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# ONE-POT SYNTHESIS OF δ-VALEROLACTONE FROM TETRAHYDROFURFURYL ALCOHOL AND δ-VALEROLACTONE AMIDATION OVER Cu/ZnO-$Al_2O_3$ CATALYST

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*It has been found that tetrahydrofurfuryl alcohol transforms into δ-valerolactone over Cu/ZnO-$Al_2O_3$ catalyst at 270–280 °C. δ-Valerolactone can be used for obtaining biodegradable polyesters and copolymers. Proposed Cu/ZnAl-1 catalyst containing 40 wt. % of CuO provides 40–50 % alcohol conversion with 80–85 % lactone selectivity under hydrogen flow at 0.1 MPa. The reaction pathway from tetrahydrofurfurol to δ-valerolactone has been proposed: it is speculated that alcohol is initially dehydrogenated into tetrahydrofurfural, which rearranges to lactone. Vapor-phase amidation of δ-valerolactone with ammonia into δ-valerolactam, as raw material for obtaining polyamide nylon-5, was also investigated. It has been shown that among studied Cu-containing oxides Cu/ZnAl-1 catalyst provides higher 80 % δ-valerolactam selectivity at 90 % lactone conversion at 280 °C under ammonia, hydrogen and steam flow with strictly certain molar ratio. The process proceeds via disclosure of lactone cycle with intermediate 5-hydroxypentamide formation.*

***Keywords:*** *catalytic dehydrogenation, tetrahydrofurfuryl alcohol, δ-valerolactone, δ-valerolactam, Cu-catalyst*

## INTRODUCTION

Currently, much research is focused on the obtaining of commodity chemicals from the renewable raw materials, which have a potential to replace oil and gas in an industrial organic synthesis. Recently, furfural was fairly added to the biomass-based platform chemicals as well as ethanol, lactic acid, and isoprene [1]. Furfural, obtained by the acidic dehydration of polypentoses, is utilized for the production of useful chemicals such as furfuryl alcohol, tetrahydrofurfuryl alcohol (THFA), furan, tetrahydrofuran and others [2]. Annual production of furfural is 0.3–0.7 Mtons [3].

Tetrahydrofurfuryl alcohol, obtained through the vapor-phase hydrogenation of furfural, is used mainly as a solvent [4]. In recent years, the catalysts for direct conversion of THFA into 1,5-pentanediol, as a component for polyesters production, have been found [5, 6]. Search of a catalyst for one-pot synthesis of δ-valerolactone (VLN) from THFA is of interest because this lactone can be polymerized into biodegradable polyesters with high mechanical properties [7–9] as well as into copolymers [10–12]. The data on direct δ-valerolactone synthesis from THFA are not numerous. This valerolactone was determined as a co-product in the THFA to tetrahydrofuran conversion over Ni-Cu [13] and Fe-Cu [14] catalysts, and also at the dehydrogenation of THFA over Cu/ZnAlCaNa catalyst [15].

δ-Valerolactone amidation with ammonia into δ-valerolactam is of specific interest for obtaining polyamide nylon-5 on the basis of furfural. Nylon-5 textile fibers are capable to absorb more moisture and generate less static buildup compared to nylon-6, obtained from ε-caprolactam [16]. Despite this advantage, nylon-5 is a minor component of the polyamide fiber industry. Literary results on δ-valerolactone amidation are in deficiency [17, 18] contrary to well-studied amidation of ε-caprolactone [19, 20].

In this work, the results concerning selective THFA dehydrogenation into δ-valerolactone and also its amidation to δ-valerolactam over several Cu-oxides are presented. The reaction pathway from THFA to δ-valerolactone is also discussed.

## EXPERIMENTAL

***Catalysts Preparation***. All chemicals used in the study were of the analytical grade. Catalyst precursors were prepared by two different methods: conventional precipitation and incipient wetness impregnation of an oxide support.

The first series of copper-based catalysts was derived from hydroxycarbonate precursors prepared by the co-precipitation of metal nitrates in aqueous solution. In short, nitrate salts $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, and if necessary, $ZrO(NO_3)_2{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$ and NaOH were dissolved in desired ratios in distilled water (the total metal concentration in the aqueous solution was 1.25 M). A 1.25 M $(NH_4)_2CO_3$ aqueous solution was then added under vigorous stirring to maintain pH ~7 at room temperature. The product slurry was aged at 60 °C for 4 h followed by standing at ambient temperature for 20 h. The resulting precipitate was washed with distilled water several times, then was filtered, dried at 110 °C for 12 h, and calcined in static air at 350 °C for 4 h. The prepared samples are named according to their composition, for instance, $Cu/ZnO\text{-}Al_2O_3$ sample was marked as Cu/ZnAl.

The $Cu/TiO_2$ sample also was prepared by the co-precipitation method. Namely, aqueous solution of $Cu(NO_3)_2$ (34 Cu mg $g^{-1}$) was added to ~2.2M $TiCl_4$ aqueous solution (103 Ti mg $g^{-1}$) under vigorous stirring. The excess of hydrochloric acid was neutralized with ammonia solution (pH ~1.5). Then, stoichiometrical quantity of urea was added and the solution was aged at 100 °C for 24 h. The obtained gel was washed and then dried at 120 °C and finally calcined to 500 °C (2 °C $min^{-1}$).

