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**Reaction Kinetics, Mechanisms and
Catalysis**

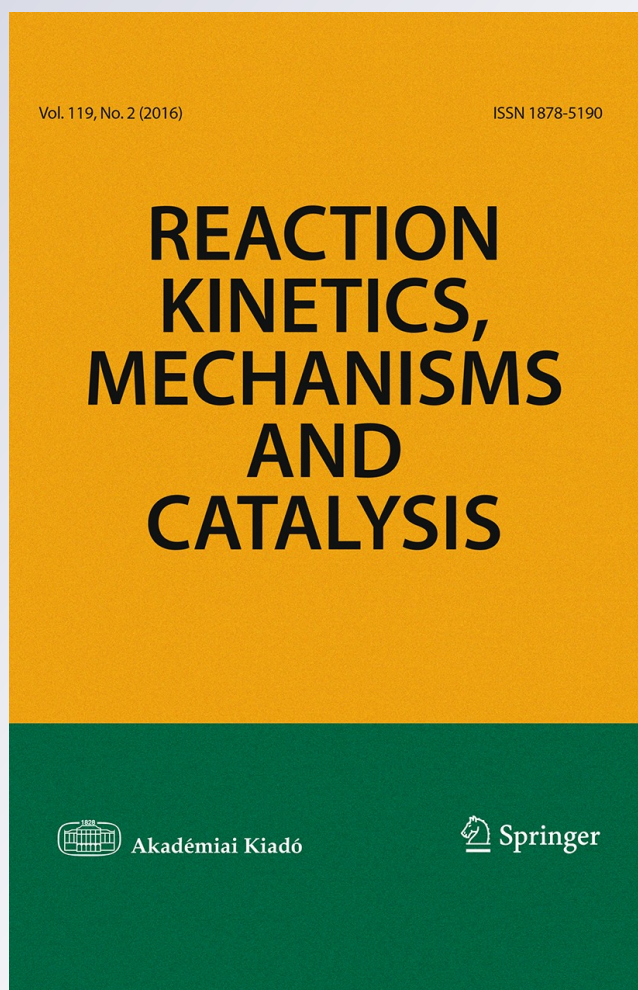
ISSN 1878-5190

Volume 119

Number 2

Reac Kinet Mech Cat (2016) 119:569-584

DOI 10.1007/s11144-016-1067-9



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Pt supported TiO₂-nanofibers and TiO₂-nanopowder as catalysts for glycerol oxidation

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Received: 7 June 2016 / Accepted: 11 August 2016 / Published online: 19 August 2016
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Abstract Novel TiO₂ nanofiber supported platinum catalysts Pt/NF–TiO₂ were synthesized and compared with TiO₂ nanopowder supported catalysts Pt/NP–TiO₂ in selective glycerol oxidation. It was found that Pt/NF–TiO₂ and Pt/NP–TiO₂ composites are catalytically active in alkaline glycerol solutions; glyceric acid is obtained as the main product of reaction. Catalyst activity and selectivity dependency on NaOH initial concentration, oxygen pressure and n(glycerol)/n(Pt) ratio were studied. Selectivity to glyceric acid of 63 % with full glycerol conversion and selectivity of 68 % with 95 % glycerol conversion is obtained correspondingly over Pt/NF–TiO₂ and Pt/NP–TiO₂ catalysts.

Keywords Biodiesel · Glycerol · Oxidation · Pt · Catalysts

Introduction

Glycerol overproduction because of increasing biodiesel manufacturing is predicted to reach about 31 billion litres in 2015. Glycerol is the main by-product of biodiesel manufacturing, where its yield equals about 10 % [1]. There is no need to do calculations to see that glycerol is obtained in huge amounts. Conventionally, glycerol is used in food, pharmaceutical and cosmetic industries, but these industries can consume only a small part of the produced glycerol, so now other applications are studied very extensively. The essence of the most of the methods is conversion

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of glycerol to value-added products. Heterogeneous glycerol oxidation is one of these glycerol utilization methods. Many important compounds, for example glyceric acid, lactic acid, glyceraldehyde, glycolic acid, tartronic acid and others can be obtained by glycerol oxidation over supported noble metal catalysts [2–5].

Compounds obtained in glycerol oxidation have a wide application, for example, glycolic acid is used in pharmaceutical industry as skin care agent, in food industry as a flavoring agent and a preservative, it is used in adhesives and plastics, in textile industry as dyeing and tanning agent, and in organic synthesis [4, 6]. Glyceric acid, lactic acid and glyceraldehyde also have a vast application in cosmetic, food industry, organic chemistry and medicine. Glyceric and lactic acids are used in production of biodegradable polymers [5, 7–10].

