CATALYTIC SYNTHESIS OF METHYL GLYCOLATE FROM GLYOXAL METHANOL SOLUTION OVER BASE CATALYSTS

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Abstract. The process of obtaining methyl glycolate from a methanolic solution of glyoxal over solid basic catalysts based on mixed oxides of magnesium, zirconium, and aluminum has been studied. According to obtained results, the selectivity of the methyl glycolate formation increases with increasing the basicity of the catalyst. The most selective coprecipitated $MgO\text{-}ZrO_2$ provides almost 100 % methyl glycolate yield. The supported $MgO\text{-}ZrO_2/Al_2O_3$ gives to 95 % yield of methyl glycolate with the formation of the glyoxal dimethyl acetal as a by-product. This catalyst could be reused several consecutive cycles without the need for intermediate regeneration. Methyl glycolate in a high 93 % yield can be obtained at 453 K over this solid catalyst in flow mode, which may be of practical interest.

Keywords: methyl glycolate, glyoxal, solid basic catalysts, mixed oxides of magnesium and zirconium.

1. Introduction

Methyl glycolate (MG) – methyl ester of glycolic (hydroxy acetic) acid – is a good solvent and an important chemical intermediate for the chemical and pharmaceutical industries. The hydrolysis of methyl glycolate is a promising way to produce high purity glycolic acid (GA).[1] GA is practically non-toxic to humans, has bactericidal properties which makes it widely used in cosmetics and pharmaceuticals.[2,3] Methyl glycolate can be a precursor for obtaining glycolide[4] – an important monomer for the production of biodegradable and biocompatible poly-glycolide (PGA) and its copolymers which are widely used in medicine.[5-7] PGA-based plastic has good oxygen barrier properties, rigidity, heat resistance, and biodegra-dability.[8,9] The use of PGA as an environmentally friendly packaging material is limited by its high cost, but the demand for polyglycolic acid is growing annually by about 10 %.[9]

MG can be obtained by esterification of glycolic acid with methanol.[10] However, to achieve a high product yield it is necessary to remove the formed water by reactive distillation which requires appropriate technical equipment.[10] Also, MG was synthesized by the carbonylation of formaldehyde using heteropolyacids[11] as catalysts, followed by esterification with methanol. To achieve a high yield of MG (89 %) the use of polar solvents (sulfolane) is required.[11] Known methods of obtaining MG are gas-phase hydrogenation of dimethyl oxalate over several Ag- and Cu-based catalysts[12-14] and oxidative esterification of ethylene glycol in methanol on Au-based catalyst.[15,16] However, the main disadvantage of these methods is the difficulty of providing high selectivity methyl glycolate and the high cost of Ag and Au-containing catalysts.

MG can be synthesized using a methanol solution of glyoxal (GLY) (ethanedial, $C_2H_2O_2$) – a low-toxic, affordable multi-tonnage product, which is produced in the industry from acetaldehyde or ethylene glycol[17] and is a by-product (2–3 %) of lignocellulose pyrolysis.[18]

The authors[19] studied the glyoxal conversion into glycolic acid methyl ester using salts of multivalent metals (Al, Zr, Cu, Ni, Fe, Co, Cr, Pb, Mn, Ce, La, Zn, Cd, and Mg) as catalysts. They determined that catalysts containing Al^{3+} and ZrO^{2+} ions were the most active and selective. Nitrates and chlorides of these metals provided 100 % conversion of glyoxal with a selectivity of 85–87 % for methyl glycolate at 453 K. However, a dis-advantage of the above process is the difficulty of purification of the target product from homogeneous catalysts. The authors[20] studied the conversion of alcoholic solutions of glyoxal (5 %) over various heterogeneous catalysts: Amberlyst-15, industrial USY zeolites (CBV300, CBV500, CBV600, CBV712, CBV720, CBV760, and CBV780) as well as Ti-MFI, Sn-MFI, MFI-ATSn, CBV720-ATGa which were synthesized by the authors. The best results were obtained over hydrothermally synthesized tin-containing zeolite Sn-MFI, which provided up to 83 % of methyl glycolate yield. However, a rather long (6–18 hours) reaction time and using low concentration (5 %) glyoxal solutions are necessary to achieve this result.

