



## Novel Pd/CeO<sub>2</sub> and Pd-NiO/CeO<sub>2</sub> nanocomposites' catalytic activity in glycerol oxidation processes

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**Abstract.** In this work novel Pd supported on cerium oxide nanocomposites in the liquid phase glycerol oxidation with molecular oxygen was studied. Pd/CeO<sub>2</sub> and Pd-NiO/CeO<sub>2</sub> composites with different Pd loading were prepared using the extractive-pyrolytic method. In the glycerol oxidation processes it was found that Pd/CeO<sub>2</sub> and Pd-NiO/CeO<sub>2</sub> composites are catalytically active. Besides, NiO additives can significantly increase Pd/CeO<sub>2</sub> catalysts' activity and selectivity to the main product – glyceric acid. Several glycerol oxidation parameters like NaOH initial concentration, glycerol/Pd molar ratio, oxygen pressure and temperature were varied. The best yield of glyceric acid reached 71–75 mol% with full glycerol conversion.

**Key words:** catalysis, oxidation, glycerol, nanocomposites, supported catalysts.

### 1. INTRODUCTION

With the extensive search for alternative renewable energy sources and development of the biodiesel industry, glycerol has been produced in large amounts reaching considerable surplus. Glycerol is the main by-product in vegetable oil transesterification process to biodiesel and its yield is about 10 wt% [1]. Due to the high abundance of glycerol, low price and excellent functionality, glycerol utilization gains a lot of attention. Liquid phase catalytic oxidation of glycerol is one of the most promising routes to produce some high-value chemicals [2]. The most common products obtained by glycerol oxidation are glyceric acid, lactic acid and dihydroxyacetone, which find potential applications in polymer and fine chemical industries [3]. Catalytic oxidation with molecular oxygen

in the presence of supported noble metal catalysts is environmentally friendly and mild glycerol utilization method. Catalysts can be reused [4–6].

Nanoscale palladium-based catalysts have been found to be very active in the glycerol oxidation processes. Compared to Au catalysts, which are the most studied catalysts in the glycerol oxidation field, Pd is relatively cheap, abundant and it can be used in neutral solutions [2]. Up to now several different Pd supports, mainly metal oxides (C, Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, combined oxide of Zr and Ce) have been used and it has been found that Pd containing catalysts' activity and product distribution strongly depend on the nature of the support [7–10].

In this work novel Pd supported on cerium oxide composites' catalytic activity in the liquid phase glycerol oxidation with molecular oxygen was studied. CeO<sub>2</sub> is a versatile material, its wide use is attributed to ceria unique redox features, which enables the oxide to act as

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an excellent oxygen storage material [11]. In the glycerol oxidation related processes bimetallic Au-Pt and bimetallic Ag-Au, Ag-Pt, Ag-Pd catalysts supported on CeO<sub>2</sub> until now have been investigated [12,13]. Also mixed cerium-zirconium oxide as support for gold and copper or for gold and ruthenium monometallic and bimetallic catalysts have been investigated [14,15]. During this work several novel Pd/CeO<sub>2</sub> and Pd-NiO/CeO<sub>2</sub> nanocomposites with different Pd loading were prepared using the extractive-pyrolytic method. Composite compositions' as well as glycerol oxidation parameters' influence on glycerol oxidation results was investigated.

## 2. MATERIALS AND METHODS

### 2.1. Reagents and supplies

Following reagents were used for the preparation of composites' precursors: palladium in powder (99.99%, Sigma-Aldrich), HCl (35%, Lachema), HNO<sub>3</sub> (65%, Lachema), trioctylamine ((C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N) (95%, Fluka), toluene (analytical grade, Stanchem). In the composites' synthesis CeO<sub>2</sub> nanopowder (Sigma-Aldrich) was used as support.

In the glycerol oxidation experiments glycerol (≥98%, Fluka), NaOH (reagent grade, Sigma-Aldrich) and oxygen (98%, AGA) were used.

For the identification of the possible products of the glycerol oxidation several standard substances as follows 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, Fluka), formate standard for IC (1.000 g/L, Fluka). For an eluent preparation trifluoroacetic acid (LC/MS, Fisher Scientific) was used. For solutions' preparation water purified by the MilliporeDirect-Q 3 UV water purification system was used.