The second series of copper-based catalysts was prepared by incipient wetness impregnation of oxide supports with metal nitrate solutions. Calculated quantities of aqueous solution of $Cu(NO_3)_2$ and if necessary, $Zn(NO_3)_2{\cdot}6H_2O$ were added to different supports: silica ($SiO_2$, NewSil, China) at a liquid/solid ratio of 3.2 cc $g^{-1}$; γ-alumina ($Al_2O_3$, NTC “Alvigo”, Ukraine) at the liquid/solid ratio of 0.8 cc $g^{-1}$; acidic $ZrO_2\text{-}SiO_2$ (molar ratio Zr:Si = 1:2) mixed oxide, which was prepared as described in the article [21], at the liquid/solid ratio of 0.5 cc $g^{-1}$. After impregnation, all catalysts were dried at 110 °C for 2 h and calcined at 350 °C for 4 h.

***Characterization.*** Textural parameters of all samples were determined using a standard technique of low-temperature nitrogen adsorption (Quantachrome Nova 2200e Surface Area and Pore Size Analyser). Specific surface area, average pore radius, and total pore volume were calculated from the adsorption-desorption isotherms using the BET method.

The X-ray diffraction (XRD) patterns were recorded on a DRON-4-07 diffractometer ($CuK_\alpha$ radiation). Diffraction patterns were identified by comparing with those from the JCPDS (Joint Committee of Powder Diffraction Standards) database.

The TPR profiles of hydrogen formation from ethanol and THFA, absorbed on Cu/ZnAlZr sample, were recorded using a modernized monopole mass-spectrometer MX-7304A (Ukraine). Preliminary, a sample (5–7 mg) was reduced in $H_2$ flow at 180–220 °C in a quartz cuvette. Then, the cuvette was degassed and adsorption of alcohol at 20 °C was provided. Further the cuvette was vacuumed repeatedly, and a desorption mass-spectrum of alcohol transformation products was recorded in mass-diapason 2–84 a.u.m. with sweep rate 2 a.u.m. $s^{-1}$ at heating sample (10 °C $min^{-1}$).

***Catalyst testing and product analysis.*** Catalytic experiments were performed in a fixed-bed flow stainless-steel reactor under atmospheric pressure. Catalyst powder was pressed into pellets and then crushed to 1–2 mm grains. Prior to the catalytic test, the sample was reduced *in situ* with hydrogen flow (30 ml $min^{-1}$) at 180–220 °C for 2 h.

The conversion of tetrahydrofurfuryl alcohol (Merck, ≥ 98 %) into δ-valerolactone was carried out at 260–300 °C under hydrogen flow. Usually, 2 $cm^3$ (1–2.4 g) of the catalyst was loaded into 8 mm inner diameter reactor. Feed rate of liquid THFA was varied, using a syringe pump Orion M361, in the interval of LHSV = 0.3–0.9 $h^{-1}$. It corresponded to the load on catalyst from 3.5 to 14 mmol THFA $g_{cat}^{-1}$ $h^{-1}$. $H_2$/THFA molar ratio varied from 1 to 25.

The amidation of δ-valerolactone (Acros Organics, 99 %) and ε-caprolactone (Alfa Aesar, 99 %) with ammonia was performed at 250–280 °C in the presence of water vapor and hydrogen. Usually, 5 $cm^3$ (3–6 g) of the catalyst was placed into 12 mm inner diameter reactor. The δ-valerolactone feed rate was 0.5 mmol VLN $g_{cat}^{-1}$ $h^{-1}$. δ-Valerolactone and water were pumped into reactor separately. The reaction products are collected in an ice-cooled condenser and analyzed by $^{13}C$ NMR (Bruker

Avance-400) and gas chromatography (Chrom-5 with 50 m capillary column) methods. The values of THFA conversion and product selectivity (*S*, wt. %) were calculated from chromatograms with preliminary calibration using THFA, δ-valerolactone, ε-caprolactone and ε-caprolactam.

## RESULTS AND DISCUSSION

The samples are characterized by developed surface (75–300 $m^2g^{-1}$) and pore diameter in the interval of 2.4–19.4 nm (Table 1).