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Therefore, the development of effective catalysts and the search for optimal conditions obtaining methyl glycolate remains an actual task. The process of obtaining glycolic acid and its methyl ester from glyoxal over several solid acids and basic catalysts based on mixed oxides of aluminum, tin, titanium, zirconium, and magnesium we investigated in our previous work.[21] It was found that the yield of methyl glycolate over the studied basic catalysts was much higher (89 %) than over acid catalysts (29 %) after 3 h of the reaction at 373 K. The most effective was the $MgO\text{-}ZrO_2$ catalyst, which provided practically 100 % yield of methyl glycolate (1 h of the reaction at 423 K).

In this work, we have used several $MgO\text{-}ZrO_2$ catalysts for glyoxal conversion into methyl glycolate.

2. Experimental

2.1. Catalyst synthesis

Mixed oxides catalysts were synthesized *via* two methods: by calcination of hydroxides obtained by coprecipitation from solutions of the corresponding salts and by impregnation of commercial granulated $\gamma\text{-}Al_2O_3$ (Alvigo) as support with appropriate salt solutions followed by heat treatment to form the deposited oxide phase.

According to the first method, magnesium nitrate $(Mg(NO_3)_2 \cdot 6H_2O)$ and zirconium(IV) oxynitrate $(ZrO(NO_3)_2 \cdot H_2O)$ were dissolved in deionized water and ammonia water was added to the mixed solution under stirring until the pH value reached 10.0. The obtained precipitate of hydroxides was aged for 20 h at 353 K, filtered, washed with distilled water (to $pH \approx 7$ of the filtrate), and extruded in the wet state through a hole with a diameter of 2 mm. Then wet granules were dried (383 K) and calcined for 2 hours at 873 K.

The supported samples with a different oxides content (from 5 to 20 wt %) were synthesized by impregnation of granular aluminum oxide (fraction of $0.5 - 2$ mm) with calculated amounts of aqueous solutions of magnesium and zirconium nitrates. The volume of the latter was determined experimentally (by moisture absorption). Then, the samples were dried at 383 K and calcined at 873 K, 2 h (a heating rate was 5°/min). They were designated as $x(MgO\text{-}ZrO_2)/Al_2O_3$ where the x in the sample designation corresponds to supported oxide content in wt%.

The highest strength of base and acid sites of oxides was determined using the Hammett indicators method (Aldrich).[22] The total content of base or acid sites was determined by reverse titration of 2,4-dinitrophenol or *n*-butylamine, adsorbed on the sample surface, with 0.05 M solution KOH or HCl, respectively, in the presence of bromothymol blue as an indicator. The computational error for content sites determination is 0.05 mmol/g.

The crystal structure of the synthesized samples was studied by X-ray powder diffraction (XRD) using DRON-4-07 diffractometer with CuK α radiation. Diffraction patterns were identified by comparing them with those from the JCPDS (Joint Committee of Powder Diffraction Standards) database.

The porous structure of the samples was studied using the nitrogen adsorption-desorption technique (Quantachrome Nova 2200e Surface Area and Pore Size Analyser). The specific surface area (S), total pore volume (V_Σ), mesopore volume (V_{me}), average pore radius (R_{av}), and mesopore radius (r_{me}) of the samples were calculated from the adsorption-desorption isotherms of nitrogen using the BET and BJH methods, respectively. The pore size distribution (PSD) curves were plotted using the desorption branches of the isotherms.

2.2. Catalytic tests

The starting materials for catalytic studies were methanol (99 %, Merck) and glyoxal in the form of an anhydrous trimer (Sigma-Aldrich, 95 %) or 40 % aqueous solution (commercially available).

