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Vapor-phase oxidation of ethylene glycol methanolic solution into methyl glycolate over CuO-containing catalysts

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The gas-phase oxidation of ethylene glycol and methanol mixture into methyl glycolate $C_2H_6O_2+CH_3OH+O_2 = C_3H_6O_3+2H_2O$ over synthesized copper-containing catalysts was studied. Methyl glycolate can be considered as raw material for obtaining biodegradable polyglycolide. The CuO-containing samples were synthesized by impregnation of granular oxide-supports (γ-Al_2O_3, SiO_2 and MgO-ZrO_2) with the calculated amount of aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ followed by heat treatment at 400 °C. In such way the supported CuO-Me_xO_y /Al_2O_3 (Me = Mg, Ti, Cr, Co, Zn, Zr, Ag) samples have been prepared. Catalytic experiments were performed in a stainless-steel flow reactor with a fixed bed of catalyst at 200-270 °C and atmospheric pressure. Oxygen of air was used as an oxidant. The reaction products were analyzed using ^{13}C NMR spectroscopy and gas chromatography. It was found that CuO/Al_2O_3 catalyst provides ~ 100% ethylene glycol conversion with 56% selectivity towards methyl glycolate at 220 °C. The main by-products are methoxymethanol, 1,1-dimethoxymethane, methyl methoxyacetate, and methyl formate. Use of silica as catalyst support leads to a significant decrease of the ethylene glycol conversion to 57 % for CuO/SiO_2, but methyl glycolate selectivity does not change significantly. Promotion of CuO/Al_2O_3 with MgO increases methyl glycolate yield to 64%. According to the scheme of ethylene glycol sequential oxidation the increase in selectivity for methyl glycolate over CuO-MgO/Al_2O_3 catalyst is caused by the basic sites that promote intramolecular Cannizzaro rearrangement of the intermediate reaction product – glyoxal hemiacetal to methyl glycolate. It's found that mixed CuO-CrO_3 oxide supported by γ-Al_2O_3 provides 80 % methyl glycolate selectivity with 95-100% ethylene glycol conversion at 200-210 °C.

Keywords: methyl glycolate, ethylene glycol, copper-containing catalysts, gas-phase oxidation

Introduction

Methyl glycolate (MG) - hydroxyacetic acid methyl ester can be considered as raw material for obtaining biodegradable polyglycolide [1,2]. The two-step synthesis of MG by the carbonylation of formaldehyde (24 MPa) in the presence of water and acid catalysts (Nafion NR-50 or $H_3PW_{12}O_{40}$) to obtain at first glycolic acid and then its following esterification with methyl alcohol was described in [3,4]. Condensation of formaldehyde and methyl formate to methyl glycolate using heteropolyacids was proposed by authors [5]. In [6] p-toluenesulfonic acid as a catalyst was used for this condensation. The reaction was carried out in an autoclave at 140 °C, with a molar ratio of formaldehyde/methyl formate = 0.65. The source of formaldehyde was trioxane. After reaction time of 3 h MG yield was 31% [6].

MG can be obtained by the vapor-phase selective hydrogenation of dimethyl oxalate using Ag/SiO_2, Ag/SBA-15, Ag/AC-N-3, Cu/RGO and others catalysts [7-13]. It should be noted that this method provides enough high selectivity for methyl glycolate (96-99%). However, the low (0.4 vol. %) content of dimethyl oxalate in the initial vapor-gas mixture causes low productivity of the catalyst (about 0.02 g of MG/L_{cat}/h) [12].

The authors of [14] synthesized methyl glycolate from the glyoxal (40% aqueous solution) and methanol at 180°C for 0.5h in an autoclave using $Al(NO_3)_3$ $9H_2O$, $AlCl_3 \cdot 9H_2O$ and $ZrOCl_2 \cdot 2H_2O$. The MG yield was in the interval of 85–87mol%. According to [15], the MG synthesis was carried out by oxidation of mannose and glucose in methanol at 100–120°C/1 MPa oxygen in the presence of MoO_3 and Au/TiO_2. The maximum methyl glycolate yield of 39mol% was achieved for mannose at 120 °C for 4 h. Authors [16] described the liquid-phase oxidation of propylene glycol-methanol mixture in autoclave under 3 MPa O_2 pressure at 100°C. The supported Au/oxides were used. On Au/ZnO the MG selectivity achieved 94 mol% at low 18% ethylene glycol conversion.

