



J. Serb. Chem. Soc. 78 (9) 1359–1372 (2013)
JSCS–4503

Journal of
the Serbian
Chemical Society

JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

UDC 547.426.1+66.094.3+544.478+
546.92:547.474.3:66.061

Original scientific paper

Selective liquid phase oxidation of glycerol to glyceric acid over novel supported Pt catalysts

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(Received 3 December 2012, revised 26 February 2013)

Abstract: Several supported platinum catalysts were prepared by the extractive–pyrolytic method for the selective production of glyceric acid from glycerol. Al₂O₃, Y₂O₃, Lu₂O₃, ZrO₂–Y₂O₃, TiO₂, SG, Fe₂O₃, γ-AlO(OH) and C were used as the catalyst supports. Glycerol oxidation was performed in alkaline solutions and oxygen was used as the oxidant. The optimal catalyst preparation parameters and glycerol oxidation conditions to obtain glyceric acid were determined. The best result (57 % selectivity to glyceric acid with 92 % glycerol conversion) was achieved on a 4.8 % Pt/Al₂O₃ catalyst.

Keywords: glycerol oxidation; supported platinum catalysts; glyceric acid; extractive–pyrolytic method.

INTRODUCTION

Glycerol, which is potentially a valuable building block, is obtained as a by-product in the production of biodiesel. Glycerol is produced in large amounts during the transesterification of fatty acids into biodiesel – its yield can reach approximately 10 %.^{1,2} In recent years, because of increasing biodiesel production, glycerol utilization has become a significant problem. The possibilities of glycerol transformation into useful compounds,^{1–28} materials,^{5,29–31} or energy sources^{5,32–34} are being investigated. With green chemistry and environmentally friendly manufacturing in mind, the selective oxidation of glycerol using supported noble metal catalysts has attracted much attention. Liquid phase oxidation of glycerol with oxygen or air over heterogeneous Pt, Pd or Au catalysts affords many important compounds – glyceric acid (GLYA), lactic acid (LACT), tartaric acid (TART), glycolic acid (GLYC), dihydroxyacetone (DIHA), glycerol-

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doi: 10.2298/JSC121203037S

dehyde (GLYAD), *etc.*^{1,6-12,14-26} Glyceric acid and its derivatives are important compounds as raw materials for chemical products, such as bioplastics, pharmaceuticals for acceleration of alcohol metabolism or liver disease treatment and cosmetics.^{3,9,11}

Most of the studies concerning the heterogeneous oxidation of glycerol were dedicated to the selective oxidation of glycerol over supported gold catalysts using oxygen as the oxidant.¹²⁻¹⁴ Gold catalysts are very selective to glyceric acid. Using an Au/C catalyst, Carretin *et al.* reported a selectivity to glyceric acid of 100 % at a glycerol conversion of 56 %.¹⁴ For gold catalysts, many supports have been investigated, *i.e.*, carbon materials, several metal oxides and polymers.^{8,15,16} The main drawback of gold catalysts is that they are active only in the presence of base, whereas platinum catalysts work in basic, acidic and neutral conditions.¹⁷⁻¹⁹

Liang *et al.*⁶ reported that multi-wall carbon nanotubes (MWNT)-supported Pt catalysts were more active and selective than Pt/activated carbon (AC) catalysts, but this type of support is expensive and the preparation of catalyst is complicated, so in further studies, the authors returned to activated carbon. Liang *et al.* compared glycerol oxidation over 5 % Pt/MWNT catalyst under alkaline and base-free conditions.⁸ The 5 % Pt/MWNT catalyst in a base-free aqueous solution was more selective to glyceric acid (68 %) at the same glycerol conversion (90 %). The authors also concluded that the activity and selectivity to glyceric acid increased with decreasing particle size of the carbon support (from 253 to 9 μm). The most active were catalysts with a Pt particle size of less than 6 nm.^{1,6,8}

A general drawback of platinum-containing catalysts is poisoning with molecular oxygen and deactivation. Therefore, Pt catalysts are used in oxidation processes at low partial pressures of oxygen or the platinum is alloyed with gold, thereby allowing higher oxygen partial pressures. Prati *et al.*²⁰⁻²³ reported that in the alkaline solutions at 3 atm bimetallic Pt–Au/C catalysts were more active and selective to glyceric acid compared with Pt/C catalysts. For example, in the presence of 1 %Pt–Au/C, the glycerol conversion was 46 % higher than in the presence of 1 %Pt/C and the selectivity to glyceric acid was increased by 13 %.²²

It is obvious that during the past years, many authors dedicated their time to the investigation of glycerol oxidation only in base-free solutions because these, together with recyclable catalysts, are the environmentally friendly route.^{1,8,23-25}