**Table 1.** Composition and textural parameters of prepared oxides

| Sample | Composition, molar ratio | BET surface area, $m^2\ g^{-1}$ | Pore volume, $cm^3\ g^{-1}$ | Average pore radius, nm | Bulk density, $g\ cm^{-3}$ |
|---|---|---|---|---|---|
| Cu/ZnAl-1 | $CuO:ZnO:Al_2O_3=10:5:1$ | 150 | 0.38 | 7.3 | 0.7 |
| Cu/ZnAl-2 | $CuO:ZnO:Al_2O_3=5:5:1$ | 75 | 0.29 | 7.7 | 1.0 |
| $Cu\text{-}Zn/Al_2O_3$ | $CuO:ZnO:Al_2O_3=10:5:1$ | 160 | 0.42 | 5.2 | 0.7 |
| Cu/ZnZrAl | $CuO:ZnO:ZrO_2:Al_2O_3=6:1:2:2$ | 140 | 0.31 | 4.3 | 1.2 |
| Cu/ZnAlCaNa | $CuO:ZnO:Al_2O_3:CaO:Na_2O=$ 59:33:3:1:0.5 | 110 | 0.54 | 9.7 | 0.7 |
| $Cu/Al_2O_3$ | $CuO:Al_2O_3=1:1.7$ | 100 | 0.31 | 5.0 | 0.7 |
| Cu/Al | $CuO:Al_2O_3=1:1.7$ | 300 | 0.30 | 2.0 | 0.7 |
| Cu/Ti | $CuO:TiO_2=1:3$ | 150 | 0.53 | 7.1 | 0.7 |
| $Cu/SiO_2$ | $CuO:SiO_2=1:4.4$ | 120 | 0.43 | 7.2 | 0.6 |
| $Cu/ZrO_2\text{-}SiO_2$ | $CuO:ZrO_2:SiO_2=1:3:6$ | 300 | 0.18 | 1.2 | 1.2 |
| $\gamma\text{-}Al_2O_3$ | – | 280 | 0.82 | 5.3 | 0.5 |

The XRD patterns of $Cu/Al_2O_3$ and Cu/ZnAl-1 catalysts calcined at 350 °C are shown in Fig. 1. According to JCPDS, the XRD pattern of $Cu/Al_2O_3$ catalyst exhibits intense peaks at $2\theta = 32.5°$, 35.5°, 38.7°, 48.7°, 53.5°, 58.2°, 61.5°, 66.2°, 68.1°, 71.7° and 75.5° corresponding to bulk CuO phase and very small peaks at $2\theta = 32.75°$, 45.6°, 61.7°, 66.9°, 72.8°, 75.5° attributable to $Al_2O_3$. The CuO crystallite size calculated from peak half-width using Sherrer equation is 30 nm for the $Cu/Al_2O_3$ sample.

The characteristic peaks of ZnO ($2\theta = 31.7°$, 34.4°, 47.6°, 56.6°) have been indicated in the diffractogram of Cu/ZnAl-1 sample in addition to CuO and $Al_2O_3$ (Fig. 1). However, the lines ascribed to ZnO and $Al_2O_3$ are weak. This is due to the fact that zinc and aluminum oxides are presented in highly disordered or amorphous states because of the relatively low calcination temperature (350 °C), or that the crystallite size is too small to be detected due to line-broadening. Also the broader peaks of CuO in the Cu/ZnAl-1 catalyst compared with those of the $Cu/Al_2O_3$ indicate that the crystallite sizes of CuO are very fine. The average particle size of CuO for Cu/ZnAl-1 catalysts is 5–10 nm. This is explained by the formation of aurichalcite $(Cu,Zn)_5(CO_3)_2(OH)_6$ phase in the catalyst precursors because of the interexchange between Cu and Zn at the atom level [22].

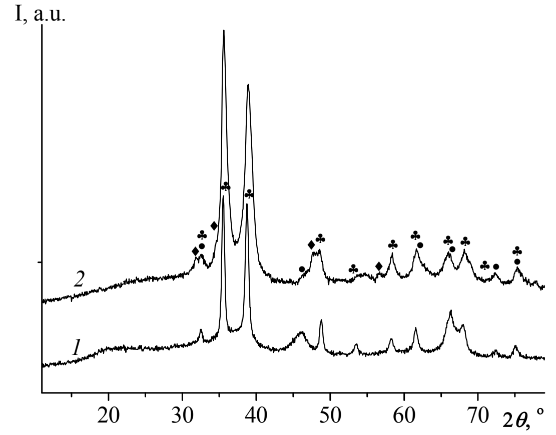


**Fig. 1.** XRD patterns of $Cu/Al_2O_3$ (*1*) and Cu/ZnAl-1 (*2*) samples after calcination (● – $\gamma\text{-}Al_2O_3$, ♣ – CuO, ♦ – ZnO)

The XRD patterns of $Cu/Al_2O_3$ and Cu/ZnAl-1 samples reduced under hydrogen flow are shown in Fig. 2. The analysis indicates that $Cu^{2+}$ ions were converted to metallic copper ($Cu^0$) with characteristic reflex at $2\theta = 43.3°$, 50.4°, and 74.1° after the sample reduction (Fig. 2). There are no peaks related to any other Cu-containing phases like $Cu_2O$ ($2\theta = 36.5°$, 61.5°) or $CuAl_2O_4$, $CuAlO_2$,

$CuAl_4O_7$. According to Scherrer equation, the average $Cu^0$ crystal size is 40 and 10–12 nm for $Cu/Al_2O_3$ and Cu/ZnAl-1 catalysts, respectively.