Batch catalytic tests were performed under autogenous pressure in rotated steel autoclave (60 rpm) with Teflon liners (25 mL) for 0.5–5 hours at 373–453 K. Usually, 8.0 g of 20 wt % glyoxal solution in methanol (prepared from anhydrous glyoxal trimer) and 0.64 g (8 wt %) of a catalyst were placed into the reactor. The mixture was allowed to react under stirring for 30 min to 1 h. Then, the reaction was quenched using an ice bath and the catalyst was removed using a paper filter.

Catalytic experiments were also performed in flow mode. A fixed-bed stainless-steel reactor with 8 mm inner diameter and 160 mm length was used. As rule, 3 cm³ (1.6 g) of catalyst was charged into the reactor. 15 wt % methanol solution of glyoxal was prepared from 40 % glyoxal aqueous solution. Previously the latter was concentrated by distilling water at 313 K and under residual pressure up to 20 mbar. The final solution contained 15 wt % glyoxal, 78.5 wt % methanol, and 6.5 wt % water. Before the introduction of the feedstock, the sample was heated in an N_2 flow (10 mL/min) to the desired temperature. The reaction was conducted under N_2 (10 mL/min) at 453 K and 2.6 MPa preventing liquid to gaseous phase transfer. The feed rate of feedstock was varied in the interval of $LHSV = 2\text{–}6\ h^{-1}$. It corresponded to the load on the catalyst (L) from 4.1 to 12.3 mmol glyoxal/mL$_{cat}$/h.

^{13}C NMR spectroscopy (Bruker Avance 400, Karlsruhe, Germany) was used to identify products and

evaluate glyoxal conversion. To assign the observed peaks in the spectra, the database of spectra of organic compounds (SDBS, National Institute of Advanced Industrial Science and Technology, Japan, www.aist.go.jp) was used. Also, the reaction products were analyzed using Agilent Technologies 7820A GC System gas chromatograph. Glycolic acid (Merck, high purity, 70 wt. % in water) and methyl glycolate (Sigma-Aldrich, 98 %) were employed as references. The conversion values of glyoxal (X) and selectivity of products (S) were calculated in mol %. Yields (Y) were calculated as $Y = S \cdot X$.

3. Results and Discussion

Chemical composition, textural properties, strength, and concentration of base sites of the synthesized catalysts are shown in Table 1.

Table 1. Textural parameters and total base properties of the synthesized catalysts

| Catalyst	S, $m^2 g^{-1}$	V_{Σ}, $cm^3 g^{-1}$	V_{me}, $cm^3 g^{-1}$)	r_{av}, nm	r_{me}, nm	$H_-(H_0)_{max}$	Total content of base/acid sites, mmol/g
MgO-ZrO$_2$ [a]	95	0.52	0.54	11.0	3.3	+17.2	1.3
5(MgO-ZrO$_2$)/Al$_2$O$_3$ [b]	225	0.72	0.77	6.4	3.9	+9.3	1.1
10(MgO-ZrO$_2$)/Al$_2$O$_3$ [b]	205	0.65	0.70	6.3	3.9	+9.3	1.2
20(MgO-ZrO$_2$)/Al$_2$O$_3$ [b]	195	0,60	0.64	6.1	3.9	+15.0	1.45
Al$_2$O$_3$	280	0.78	0.84	5.9	3.3	+3.3	1.1

[a] Synthesis by coprecipitation; [b] synthesis by impregnation
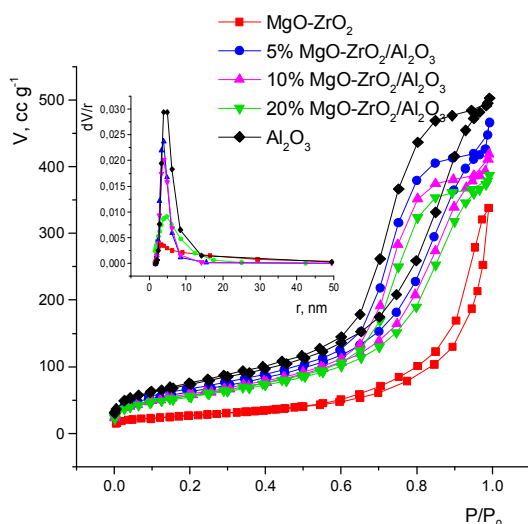
Fig. 1. Nitrogen adsorption-desorption isotherms and PSD curves for the initial Al$_2$O$_3$ and synthesized samples