### 2.2. Composites' preparation

Supported palladium composites were prepared by extractive-pyrolytic method described in [16,17]. In the case of monometallic Pd/CeO<sub>2</sub> nanocomposites, the composites' preparation started with the production of an organic precursor by the liquid extraction method. In order to obtain precursor, 20 mL of 1.0 mol/L tetrachloride palladium acid solution in 2 mol/L hydrochloric acid solution was added to 50 mL of 1 mol/L trioctylamine

solution in toluene. After shaking the mixture for 5 min, the organic phase was separated from the water phase and filtered. The obtained organic phase, which was a 0.4 mol/L [(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>NH]<sub>2</sub>PdCl<sub>4</sub> solution in toluene, was the composites' precursor and it was added to the support (CeO<sub>2</sub>). The amount of support was calculated as having a final palladium loading on the composite (0.4–2.8 wt% by weight of support). The obtained system was stirred for 10 min, during which support was impregnated by precursor. After impregnation the support and precursor mixture was dried for 20–60 min at room temperature. The dry mixture was then calcinated at 300 °C for 5 min at the atmospheric pressure. During the calcination stage, all the Pd compound in the precursor was reduced to Pd (0).

For the preparation of Pd-NiO/CeO<sub>2</sub> composites, at first NiO/CeO<sub>2</sub> composite was prepared. NiO/CeO<sub>2</sub> composite's preparation started with production of nickel-containing organic extract (precursor), which is described in details in [18]. After organic extract was prepared, support (CeO<sub>2</sub>) was impregnated in it. Following sample was dried at room temperature and calcinated at 300 °C for 30 min. After NiO/CeO<sub>2</sub> composite was produced, it was impregnated by palladium precursor, dried and calcinated in the same way as it was described in the Pd/CeO<sub>2</sub> composites' preparation. Loading of NiO was kept constant in all Pd-NiO/CeO<sub>2</sub> composites and was 5.0 wt%, while Pd loading varied from 0.4–2.8 wt%.

### 2.3. Equipment

The characterization of novel nanocomposites' morphology, crystallization, chemical content and surface area was done by scanning electron microscopy (SEM TESCAN LYRA3), X-ray diffraction (XRD), X-ray fluorescence (XRF) and BET surface area analysis method. The phase composition was determined by XRD analysis with D8 Advance, Bruker AXS system. The Pd crystallite size  $d_{Pd}$  was calculated from broadening of diffraction maxima using the Scherrer Equation (software Topas 3). Chemical analysis was performed by means of the S4 Pioneer X-ray Spectrometer (Bruker AXS). The BET specific surface area (SSA) of the composites was determined by nitrogen adsorption at –196 °C with a HROM-3 chromatograph.

The oxidation experiments of aqueous glycerol solutions with molecular oxygen in the presence of novel composites was performed in an autoclave and in a thermostated slurry bubble column reactor operated in batch mode. Glycerol oxidation process parameters like NaOH initial concentration  $c_0(\text{NaOH}) = 0\text{--}1.5$  mol/L, glycerol and palladium molar ratio  $n(\text{glycerol})/n(\text{Pd}) = 300\text{--}1000$  mol/mol, reaction temperature 45–60 °C and oxygen pressure from

1 to 6 atm were varied. Glycerol initial concentration  $c_0(\text{glycerol})$  was 0.3 mol/L. Analysis of the reaction mixture was performed by high-performance liquid chromatograph Shimadzu Nexera equipped with UV-Vis SHIMADZU SPD-20A (UV 210 nm) and ELSD-LTII detectors. A Waters IC-PAC Ion-Exclusion column (300 mm  $\times$  7.8 mm) (75 °C) was used with aqueous trifluoroacetic acid 0.045 vol% as the eluent.

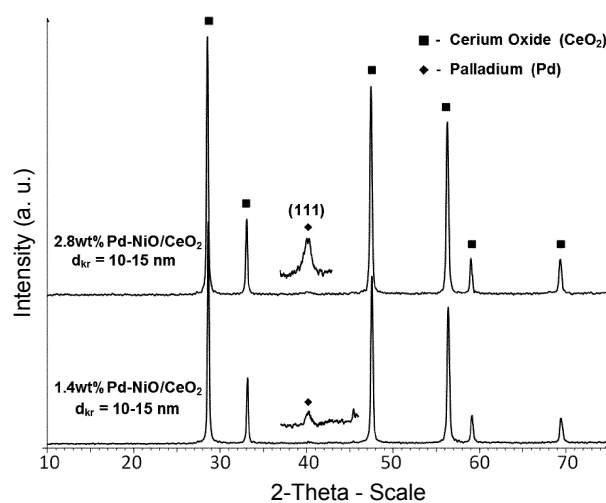
### 3. RESULTS AND DISCUSSION

#### 3.1. Composites' characterization

Figure 1 shows a typical SEM image and EDS spectra of the 1.4 wt% Pd-NiO/CeO<sub>2</sub> composite. The data testify that the composite particles form agglomerates with irregular shapes and sizes from 1–100  $\mu\text{m}$ . The EDS spectrum shows the presence of palladium and nickel in the produced composite.

