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New methods of glyceric and lactic acid production by catalytic oxidation of glycerol. New method of synthesis of a catalyst with enhanced activity and selectivity

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Rapeseed oil, which is the feedstock for biodiesel manufacturing, cannot be fully converted to biodiesel due to the forming of glycerol as the by-product. Glycerol liquid phase catalytic oxidation with molecular oxygen is one of the most promising methods for glycerol utilization. The new, extraction-pyrolytic, method for supported catalyst synthesis is worked out. It is demonstrated that the method can be used for the preparation of supported palladium and platinum catalysts for selective glycerol oxidation. It is possible to reach 72–78% yield by glyceric acid with full glycerol conversion by oxidizing glycerol in the presence of 1.25–2.5% Pd/Al_2O_3 catalyst. The yield of 54% by lactic acid with glycerol conversion ratio of 86% is reached in the presence of 1.25% Pt/Y_2O_3 catalyst.

Key words: biodiesel, glycerol, oxygen, heterogeneous catalyst

INTRODUCTION

The demand for energy continues to grow worldwide and along with it the so-called "greenhouse gas" emissions continue to rise causing a dangerous climate change. In order to mitigate the effect of the climate change a set of measures have been worked out, including energy saving and renewable energy resource proportion increase activities, for example, expanding the use of biofuel. The European biodiesel production capacity is estimated around 22 million m^3 per year.

The rapeseed oil, which is the feedstock for biodiesel manufacturing, cannot be fully converted to biodiesel due to formation of glycerol as a by-product. The volume of biodiesel manufacturing and the amount of glycerol obtained as the process by-product increases correspondingly. It significantly lowers the glycerol market price and forces to look for new, alternative ways of its application. Glycerol liquid phase catalytic oxidation with molecular oxygen is one of the most promising methods for glycerol utilization. Oxidation of glycerol in the presence of a supported heterogeneous catalyst makes it possible to get a number of important and valuable compounds that are either end-products or feedstock in various organic synthesis processes. These methods are environmentally friendly, as oxygen is the possible "greenest" oxidizer and the only glycerol oxidation by-product is water.

Platinum group metals are the classical supported heterogeneous catalysts [1, 2, 3] used in the processes of liquid-phase oxidation of alcohols and aldehydes, including glycerol.

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Carbon based carriers (activated carbon, graphite, carbon black) are usually used in the synthesis of supported Pt and Pd catalysts; metal oxide based carriers are used less frequently. Despite the variety of supported Pd, Pt and Au catalysts, glycerol oxidation products are mostly obtained in a mixture. This mixture contains such valuable products as glyceric, lactic, tartronic, glycolic and ketomalonic acids as well as dihydroxyacetone, which all are highly priced on the market individually, but it is too difficult and expensive to extract them from the reaction mixture obtained. The only possible solution is to develop a selective catalyst and to find appropriate oxidation reaction conditions which would facilitate domination of one specific product in the reaction mixture. Glycerol utilization by obtaining other valuable products can significantly decrease the net cost of the biofuel manufacturing.

Glyceric acid is one of the most important products obtained by glycerol oxidation. It is being used as a raw material for cosmetics manufacturing [4, 5], biodegradable surfactants and biodegradable polymers [6, 7, 8]. Up to now, the highest yield by glyceric acid has been reached by authors of the work [1]. There glycerol oxidation in the presence of 5% Pd/C catalyst resulted in 100% glycerol conversion and glyceric acids selectivity of 70%.

Lactic acid has always had an important role in food, cosmetic and pharmaceutical industries. Recently, lactic acid found its application in production of biodegradable polymers, which can also be used in medicine. Until now, production of lactic acid by oxidizing glycerol in the presence of noble metal catalysts has not been studied so widely as production of glyceric acid. In [9] lactic acid has been obtained with selectivity of 33–80% when glycerol conversion was in the range of 70–12%. It can be seen that selectivity to lactic acid decreases with increase in glycerol conversion, and the best selectivity to lactic acid was 80% when glycerol conversion was 12%. The highest selectivity to lactic acid (85%) was obtained by Shen et al. [10], it was reached while oxidizing glycerol in the presence of Au-Pt/TiO_2 catalyst; unfortunately, glycerol conversion was also low (30%). The yield by lactic acid was 25%.