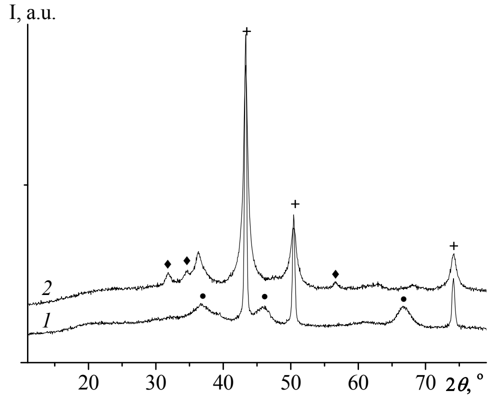


**Fig. 2.** XRD patterns of $Cu/Al_2O_3$ (*1*) and Cu/ZnAl (*2*) samples after reduction (● – $\gamma$-$Al_2O_3$, + – $Cu^0$, ♦ – ZnO)

***Dehydrogenation of tetrahydrofurfuryl alcohol: $C_5H_{10}O_2 = C_5H_8O_2 + H_2$.*** The results on THFA transformation over studied Cu-oxides at 270 °C under hydrogen flow are presented in Table 2. The best selectivity of 90 % towards δ-valerolactone at 40 % THFA conversion is observed on the Cu/ZnAl-1 catalyst. The lower copper content in Cu/ZnAl-2 sample results in decreasing THFA conversion up to 36 % (Table 2). In contrast to precipitated Cu/ZnAl-1 catalyst, supported $Cu$-$Zn/Al_2O_3$ sample shows twice low (19 %) THFA conversion (Table 2). Five-component Cu/ZnAlCaNa sample, with the composition similar to catalyst tested in [15], provides 39 % THFA conversion with 87 % VLN selectivity that is close to simpler three-component Cu/ZnAl-1 catalyst (Table 2). Co-precipitated Cu/ZnZrAl sample with $Zr^{4+}$ ions which effectively catalyzes the transformation of ethanol to ethyl acetate [23] showed also the lower 29 % THFA conversion than Cu/ZnAl-1 catalyst (Table 2).

According to the thermodynamic calculation of equilibrium content in THFA–δ-valerolactone–$H_2$ system, the dehydrogenation of THFA is low endothermic process ($\Delta H_R^{280\,°C} = +3.5$ kJ/mol), and THFA conversion can achieve of 73 % at 280 °C and atmospheric pressure.

As expected, THFA conversion declined from 40 % to 20 % on Cu/ZnAl-1 catalyst due to increase of pressure in the experiments from 0.10 to 0.25 MPa (Table 2). Also, THFA conversion and especially VLN selectivity decline in the experiments without $H_2$ flow (Table 2). As a rule, the THFA transformation experiments are performed under hydrogen flow, which prevents coke formation on the surface of catalyst [13, 15, 19].

**Table 2.** Effect of catalyst on THFA conversion[a]

| **Catalyst** | **X, %** | **Selectivity, wt. %[b]** | | | **VLN yield, %** |
|---|---|---|---|---|---|
| | | **VLN** | **2HTHP** | **Others** | |
| Cu/ZnAl-1 | 40 | 90 | 2 | 8 | 36 |
| Cu/ZnAl-1[c] | 20 | 80 | 3 | 17 | 16 |
| Cu/ZnAl-1[d] | 34 | 55 | 26 | 19 | 19 |
| Cu/ZnAl-2 | 36 | 85 | 2 | 13 | 31 |
| $Cu$-$Zn/Al_2O_3$ | 19 | 85 | 4 | 11 | 16 |
| Cu/ZnAlCaNa | 39 | 87 | 2 | 11 | 34 |
| Cu/ZnZrAl | 29 | 83 | 3 | 14 | 24 |
| $Cu/Al_2O_3$ | 77 | 36 | 0 | 64 | 28 |
| Cu/Al | 78 | 17 | 0 | 83 | 13 |
| $Cu/SiO_2$ | 13 | 81 | 11 | 8 | 11 |
| $\gamma$-$Al_2O_3$ | 97 | 2 | 0 | 98 | 2 |

[a] Experimental conditions: 270 °C; 5 mmol THFA $g_{cat}^{-1}$ $h^{-1}$, $H_2$/THFA = 25, mol

[b] VLN, δ-valerolactone; 2HTHP, 2-hydroxytetrahydropyran

[c] 0.25 MPa

[d] Without $H_2$ flow

The supported and precipitated $Cu/Al_2O_3$ samples provide the higher 77–78 % THFA conversion in comparison with Cu/ZnAl-1 (Table 2), but the main products are 3,4-dihydro-*2H*-pyran and tetrahydropyran whereas over pure $Al_2O_3$ the main product is 3,4-dihydro-*2H*-pyran. Obviously, basic ZnO oxide is an important component of Cu/ZnAl-1 catalyst which promotes the VLN formation. The $Cu/SiO_2$ sample demonstrates 81 % VLN selectivity, however at the low 13 % THFA conversion (Table 2). Thus, we have used selective Cu/ZnAl-1 catalyst for a more detailed study.

THFA conversion increases from 32 to 58 % on Cu/ZnAl-1 catalyst at rising temperature from 260 to 300 °C. However, VLN selectivity declines by about 10 % (Fig. 3).

At increasing load on the catalyst from 3 up to 12.5 mmol THFA $g_{cat}^{-1}$ $h^{-1}$ the alcohol conversion decreases by 25 % (Fig. 4). It is important, VLN selectivity does not change significantly, and VLN productivity achieves 2.5 mmol $g_{cat}^{-1}$ $h^{-1}$ (Fig. 4).