In our early work [18] it was found that after thermal treatment at 300 °C NiO/CeO<sub>2</sub> composite was x-ray amorphous. XRD pattern of the 1.4 wt% Pd-NiO/CeO<sub>2</sub> and 2.8 wt% Pd-NiO/CeO<sub>2</sub> composites shown in Fig. 2 approves the presence of Pd. X-ray diffraction analysis presents that with the increase of Pd loading, the characteristic Pd (111) peak becomes more apparent.

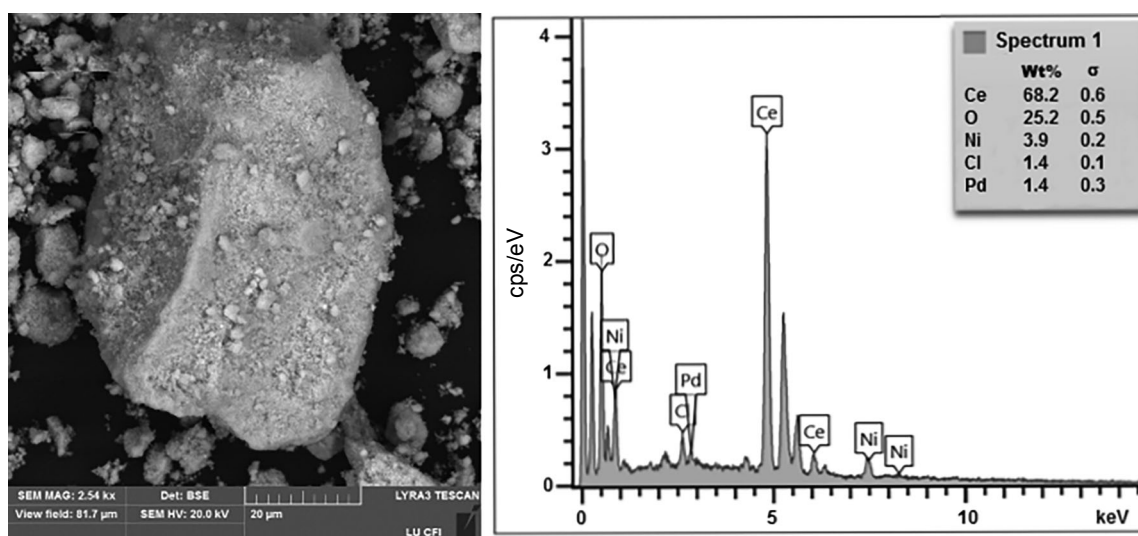
In Table 1 results of specific surface area and size of Pd crystallites  $d_{\text{Pd}}$  measurements for some Pd/CeO<sub>2</sub> and Pd-NiO/CeO<sub>2</sub> composites as well as support are shown. As it can be seen from Table 1, surface area decreases with increasing content of Pd in both cases – promoted with NiO and non-promoted Pd composites. Surface



**Fig. 2.** XRD pattern of the 1.4 wt% Pd-NiO/CeO<sub>2</sub> and 2.8 wt% Pd-NiO/CeO<sub>2</sub> composites.

**Table 1.** Specific surface areas and size of Pd crystallites of some synthesized composites

Composite	SSA (m <sup>2</sup> /g)	$d_{\text{Pd}}$ (nm)
CeO <sub>2</sub>	26	–
NiO/CeO <sub>2</sub>	29	–
0.7 wt% Pd/CeO <sub>2</sub>	26	–
2.8 wt% Pd/CeO <sub>2</sub>	16	10–15
0.7 wt% Pd-NiO/CeO <sub>2</sub>	28	–
1.4 wt% Pd-NiO/CeO <sub>2</sub>	22	10–15
2.8 wt% Pd-NiO/CeO <sub>2</sub>	19	10–15



**Fig. 1.** SEM image (left) and EDS analysis (right) of the 1.4 wt% Pd-NiO/CeO<sub>2</sub> composite.

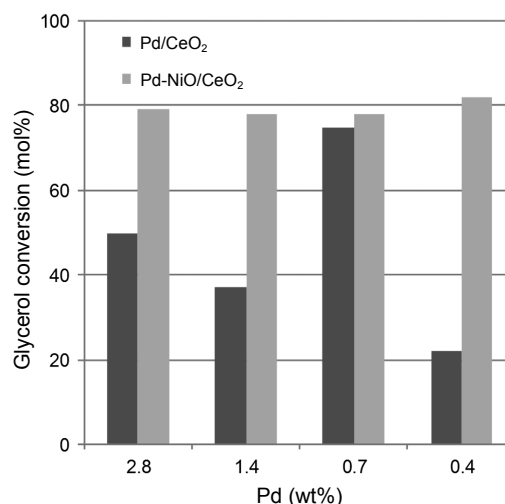
areas of non-promoted and promoted Pd composites with the same Pd loading are similar. Pd crystallite sizes determined by XRD for 1.4 and 2.8 wt% Pd containing composites are also similar (10–15 nm).