New, simple and cost-effective methods of glyceric and lactic acids selective syntheses by oxidation of glycerol with air or molecular oxygen in the presence of palladium and platinum catalysts are developed in this work. A new, extraction-pyrolytic, method of supported catalyst synthesis is worked out. This method allows us to obtain catalysts that are more active and selective than those catalysts that are synthesized by conventional methods.

EXPERIMENTAL

Materials

The following reagents were used for the preparation of catalyst precursors: platinum in powder (99.99%; Sigma-Aldrich), palladium in powder (99.9%; Aldrich), HCl (35%; Lachema); HNO_3 (65%; Lachema), trioctylamine ($(C_8H_{17})_3N$) (95%; Fluka), toluene (analytical grade; Stanchem). In the synthesis of the catalysts several powders were used as carriers – Al_2O_3, Y_2O_3 and Si_3N_4 (obtained in plasma by the procedure described in [11]), ZrO_2–Y_2O_3 (nanopowder of zirconium oxide (86%) which is stabilized with yttrium oxide (14%) and prepared by the procedure described in [12]), nanoporous microgranulars of α-Al_2O_3 (Al_2O_3(g)) [13], TiO_2 (nanopowder of titanium dioxide prepared by the sol–gel method described in [14]), C (Norit®, Sigma-Aldrich), SG – silica gel obtained through the sol–gel technology from S. I. Vavilov State Optical Institute (St. Peterburg, Russia) [15], pyrex borosilicate glass was ground in a ball grinder, sifted and the fraction with particle size less than 90 μm was used. Glycerol (≥98%; Fluka), NaOH (reagent grade, Sigma-Aldrich) and oxygen (98%; AGA SIA) were used in the glycerol oxidation experiments. H_2SO_4 (95–98%; Sigma-Aldrich) was used in the samples of the reaction mixture preparation and analysis. For the identification of the possible products of glycerol oxidation several following compounds were used: DL-glyceraldehyde dimer (≥97%; Aldrich), 1,3-dihydroxyacetone dimer (≥97%; Aldrich), glyceric acid calcium salt hydrate (≥99%; Fluka), sodium β-hydroxypyruvate hydrate (≥97%; Fluka), lithium lactate (≥97%; Fluka), tartronic acid (≥98%; Alfa Aesar), sodium mesoxalate monohydrate (≥98%; Aldrich), glycolic acid (≥99%; Acros organics), glyoxylic acid monohydrate (≥98%; Aldrich), oxalate standard for IC (1.000 g/L; Fluka), acetate standard for IC (1.000 g/L; Fluka), formate standard for IC (1.000 g/L; Fluka).

Catalyst preparation

The process of catalyst preparation by the extractive-pyrolytic method was started with the production of a precursor by the liquid extraction method. In order to produce a precursor an aqueous solution of tetrachloride palladium acid (H_2PdCl_4) or hexachloride platinum acid (H_2PtCl_6), or gold tetrachloride acid ($HAuCl_4$) in 2 M hydrochloric acid was added to the 1 M trioctylamine$(C_8H_{17})_3N$ solution in toluene. After shaking the mixture for 3–5 minutes, the organic phase was separated from the aqueous phase and filtered. The analysis of the aqueous solutions after extraction using a HITACHI 180-50 atomic absorption spectrometer evidenced that the metals had been completely extracted into the organic phase. The obtained organic extract (c_{Me} = 0.4 M) is the catalyst precursor. Different volumes of the precursor were used to impregnate the carrier in order to produce catalysts. Metal loading in the catalyst was within the range of 0.1 and 10 wt% of carrier weight. After impregnation the mixture was dried for 5 minutes at 20–110 °C to remove the solvent. The dry mixture was heated up at the rate 10 K/min and calcinated at 300 °C, 400 °C or 500 °C for 5–120 minutes in air.