In this paper the results on vapor-phase oxidation of ethylene glycol in the presence of methanol vapour into methyl glycolate over supported copper-containing catalysts are presented.

Experiment

Preparation of catalyst

The samples of Cu-containing oxides were synthesized by impregnation of granular oxide-support (fraction 0.5 – 2 mm) with calculated amount of aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$. In such way the samples of $CuO\text{-}Me_xO_y/Al_2O_3$ (Me = Mg, Ti, Cr, Co, Zn, Zr, Ag) have been prepared using a compatible solution of copper nitrate with the corresponding metal salt: $Mg(NO_3)_2{\cdot}6H_2O$, $TiCl_4$, $(NH_4)_2Cr_2O_7$, $Co(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $ZrO(NO_3)_2{\cdot}5H_2O$, $AgNO_3$. The need solution volume was determined by moisture absorption, as rule, 0.6 cm^3 of solution on 1 g of Al_2O_3 was used. Then samples were dried at 120 °C and calcined at 400 °C for 4 h. As oxide-supports were used $\gamma\text{-}Al_2O_3$ (Ukraine, $S_{BET} = 280$ m^2/g, $r_{av} = 5.3$ nm, $V_\Sigma = 0.82$ cm^3/g, $H_0 \leq +3.3$, $C_{acid\ site} = 1.1 \pm 0.05$ mmol/g), SiO_2 (silica gel, China, $S_{BET} = 380$ m^2/g, $r_{av} = 4.9$ nm, $V_p = 0.97$ cm^3/g, $H_0 = +1.5$, $C_{acid\ site} = 1.2 \pm 0.05$ mmol/g) and mixed magnesium and zirconium oxide (atomic ratio Mg: Zr = 7.5: 1, $S_{BET} = 70$ m^2/g, $r_{av} = 7.3$ nm, $V_\Sigma = 0.25$ cm^3/g, $H\_ \leq +27.0$, $C_{basic\ site} = 0.8 \pm 0.05$ mmol/g). The $MgO\text{-}ZrO_2$ support was synthesized by co-precipitation from Mg $(NO_3)_2$ and $ZrO(NO_3)_2$ solutions according to [18]. A sample marked $40CuO/Al_2O_3$ means that the sample contains 40 wt.% CuO concerning to Al_2O_3.

The textural parameters of samples were determined from the N_2 adsorption-desorption isotherms by BET method (Quantachrome Nova 2200e Surface Area and Pore Size Analyzer). The X-ray powder diffraction analysis of obtained samples was performed with a DRON-4-07 diffractometer (CuKα).

Catalytic test

Methanol (Merk) and ethylene glycol (chemical purity) were used. Catalytic experiments were performed in a stainless-steel flow reactor (8 mm inner diameter) with a fixed bed of catalyst (3 cm^3) at 200-270°C and atmospheric pressure. Oxygen of air use as oxidant. 20% methanol solution of ethylene glycol was fed into the evaporator using an Orion M-361 syringe pump. At that in evaporator need air flow was fed also. The heated vapor-gas mixture flowed through the reactor at space velocity GHSV= 320–1250 h^{-1} that corresponded to contact time τ= 3–11 s. The molar ratio of ethylene glycol: oxygen was 1: 1.5. The load on a catalyst was varied from 0.9 to 3.5 mmol EG/cm^3_{cat} /h. The reaction products were condensed in an ice-cooled receiver and analyzed using ^{13}C NMR spectroscopy (Bruker Avance-400) and gas chromatography (Agilent 7820A). The conversion (X) of ethylene glycol and selectivity (S) of products were calculated in wt.% from chromatograms.