Since 1993, when Kimura *et al.*¹⁷ reported glycerol oxidation over Pt/C, mainly carbon material supports have been studied for monometallic Pt catalysts, *i.e.*, activated carbon, graphite and MWNT. Recently, several authors reported about selective glycerol oxidation over bimetallic Au–Pt catalysts supported on MgO, Mg(OH)₂,^{35,36} H-mordenite³⁷ and Al₂O₃.³⁸ The preparations of Pt catalysts are based on 3 methods – impregnation, immobilization and ion

exchange.^{1,6,8,11,18} Recently, a new extractive-pyrolytic method was described³⁹ for the preparation of a fine-disperse platinum coating on nanopowder supports, such as Al_2O_3 , $\gamma\text{-AlO}(\text{OH})$, Y_2O_3 , CeO_2 and SiO_2 . It was determined that the Pt particles were spherical and depending on the nature of the supports nature and parameters for the preparation of the catalyst, the sizes of the Pt crystallites range from 5 to 35 nm.

Herein, the results of an investigation of glycerol oxidation by molecular oxygen over novel Pt catalysts to obtain glyceric acid are reported. The catalysts were prepared by the new extractive-pyrolytic method and Al_2O_3 , Y_2O_3 , Lu_2O_3 , $\text{ZrO}_2\text{-Y}_2\text{O}_3$, TiO_2 , silica gel (SG), Fe_2O_3 , $\gamma\text{-AlO}(\text{OH})$ and AC were used as the supports.

EXPERIMENTAL

Materials

The following reagents were used for the preparation of the catalysts precursors: platinum powder (99.99 %; Sigma-Aldrich), HCl (35 %; Lachema); HNO_3 (65 %; Lachema), trioctylamine ($(\text{C}_8\text{H}_{17})_3\text{N}$) (95 %; Fluka) and toluene (analytical grade; Stanchem). For the synthesis of the catalysts, several powders were used as supports – Al_2O_3 and Y_2O_3 (nanopowders of aluminium and yttrium oxide obtained in plasma by procedure described in the literature³⁹), $\text{ZrO}_2\text{-Y}_2\text{O}_3$ (nanopowder of zirconium oxide (86 %), which was stabilized with yttrium oxide (14 %) and prepared by a literature procedure⁴⁰), Fe_2O_3 (nanopowder of iron (III) oxide prepared by the extractive-pyrolytic method described in the literature⁴¹), TiO_2 (nanopowder of titanium dioxide prepared by the sol-gel method described previously⁴²), Lu_2O_3 nanopowder (Sigma-Aldrich), $\gamma\text{-AlO}(\text{OH})$ nanopowder (boehmite, PURAL[®] SB, Sasol, Germany); $\gamma\text{-Al}_2\text{O}_3$ (nanopowder of aluminium oxide obtained in burning commercial $\gamma\text{-AlO}(\text{OH})$, C (Norit[®], Sigma-Aldrich), SG – silica gel obtained through sol-gel technology from S. I. Vavilov State Optical Institute (St. Petersburg, Russia)⁴³. 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 glycerol oxidation, several possible products 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), tartaric acid (≥ 98 %; Alfa Aesar), sodium mesoxalate monohydrate (≥ 98 %; Aldrich), glycolic acid (≥ 99 %; Acros Organics), glyoxylic acid monohydrate (≥ 98 %; Aldrich), oxalic acid (98 %; Aldrich), acetate standard for IC (1.000 g L^{-1} ; Fluka) and formate standard for IC (1.000 g L^{-1} ; Fluka).

Catalyst preparation and characterization

Supported platinum catalysts were prepared by the extractive-pyrolytic method.^{39,44} In order to obtain platinum-containing organic extracts by the liquid extraction method, chloroplatinic acid (H_2PtCl_6) solution in hydrochloric acid (2 M HCl) was added to the trioctylamine ($(\text{C}_8\text{H}_{17})_3\text{N}$) solution in toluene. After shaking the mixture for 3 min, the organic phase was separated from the aqueous phase and filtered. The analysis of the aqueous solution after extraction using a Hitachi 180-50 atomic absorption spectrometer evidenced that the platinum had been completely extracted into the organic phase. The obtained organic phase, which was a solution of $[(\text{C}_8\text{H}_{17})_3\text{NH}]_2\text{PtCl}_6$ in toluene, is a precursor. The precursor was added to the

support. Alkylammonium salts are typical cationic surfactants and wet properly surfaces of different nature.⁴⁵ To uniformly distribute the precursor over the carrier surface, the mixture was thoroughly stirred, then dried to remove the solvent and calcinated. In the preparation of the catalyst, several parameters, *i.e.*, the concentration of the precursor (0.016–0.4 M), impregnation time of the supports with the precursor (5–180 min), the temperature and time of drying (18–110 °C and 3–120 min, respectively) and the temperature and time of calcination (300–500 °C and 5–120 min, respectively), were varied.