### 3.2. Glycerol oxidation

Glycerol oxidation with molecular oxygen tests in the presence of novel Pd supported composites showed that these composites are catalytically active for the glycerol conversion into other products. By comparing Pd/CeO<sub>2</sub> and Pd-NiO/CeO<sub>2</sub> composites, it was found that NiO additives can significantly increase Pd/CeO<sub>2</sub> composites' activity. From Fig. 3 it can be seen, that regardless of Pd loading glycerol conversion in the presence of NiO containing composites was greater. This could be explained by NiO promotional effect caused by synergy, which occurs between Pd and NiO particles reported in [19]. Testing composite NiO/CeO<sub>2</sub> without Pd in the glycerol oxidation experiments, it was found that it doesn't show catalytic activity.

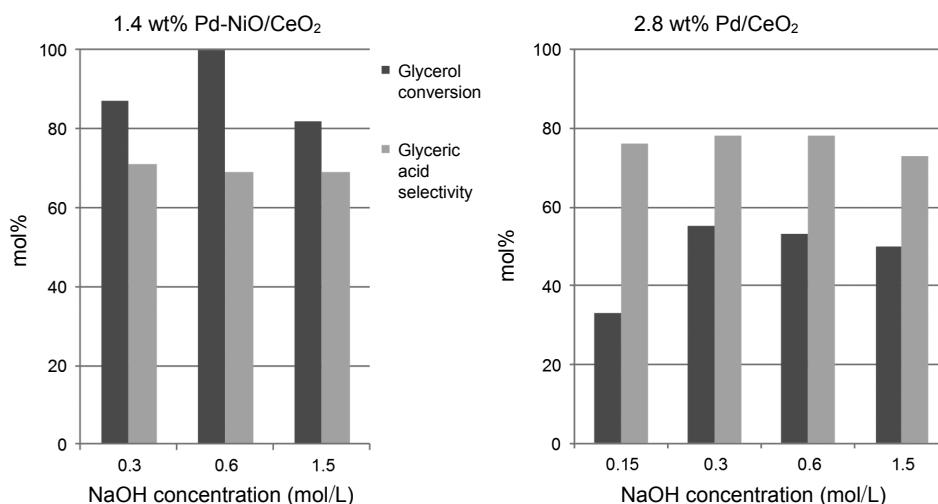
The main glycerol oxidation product over all Pd containing composites was glyceric acid. By-products were lactic, tartronic, glycolic, oxalic, acetic and formic acids. Comparing Pd containing composites' activity depending on Pd loading, from Fig. 3 it can be seen that, in the case of Pd-NiO/CeO<sub>2</sub> composites, glycerol conversion was similar in all cases (74–82 mol%), while non-promoted composites activities' dependence on Pd loading was ambiguous.

Using one of the promoted composites (1.4 wt% Pd-NiO/CeO<sub>2</sub>) as well as one of non-promoted composites (2.8 wt% Pd/CeO<sub>2</sub>), influence of NaOH was determined (Fig. 4 (left) and (right), respectively). At first,



**Fig. 3.** Glycerol conversion in the presence of Pd/CeO<sub>2</sub> and Pd-NiO/CeO<sub>2</sub> composites depending on Pd loading (oxidation conditions:  $c_0(\text{glycerol}) = 0.3 \text{ mol/L}$ ,  $c_0(\text{NaOH}) = 1.5 \text{ mol/L}$ ,  $n(\text{glycerol})/n(\text{Pd}) = 300 \text{ mol/mol}$ ,  $p\text{O}_2 = 1 \text{ atm}$ ,  $60 \text{ }^\circ\text{C}$ , reaction time 5 h).

it was experimentally tested that non-promoted as well as promoted Pd containing composites are inactive in base-free glycerol solutions, so base is needed to initiate the reaction. NaOH initial concentration was varied in the range 0.3–1.5 mol/L. From Fig. 4 it can be seen that optimal NaOH initial concentration in the case of promoted composite was 0.6 mol/L, when full glycerol conversion was reached. If NaOH concentration was increased until 1.5 mol/L, glycerol conversion decreased by almost 20 mol%, which could be related with greater media viscosity determined by NaOH and also with



