TWO-STAGE CONVERSION OF GLYCEROL INTO PROPYLENE GLYCOL OVER Cu/Al\textsubscript{2}O\textsubscript{3} CATALYST

Institute of Sorption and Problems of Endoeology of the National Academy of Sciences, 13, General Naumov str., 03164 Kyiv, Ukraine; brei@ukr.net

Received: October, 28, 2014 / Revised: December 08, 2014 / Accepted: February 18, 2015

Abstract. The conversion of 30 % glycerol mixture in ethanol over Cu/Al\textsubscript{2}O\textsubscript{3} catalyst at 493 K/0.1MPa was studied under Ar-H\textsubscript{2} flow with different H\textsubscript{2} content. It was shown, that 84 % selectivity towards hydroxyacetone is achieved at using 2.5 % H\textsubscript{2} concentration in a carrier gas. Then the product obtained at 493 K has been hydrogenated into a propylene glycol at 448 K in pure H\textsubscript{2} flow under 1.2 MPa. 89 % selectivity towards propylene glycol was achieved at moderate consumption of hydrogen H\textsubscript{2}/C\textsubscript{3}H\textsubscript{8}O\textsubscript{3} = 4 (mol). Two-stage conversion of glycerol into the propylene glycol at different pressure is proposed.

Keywords: glycerol dehydration, Cu/Al\textsubscript{2}O\textsubscript{3} catalyst, hydroxyacetone, propylene glycol.

1. Introduction

Currently, the propylene glycol (PG) is a large-scale product (0.9·10\textsuperscript{6} 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 H\textsubscript{2}/C\textsubscript{3}H\textsubscript{8}O\textsubscript{3} = 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 m\textsuperscript{3}/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, acetonyl acetate [16].

2. Experimental

30 wt % solution of glycerol in anhydrous ethanol was used as a reagent. The Cu/Al\textsubscript{2}O\textsubscript{3} and CuO-Cr\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalysts (atomic ratio of Cu:Al = 3:4; \( S = 165 \text{ m}^2/\text{g} \); \( V_p = 0.31 \text{ cm}^3/\text{g} \); \( D_p = 7.5 \text{ nm} \)) 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 cm\textsuperscript{3}). Before the experiment, the catalyst was reduced in H\textsubscript{2} 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+H\textsubscript{2}) varied from 0 to 100 %. A pump Waters 590 was used for feeding 30 % glycerol solution in the reactor under LHSV = 2 h\textsuperscript{-1}, that corresponds to the load on the catalyst of 7 mmol C\textsubscript{3}H\textsubscript{8}O\textsubscript{3}/g\textsubscript{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\textsuperscript{-1}) under hydrogen flow of 90 cm\textsuperscript{3}/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:

$$\text{C}_3\text{H}_8\text{O}_3 = \text{C}_3\text{H}_6\text{O}_2 + \text{H}_2\text{O}$$

In our experiments the Cu/Al$_2$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 CuO/Al$_2$O$_3$ catalyst also demonstrated better selectivity towards acetol than CuO-Cr$_2$O$_3$/Al$_2$O$_3$. Therefore we used ethanol-glycerol mixture and CuO/Al$_2$O$_3$ catalyst for the further investigation.

![Fig. 1. Selectivity towards acetol as the function of time (493 K, 0.1 MPa, 7 mmol C$_3$H$_6$O$_2$/g-cat/h); glycerol-ethanol mixture over CuO/Al$_2$O$_3$ (1) and CuO-Cr$_2$O$_3$/Al$_2$O$_3$ (2); glycerol-water mixture over CuO/Al$_2$O$_3$ (3) and CuO-Cr$_2$O$_3$/Al$_2$O$_3$ (4).](image-url)

The composition of glycerol dehydration product of by-products decreases as well. Maximal content of 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 H$_2$ flow could depress the by-product formation. According to generally adopted scheme of glycerol transformation over the Cu-containing catalysts intermediate products are glyceraldehyde and pipiraldehyde [3-14]. Obviously, high H$_2$ excess retards glycerol dehydrogenation and accelerates hydrogenation of pipiraldehyde 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.
Two-stage Conversion of Glycerol into Propylene Glycol over Cu/Al$_2$O$_3$ Catalyst

