТОРІ

Анотація. Досліджено перетворення 30 % розчину гліцерину в етанолі на $\text{Cu}/\text{Al}_2\text{O}_3$ каталізаторі при 493 K/0,1 МПа в потоці $\text{Ar}-\text{H}_2$ з різним вмістом H_2 . Показано, що 84 % селективність за гідроксиацетоном досягається при концентрації H_2 в газі-носії 2,5%. Проведено гідрування отриманого продукту в пропіленгліколі при температурі 448 K в потоці чистого H_2 при 1,2 МПа. При середній витраті водню $\text{H}_2/\text{C}_3\text{H}_8\text{O}_2 = 4$ моль досягнуто 89% селективності відносно пропіленгліколю. Показана можливість двостадійного перетворення гліцерину в пропіленгліколь за різних тисків.

Ключові слова: дегідрований гліцерин, каталізатор $\text{Cu}/\text{Al}_2\text{O}_3$, гідроксиацетон, пропіленгліколь.