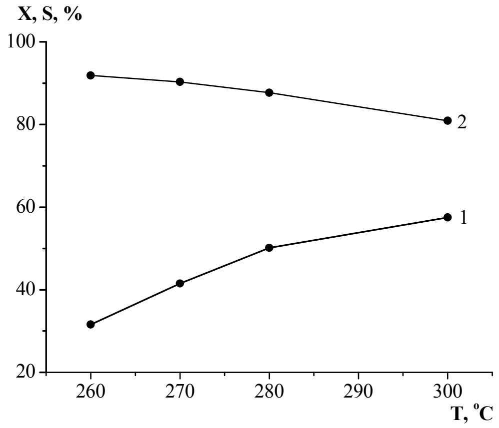


**Fig. 3.** Tetrahydrofurfuryl alcohol conversion (*1*) and δ-valerolactone selectivity (*2*) over Cu/ZnAl-1 at different temperatures (5 mmol THFA $g_{cat}^{-1}$ $h^{-1}$; $H_2$/THFA = 25, mol)

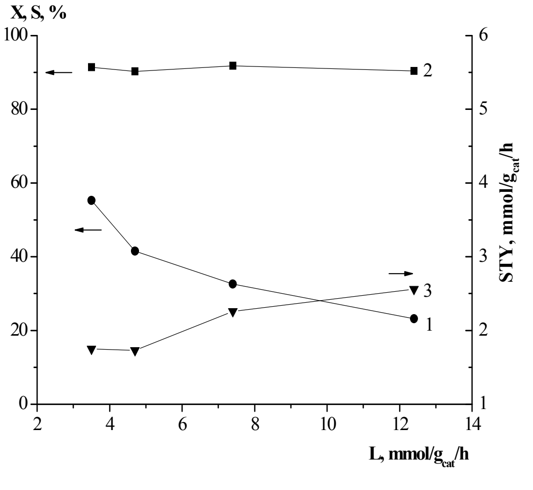


**Fig. 4.** Tetrahydrofurfuryl alcohol conversion (*1*), δ-valerolactone selectivity (*2*) and productivity (*3*) at different loads over Cu/ZnAl-1 catalyst (270 °C, $H_2$/THFA = 25, mol; GHSV = 1950–2130 $h^{-1}$)

As noted above, hydrogen flow promotes stable work of a catalyst during THFA conversion. The performed experiments have shown that at increase of $H_2$/THFA molar ratio from 1 to 25 the conversion can be raised for 10 % (Fig. 5). Under hydrogen flow with $H_2$/THFA = 15 the catalyst loses about 10 % of its activity after 8 h (Fig. 6). The gas hourly space velocity GHSV = 1280 $h^{-1}$ and time of contact of ~3 s correspond to such $H_2$/THFA ratio.

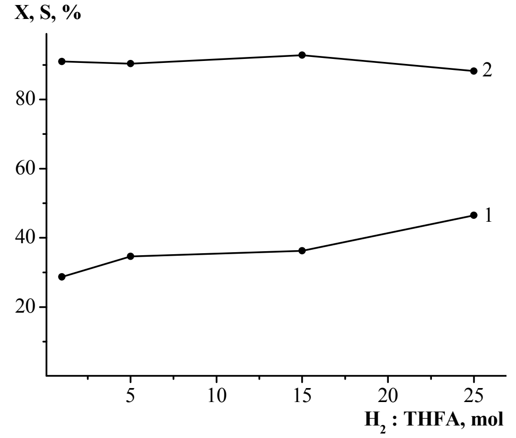


**Fig. 5.** Tetrahydrofurfuryl alcohol conversion (*1*) and δ-valerolactone selectivity (*2*) over Cu/ZnAl-1 at different $H_2$/THFA molar ratios (270 °C; 5 mmol THFA $g_{cat}^{-1}$ $h^{-1}$)

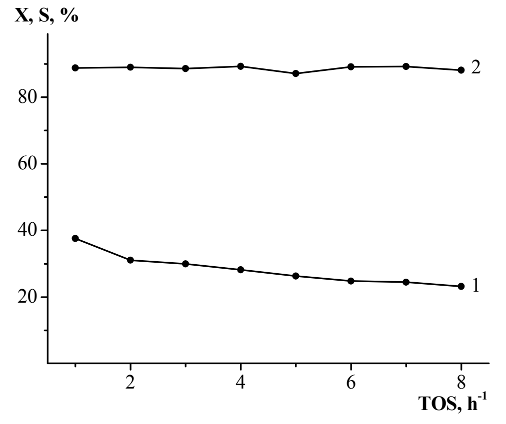
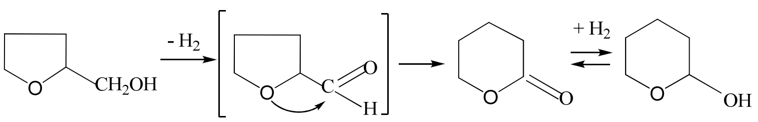


**Fig. 6.** Tetrahydrofurfuryl alcohol conversion (*1*) and δ-valerolactone selectivity (*2*) *vs* time on stream over Cu/ZnAl-1 catalyst (270 °C; 5 mmol THFA $g_{cat}^{-1}$ $h^{-1}$; $H_2$/THFA = 15, mol)