Example of catalyst precursor preparation. To 48.25 mL of 1 M trioctylamine solution in toluene, 38.7 mL of 0.5 M chloroplatinic acid solution in 2 M HCl was added. After shaking the mixture for 3 min, organic phase was separated and filtrated. During extraction, the precursor, which was a 0.4 M solution of $[(C_8H_{17})NH]_2PtCl_6$ in toluene was formed.

Example of 2.4 % Pt/Al₂O₃ catalyst preparation. To 1.0 g Al₂O₃ powder, 0.32 mL of a 0.4 M precursor solution was added. The obtained mixture was stirred until the support had been completely impregnated with precursor and then dried for 5 min at a temperature between 80–100 °C. After drying, the mixture was heated at a rate of 10 °C min⁻¹ and calcinated at 300 °C for 5 min under atmospheric pressure.

Catalyst characterization

The prepared catalysts were characterized by X-ray diffraction (XRD) analysis using a Bruker AXS D-8 Advance diffractometer with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) over a wide range of Bragg angles ($10^\circ < 2\theta < 75^\circ$) at a scanning rate of 0.02° s⁻¹ at room temperature. Specific surface area (SSA) of the powders was measured using HROM-3 chromatograph (Laboratorni Pstroje, Praha) at the liquid nitrogen temperature and calculated by the Brunauer–Emmett–Teller (BET) method.

Glycerol oxidation

The oxidation was performed at elevated temperatures using a thermostatted slurry bubble reactor (50 mL capacity), equipped with gas supply system. After the catalyst had been fed into the reactor, the desired amount of distilled water and an aqueous solution of glycerol were added. If necessary, an aqueous solution of NaOH was added to the reaction mixture. When the required temperature had been reached, the oxygen supply to the reactor was turned on (300 mL min⁻¹). Samples were removed periodically and analysed by high-performance liquid chromatograph (HPLC). Several glycerol oxidation process parameters like NaOH initial concentration (0–1.5 M), glycerol and platinum molar ratio (300–500 mol/mol) as well as oxidation temperature (50–65 °C) were varied.

Example of glycerol oxidation over 4.8 % Pt/Al₂O₃ catalyst in basic solution. Oxidation conditions: initial concentration of glycerol $c_0(C_3H_8O_3) = 0.3 \text{ mol dm}^{-3}$; initial concentration of sodium hydroxide $c_0(NaOH) = 0.7 \text{ mol dm}^{-3}$; glycerol and platinum molar ratio $n(C_3H_8O_3)/n(Pt) = 300$; oxygen partial pressure $p_{O_2} = 1 \text{ atm}$; oxidation temperature 60 °C. 0.0585 g of dry 4.8 % Pt/Al₂O₃ catalyst, 11.77 mL of distilled water and 1.13 mL of 3.99 M aqueous glycerol solution were added into the reactor on the thermostatted stage (10 min). After that an oxygen supply to the reactor was turned on (300 mL min⁻¹) and 2.10 mL of an aqueous 5.00 M NaOH solution was added.

Product analysis

Analysis of the reaction mixture was performed on a Waters 2487 HPLC instrument equipped with an ultraviolet (UV 210 nm) and a refractive index (RI) detector.

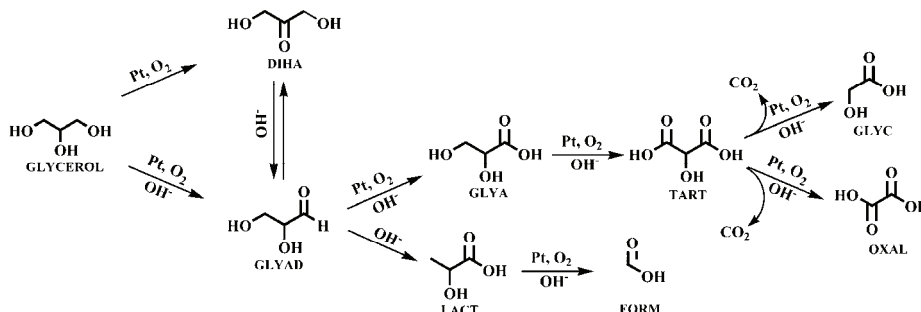
The reactants and the products were separated on an anion exclusion column (IC-PAK Ion-Exclusion 50 A, 7 μm (300 mm \times 7.8 mm)) maintained at 60 °C. The eluent was 2.5 mM

H₂SO₄ solution. Filtered samples of the reaction mixtures (20 μ L) were diluted 50 times with eluent. The injection volume was 10 μ L, and run time and eluent flow rate were set at 20 min and 0.6 mL min⁻¹, respectively. The possible products were identified by comparison with original samples.

RESULTS AND DISCUSSION

Influence of catalyst support and Pt loading on glycerol oxidation

Several products were obtained in the oxidation process, *i.e.*, glyceric acid, tartronic acid, lactic acid, glyceraldehyde, dihydroxyacetone, glycolic acid, oxalic acid and formic acid. The reaction pathways are presented in Scheme 1.