**Fig. 4.** NaOH initial concentration influence on the glycerol oxidation results in the presence of 1.4 wt% Pd-NiO/CeO<sub>2</sub> composite (left) and 2.8 wt% Pd/CeO<sub>2</sub> composite (right) (oxidation conditions:  $c_0(\text{glycerol}) = 0.3 \text{ mol/L}$ ,  $n(\text{glycerol})/n(\text{Pd}) = 300 \text{ mol/mol}$ ,  $p\text{O}_2 = 1 \text{ atm}$ ,  $60 \text{ }^\circ\text{C}$ , reaction time 5 h).

lower oxygen dissolution in the liquid medium [20]. In the presence of Pd/CeO<sub>2</sub> composite it was found out that optimal concentration of NaOH was 0.3 mol/L. Selectivity of Pd containing composites to the main product – glyceric acid – was similar for both composites – selectivity didn't depend on the change of NaOH concentration, neither on glycerol conversion. In further experiments only the most active composite – 1.4 wt% Pd-NiO/CeO<sub>2</sub> – was used.

Investigating the influence of composites' amount in the reaction mixture, glycerol/Pd molar ratio in the range from 300 to 1000 mol/mol was varied (Table 2). Glycerol/Pd molar ratio increase from 300 to 500 didn't influence glycerol oxidation results, when oxidation was carried out at atmospheric pressure. Obtained glycerol conversion and glyceric acid selectivity was similar at both ratios. Glycerol/Pd molar ratio increase until 1000 mol/mol, as suspected, significantly reduced glycerol conversion. Conversion decreased more than two times – from 74–32 mol%.

Using small amounts of 1.4 wt% Pd-NiO/CeO<sub>2</sub> composite (n(glycerol)/n(Pd) = 1000 mol/mol), oxygen

pressure influence on glycerol oxidation was also studied (Table 2). Oxygen pressure was varied in the range from 1 to 6 atm. As it can be seen from Table 2, high oxygen pressure (above 1 atm) causes deactivation of catalyst surface and therefore is not allowed. It coincides with the literature where it is said that one of the significant platinum group metal disadvantages is their over-oxidation at high oxygen pressures. Over-oxidation, which is the coverage of surface sites by oxygen, leads to catalyst deactivation and a slowdown of alcohol oxidation [21,22].

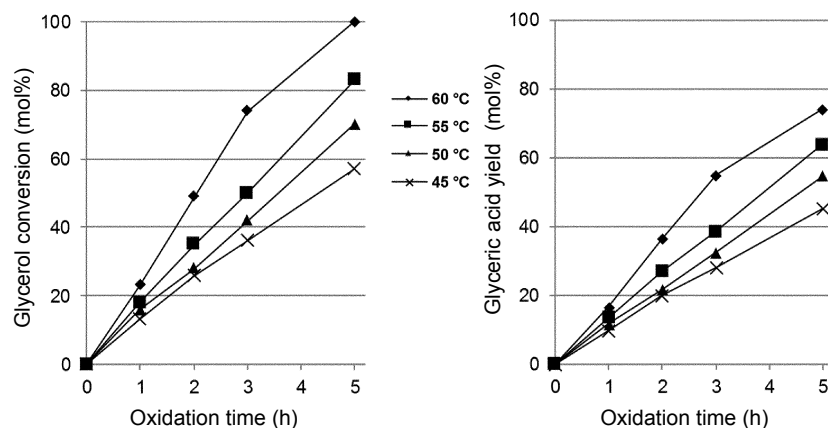
Glycerol/Pd molar ratio of 500 mol/mol and oxidation at atmospheric pressure was found to be optimal conditions. Extending glycerol oxidation duration from 3–5 h at mentioned conditions, full glycerol conversion was reached with glyceric acid selectivity of 74 mol%.

In this work also influence of oxidation temperature at pO<sub>2</sub> = 1 atm was investigated. Oxidation temperature was varied in the range from 45–60 °C. Glycerol conversion and glyceric acid yield dependence on temperature using 1.4 wt% Pd-NiO/CeO<sub>2</sub> composite as catalyst is shown in Fig. 5 (left) and (right), respectively.