***Route of THFA transformation into δ-valerolactone.*** Authors [24] have supposed that at the first stage of THFA transformation over $Cu/Al_2O_3$ catalyst its rearrangement into 2-hydroxytetrahydropyran, and then δ-valerolactone is formed through dehydrogenation of this cyclic hemiacetal. Really, δ-valerolactone was obtained via the dehydrogenation of preliminarily synthesized 2-hydroxytetrahydropyran on $Cu/Al_2O_3$ catalyst [24]. It is also known [25] that dehydrogenation of THFA proceeds hardly in comparison with other primary alcohols. The rate constant of THFA dehydrogenation was determined as 7.9 mmol $g_{cat}^{-1}$ $h^{-1}$ only, whereas for ethanol $k = 663$ mmol $g_{cat}^{-1}$ $h^{-1}$ at 360 °C over $ZnO\text{-}Cr_2O_3$ catalyst [25].

As known, copper is a classical catalyst of alcohol dehydrogenation. The emission of hydrogen is observed in the desorption mass-spectra of ethanol adsorbed on previously reduced Cu/ZnZrAl sample (Fig. 7 *a*). Peaks of formed hydrogen ($m/e = 2$) as well as acetaldehyde ($m/e = 44$, 29) are recorded at 170 °C (Fig. 7 *a*). The emission of $H_2$ is observed also at 180 °C in the TPR mass-spectrum of THFA adsorbed on reduced Cu/ZnZrAl catalyst (Fig. 7 *b*). So, THFA molecules are dehydrogenated on the Cu-sites. The peaks of 28, 41 and 43 a.u.m., observed at 210 °C, should be assigned to formed intermediate compound (Fig. 7 *b*).

Thus, the key stage of THFA transformation is dehydrogenation into unstable tetrahydrofurfural on the Cu-sites of catalyst. This hypothesis is confirmed by our results (Table 2) and also by data [14], according to them, THFA conversion rises at increasing of Cu content in the catalysts. Further, δ-valerolactone can be formed via the cycle expansion with hydride ion transfer as shown in Scheme 1:



**Scheme 1.** Probable reaction route of tetrahydrofurfuryl alcohol transformation into δ-valerolactone

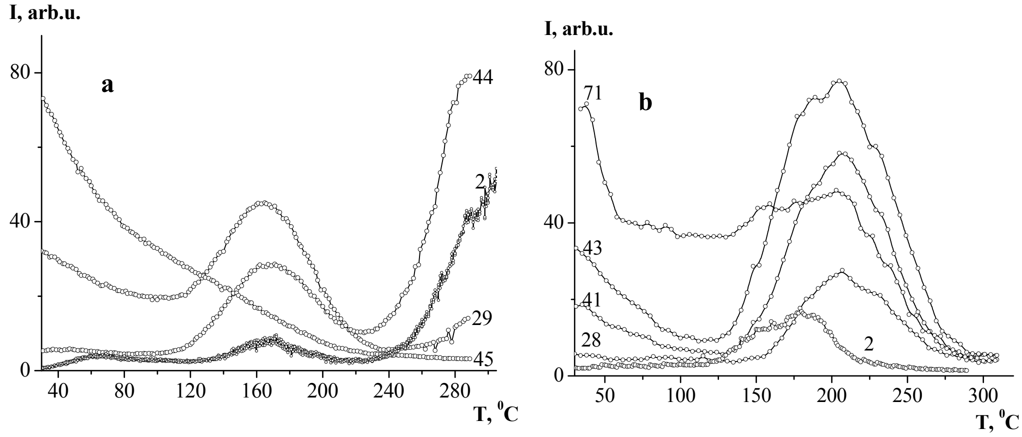


**Fig. 7.** TPR profiles of ethanol (*a*) and THFA (*b*) transformation on Cu/ZnZrAl ($H_2$ – 2 a.u.m.; $C_2H_5OH$ – 45 a.u.m.; $C_2H_4O$ – 44, 29 a.u.m.; tetrahydrofurfuryl alcohol – 71 a.u.m.; intermediate compound – 28, 41 and 43 a.u.m.)

***Amidation of δ-valerolactone: $C_5H_8O_2 + NH_3 = C_5H_9NO + H_2O$.*** Vapour-phase amidation of lactones, in particular δ-valerolactone, is a rather complicated process, which is realized under ammonia, hydrogen and steam flow conditions at 260–280 °C [19, 20]. Therefore at first, we have studied the reaction of more available ε-caprolactone (CLN) with ammonia according to the procedure described in patent [20]. The results on CLN amidation over the Cu-containing oxides are presented in Table 3. Cu/ZnAl-1 catalyst provides the formation of predominantly ε-caprolactam (CLM) at 96–98 % CLN conversion under GHSV = 325–360 $h^{-1}$ (Table 3). Contact time of reagents with the catalyst was about 10 s. It is important to use the molar ratio of ammonia, water and hydrogen to CLN close to 5, 10 and 15, respectively (Table 3). The decrease of $H_2O$/CLN ratio by half leads to lowering both CLN conversion and CLM selectivity from 98 to 93 % and from 65 to 57 %, accordingly (Table 3). The decline of $NH_3$/CLN ratio results in CLM selectivity decreasing, for example, to 10 % at $NH_3$/CLN = 1 for the Cu/ZnAl-1 catalyst (Table 3). Similar result was also obtained by authors [19], when ammonia content in the reaction mixture was decreased. In case of carrying out reaction in the absence of hydrogen flow, ε-caprolactone conversion declines from 96 to 89 % as shown for Cu/ZnAl-2 catalyst (Table 3).