All synthesized samples are characterized by a mesoporous structure (mesopores radius from 3.3 to 3.9 nm) with a fairly developed surface of 95–225 m^2/g (Table 1). The initial γ-Al$_2$O$_3$ support is weakly acid oxide with $H_{0max} = +3.3$. The deposition of 5–20 wt. % mixed magnesium and zirconium oxide to alumina surface, as a result, gives samples with the basic centers with H_{-max} from +9.3 to +15 (Table 1). Coprecipitated mixed oxide MgO-ZrO$_2$ is characterized by stronger basic centers with $H_- \leq +17.2$ but a smaller specific surface area (Table 1). The nitrogen adsorption-desorption isotherms and pore size distribution curves for the bulk coprecipitated MgO-

ZrO$_2$ and supported MgO-ZrO$_2$/Al$_2$O$_3$ samples are shown in Fig. 1. Isotherms of all samples belong to type IV according to the IUPAC classification, which is characteristic of mesoporous materials. This fact is also confirmed by curves of the pore size distribution (inset to Fig. 1). The supported MgO-ZrO$_2$/Al$_2$O$_3$ catalysts are characterized by a narrower pore size distribution due to the corresponding characteristics of the initial support – γ-Al$_2$O$_3$.
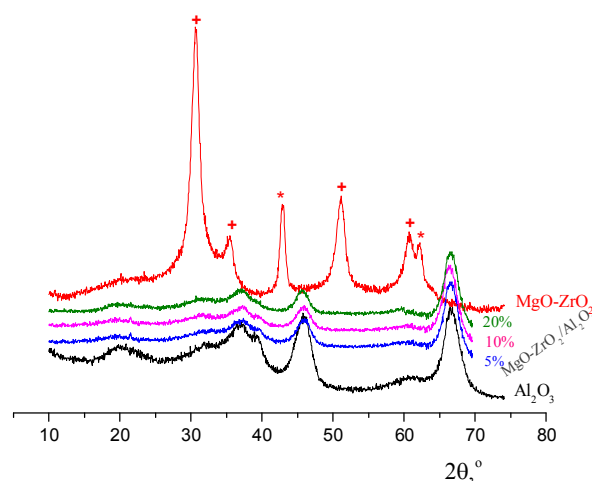
Fig. 2. XRD patterns of MgO-ZrO$_2$ and xMgO-ZrO$_2$/Al$_2$O$_3$ samples (+ – Mg$_2$Zr$_5$O$_{12}$; * – MgO)

According to XRD analysis (Fig. 2), all supported MgO-ZrO$_2$/Al$_2$O$_3$ catalysts remain in the amorphous state. The diffractograms of supported samples do not show peaks inherent in the synthesized bulk MgO-ZrO$_2$. The

latter contains two phases: MgO in the periclase form (peaks at $2\theta = 42.9°$ and $62.2°$) and $Mg_2Zr_5O_{12}$ (peaks at $2\theta = 30.6°$; $35.1°$, $50.9°$, and $60.8°$).

Synthesized samples were tested in the conversion of 20 wt. % glyoxal-methanol solution into methyl glycolate. The results are summarized in Table 2.