Scheme 1. Reaction pathway for glycerol oxidation in the presence of Pt-supported catalysts.

The results for the oxidation of glycerol over the different novel Pt catalysts are given in Table I. The activity of the catalysts was estimated by glycerol conversion. The most active catalysts with glycerol conversion above 83 % were 1.2 % Pt/Y₂O₃, Pt/ZrO₂-Y₂O₃, Pt/ γ -Al₂O₃, 1.2 % Pt/SG, 4.8 % Pt/ γ -AlO(OH) and 2.4 % Pt/Lu₂O₃. For almost all these catalysts, the Pt crystallite size d_{Pt} was less than 10 nm. As was reported previously,³⁹ X-ray diffraction analyses showed that with increasing Pt loading, the characteristic peak Pt(111) became more apparent. In the case of Pt loading less than 2.4 %, this Pt peak was almost fully overlapped by peaks arising from some of the supports, which makes the determination of the average crystallite size of the metal in the catalyst impossible. As was mentioned above, Liang *et al.*^{1,6,8} who investigated the influence of Pt particle size on the activity and selectivity of Pt/C and Pt/MWNTs catalysts, concluded that catalysts with Pt particle sizes less than 6 nm were the most active. Simultaneously, the selectivity to glyceric acid gradually increased with increasing size of the Pt particles. They considered that the lower activity of the larger-sized Pt particles was due to their lower metal surface area, which restricted the adsorption of substrate. In the study, the specific surface area (SSA) of the supports and catalysts, determined by the BET method, were different depending on the nature of the support. The data presented in Table I show that the carbon support (337 m² g⁻¹) and the Pt catalysts on the carbon support (161–213 m² g⁻¹) have the

TABLE I. Effect of the nature of the catalyst support and the platinum loading on glycerol conversion and oxidation product selectivity; reaction conditions: $c_0(\text{C}_3\text{H}_8\text{O}_3) = 0.3 \text{ M}$, $c_0(\text{NaOH}) = 1.5 \text{ M}$, $n(\text{C}_3\text{H}_8\text{O}_3)/n(\text{Pt}) = 300$, $T = 60 \text{ }^\circ\text{C}$, $P_{\text{O}_2} = 1 \text{ atm}$ and reaction time = 7 h; Catalyst calcination temperature and time: 300 $^\circ\text{C}$ and 5 min, respectively

Catalyst support	Pt wt. %	d_{Pt} nm	SSA of catalyst $\text{m}^2 \text{g}^{-1}$	SSA of support $\text{m}^2 \text{g}^{-1}$	Glycerol conversion %	Selectivity, mol %					
						GLYA	TART	LACT	GLYC	OXAL	FORM
Al_2O_3	0.6	–	–	41	64	41	27	17	10	3	2
	1.2	–	41	–	69	51	17	16	12	2	2
	2.4	>15	42	–	69	49	9	24	13	2	3
Y_2O_3	4.8	20	44	–	73	53	14	19	10	2	2
	0.6	–	18	21	65	14	28	42	3	13	0
	1.2	–	16	–	88	38	11	42	6	2	1
$\text{ZrO}_2\text{-Y}_2\text{O}_3$	2.4	–	20	–	66	54	9	27	6	3	1
	4.8	7	–	–	70	50	8	30	8	2	2
	1.2	8	60	65	87	20	31	34	8	5	2
$\gamma\text{-Al}_2\text{O}_3$	2.4	10	58	–	91	39	22	24	10	3	2
	4.8	10	56	–	85	47	14	24	12	2	1
	1.2	–	105	122	87	19	40	25	7	8	1
C	2.4	5	100	–	94	48	19	20	10	2	1
	4.8	10	102	–	89	46	17	22	11	3	1
	1.2	–	213	337	49	62	6	19	11	2	0
Lu_2O_3	4.8	20	161	–	68	37	18	30	9	4	2
	2.4	–	14	16	84	44	13	28	12	2	1
	4.8	23	14	–	65	55	11	20	11	2	1
Fe_2O_3	2.4	–	34	39	31	37	2	0	60	1	0
	4.8	8	30	–	56	36	2	8	53	1	0
	1.2	9	51	51	93	35	23	25	9	4	4
TiO_2	2.4	12	56	–	58	36	22	26	9	3	4
	4.8	25	66	135	76	62	7	19	8	2	2
	4.8	5	115	146	83	47	19	18	11	3	1