Results and Discussion

The nitrogen adsorption-desorption isotherms for studied oxides belong to type IV as it's shown for $40CuO/Al_2O_3$ (Fig. 1). The isotherm is characterized by a wide hysteresis loop in the range of relative N_2 pressure 0.4–0.9, which indicates on a substantial part of mesopores in the Al_2O_3 support. The calculated pore size distribution confirms this fact also (Fig. 1). The calculated from the adsorption-desorption isotherm values of S_{BET}, V_Σ and r_{av} for $40CuO/Al_2O_3$ are equal to 160 m^2/g, 0.42 cm^3/g and 5.4 nm respectively. It should be noted, that the specific surface area and pore volume of the supported oxides become almost half smaller as to the initial $\gamma\text{-}Al_2O_3$ due to filling alumina pores with CuO supported.

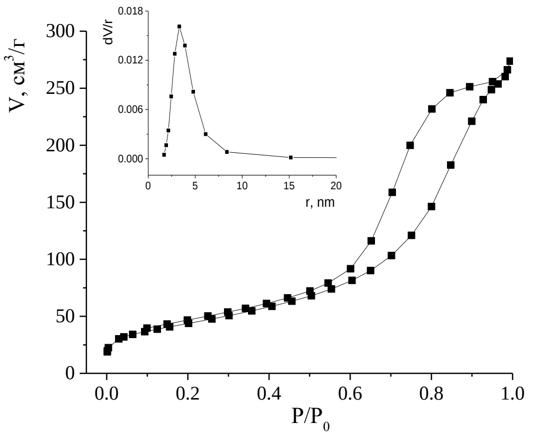


Fig. 1. Nitrogen adsorption–desorption isotherm and pore-size-distribution plot for $40CuO/Al_2O_3$ catalyst

According to XRD analysis of $40CuO/Al_2O_3$, CuO supported is in the crystalline state. The peaks at 2θ = 32.5, 35.5, 38.7, 48.7, 53.5, 58.2, 61.5, 66.2, 68.1, 71.7 and 75.5° on XRD pattern of the sample (Fig. 2) are correspond to the CuO phase (JCPDS). The average calculated crystallite size of CuO, determined by the peak (202) at 2θ = 48.7°, is 22–24 nm.

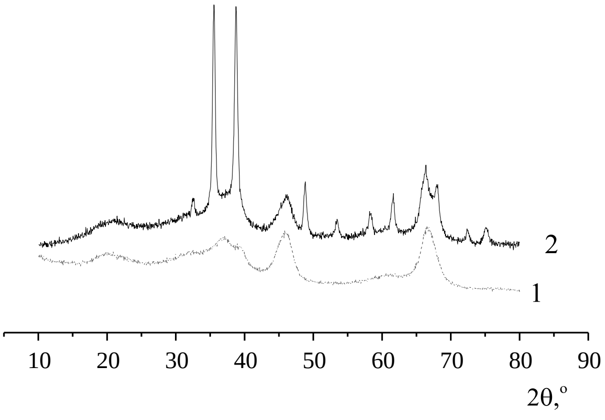


Fig. 2. XRD patterns of $\gamma\text{-}Al_2O_3$ (1) and $40CuO/Al_2O_3$ (2)

The EG conversion and MG selectivity values at different temperatures for $40CuO/Al_2O_3$ catalyst are presented in Fig. 3. The conversion of ethylene glycol at 210–240°C is at the level of 98–100%. Selectivity towards methyl glycolate has maximum of 56% at 220°C (Fig. 3).

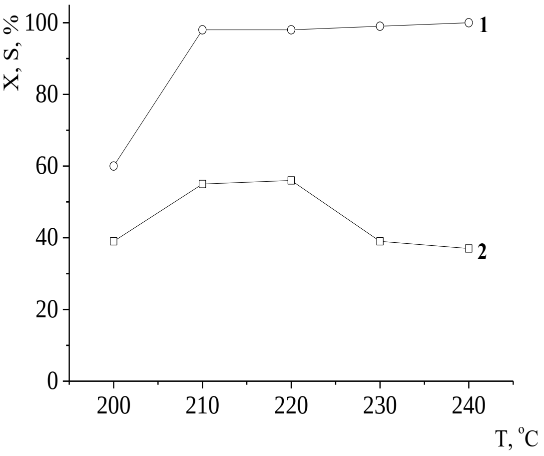


Fig. 3. Ethylene glycol conversion (1) and methyl glycolate selectivity (2) on $40CuO/Al_2O_3$ catalyst at different temperatures (L = 1.6 mmol $EG/cm^3_{cat}/h$)