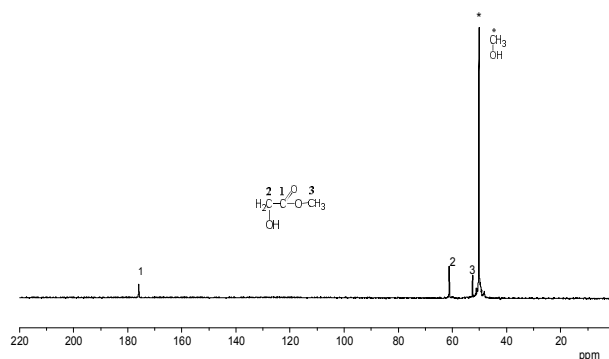**Table 2.** Glyoxal conversion to methyl glycolate over various catalysts [a]

Catalyst	X_{GL}, %	S, mol %		Y_{MG}, %
		Methyl glycolate	Glyoxal dimethyl acetal	
–	48	92	8	44
Al_2O_3	89	76	24	68
$5(MgO\text{-}ZrO_2)/Al_2O_3$	96	92	8	88
$10(MgO\text{-}ZrO_2)/Al_2O_3$	96	95	5	91
$20(MgO\text{-}ZrO_2)/Al_2O_3$	97	98	2	95
$MgO\text{-}ZrO_2$	100	100	0	100

[a] Reaction conditions: 8.0 g of 20 wt. % glyoxal-methanol solution, 0.64 g catalyst, 423 K, 1 h

So, a slight conversion of glyoxal (about 48 %) is observed under these conditions without a catalyst. It was observed that pure Al_2O_3 catalyst provides 24 % selectivity towards glyoxal dimethyl acetal (GLYDMA) (1,1,2,2-tetramethoxyethane, $C_6H_{14}O_4$) with 96 % glyoxal conversion at 423 K. It is known that the formation of acetals is catalyzed by acids.[23] According to obtained results, the selectivity of the methyl glycolate formation increases with increasing the basicity of the catalyst. On the supported $MgO\text{-}ZrO_2/Al_2O_3$ catalysts, which are characterized by higher basicity compared to pure Al_2O_3, the conversion of glyoxal is 96–97 %. The selectivity for methyl glycolate increases to 92–98 % (Table 2). However, a small amount of glyoxal dimethyl acetal (2–8 %) is also formed (Table 2). Practically 100 % selectivity for the target product at 100 % glyoxal conversion was provided by a coprecipitated $MgO\text{-}ZrO_2$ catalyst under these conditions (Table 2). Only peaks of methyl glycolate and methanol are present in the ^{13}C NMR spectrum of the product obtained over this catalyst (Fig. 3). This catalyst is characterized by stronger basic centers H_{-max} from +17.2 (Table 1). It is known[19] that the Cannizaro type reaction on which the formation of methyl glycolate from glyoxal is based can be catalyzed by strong bases.

However, the preparation of coprecipitated MgO-ZrO_2 catalyst is a somewhat more complicated procedure in comparison with the synthesis of supported MgO-ZrO_2/Al_2O_3 catalysts synthesized by a simple impregnation method. The supported 20MgO-ZrO_2/Al_2O_3 catalyst provided a 95 % yield of methyl glycolate with the formation of only 2 % of the by-product (Table 2). Due to the above-mentioned advantage, this catalyst may be more promising for possible practical use, in particular in flow mode. To assess the potential of the 20MgO-ZrO_2/Al_2O_3 catalyst for practical application, its operation stability was evaluated. For this, the separated catalyst was used several consecutive cycles without intermediate regeneration (Fig. 4). As the results showed, the yield of

methyl glycolate in the sixth cycle of the catalyst decreased by 11 %, and after regeneration by calcination in the air (823 K, 2 h), the catalyst almost completely restores its activity.
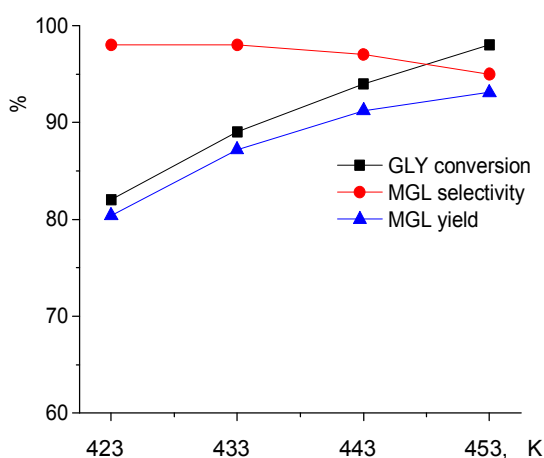