After the catalyst preparation the chemical composition of the prepared materials was determined by an X-ray fluorescent spectrometer S4 Pioneer. The prepared catalysts were characterized by X-ray diffraction (XRD) using a diffractometer D-8 Advance (Bruker AXS) with CuK_α radiation ($\lambda = 1.5418$ Å) in a wide range of Bragg angles ($10^\circ < 2\theta < 75^\circ$) with a scanning rate of 0.02 °/s at room temperature. The average crystallite size was calculated from X-ray line broadening using (111) peaks and the Scherrer equation. Specific surface area (S.S.A.) of the powders was measured using the HROM-3 chromatograph by the BET method at the temperature of liquid nitrogen. A mixture of argon and helium was used as an adsorbate gas. TEM measurements were carried out with a JEM-1230 instrument operating at 100 kV. The powder samples of the catalysts were ultrasonically dispersed in ethanol and the suspension was deposited on a copper grid coated with a porous carbon film. Histograms of particle size distribution were obtained by counting onto the micrographs at least 300 particles, and the mean particle diameter (d_{Pd}) was calculated using the formula, $d_{Pd} = \sum d_i n_i \Big/ \sum n_i$, where n_i was the number of particles of diameter d_i.

Glycerol oxidation

Oxidation of glycerol by molecular oxygen in the presence of supported catalysts in alkaline medium has been performed in a thermostatted slurry bubble column reactor operated in the batch mode. The total reactor volume was 50 mL, the total reaction mixture volume was 15 mL. The oxidation has been performed as follows: the required quantities of dry catalyst, distilled water and 3.0 M glycerol aqueous solution were fed into the reactor during thermostatting (10 min). The supply of oxygen to the reactor has been switched on (oxygen flow = 300 mL/min) and the required volume of 5.0 M sodium hydroxide water solution has been added. The oxidation process started at the moment of the addition of sodium hydroxide. In order to determine the concentration of reaction products, liquid samples were collected periodically from the reaction mixture after a certain period of time. Reaction mixture samples were filtered for separation of catalysts. The filtered samples were analyzed by a high performance liquid chromatographic (HPLC) method.

RESULTS AND DISCUSSION

Production of glyceric acid

The new catalyst activity was tested oxidizing glycerol in alkaline water solutions. In the presence of supported Pd catalysts the main oxidation product was glyceric acid, but lactic, tartronic and oxalic acids were obtained as by-products. From Table 1, which shows the comparison of Pd catalysts activity and selectivity, it can be seen that the carrier type and Pd loading in the catalyst significantly affected the product yield and selectivity. If the palladium weight loading was from 1 to 5%, the studied catalysts selectivity to glyceric acid was high and ranged from 77 to 89%. The influence of palladium loading varied depending on the carrier type. In the presence of Pd/C, Pd/PYR or Pd/Al_2O_3(g) catalysts, glycerol conversion decreased with an increase of palladium loading. In the case of Y_2O_3 as a carrier, catalyst activity increased with a Pd loading increase from 0.1 to 5%, but dropped sharply at the palladium weight loading of 10%. With Al_2O_3 as a carrier the highest catalyst activity was achieved when the Pd weight loading was between 1 and 2.5%. Analyzing the data in Table 1,

Table 1. **Effect of catalyst carrier type and palladium weight loading on the glycerol conversion and oxidation product selectivity**

Support	Pd, wt%	Glycerol conv., %	Selectivity, mol%					S.S.A of catalyst, m²/g	d_{Pd} nm by XRD and TEM*
			Glyceric acid	Lactic acid	Tartronic acid	Glycolic acid	Oxalic acid		
Si_3N_4	1^b	1	89	0	7	0	4		
TiO_2	1^b	15	89	0	4	5	2		
C	0.1^b	42	73	0	13	9	5		
	1^b	14	73	5	5	13	4	31	20
	5^b	7	78	6	6	7	3	30	30
PYR^a	0.5^c	53	53	13	19	5	10	15	10
	1.5^c	24	72	8	9	6	5	14	35
	2.5^c	17	76	8	7	6	3	18	45
	10^c	4	81	0	6	7	6	16	50
Y_2O_3	0.1^b	2	90	0	10	0	0		
	1^b	8	77	0	5	14	4		
	5^b	37	75	10	6	6	3	23	18
	10^b	2	40	2	3	50	5		
Al_2O_3(g)	0.1^b	68	48	7	32	5	8		
	2.5^b	34	70	15	5	7	3	37	28
	5^b	18	80	10	0	7	3	37	35
Al_2O_3	0.1^b	4	40	28	25	0	7	48	
	1^b	75	73	10	8	6	3	48	
	5^b	29	75	11	5	6	3	49	
	1.25^c	70	74	8	9	6	3	42	21*
	2.5^c	74	66	17	8	5	4	36	21*
	5^c	33	73	9	7	7	4	40	29*