**Table 3.** Effect of catalyst on ε-caprolactone conversion and selectivity towards ε-caprolactam[a]

| Catalyst | GHSV, $h^{-1}$ | Molar ratio | | | *X*, % | *S*, % |
|---|---|---|---|---|---|---|
| | | $NH_3$/CLN | $H_20$/CLN | $H_2$/CLN | | |
| Cu/ZnAl-1 | 325 | 6 | 10 | 15 | 98 | 65 |
| Cu/ZnAl-1 | 360 | 6 | 5 | 22 | 93 | 57 |
| Cu/ZnAl-1 | 180 | 2.5 | 5 | 10 | 97 | 34 |
| Cu/ZnAl-1 | 120 | 1 | 5 | 5 | 97 | 10 |
| Cu/ZnAl-2 | 325 | 5 | 10 | 18 | 96 | 64 |
| Cu/ZnAl-2 | 160 | 5 | 10 | 0 | 89 | 65 |
| Cu/Ti | 325 | 5 | 10 | 15 | 98 | 66 |

[a] Experimental conditions: 260 °C, 0.5 mmol $C_6H_{10}O_2$ $g_{cat}^{-1}$ $h^{-1}$

The time on stream data have shown that $Cu/TiO_2$ catalyst is the most stable, keeping the initial activity during 10 h. Other samples begin to lose their activity after 9 h. The best result on CLN amidation over $Cu/TiO_2$ catalyst was also observed in patent [20].

The obtained results concerning δ-valerolactone amidation over the Cu-containing oxides are presented in Table 4. In the experiments, similar reagents ratios and contact time were kept as for the CLN amidation. However, water and VLN have been fed into a reactor by separate flows, because VLN easily hydrates to 5-hydroxyvaleric acid [26]. Cu/ZnAl-1 catalyst provides the best (80 %) selectivity towards δ-valerolactam with 79 % VLN conversion at 260 °C (Table 4). $Cu/TiO_2$ sample shows 52 % VLM selectivity at 91 % VLN conversion (Table 4). Thus, Cu/ZnAl-1 is a more suitable catalyst for the VLN amidation than $Cu/TiO_2$, which shows the best result for the CLN amidation (Table 3).

**Table 4.** Effect of catalyst on δ-valerolactone conversion and selectivity towards δ-valerolactam[a]

| Catalyst | GHSV, $h^{-1}$ | Molar ratio | | | *X*, % | S, %[b] | | |
|---|---|---|---|---|---|---|---|---|
| | | $NH_3$/VLN | $H_2O$/VLN | $H_2$/VLN | | VLM | 5-HA | NP |
| Cu/ZnAl-1 | 325 | 5 | 10 | 18 | 79 | 80 | 12 | 8 |
| Cu/ZnAl-1 | 350 | 5 | 5 | 22 | 95 | 65 | 0 | 35 |
| Cu/ZnAl-1 | 170 | 1 | 10 | 5 | 100 | 18 | 66 | 16 |
| Cu/Ti | 326 | 5 | 10 | 15 | 91 | 52 | 16 | 32 |
| $Cu/ZrO_2$-$SiO_2$ | 320 | 5 | 6 | 18 | 100 | 9 | 89 | 2 |

[a] Experimental conditions: 260 °C, 0.5 mmol $C_5H_8O_2$ $g_{cat}^{-1}$ $h^{-1}$

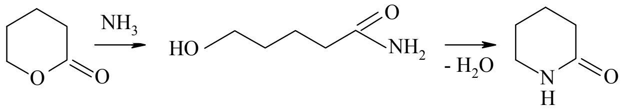
[b] VLM – δ-valerolactam; 5-HA – 5-hydroxypentamide; NP – non specified products

With decreasing molar ratios of water from 10 to 5 and ammonia from 5 to 1, VLM selectivity declines from 80 to 65 % and from 80 to 18 %, respectively (Table 4). The formation of 5-hydroxypentamide on Cu/ZnAl-1 is observed at ammonia deficit (Table 4). This amide is also formed mainly over acidic mixed oxide $Cu/ZrO_2$-$SiO_2$ (Table 4). For the VLN amidation, we observed a 2–3 h period of catalyst load aging as it happened for the CLN amidation reaction.

The VLN conversion and VLM yield increase from 80 to 92 % and from 64 to 74 %, respectively at raising temperature from 250 to 280 °C (Fig. 8). The selectivity towards δ-valerolactam kept on the level of 80 %.