Fig. 3. ^{13}C NMR spectrum of the conversion product of methanolic glyoxal solution obtained at 423 K and 1 h over MgO-ZrO_2 catalyst
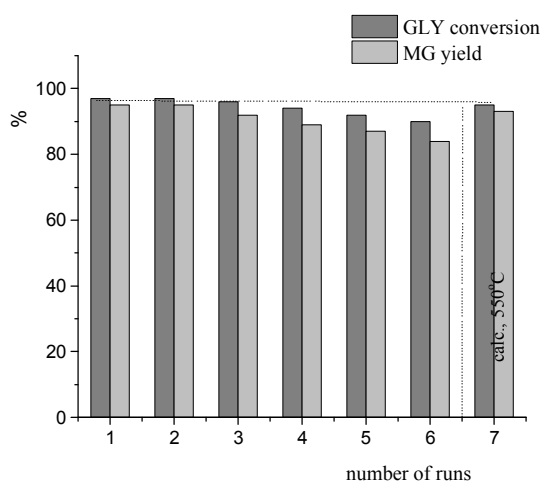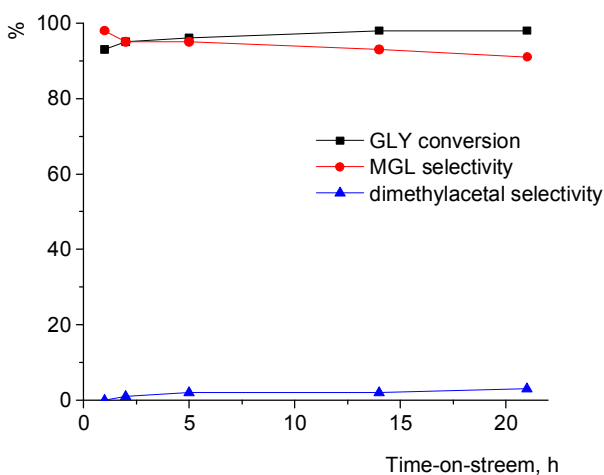

Fig. 4. The glyoxal conversion and the methyl glycolate yield over 20(MgO-ZrO_2)/Al_2O_3 catalyst depending on its operation cycle (*1 h in an autoclave at 423 K*)

To be able to carry out the process in flow mode, it is important to achieve a high yield of the target product in a relatively short reaction time. The catalyst 20MgO-ZrO_2/Al_2O_3 provided an 80–93 % yield of methyl glycolate depending on the temperature after 30 min of reaction (Fig. 5). With an elevation of temperature, the glyoxal conversion increases, the methyl glycolate selectivity decreases slightly (Fig. 5) as well the color of the product intensifies. Therefore, the process should be carried out not higher than at 453 K.

Further, the conditions were selected for methyl glycolate obtained from glyoxal on this catalyst in flow mode. The latter is more promising for industrial production.
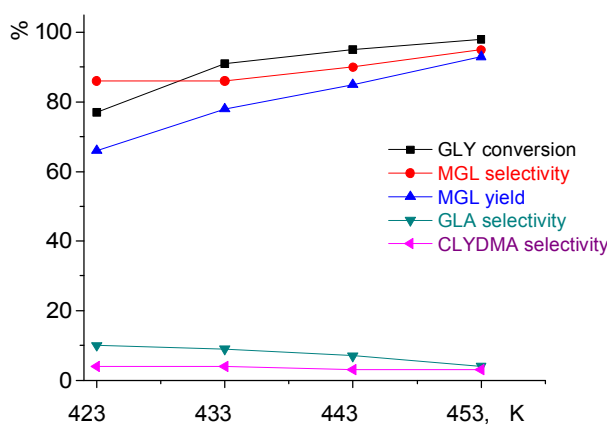
The effect of LHSV was studied for glyoxal conversion at 423 K. It was observed that the best result was achieved when LHSV = 3 h^{-1} (L = 6.2 mmol glyoxal/mL$_{cat}$/h). In these conditions, conversion of glyoxal is 77 % and methyl glycolate selectivity is equal to 86 %. The influence of reaction temperature on the transformation of glyoxal was also studied. As may be seen from Fig. 6, the most suitable temperature is 453 K, which gave the highest selectivity for methyl glycolate (95 %) and the highest yield of methyl glycolate (93 %) with 98 % conversion of glyoxal. The productivity of the catalyst, in this case, is 5.7 mmol MG/mL$_{cat}$/h. The by-products are glycolic acid and glyoxal dimethyl acetal (Fig. 6).