**Table 2.** Glycerol/Pd molar ratio and oxygen pressure influence on the glycerol oxidation results in the presence of 1.4 wt% Pd-NiO/CeO<sub>2</sub> composite

n(glycerol)/n(Pd) (mol/mol)	pO <sub>2</sub> (atm)	Glycerol conversion (mol%)	Product selectivity (mol%)			
			Glyceric acid	Lactic acid	Tartronic acid	Glycolic acid
300	1	77	74	11	5	6
500	1	74	74	12	5	5
500*	1	100	74	11	6	6
1000	1	32	78	9	4	6
1000	3	22	72	5	3	15
1000	6	24	73	4	3	16

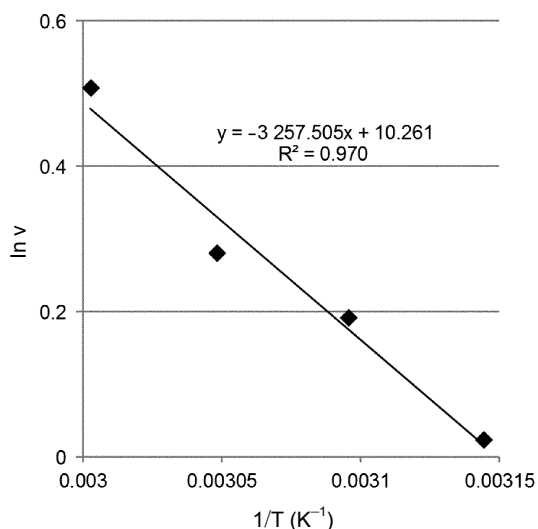
Oxidation conditions: c<sub>0</sub>(glycerol) = 0.3 mol/L, c<sub>0</sub>(NaOH) = 0.6 mol/L, 60 °C, reaction time 3 h (\* 5 h). Total selectivity of by-products as oxalic acid, acetic acid and formic acid didn't exceed 5 mol%.



**Fig. 5.** Temperature influence on glycerol conversion (left) and glyceric acid yield (right) in the presence of 1.4 wt% Pd-NiO/CeO<sub>2</sub> composite (oxidation conditions: c<sub>0</sub>(glycerol) = 0.3 mol/L, c<sub>0</sub>(NaOH) = 0.6 mol/L, n(glycerol)/n(Pd) = 500 mol/mol, pO<sub>2</sub> = 1 atm).

It was concluded that higher oxidation temperature leads to greater glycerol conversion. Increasing temperature from 45–60 °C, glycerol conversion rose by 40 mol%. Selectivity to glyceric acid at different temperatures and different glycerol conversions was similar. Thereby the greatest yields of glyceric acid (see Fig. 5 (right)) was reached at the 60 °C temperature when glycerol conversion was complete. The best yield of glyceric acid was 74 mol%. Obtained glyceric acid yield was greater than that reached previously in [23], where in the presence of similar Pt containing catalyst (4.8 wt% Pt-NiO/CeO<sub>2</sub>) yield of glyceric acid was 68 mol% (glycerol oxidation conditions were as follows:  $c_0(\text{glycerol}) = 0.3 \text{ mol/L}$ ,  $c_0(\text{NaOH}) = 1.5 \text{ mol/L}$ ,  $n(\text{glycerol})/n(\text{Pt}) = 1000 \text{ mol/mol}$ ,  $p\text{O}_2 = 6 \text{ atm}$ ,  $t = 70 \text{ °C}$ , oxidation time 3 h). Besides oxidation in the presence of novel 1.4 wt% Pd-NiO/CeO<sub>2</sub> composite was milder method – it required lower temperature and oxygen pressure, smaller initial NaOH concentration.

Fig. 6 represents an Arrhenius type plot of reaction rate versus temperature. Apparent activation energy was calculated from the Arrhenius type plot and was found to be about  $27 \pm 3 \text{ kJ/mol}$ . The low value of activation energy testifies that the oxidation process occurs in the transition region, where the mass transfer rate approximately equals to the chemical reaction rate.



**Fig. 6.** Arrhenius type plot illustrating the influence of temperature on glycerol oxidation rate in the presence of 1.4 wt% Pd-NiO/CeO<sub>2</sub> composite (reaction conditions:  $c_0(\text{glycerol}) = 0.3 \text{ mol/L}$ ,  $c_0(\text{NaOH}) = 0.6 \text{ mol/L}$ ,  $n(\text{glycerol})/n(\text{Pt}) = 500 \text{ mol/mol}$ ,  $p\text{O}_2 = 1 \text{ atm}$ , reaction time 60 min).