Reaction conditions: c_0(glycerol) = 0.3 M, c_0(NaOH) = 1.5 M, n(glycerol)/n(Pd) = 300, 60 °C, P_{O_2} = 1 atm, reaction time 7 h; ^{a} Pyrex borosilicate glass; catalyst calcination temperature: ^{b} 400 °C, ^{c} 300 °C; calcination time 5 min.

under the given conditions the most active were catalysts with Al_2O_3 nanopowder as a carrier: 2.5% Pd/Al_2O_3, 1.25% Pd/Al_2O_3 and 1% Pd/Al_2O_3. In the presence of the most active catalysts selectivity to glyceric acid ranged from 66 to 74%, but glycerol conversion was 70–75%. Typical TEM microphotography and the corresponding histograms of new catalysts with Al_2O_3 nanopowder as a carrier are presented in Fig. 1. Electronic microscopy revealed that palladium in the synthesized 1.25–5% Pd/Al_2O_3 catalysts was represented by spherical nanoparticles that are grouped in the loosely coupled aggregates. Pd particle size distribution for the catalyst containing 5% metal is observed in a wider interval than for the most active catalysts which contains 1.25–2.5% Pd. Fraction of Pd particles up to 25 nm in size in the 1.25–2.5% Pd/Al_2O_3 catalysts is 64–68%, but in the 5% Pd/Al_2O_3 catalyst this fraction is 36%. The glycerol conversion increase in the presence of Pd-supported catalysts can be explained by a decrease of Pd particle size. According to the data presented in Table 1 and Fig. 1, glycerol conversion increased from 33 to 70–74% in the presence of the Pd/Al_2O_3 when the Pd particle size decreased from 29 to 21 nm. Similarly in the presence of the Pd/PYR and Pd/C catalysts glycerol conversion increased respectively from 4 to 53% or from 7 to 14% when the Pd particle size decreases from 50 to 10 nm or from 30 to 20 nm. The results obtained in this study are consistent with the data of [16], which shows a similar effect for the monometallic 1% Pd/C and bimetallic 1% (Au–Pd)/C catalysts.

Varying the glycerol oxidation parameters in the presence of the most active catalysts, optimal conditions for the selective glyceric acid production were found (Table 2). It can be seen from the data presented in Table 2 that the full glycerol conversion with 76–78% selectivity to glyceric acid was reached in the presence of 1.25% Pd/Al_2O_3 and 2.5% Pd/Al_2O_3 catalysts, when the NaOH concentration was equal to 0.7 M and n(glycerol)/n(Pd) = 300–400 mol/mol.