largest surface areas. However, catalysts of this type were less active than catalysts with Y_2O_3 , $\text{ZrO}_2\text{-Y}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, SG, $\gamma\text{-AlO(OH)}$ and Lu_2O_3 as supports. It was shown in earlier investigations of glycerol oxidation in the presence of gold catalysts supported on different carbons,^{46,47} CeO_2 ,⁴⁸ Nb_2O_5 , V_2O_5 , Ta_2O_5 and Al_2O_3 ⁴⁶ that there was no direct dependency between specific surface area of the support and the catalytic properties of gold. The results presented in Table I confirm this statement. For example, the glycerol conversions with the 4.8 % Pt/ $\text{ZrO}_2\text{-Y}_2\text{O}_3$ and 4.8 % Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalysts, having $d_{\text{Pt}} = 10$ nm, are the same (85–89 %) but the specific surface areas of the supports and catalysts differ two-fold. Moreover, the activities of the 4.8 % Pt/ Al_2O_3 and 4.8 % Pt/ Y_2O_3 catalysts were similar, but the d_{Pt} of the 4.8 % Pt/ Al_2O_3 catalyst was 3 times greater and the SSA of the support was 2 times greater than the corresponding values for the 4.8 % Pt/ Y_2O_3 catalyst.

The data in Table I show that depending on the nature of the catalyst support and the loading of Pt on the support, glyceric acid, lactic acid, tartronic acid or glycolic acid were produced as the main product. It is visible from Table I that in the presence of catalysts with Al_2O_3 , Lu_2O_3 , TiO_2 , SG, $\gamma\text{-AlO(OH)}$ and C as supports, glyceric acid was the main product regardless of the Pt loading. The Pt/ Fe_2O_3 catalyst was selective to glycolic acid. When Y_2O_3 , $\text{ZrO}_2\text{-Y}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ were used as supports, the selectivity of the catalyst was dependent on the Pt loading. If the Pt loading was 2.4–4.8 %, the main product of glycerol oxidation was glyceric acid. Decreasing the Pt content in the catalyst from 2.4 to 0.6 % led to changes in the main product of the reaction. Over the 0.6–1.2 % Pt/ Y_2O_3 catalyst, the main product was lactic acid with a selectivity of 42 %, but the 1.2 % Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyst was the most selective to tartronic acid (40 %). 1.2 % Pt/($\text{ZrO}_2\text{-Y}_2\text{O}_3$) catalyst was not selective; the amounts of formed glyceric, tartronic and lactic acids were similar.

It could be concluded from Table I that the most effective Pt catalysts to produce glyceric acid are Pt/ TiO_2 , Pt/ Al_2O_3 , Pt/ Y_2O_3 , Pt/ Lu_2O_3 , Pt/ $\text{ZrO}_2\text{-Y}_2\text{O}_3$ and Pt/ $\gamma\text{-Al}_2\text{O}_3$. The catalysts with a Pt loading of 2.4–4.8 % were both active (glycerol conversion for these catalysts was 65–94 %) and selective to glyceric acid (39–62 %). The Pt/ Al_2O_3 and Pt/ Y_2O_3 catalysts were used in the further investigation to determine how the catalyst preparation and glycerol oxidation parameters affect the activity and selectivity of the catalysts.

Effect of the catalyst preparation parameters on the activity and selectivity of the catalyst

The experiment results showed that some catalyst preparation parameters, such as concentration of precursor, impregnation time of the supports with the precursor, temperature and drying time did not significantly influence the activity and selectivity of the catalyst. In the further investigation these preparation para-

meters were kept constant: concentration of precursor 0.4 M, support impregnation time with precursor 10 min, temperature and drying time 80–100 °C and 10 min, respectively. The calcination temperature and time considerably influenced the activity and selectivity of the catalyst, as given in Table II.

TABLE II. Effect of catalysts calcination temperature on glycerol conversion and oxidation product selectivity; reaction conditions: $c_0(\text{C}_3\text{H}_8\text{O}_3) = 0.3 \text{ mol dm}^{-3}$, $c_0(\text{NaOH}) = 1.5 \text{ mol dm}^{-3}$, $n(\text{C}_3\text{H}_8\text{O}_3)/n(\text{Pt}) = 300$, $T = 60 \text{ °C}$, $p_{\text{O}_2} = 1 \text{ atm}$ and reaction time = 7 h; Pt catalyst calcination time = 5 min

Catalyst	Calcination temperature, °C	Glycerol conversion, %	Selectivity, %					
			GLYA	TART	LACT	GLYC	OXAL	FORM
1.2 % Pt/Al ₂ O ₃	300	69	51	17	16	12	1	3
	400	54	7	26	57	0	6	4
	500	61	18	23	49	0	4	6
2.4 % Pt/Al ₂ O ₃	300	69	50	9	24	13	1	3
	400	56	6	26	57	0	6	5
	500	54	20	14	58	0	2	6
4.8 % Pt/Al ₂ O ₃	300	75	53	13	19	10	3	2
	400	16	15	2	65	15	0	3
	500	22	15	3	67	12	0	3
1.2 % Pt/Y ₂ O ₃	300	88	38	11	42	6	2	1
	400	87	8	18	62	6	5	1
	500	85	10	16	62	6	5	1
2.4 % Pt/Y ₂ O ₃	300	66	54	9	27	6	3	1
	400	59	12	29	49	0	6	4
	500	87	25	15	48	8	3	1