With increasing the load on $40CuO/Al_2O_3$ catalyst from 1.6 to 3.5 mmol $EG/cm^3_{cat}/h$, ethylene glycol conversion decreases from 98 to 75% (Fig. 4). The selectivity for methyl glycolate is 56–58% at load ranges from 1.6 to 2.5 mmol $EG/ml_{cat}/h$, but at L = 3.5 mmol $EG/ml_{cat}/h$ the selectivity decreases to 47% (Fig. 4).

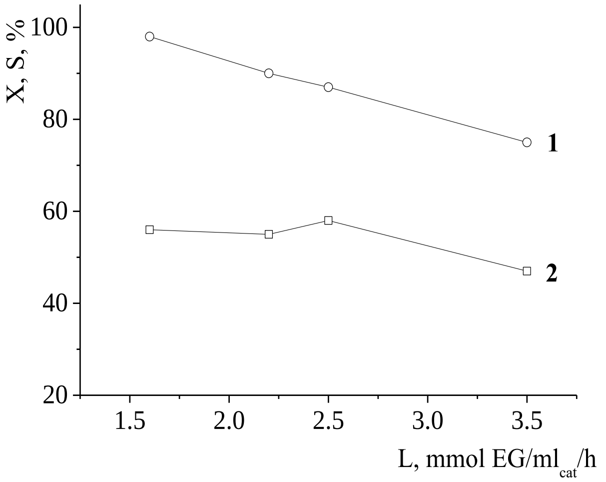


Fig. 4. Ethylene glycol conversion (1) and methyl glycolate selectivity (2) on $40CuO/Al_2O_3$ at different loads on catalyst (220 °C)

Therefore, the optimal temperature and load on catalyst, that provide the highest 55% methyl glycolate yield on $40CuO/Al_2O_3$ catalyst, are 220°C and 1.6 mmol $EG/ml_{cat}/h$, respectively.

The values of EG conversion and MG selectivity for $40CuO/Al_2O_3$ catalyst do not change significantly for at least 12 hours' reaction (Fig. 5). It should be noted that initially, during 1-2 h, the catalyst provides only 20-40% of MG selectivity. After 3 h work of catalyst, the selectivity reaches ~55% and remains constant (Fig. 5).

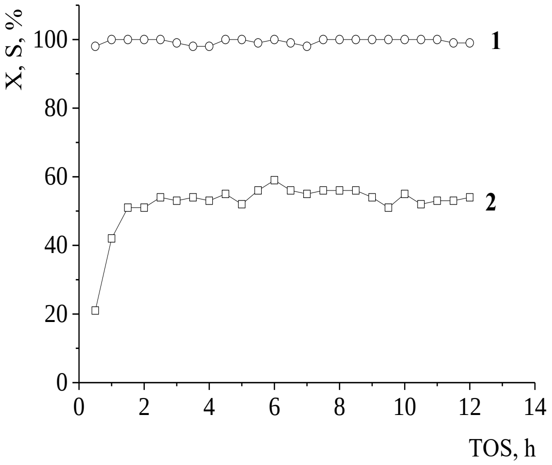


Fig. 5. Ethylene glycol conversion (1) and methyl glycolate selectivity (2) with time on stream on $40CuO/Al_2O_3$ (220°C, 1.6 mmol $EG/cm^3_{cat}/h$).

In order to improve the methyl glycolate selectivity, the ethylene glycol oxidation, the CuO/Al_2O_3 catalyst was promoted with magnesium, titanium, chromium, cobalt, zinc, zirconium, silver oxides. Also, the CuO/SiO_2, CuO-MgO/SiO_2, CuO/MgO-ZrO_2, CuO-ZnO-ZrO_2-Al_2O_3 and CuO-ZnO-Al_2O_3 (catalyst for methanol synthesis) were tested in this reaction. The results are presented in Table 1.