#### 4. CONCLUSIONS

It was found that Pd/CeO<sub>2</sub> and Pd-NiO/CeO<sub>2</sub> composites are catalytically active in the glycerol oxidation processes. NiO additives can significantly increase Pd/CeO<sub>2</sub> catalysts' performance and yield of the main product – glyceric acid. Decreasing NaOH initial concentration from 1.5–0.6 mol/L, glycerol conversion was improved when Pd-NiO/CeO<sub>2</sub> composite was used. The change of glycerol/Pd molar ratio showed that the ratio 500 mol/mol was optimal. Oxygen pressure above 1 atm was not allowed, because of catalyst's deactivation. The best yield of the main product – glyceric acid – was 74 mol% with full glycerol conversion and it was achieved in the presence of 1.4 wt% Pd-NiO/CeO<sub>2</sub> composite at the following oxidation parameters:  $c_0(\text{glycerol}) = 0.3 \text{ mol/L}$ ,  $c_0(\text{NaOH}) = 0.6 \text{ mol/L}$ ,  $n(\text{glycerol})/n(\text{Pt}) = 500 \text{ mol/mol}$ ,  $p\text{O}_2 = 1 \text{ atm}$ , 60 °C.

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#### REFERENCES

1. Malleshham, B., Sudarsanam, P., Reddy, B. V. S., and Reddy, B. M. Development of cerium promoted copper-magnesium catalysts for biomass valorization: selective hydrogenolysis of bioglycerol. *Appl. Catal. B Environ.*, 2016, **181**, 47–57.
2. Bee, S., Hamid, A., Basiron, N., Yehye, W. A., Sudarsanam, P., and Bhargava, S. K. Nanoscale Pd-based catalysts for selective oxidation of glycerol with molecular oxygen: structure – activity correlations. *Polyhedron*, 2016, **120**, 124–133.
3. Dou, J., Zhang, B., Liu, H., Hong, J., Yin, S., Huang, Y., and Xu, R. Carbon supported Pt<sub>9</sub>Sn<sub>1</sub> nanoparticles as an efficient nanocatalyst for glycerol oxidation. *Appl. Catal. B Environ.*, 2016, **180**, 78–85.
4. Cornaja, S., Dubencovs, K., Kulikova, L., Serga, V., Kampars, V., Zizkuna, S., Stepanova, O., Sproge, E., and Cvetkovs, A. Process for the preparation of lactic acid from glycerol. *Pat. EP2606968B1* (20.01.2016).
5. Painter, R. M., Pearson, D. M., and Waymouth, R. M. Selective catalytic oxidation of glycerol to dihydroxyacetone. *Angew. Chemie Int. Ed.*, 2010, **49**, 9456–9459.
6. Gil, S., Marchena, M., Fernández, C. M., Sánchez-Silva, L., Romero, A., and Valverde, J. L. Catalytic oxidation of crude glycerol using catalysts based on Au supported on carbonaceous materials. *Appl. Catal. A Gen.*, 2013, **450**, 189–203.