From Table II it is visible that the 4.8 % Pt/Al₂O₃ catalyst prepared with a calcination temperature of 300 °C demonstrated the highest activity and selectivity to glyceric acid. On increasing the catalyst calcination temperature from 300 to 500 °C, the glycerol conversion for the 4.8 % Pt/Al₂O₃ catalyst decreased from 75 to 22 % and the selectivity to glyceric acid decreased from 53 to 15 %. Meanwhile, the selectivity to lactic acid rose from 19 to 67 %. The changes in the glycerol conversion in the presence of the 1.2–2.4 % Pt/Al₂O₃ catalysts were not so drastic (69–54 %) in comparison with those observed in the presence of the 4.8 % Pt/Al₂O₃ catalyst. The data presented in Table III showed the Pt/Al₂O₃ catalysts became more active when the catalyst calcination time was extended from 5 to 120 min. The glycerol conversion increased by 9–19 %. The selectivity of the 4.8 % Pt/Al₂O₃ catalyst to glyceric acid also increased from 53 to 59 % with increasing calcination time, but the 1.2–2.4 % Pt/Al₂O₃ catalysts became non-selective.

It can be seen from the data presented in Tables II and III that in the glycerol oxidation processes over the Pt/Y₂O₃ catalysts, the effect of calcination temperature and time on catalyst activity and selectivity was different and depended on

the Pt loading. Using the 1.2 % Pt/Y₂O₃ catalyst, the glycerol conversion was in the range from 83 to 88% and was independent of the temperature and time of calcination. The main product of the reaction was lactic acid and the selectivity increased with increasing temperature and time of calcination. The 1.2 % Pt/Y₂O₃ catalyst calcinated at 400–500 °C was the most selective catalyst to lactic acid (62 %, with a glycerol conversion of 85–87 %). In the presence of the 2.4 % Pt/Y₂O₃ catalyst, the main product obtained was glyceric acid and the glycerol conversion was higher when the catalyst was prepared with a calcination temperature of 300 °C and a calcination time of 120 min.

TABLE III. Effect of catalyst calcination time on glycerol conversion and oxidation product selectivity; reaction conditions: $c_0(\text{C}_3\text{H}_8\text{O}_3) = 0.3 \text{ mol dm}^{-3}$, $c_0(\text{NaOH}) = 1.5 \text{ mol dm}^{-3}$, $n(\text{C}_3\text{H}_8\text{O}_3)/n(\text{Pt}) = 300$, $T = 60 \text{ }^\circ\text{C}$; $p_{\text{O}_2} = 1 \text{ atm}$ and reaction time = 7 h; Pt catalyst calcination temperature: 300 °C

Catalyst	Calcination time, °C	Glycerol conversion, %	Selectivity, %					
			GLYA	TART	LACT	GLYC	OXAL	FORM
1.2 %Pt/Al ₂ O ₃	5	69	51	17	16	12	1	3
	30	86	26	27	29	11	7	0
	120	88	27	31	24	11	6	1
2.4 %Pt/Al ₂ O ₃	5	69	50	9	24	13	1	3
	30	89	36	20	28	12	3	1
	120	88	35	21	29	11	3	1
4.8 %Pt/Al ₂ O ₃	5	73	53	14	19	10	2	2
	120	82	59	10	20	7	1	3
1.2 %Pt/Y ₂ O ₃	5	88	38	11	42	6	2	1
	30	83	18	25	43	8	5	1
	120	83	8	23	55	7	7	0
2.4 %Pt/Y ₂ O ₃	5	66	54	9	27	6	3	1
	30	87	41	21	24	11	2	1
	120	84	46	14	27	10	2	1

By comparing the data presented in Tables II and III, it could be concluded that the most effective catalyst for glycerol oxidation to glyceric acid was the 4.8 % Pt/Al₂O₃ catalyst that had been calcinated at 300 °C for 120 min.

Effect of glycerol oxidation parameters on the glycerol conversion and oxidation selectivity in the presence of the 4.8 % Pt/Al₂O₃ catalyst

It was reported^{23,49–51} that catalysts based on platinum group metals suffered oxygen poisoning proportional to the oxygen partial pressure. When using Pt catalysts, a low oxygen partial pressure must be applied to limit the rate of oxygen supply to the surface of such catalysts. Under these conditions, the oxidation process must be performed in the oxygen transport limited region when the temperature effect on the oxidation ratio is insignificant. To investigate influence of oxygen partial pressure on glycerol oxidation, experiments were performed under the following conditions: $c_0(\text{C}_3\text{H}_8\text{O}_3) = 0.3 \text{ mol dm}^{-3}$;

TABLE IV. Glycerol oxidation; effect of p_{O_2} , $n(C_3H_8O_3)/n(Pt)$ and initial NaOH concentration; reaction conditions: $T = 60$ °C; reaction time, 7 h; catalyst: 4.8 % Pt/Al₂O₃; catalyst calcination temperature and time: 300 °C and 120 min, respectively