Fig. 5. Glyoxal conversion, selectivity, and yield of methyl glycolate over 20(MgO-ZrO_2)/Al_2O_3 catalyst at different temperatures (*reaction time 30 min*)

Fig. 6. Glyoxal conversion, methyl glycolate selectivity and yield, glycolic acid and glyoxal dimethyl acetal selectivities over 20(MgO-ZrO_2)/Al_2O_3 catalyst at different temperatures (*L = 6.2 mmol glyoxal/mL$_{cat}$/h*)

The stability of 20(MgO-ZrO_2)/Al_2O_3 catalyst with time on stream was studied at 453 K (Fig. 7). One can see that glyoxal conversion is at a level of 91–98 % and methyl glycolate selectivity declines slightly from 98 to 91 %. Also, a small amount of glyoxal dimethyl acetal (1–3 % of selectivity) was formed. It points to minor deactivation of catalyst in a period of 20 h.

Under these conditions, the methyl glycolate yield has reached a maximum of 93 %, which corresponds to the productivity of 5.7 mmol MG /mL$_{cat}$/h. This may be interesting for practical application.

4. Conclusions

Therefore, the results of the studies indicate that the synthesized solid catalysts based on magnesium and zirconium oxides are quite effective in the conversion of methanolic glyoxal solution into methyl glycolate. The

Fig. 7. Glyoxal conversion and products selectivity with time on stream over 20(MgO-ZrO_2)/Al_2O_3 (*T = 453 K, L = 6.2 mmol glyoxal/mL$_{cat}$/h*)

most selective coprecipitated MgO-ZrO$_2$ catalyst after 1 h of the reaction in a rotated autoclave at 423 K of provides almost 100 % methyl glycolate yield. The supported MgO-ZrO$_2$/Al$_2$O$_3$ catalyst synthesized by a simple impregnation method under these conditions provided a 95 % yield of methyl glycolate with the formation of only 2 % of the by-product. Methyl glycolate in high 93 % yield can be obtained in flow mode on this catalyst at 453 K, which may be of practical interest.

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КАТАЛІТИЧНИЙ СИНТЕЗ МЕТИЛГЛІКОЛАТУ З МЕТАНОЛЬНОГО РОЗЧИНУ ГЛІОКСАЛЮ НА ОСНÓВНИХ КАТАЛІЗАТОРАХ

Анотація. *Досліджено процес одержання метил-гліколату з метанольного розчину гліоксалю на твердих основних каталізаторах на основі змішаних оксидів алюмінію, цирконію та магнію. Селективність утворення метилгліколату зростає зі збільшенням основності каталізатора. Найбільш селективний співосаджений MgO-ZrO$_2$ каталізатор забезпечує практично 100 % вихід метилгліколату. На MgO-ZrO$_2$/Al$_2$O$_3$ спостерігається 95%-й вихід метилгліколату з утворенням гліоксальдиметилацеталю як побічного продукту. Метилгліколат з високим виходом 93 % можна отримувати в проточному режимі, що може представляти практичний інтерес.*

Ключові слова: *метилгліколат, тверді основні каталі-затори, змішані оксиди магнію і цирконію.*