The addition of zirconium, zinc or magnesium oxides to copper oxide on γ-Al_2O_3 ($20CuO$-$10ZnO/Al_2O_3$, $20CuO$-$20ZrO_2/Al_2O_3$, $20CuO$-$2.5MgO/Al_2O_3$ samples) increases the methyl glycolate yield by 5–9 % compared with $40CuO/Al_2O_3$. Other tested samples provide the target product yield at the level of 13–58 % (Table 1). It can be noted that methyl glycolate selectivity is sufficiently high on CuO/MgO-ZrO_2 (74 %), CuO-ZnO-ZrO_2-Al_2O_3 (76 %) and $20CuO$-$10MgO/Al_2O_3$ (77 %) oxides, however, the ethy- lene glycol conversion is much less than that over other samples (Table 1).

The using of silica as catalyst support leads to a significant decrease of the ethylene glycol conversion from 98 % for $40CuO/Al_2O_3$ to 57 % for $40CuO/SiO_2$ while the methyl glycolate selectivity does not change significantly (Table 1). A similar situation is observed when comparing of $20CuO$-$5MgO/Al_2O_3$ and $20CuO$-$5MgO/SiO_2$ samples (Table 1). Methyl glycolate yield of 64 % is observed on CuO-MgO/Al_2O_3 catalyst containing 20 wt. % of CuO and 2.5 wt. % of MgO at 220C (Table 1).

In Table 2 are presented the contents of EG oxidation products (without methanol) on three suitable catalysts.

Table 1 **Ethylene glycol oxidation over CuO-containing catalysts** [1]

Catalyst	X_{EG}, %	S_{MG}, wt. %	Y_{MG}, wt. %
$40CuO/Al_2O_3$	98	56	55
$45CuO$-$0.44Ag_2O/Al_2O_3$	96	55	53
$20CuO$-$10ZnO/Al_2O_3$	90	67	60
$15CuO$-$30ZrO_2/Al_2O_3$	95	52	49
$20CuO$-$20ZrO_2/Al_2O_3$	99	64	63
$20CuO$-$15ZrO_2/Al_2O_3$	96	57	55
$20CuO$-$12TiO_2/Al_2O_3$	96	46	44
$15CuO$-$1.5Co_3O_4/Al_2O_3$	82	46	38
$20CuO$-$1.5MgO/Al_2O_3$	89	66	59
$20CuO$-$2.5MgO/Al_2O_3$	90	71	64
$20CuO$-$5MgO/Al_2O_3$	81	72	58
$20CuO$-$10MgO/Al_2O_3$	59	77	45
CuO-ZnO-ZrO_2-Al_2O_3	63	76	48
CuO-ZnO-Al_2O_3	50	25	13
$40CuO/SiO_2$	57	54	31
$20CuO$-$5MgO/SiO_2$	65	63	41
$35CuO/MgO$-ZrO_2	24	74	18

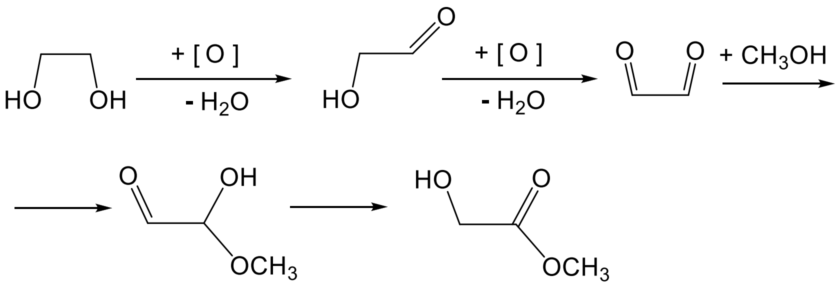
[1] *Reaction conditions*: 20 wt. % EG methanol solution, T = 220°C, L = 1.6 mmol EG/ml_{cat}/h, molar ratio EG : O_2 = 1 : 1.5.