$n(C_3H_8O_3)/n(Pt)$	$c_0(NaOH)$ mol dm ⁻³	Glycerol conversion %	Selectivity, %							
			GLYA	GLYAD	DIHA	TART	LACT	GLYC	OXAL	FORM
300	0.7	92	57	-	-	12	17	9	3	2
500		92	52	-	-	12	21	12	2	1
500 ^a		44	55	-	-	3	29	10	2	1
500 ^b		85	50	-	-	23	10	9	7	1
300	1.5	82	59	-	-	10	20	7	1	3
500		57	63	-	-	7	17	9	1	3
300	-	49	47	32	8	-	-	9	2	2

^a $p_{O_2} = 0.2$ atm; ^b $p_{O_2} = 3$ atm

$c_0(\text{NaOH}) = 0.7 \text{ mol dm}^{-3}$; $n(\text{C}_3\text{H}_8\text{O}_3)/n(\text{Pt}) = 500$. From the data presented in Table IV, it could be seen that the best result was attained when $p_{\text{O}_2} = 1 \text{ atm}$ was applied. The glycerol conversion increased by 7 % when the oxidation was realized at $p_{\text{O}_2} = 3 \text{ atm}$ in comparison with that at $p_{\text{O}_2} = 1 \text{ atm}$. Moreover, it was found that with further oxidation, the glycerol conversion did not change but the selectivity to glyceric acid decreased. It was impossible to reach a conversion above 45 % when glycerol was oxidised at $p_{\text{O}_2} = 0.2 \text{ atm}$. Atmospheric oxygen pressure was used in the further studies on the effect of other oxidation parameters on glycerol conversion and oxidation selectivity.

Data from Table IV show that at $p_{\text{O}_2} = 1 \text{ atm}$, a higher glycerol conversion of 92 % was reached when the initial concentration of NaOH was 0.7 M, which was not dependent on the $n(\text{C}_3\text{H}_8\text{O}_3)/n(\text{Pt})$ ratio. In a 1.5 M NaOH solution, the glycerol conversion decreased by 25 % if the $n(\text{C}_3\text{H}_8\text{O}_3)/n(\text{Pt})$ was increased from 300 to 500. Selectivity to the main product, glyceric acid, was similar and ranged from 52 to 59 % in both aqueous 0.7 and 1.5 M NaOH solutions when the glycerol conversion was 82–92 %, respectively. In addition, in the base-free solution, the glycerol conversion decreased noticeably to 49 % and the selectivity to glyceric acid decreased from 59–57 to 47 % with new products, such as glyceraldehyde and dihydroxyacetone, being formed. As was mentioned above, Liang *et al.*⁸ reported that a 5 % Pt/MWNTs catalyst in a base-free aqueous solution was more selective to glyceric acid (68 %) at the same glycerol conversion (90 %). This apparent contradiction with the present results could be explained by an effect of the nature of the support on glycerol oxidation.

The influence of temperature on the oxidation rate of glycerol data is shown in Fig. 1, from which it could be seen that temperature had almost no effect.

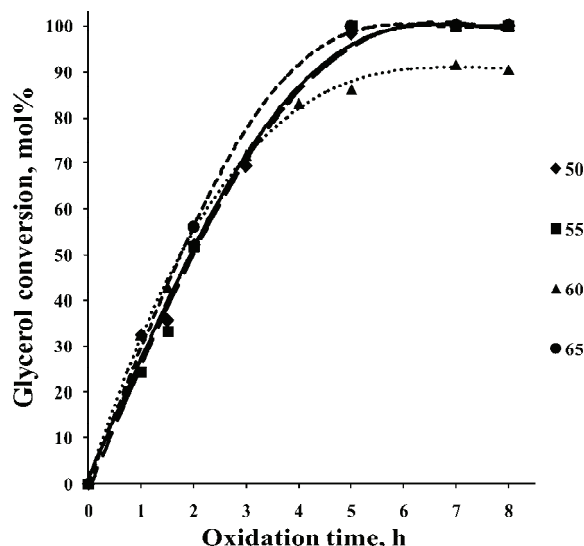


Fig. 1. Effect of temperature on glycerol oxidation over the 4.8 % Pt/Al₂O₃ catalyst. Reaction conditions: $c_0(\text{C}_3\text{H}_8\text{O}_3) = 0.3 \text{ mol dm}^{-3}$, $c_0(\text{NaOH}) = 1.5 \text{ mol dm}^{-3}$, $n(\text{C}_3\text{H}_8\text{O}_3)/n(\text{Pt}) = 300$ and $p_{\text{O}_2} = 1 \text{ atm}$.