7. Chornaja, S., Dubencov, K., Kampars, V., Stepanova, O., Zhizhkun, S., Serga, V., and Kulikova, L. Oxidation of glycerol with oxygen in alkaline aqueous solutions in the presence of supported palladium catalysts prepared by the extractive-pyrolytic method. *React. Kinet. Mech. Catal.*, 2013, **108**, 341–357.
8. Namdeo, A., Mahajani, S. M., and Suresh, A. K. Palladium catalysed oxidation of glycerol – effect of catalyst support. *Mol. Catal. A: Chem.*, 2016, **421**, 45–56.
9. Gross, E. and Somorjai, G. A. The impact of electronic charge on catalytic reactivity and selectivity of metal-oxide supported metallic nanoparticles. *Top. Catal.*, 2013, **56**, 1049–1058.
10. Olmos, C. M., Chinchilla, L. E., Rodrigues, E. G., Delgado, J. J., Hungria, A. B., Blanco, G., Pereira, M. F. R., Orfao, J. J. M., Calvino, J. J., and Chen, X. Synergistic effect of bimetallic Au-Pd supported on ceria-zirconia mixed oxide catalysts for selective oxidation of glycerol. *Appl. Catal. B Environ.*, 2016, **197**, 222–235.
11. Pantaleo, G., Parola, V. L., Deganello, F., Singha, R. K., Bal, R., and Venezia, A. M. G. Ni/CeO<sub>2</sub> catalysts for methane partial oxidation: synthesis driven structural and catalytic effects. *Appl. Catal. B Environ.*, 2016, **189**, 233–241.
12. Purushothaman, R. K. P., van Haveren, J., van Es, D. S., Melián-Cabrera, I., Meeldijk, J. D., and Heeres, H. J. An efficient one pot conversion of glycerol to lactic acid using bimetallic gold-platinum catalysts on a nanocrystalline CeO<sub>2</sub> support. *Appl. Catal. B Environ.*, 2014, **147**, 92–100.
13. Zaid, S., Skrzyńska, E., Addad, A., Nandi, S., Jalowiecki-Duhamel, L., Girardon, J. S., Capron, M., and Dumeignil, F. Development of silver based catalysts promoted by noble metal M (M = Au, Pd or Pt) for glycerol oxidation in liquid phase. *Top. Catal.*, 2017, **60**(15–16), 1072–1081.
14. Kaminski, P., Ziolek, M., and van Bokhoven, J. A. Mesoporous cerium–zirconium oxides modified with gold and copper – synthesis, characterization and performance in selective oxidation of glycerol. *RSC Adv.*, 2017, **7**, 7801–7819.
15. Chinchilla, L. E., Olmos, C. M., Villa, A., Carlsson, A., Prati, L., Chen, X., Blanco, G., Calvino, J. J., and Hungria, A. B. Ru-modified Au catalysts supported on ceria-zirconia for the selective oxidation of glycerol. *Catal. Today*, 2015, **253**, 178–189.
16. Serga, V., Kulikova, L., Cvetkov, A., and Krumina, A. EPM fine-disperse platinum coating on powder carriers. *IOP Conf. Ser. Mater. Sci. Eng.*, 2012, **38**, 12062–12065.
17. Palcevskis, E., Kulikova, L., Serga, V., Cvetkovs, A., Chornaja, S., Sproge, E., and Dubencovs, K. Catalyst materials based on plasma-processed alumina nanopowder. *J. Serbian Chem. Soc.*, 2012, **77**, 1799–1806.
18. Serga, V., Cvetkovs, A., Krumina, A., Chornaja, S., Kunakovs, J., and Maiorov, M. Production of CeO<sub>2</sub>/NiO and CeO<sub>2</sub>/NiO-Pt nanocomposites by EPM. *Int. J. New Technol. Res.*, 2016, **2**, 123–127.
19. Li, Y., Chen, S., Xu, J., Zhang, H., Zhao, Y., Wang, Y., and Liu, Z. Ni promoted Pt and Pd catalysts for glycerol oxidation to lactic acid. *Clean – Soil, Air, Water*, 2014, **42**, 1140–1144.
20. Sipos, P., Hefter, G., and May, P. Viscosities and densities of highly concentrated aqueous MOH solutions (M<sup>+</sup> = Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Cs<sup>+</sup>, (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>) at 25.0 °C. *J. Chem. Eng. Data*, 2000, **45**, 613–617.
21. Keresszegi, C., Mallat, T., Grunwaldt, J. D., and Baiker, A. A simple discrimination of the promoter effect in alcohol oxidation and dehydrogenation over platinum and palladium. *J. Catal.*, 2004, **225**, 138–146.
22. Villa, A., Wang, D., Veith, G. M., and Prati, L. Bismuth as a modifier of Au–Pd catalyst: enhancing selectivity in alcohol oxidation by suppressing parallel reaction. *J. Catal.*, 2012, **292**, 73–80.
23. Chornaja, S., Sile, E., Dubencovs, K., Bariss, H., Zhizhkuna, S., Serga, V., and Kampars, V. NiO and CoO<sub>x</sub> promoted Pt catalysts for glycerol oxidation. *Key Eng. Mater.*, 2017, **721**, 76–81.

## Uudsete Pd/CeO<sub>2</sub> ja Pd-NiO/CeO<sub>2</sub> nanokomposiitide katalüütiline aktiivsus oksüdatsiooniprotsessidel glütseroolis

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On käsitletud uudsete, tseeriumoksiidimmobiliseeritud pallaadiumi nanoosakeste katalüütilist aktiivsust vedelfaas-oksüdatsioonil (glütserool) molekulaarhappikuga. Kasutades ekstraktsioonipürolüütilist meetodit, valmistati erineva Pd sisaldusega Pd/CeO<sub>2</sub> ja Pd-NiO/CeO<sub>2</sub> komposiidid. Oksüdatsiooniprotsessil glütseroolis leiti, et Pd/CeO<sub>2</sub> ja Pd-NiO/CeO<sub>2</sub> komposiitidel on katalüütiline aktiivsus, kusjuures NiO lisand suurendab märkimisväärselt Pd/CeO<sub>2</sub> katalüütilist aktiivsust ning selektiivsust põhiprodukti glütseerhappe suhtes. Varieeriti mitmeid eksperimendiparameetreid, nagu NaOH algkontsentratsioon, glütserool/Pd moolsuhe, happikurõhk ja temperatuur. Glütseerhappe saagikuseks saadi 71–75 mol% glütserooli täielikul konversioonil.