Table 2. **Product content of ethylene glycol conversion** [1]

Catalyst	Content of reaction products, mol. % [2]							X_{EG}, %	S_{MG}, mol. %
	EG	**MG**	MA	MF	MM	DMM	ME		
$40CuO/Al_2O_3$	1	**65**	4	13	8	2	7	99	66
CuO-ZnO-ZrO_2-Al_2O_3	42	**51**	2	0	5	0	0	58	88
$20CuO$-$5MgO/Al_2O_3$	18	**50**	0	6	20	0	6	82	60

[1] Reaction conditions: 20 wt. % EG methanol solution, 220°C, 1.6 mmol EG/ml_{cat}/h, molar ratio EG : O_2 = 1 : 1.5; [2] EG – ethylene glycol, MG – methyl glycolate, MA – methyl methoxyacetate, MF – methyl formate, MM – methoxymethanol, DMM – 1,1-dimethoxymethane, ME-1-methoxyethanol

Sequential oxidation of propylene glycol to methyl glycolate is described by sum reaction $C_2H_6O_2$ + CH_3OH + O_2 = $C_3H_6O_3$ + $2H_2O$ and includes at least three stages. In opinion authors [16], ethylene glycol is oxidized on the Au/ZnO catalyst initially to glycolaldehyde that forms the hemiacetal with methanol. Next, this hemiacetal is oxidized to methyl glycolate. According to another scheme, proposed for the propylene glycol and glycerol oxidative esterification into alkyl lactates [18, 19], the EG converting to MG could be include the sequential oxidation to glyoxal via glycolic aldehyde, the formation of glyoxal hemiacetal with methanol. Then the hemiacetal rearrangements into MG by Cannizzaro on basic sites of catalyst:



The process follows Mars - van Krevelen's scheme, that the oxidant is atomic oxygen of copper oxide lattice: $2CuO = Cu_2O + O$. Copper oxide (I) is oxidized to CuO by air oxygen. The increase of methyl glycolate yield on basic $CuO\text{-}MgO/Al_2O_3$ catalyst, and twice decreasing one on $CuO\text{-}MgO/SiO_2$ with more acidic support – silica, confirms the Cannizzaro intermolecular rearrangement (Table 1).

The by-products of studied EG oxidation are methyl methoxyacetate, methyl formate, hemi- and full acetals of formaldehyde and acetaldehyde with methanol (methoxymethanol, 1,1-dimethoxymethane, 1-methoxyethanol, 1,1-dimethoxyethane). It should be noted that methyl formate, methoxymethanol and 1,1-dimethoxymethane are formed from formaldehyde, producing by aldol decondensation of glycolaldehyde. According to the calculations using Aspen HYSYS program of equilibrium $OHCH_2CHO \leftrightarrow 2HCHO$, the formaldehyde content may be 36 mol. % at 240 °C. That is, the reaction rate of glycolaldehyde de-condensation competes with its oxidation into glyoxal. The acetaldehyde is formed at dehydration of ethylene glycol.

At testing various supported oxides in the TPR oxidation of cyclohexanol to cyclohexane, we have found a promising $CuO\text{-}CrO_3/Al_2O_3$ sample that catalyzes the oxidation without cyclohexanol dehydration to cyclohexene in fact [20]. This sample turned out to be active and selective in studied EG oxidation: 80% methyl glycolate selectivity is observed at 200^0C with 100% ethylene glycol conversion. Also, $CuO\text{-}CrO_3/Al_2O_3$ catalyst provides 95-100% ethylene glycol conversion at higher load on a catalyst, up to 2.3 mmol EG/cm^3_{cat}/h, in comparison with other studied samples (Fig. 6).