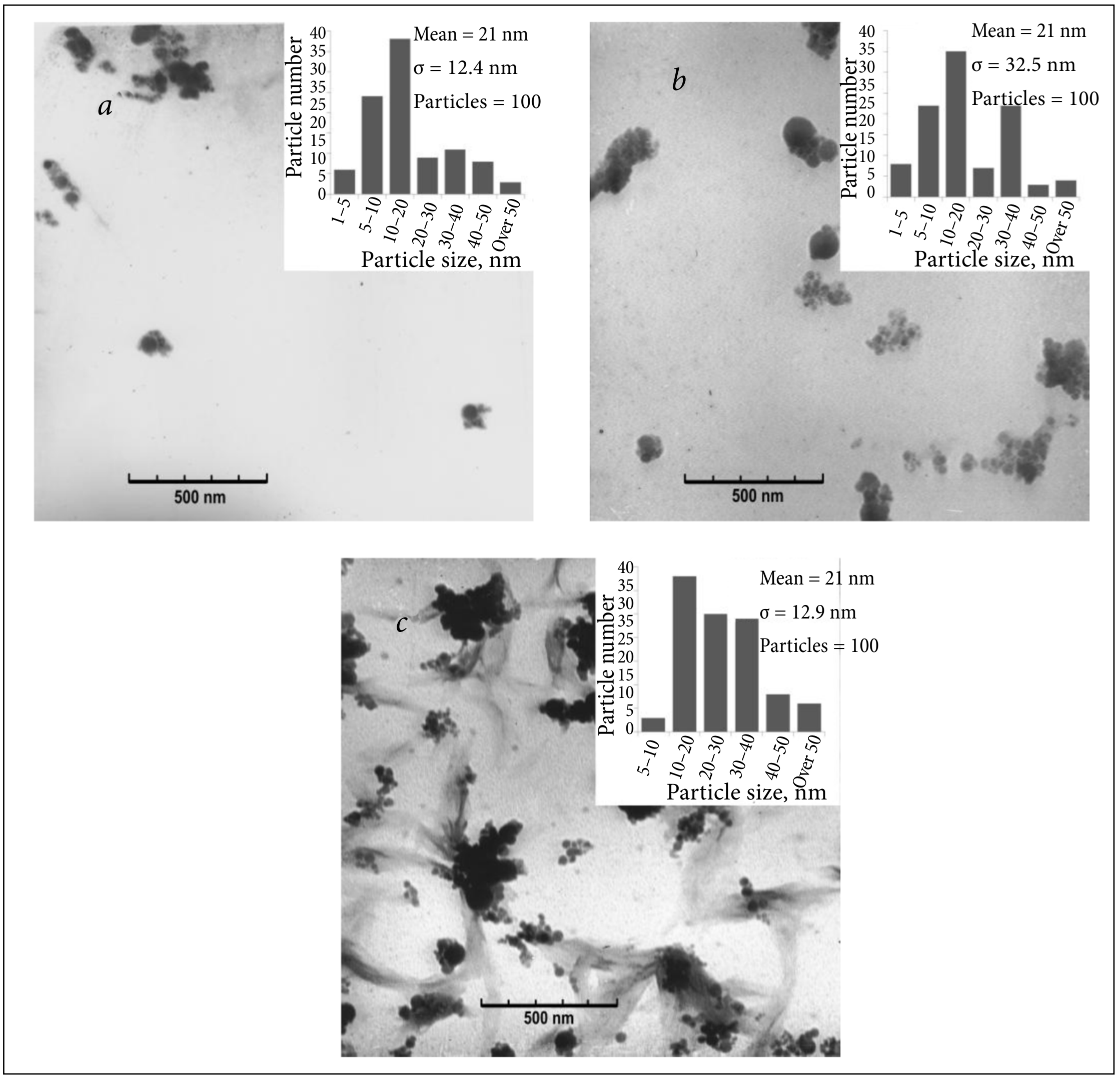

Fig. 1. TEM images of 1.25% Pd/Al_2O_3 (*a*); 2.5% Pd/Al_2O_3 (*b*); 5% Pd/Al_2O_3 (*c*)

Table 2. **Effect of the oxidation parameters on the glycerol conversion and selectivity to glyceric acid**

Catalyst	c_0(NaOH), M	n(glyc)/n(Pd), mol/mol	t, h	Glycerol conv., %	Selectivity to glyceric acid, mol%
1.25% Pd/Al_2O_3	0.7	400	7.5	100	76
1.25% Pd/Al_2O_3	1.5	400	7.5	92	74
2.5% Pd/Al_2O_3	0.7	300	10.0	100	78
2.5% Pd/Al_2O_3	0.7	400	10.0	93	77

Reaction conditions: c_0(glycerol) = 0.3 M, c_0(NaOH) = 1.5 M, n(glycerol)/n(Pd) = 300, 60 °C, P_{O_2} = 1 atm. Catalyst calcination temperature and time: 300 °C and 5 min, respectively.

It is known that the main disadvantage of catalysts based on Pd is their deactivation due to oxygen poisoning [17, 18]. The glycerol oxidation was carried out repeatedly with the used 1.25% Pd/Al_2O_3 catalyst. The results of the reuse experiment indicated that the catalyst does not deactivate in the first oxidation process. Glycerol conversion for the reused 1.25% Pd/Al_2O_3 catalyst was the same (69–70%), but the selectivity to glyceric acid reduced from 74 to 67%.