Table 1

<table>
<thead>
<tr>
<th>H$_2$ flow, cm$^3$/min</th>
<th>GHSV, h$^{-1}$</th>
<th>H$_2$/C$_3$H$_8$O$_3$, mol</th>
<th>HA, wt %</th>
<th>PG, wt %</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>2690</td>
<td>2</td>
<td>36</td>
<td>23</td>
<td>41</td>
</tr>
<tr>
<td>44</td>
<td>2320</td>
<td>3</td>
<td>39</td>
<td>28</td>
<td>33</td>
</tr>
<tr>
<td>74</td>
<td>5650</td>
<td>5</td>
<td>53</td>
<td>30</td>
<td>17</td>
</tr>
<tr>
<td>222</td>
<td>16680</td>
<td>16</td>
<td>46</td>
<td>39</td>
<td>15</td>
</tr>
</tbody>
</table>

Note: * 493 K; 0.1 MPa; 7 mmol C$_3$H$_8$O$_3$/g$_{cat}$/h; HA – hydroxyacetone; PG – propylene glycol; other – ethyl lactate and ketals.

Table 2

<table>
<thead>
<tr>
<th>H$_2$ content, vol %</th>
<th>H$_2$/C$_3$H$_8$O$_3$, mol</th>
<th>HA, %</th>
<th>PG, %</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2</td>
<td>36</td>
<td>23</td>
<td>41</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>48</td>
<td>21</td>
<td>31</td>
</tr>
<tr>
<td>30</td>
<td>0.7</td>
<td>69</td>
<td>18</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>0.13</td>
<td>72</td>
<td>16</td>
<td>12</td>
</tr>
<tr>
<td>2.5</td>
<td>0.05</td>
<td>84</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>2.5**</td>
<td>0.05</td>
<td>85</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>71</td>
<td>14</td>
<td>15</td>
</tr>
</tbody>
</table>

Notes: * 493 K, 0.1 MPa, 7 mmol C$_3$H$_8$O$_3$/g$_{cat}$/h, GHSV=2690 h$^{-1}$; ** 493 K, 0.1 MPa, 11 mmol C$_3$H$_8$O$_3$/g$_{cat}$/h, GHSV = 2690 h$^{-1}$

Table 3

<table>
<thead>
<tr>
<th>T, K</th>
<th>PG, %</th>
<th>HA, %</th>
<th>EL, %</th>
<th>NS, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>493</td>
<td>29</td>
<td>33</td>
<td>12</td>
<td>26</td>
</tr>
<tr>
<td>468</td>
<td>58</td>
<td>25</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>448</td>
<td>89</td>
<td>7</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>448**</td>
<td>81</td>
<td>12</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

Notes: * 1.2 MPa; H$_2$/C$_3$H$_8$O$_3$ = 4; LHSV = 3 h$^{-1}$; EL – ethyl lactate; NS – non specified products; ** 0.1 MPa H$_2$/C$_3$H$_8$O$_3$ = 46; LHSV = 3h$^{-1}$ [10]

Fig. 2. Changes in acetol selectivity with time at 493 K under 7 mmol C$_3$H$_8$O$_3$/g$_{cat}$/h: 6 vol % H$_2$ (1); 0 vol % H$_2$ (2) and 2.5 vol % H$_2$ (3)
3.2. Hydrogenation of Hydroxyacetone into Propylene Glycol:
\[ C_3H_6O_2 + H_2 = C_3H_8O_2 \]

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 Cu/Al\(_2\)O\(_3\) catalyst was used. The hydrogenation is performed under \( H_2 \) flow of 90 cm\(^3\)/min that corresponds to \( H_2/\text{acetol} = 4 \) 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 \( H_2/\text{glycerol} \) 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 results on hydrogenation of glycerol [10] (448 K, 0.1 MPa \( H_2/\text{C}_3\text{H}_6\text{O}_2 = 46 \); LHSV = 3 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 \( H_2 \) content. 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 Cu/Al\(_2\)O\(_3\) catalyst at 493 K was studied under Ar-\( H_2 \) 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 Cu/Al\(_2\)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.

References