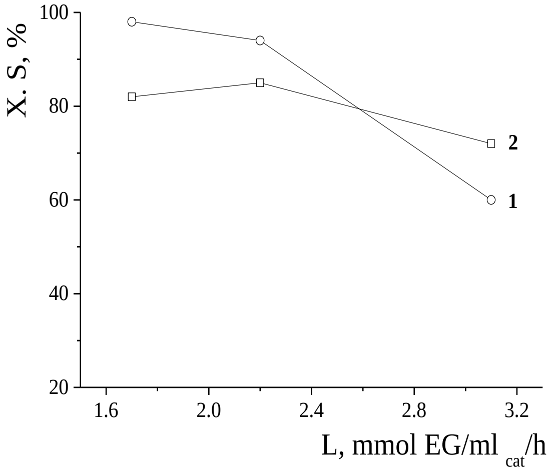


Fig. 6. Ethylene glycol conversion (1) and methyl glycolate selectivity (2) on $CuO\text{-}CrO_3/Al_2O_3$ catalyst at different loads on catalyst (200 C)

Conclusion

Thus, it's found that mixed $CuO\text{-}CrO_3$ oxide supported by $\gamma\text{-}Al_2O_3$ may be a suitable catalyst for the vapor-phase ethylene glycol oxidative esterification with methanol into methyl glycolate at $200\text{-}210^0C$. The catalyst provides 80 % methyl glycolate selectivity with 95-100% ethylene glycol conversion at loads on the catalyst up to 2.3 mmol EG/cm^3_{cat}/h.

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Парофазне окиснення метанольного розчину етиленгліколю до метилгліколату на мідьвмісних каталізаторах

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В роботі наведено результати парофазного окиснення етиленгліколю в метанолі $C_2H_6O_2+CH_3OH+O_2 = C_3H_6O_3+2H_2O$ на оксидних мідьвмісних каталізаторах в проточному реакторі для одержання метилгліколату. Метилгліколат можна розглядати як сировину для одержання гліколіду – мономеру для виробництва біодеструктуючого полігліколіду. Зразки нанесених мідьвмісних каталізаторів синтезували просочуванням гранул вибраного оксиду-носія (γ-Al_2O_3, SiO_2 та MgO-ZrO_2) розрахованою кількістю водного розчину $Cu(NO_3)_2 \cdot 3H_2O$, а для зразків CuO-Me_xO_y/Al_2O_3 (Me = Mg, Ti, Cr, Co, Zn, Zr, Ag) сумісним розчином нітрату міді з сіллю відповідного металу з наступною термообробкою для утворення нанесеної оксидної фази. Каталітичні експерименти здійснювали в проточному реакторі з нерухомим шаром каталізатору за температур 200–270 °C і атмосферного тиску. Окиснювачем слугував кисень повітря. Продукти реакції аналізували з використанням ^{13}C ЯМР спектроскопії та газової хроматографії. Виявлено, що CuO/Al_2O_3 каталізатор забезпечує майже 100 % конверсію етиленгліколю із 56% селективністю за метилгліколатом при 220°C. Основними побічними продуктами окиснення етиленгліколю є метоксиметанол, 1.1-диметоксиметан, метилметоксиацетат та метилформіат. Використання кремнезему як оксиду-носія призводить до значного зниження конверсії етиленгліколю (57 % для CuO/SiO_2 каталізатора), тоді як селективність за метилгліколатом істотно не змінюється. Введення до складу CuO/Al_2O_3 каталізатора оксидів цирконію, цинку і магнію сприяє перебігу цільової реакції. Встановлено, що найбільший вихід метилгліколату - 64 % з 90 % конверсією етиленгліколю спостерігається на CuO-MgO/Al_2O_3, що містить 20 мас. % оксиду міді і 2.5 мас. % оксиду магнію. Згідно наведеної схеми послідовного окислення етиленгліколю збільшення селективності за метилгліколатом на CuO-MgO/Al_2O_3 каталізаторі зумовлюють основні центри, які сприяють внутрішньомолекулярному перегрупуванню Канніццаро проміжного продукту реакції – напівацеталю гліоксалю у метилгліколат. Знайдено, що змішаний CuO-CrO_3 оксид, нанесений на γ-Al_2O_3, забезпечує 80 % селективність за метилгліколатом при 95-100% конверсії етиленгліколю за температур 200-210 °C.

Ключові слова : метилгліколат, етиленгліколь, мідьвмісні каталізатори, газо-фазне окиснення