Production of lactic acid

Testing new synthesized Pt, Au and Pd catalysts supported on Y_2O_3 in glycerol oxidation processes, it was found that good selectivity to lactic acid with high glycerol conversion can be achieved by using platinum catalysts (Table 3). Oxidizing glycerol at the same conditions over 1.2% Au/Y_2O_3 catalyst was not leading to formation of lactic acid, but oxidation over 1.2% Pd/Y_2O_3 catalyst resulted in poor lactic acid selectivity. Moreover, the last two catalysts had low activity. Other products which formed in the process were the following: glyceric, tartronic, glycolic, formic and oxalic acids. Shen et al. oxidizing glycerol over Pt, Au and Pd catalysts supported on TiO_2 also concluded that Pt catalysts have the highest activity and selectivity to lactic acid. Besides, they concluded that Au addition enhances Pt catalysts performance [10]. In our case Au addition to Pt/SiO_2 catalyst improved its activity but did not influence selectivity to lactic acid.

Continuing researches with Pt catalysts supported on other materials (Table 3), it was concluded that also 1.2% Pt/ZrO_2-Y_2O_3 and 5% Pt/C had satisfactory selectivity to lactic acid as well. The best results were reached when the Pt loading on Y_2O_3 or ZrO_2-Y_2O_3 was lower than 2.4%.

In Figures 2 and 3 the catalyst calcination temperature and time influence on the catalysts selectivity to lactic acid is shown. It is visible from Fig. 2 that elevation of catalyst calcination temperature was essential in the rise of lactic acid selectivity independently of catalyst support nature. Meanwhile glycerol conversion did not change significantly (except 1.2% Pt/Y_2O_3 catalyst). In all cases catalysts calcinated above 300 °C were much more selective to lactic acid. Increasing calcination temperature from 300 to 500 °C catalyst selectivity to lactic acid rose by 20–43%.

Unlike catalysts calcination temperature, influence of the catalysts calcination time on the lactic acid selectivity was not so great (Fig. 3). All Pt-supported catalysts with prolonged calcination time were more active in the glycerol oxidation. Also the catalyst (except 2.4% Pt/Y_2O_3) selectivity to lactic acid

Table 3. **Selectivity by lactic acid in glycerol oxidation over Au, Pd and Pt catalysts**

Catalyst	Me, wt%	Glycerol conv., %	Selectivity, mol%				
			Lactic acid	Glyceric acid	Tartronic acid	Glycolic acid	Oxalic acid
Au/Y_2O_3	1.2	0.3	0	81	0	0	0
Pd/Y_2O_3	1.2	9	7	77	4	9	4
Pt/Y_2O_3	0.6	65	42	14	28	3	14
	1.2	88	42	38	11	6	2
	2.4	66	27	54	9	6	3
	4.8	70	30	50	8	8	2
Pt/Al_2O_3	0.6	64	17	41	27	10	3
	1.2	69	16	56	7	11	1
	2.4	69	24	49	9	13	2
	4.8	75	19	53	13	10	3
Pt/ZrO_2-Y_2O_3	1.2	87	34	20	31	7	5
	2.4	91	24	39	22	10	3
	4.8	85	24	47	14	12	2
Pt/C	1.2	49	19	62	6	11	2
	4.8	68	30	37	18	9	4
Pt/SiO_2	4.8	82	33	36	14	14	3
Au-Pt/SiO_2	2.5	91	33	38	22	8	0

Reaction conditions: c_0(glycerol) = 0.3 M, c_0(NaOH) = 1.5 M, n(glycerol)/n(Pt) = 300 mol/mol, 60 °C, P_{O_2} = 1 atm, reaction time 7 h. Catalyst calcination temperature and time: 300 °C and 5 min, respectively.