The changes in selectivity to glyceric acid with oxidation time at different temperatures are shown in Fig. 2. Analyzing the data shown in Figs. 1 and 2, it could be concluded that at a glycerol conversion of 90 %, the selectivity to glyceric acid was similar (50–56 %) at 50–60 °C. At the higher temperature (65 °C), the selectivity to glyceric acid was only 40 % at the same glycerol conversion. It should be noted that only at 60 °C was the selectivity to glyceric acid higher and independent of glycerol conversion.

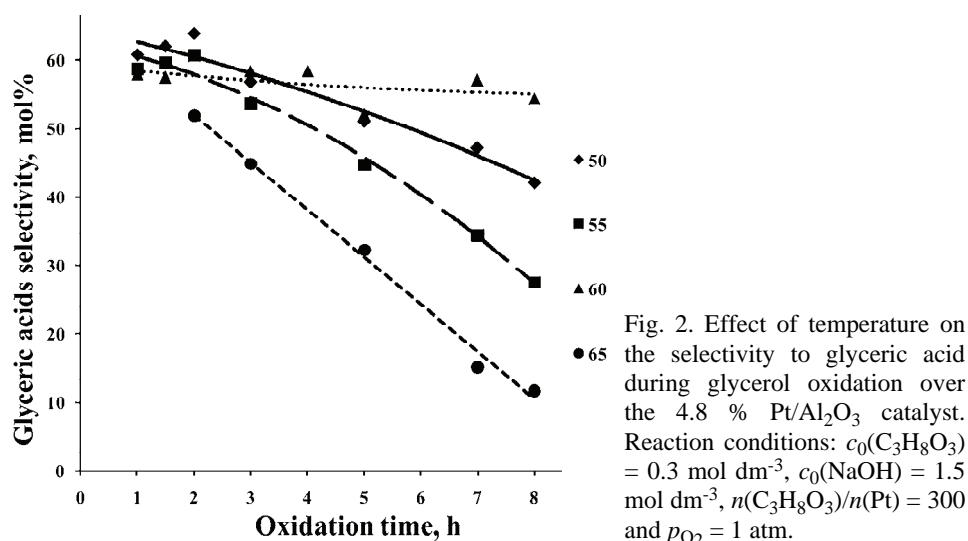


Fig. 2. Effect of temperature on the selectivity to glyceric acid during glycerol oxidation over the 4.8 % Pt/Al₂O₃ catalyst. Reaction conditions: $c_0(\text{C}_3\text{H}_8\text{O}_3) = 0.3 \text{ mol dm}^{-3}$, $c_0(\text{NaOH}) = 1.5 \text{ mol dm}^{-3}$, $n(\text{C}_3\text{H}_8\text{O}_3)/n(\text{Pt}) = 300$ and $p_{\text{O}_2} = 1 \text{ atm}$.

CONCLUSIONS

It was demonstrated that the extractive–pyrolytic method could be employed for the preparation of supported platinum catalysts for the selective oxidation of glycerol. By optimization of catalyst preparation and glycerol oxidation process parameters, the optimal conditions for the selective production of glyceric acid were found for the most effective novel 4.8 % Pt/Al₂O₃ catalyst to be: catalyst calcination temperature, 300 °C; calcination time, 120 min; $c_0(\text{C}_3\text{H}_8\text{O}_3)$, 0.3 mol dm⁻³; $c_0(\text{NaOH})$, 0.7 mol dm⁻³; $n(\text{C}_3\text{H}_8\text{O}_3)/n(\text{Pt})$, 300; temperature, 60 °C and P_{O_2} , 1 atm, when a glycerol conversion of 92 % and a selectivity to glyceric acid of 57 % were achieved.

Acknowledgment. This work was supported by the European Regional Development Fund – Project No. 2010/0304/2DP/2.1.1.1.0/10/APIA/VIAA/087.

ИЗВОД

СЕЛЕКТИВНА ОКСИДАЦИЈА ГЛИЦЕРОЛА ДО ГЛИЦЕРИНСКЕ КИСЕЛИНЕ
У ТЕЧНОЈ ФАЗИ СА Pt КАТАЛИЗАТОРИМА

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Неколико чврстих Pt катализатора за селективно добијање глицеринске киселине из глицерола су припремљени поступком који је комбинација екстракције и пиролизе. Al₂O₃, Y₂O₃, Lu₂O₃, ZrO₂-Y₂O₃, TiO₂, SG, Fe₂O₃, γ-AlO(OH) и C су коришћени као носачи катализатора. Оксидација глицерола је вршена у алкалним растворима и кисеоник је коришћен као оксиданс. Одређени су оптимални параметри за припрему катализатора и услови оксидације глицерола при којим се добија глицеринска киселина. Најбољи резултат (селективност за глицеринску киселину 57 % са конверзијом глицерола 92 %) постигнут је у присуству катализатора 4,8 % Pt/Al₂O₃.

(Примљено 3. децембра 2012, ревидирано 26 фебруара 2013)

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