Notice that the data on lactone amidation have been obtained under light load on a catalyst

(0.5 mmol $C_5H_8O_2$ $g_{cat}^{-1}h^{-1}$) because this process includes at least two stages. The presence of 5-hydroxypentamide in reaction products confirms that the process proceeds via the disclosure of lactone cycle with the hydroxyamide formation, followed by the 5-hydroxypentamide condensation, perhaps through its preliminary dehydrogenation to 5-aldehydepentamide on the Cu-sites , as it is presented in the Scheme 2:



**Scheme 2.** Reaction route of δ-valerolactone amidation into δ-valerolactam

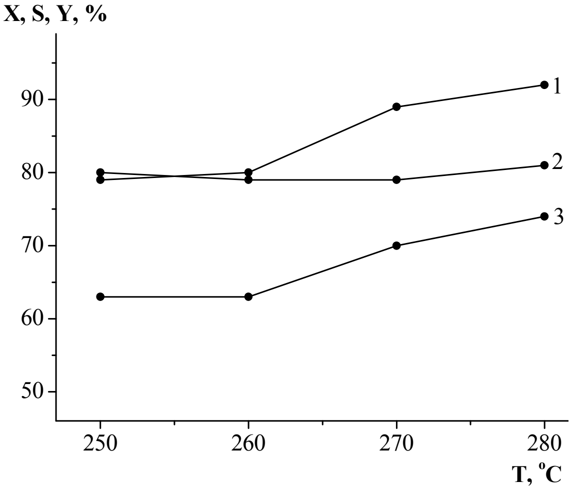


**Fig. 8.** δ-Valerolactone conversion (*1*), selectivity (*2*) and yield (*3*) of δ-valerolactam on Cu/ZnAl-1 at different temperatures (0.5 mmol $C_5H_8O_2$ $g_{cat}^{-1}$ $h^{-1}$)

## CONCLUSIONS

The vapour-phase conversion of THFA producing δ-valerolactone has been investigated over several Cu-containing oxides under hydrogen flow. Co-precipitated Cu/ZnO-$Al_2O_3$ oxide is found as selective catalyst for one-pot THFA dehydrogenation to δ-valerolactone. Cu/ZnAl-1 catalyst containing 40 wt. % of CuO provides 40–50 % THFA conversion with 80–85 % VLN selectivity at 270–280 °C. A reaction pathway from THFA to VLN has been proposed: it is speculated that THFA is initially dehydrogenated into tetrahydrofurfural, which rearranged to VLN.

The vapour-phase amidation of δ-valerolactone with ammonia into δ-valerolactam was studied over several Cu-oxides under steam and hydrogen flow. The high selectivity towards δ-valerolactam of 80 % at 80–90 % lactone conversion was achieved over Cu/ZnAl-1 catalyst at 260–280 °C. However, the lactone amidation is a quite complicated process with low space-time yield of δ-valerolactam at the level of 0.3 mmol $g_{cat}^{-1}$ $h^{-1}$. One-pot THFA dehydrogenation into δ-valerolactone might be more preferred choice for an industry.

# Одностадійний синтез δ-валеролактону з тетрагідрофурфурилового спирту та амідування δ-валеролактону на Cu/ZnO-$Al_2O_3$ каталізаторі

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*Вивчено парофазне перетворення тетрагідрофурфурилового спирту (ТГФС) у δ-валеролактон на Cu-оксидах при 260–300 °С. Знайдено, що Cu/ZnO-$Al_2O_3$ каталізатор забезпечує пряме дегідрування ТГФС до δ-валеролактону при 270–280 °С. Пропонується схема перетворення тетрагідрофурфурилового спирту: спочатку ТГФС дегідрується до тетрагідрофурфурилового альдегіду, який далі перегруповується в δ-валеролактон. Досліджено також парофазне амідування δ-валеролактону амоніаком у δ-валеролактам в потоці водню та водяної пари на Cu-оксидах при 250–280 °С. Показано, що 80 % селективність за δ-валеролактамом при 80–90 % конверсії лактону досягається на Cu/ZnO-$Al_2O_3$ каталізаторі при 260–280 °С.*

***Ключові слова**: каталітичне дегідрування, тетрагідрофурфуриловий спирт, δ-валеролактон, δ-валеролактам, Cu-каталізатор*

# Одностадийный синтез δ-валеролактона из тетрагидрофурфурилового спирта и амидирование δ-валеролактона на Cu/ZnO-$Al_2O_3$ катализаторе

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*Изучено парофазное превращение тетрагидрофурфурилового спирта (ТГФС) в δ-валеролактон на Cu-оксидах при 260–300 °С. Обнаружено, что Cu/ZnO-$Al_2O_3$ катализатор обеспечивает прямое дегидрирование ТГФС до δ-валеролактона при 270–280 °С. Предлагается схема превращения тетрагидрофурфурилового спирта: сначала ТГФС дегидрируется до тетрагидрофурфурилового альдегида, который далее перегруппировывается в δ-валеролактон. Исследовано также парофазное амидирование δ-валеролактона аммиаком в δ-валеролактам в потоке водорода и паров воды на Cu-оксидах при 250–280 °С. Показано, что 80 % селективность по δ-валеролактаму при 80–90 % конверсии лактона достигается на Cu/ZnO-$Al_2O_3$ катализаторе при 260–280 °С.*

***Ключевые слова**: каталитическое дегидрирование, тетрагидрофурфуриловый спирт, δ-валеролактон, δ-валеролактам, Cu-катализатор*

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