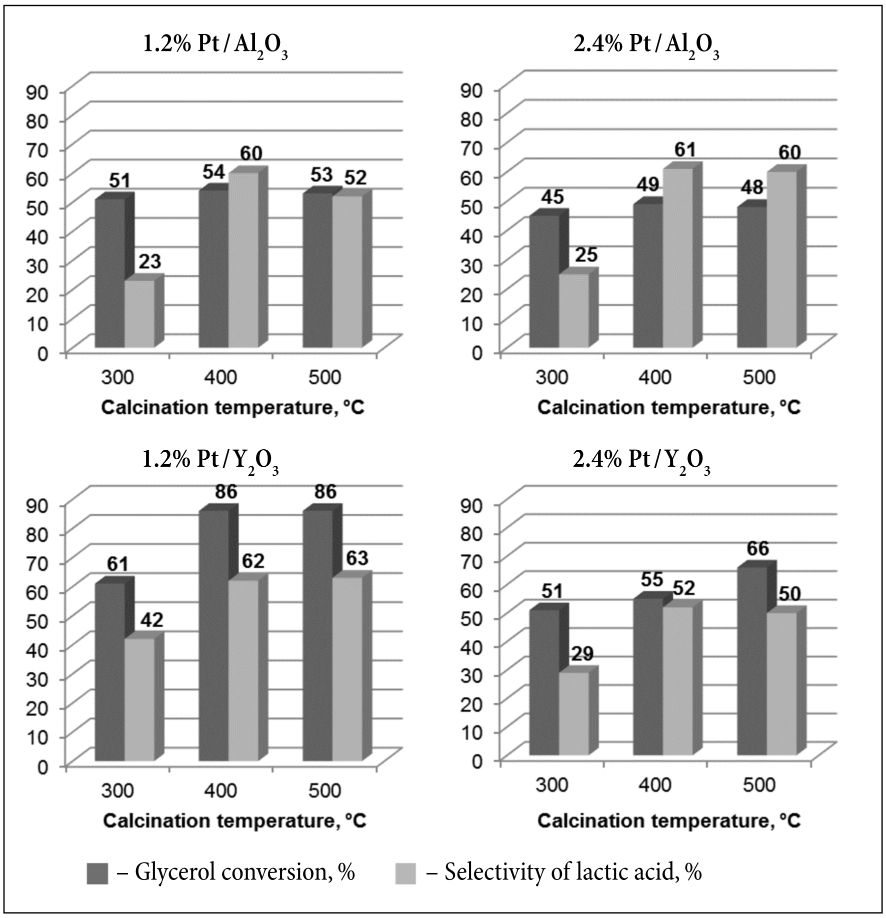

Fig. 2. Effect of the catalyst calcination temperature on the glycerol conversion and lactic acid selectivity. Reaction conditions: c_0(glycerol) = 0.3 M, c_0(NaOH) = 1.5 M, n(glycerol)/n(Pt) = 300 mol/mol, 60 °C, P_{O_2} = 1 atm, reaction time 4 h, Pt catalyst calcination time 5 min

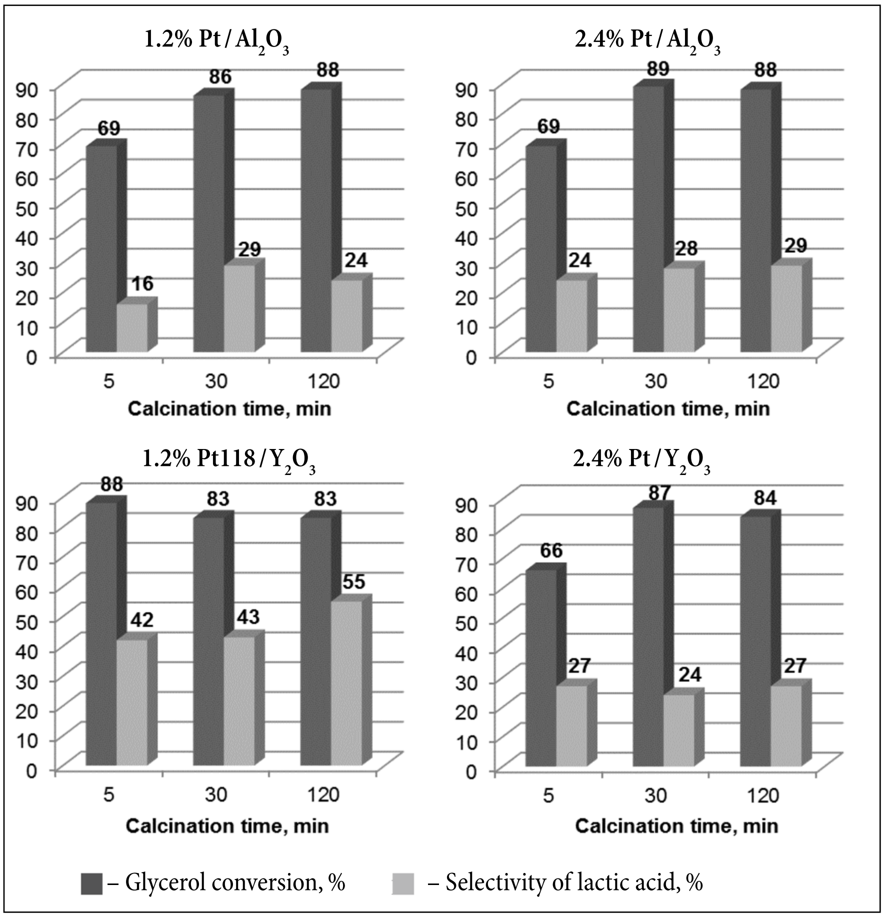

Fig. 3. Effect of the catalyst calcination time on the glycerol conversion and lactic acid selectivity. Reaction conditions: c_0(glycerol) = 0.3 M, c_0(NaOH) = 1.5 M, n(glycerol)/n(Pt) = 300 mol/mol, 60 °C; P_{O_2} = 1 atm, reaction time 7 h, Pt catalyst calcination temperature 300 °C

slightly grew with the calcination time. The biggest increase in lactic acid selectivity was 13% and it was reached oxidizing glycerol in the presence of 1.2% Pt/Y_2O_3 catalyst. Prolonging the catalyst calcination time from 5 to 120 min, the 1.2% Pt/Y_2O_3 catalyst selectivity to lactic acid rose from 42 to 55%. From Figs. 2 and 3 it is visible that the 1.2% Pt/Y_2O_3 catalyst calcinated at 400–500 °C with the calcination time 5 min was the most active (glycerol conversion 86%) and selective to lactic acid (62–63%). The yield of lactic acid was 54%. Until now the best yield of lactic acid obtained in similar oxidation conditions (1 atm pressure, 60 °C) has been 36% and it was reached using Au-Pt/CeO_2 catalyst [19].

CONCLUSIONS

The extractive-pyrolytic catalyst synthesis method provides a way for an efficient synthesis of nanostructured palladium and platinum catalysts. It is demonstrated that the method can be used for the preparation of supported palladium and platinum catalysts for selective glycerol oxidation. It is possible to reach 72–78% yield by glyceric acid with full glycerol conversion oxidizing glycerol in the presence of 1.25–2.5% Pd/Al_2O_3 catalyst. This result is 8% higher than results in other published reports. The yield of 54% by lactic acid with the glycerol conversion ratio of 86% is reached in the presence of 1.25% Pt/Y_2O_3 catalyst. Until now, the best yield by lactic acid found in publications has been 36%. The described methods of glyceric and lactic acid obtaining as well as a new catalyst synthesis method are patented in EU [20] and Latvia [21] and can be applied for glyceric and lactic acids production in an industrial scale.

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NAUJI GLICEROLIO IR PIENO RŪGŠČIŲ GAVIMO BŪDAI KATALITIŠKAI OKSIDUOJANT GLICEROLĮ. NAUJAS KATALIZATORIAUS, PASIŽYMINČIO PADIDINTU AKTYVUMU IR ATRANKUMU, SINTEZĖS BŪDAS

Santrauka

Rapsų aliejus negali būti visiškai paverstas biodyzelinu, nes jį gaminant susidaro šalutinis produktas glicerolis. Vienas perspektyviausių būdų gliceroliui utilizuoti yra jo katalizinė skystos fazės oksidacija deguonimi. Pateiktas naujas katalizatoriaus sintezės būdas. Parodyta, kad siūlomas būdas gali būti panaudotas paladžio ir platinos katalizatorių selektyviajai gamybai oksiduojant glicerolį.