Supported Pt catalysts have been found to be very active in glycerol oxidation processes. Furthermore, they show activity in alkaline water solutions as well as in base-free solutions [11–13]. Pt group metal catalysts are characterized by two significant drawbacks—metal surface overoxidation in high oxygen pressure and active site poisoning with strongly adsorbed products, which both cause deactivation of the catalyst surface during oxidation process [14]. Despite these drawbacks, supported Pt catalysts are among the best and the most effective catalysts used in glycerol oxidation. Depending on catalyst type used—monometallic, bimetallic, promoted—achieved oxidation results can strongly differ [15, 16]. In comparison to two other popular noble metal catalysts (Au and Pd), in some papers, it is concluded that Pd catalysts are more active and selective to glyceric acid than supported Pt catalysts, while Au catalysts are characterized by greater resistance against metal surface overoxidation and thereby these catalysts can be applied in higher pressures to reach higher glycerol conversion [15–17].

Up to now, several Pt supports are used, of which the most popular are metal oxides [18, 19] and activated carbon [2, 20–22]. All mentioned supports are nanopowder type supports, but gradually, the popularity of other type Pt supports increase—nanotubes, nanofibers and nanowires [21, 23–27]. Most catalysts are selective to glyceric acid [20, 23, 28–31], but in some cases, also glycolic acid [4], lactic acid [2, 3] or glyceraldehyde [5, 25, 27, 32] are obtained as the main products depending on oxidation conditions. It is well known that a support and its morphology can play a significant role in the characteristics of a catalyst, following influences catalysts selectivity and activity [33–36].

The catalytic activity of platinum supported TiO_2 nanopowders is well known in various processes including selective glycerol oxidation in aqueous solutions [2, 8, 37–39], but TiO_2 nanoparticles with other morphologies (nanofibers, nanotubes, nanowires) have not been studied in glycerol oxidation yet. Until now, the catalytic properties of these particles have been used in other processes. Therefore, many preparation techniques have already been developed [40–44]. TiO_2 nanofibers are usually synthesized via electrospinning technique in combination with hydrothermal process, calcination or sol-gel method [44–47]. Microwave assisted sintering is the most promising method for fast preparation of TiO_2 nanowires. In comparison with hydro-thermal sintering, microwave assisted preparation allows obtaining nanowires with a much shorter reaction time

[42, 48]. Modification with such elements as Au, N, Cr and other allows increasing the activity of TiO_2 nanofiber catalysts in various processes [45–51].

In this work, new Pt containing nanocomposite in glycerol oxidation is studied—Pt supported TiO_2 nanofibers (Pt/NF- TiO_2). Until now, according to literature on Pt supports that have fibrous structure, only carbon nanofibers [24] and multiwall carbon nanotubes [23, 27, 52] were known. Both catalysts are selective to glyceric acid. Previously Liang et al. reported that platinum catalysts supported on multiwall carbon nanotubes Pt/MWNTs are more active in glycerol oxidation than Pt/C catalysts [21]. Oxidation was carried out under base free conditions, and in this case selectivity to glyceric acid reached 68 % with glycerol conversion of 90 % when Pt/MWNTs catalyst was used. The authors suggest that Pt particles deposited on the external wall of MWNTs can contact easily with glycerol and oxygen, and the easier accessibility of Pt could contribute to a higher activity for glycerol oxidation. Later Zhang et al. found out that carbon nanofiber supported Pt catalysts are even more effective in glycerol oxidation to glyceric acid than Pt/MWNTs catalysts at the same oxidation conditions [24]. Oxidizing glycerol over Pt/S-CNFs catalyst, selectivity to glyceric acid was 83 % at glycerol conversion of 90 %.

In this work, differences between Pt supported TiO_2 nanofiber (Pt/NF- TiO_2) and fine-disperse platinum catalyst supported on TiO_2 nanopowder (Pt/NP- TiO_2) activity and selectivity will be investigated. Pt/NP- TiO_2 catalyst has already been studied in our previous works [2, 5].

Experimental

Preparation of platinum catalyst supported on TiO_2 nanopowder (Pt/NP- TiO_2)

Supported Pt/NP- TiO_2 catalyst was prepared by extractive-pyrolytic method described in [2]. The process of catalyst preparation by the extractive-pyrolytic method was started with production of a precursor by the liquid extraction method. In order to produce the precursor, an aqueous solution of hexachloride platinum acid (H_2PtCl_6) in 2.0 mol/L hydrochloric acid was added to 1.0 mol/L trioctylamine (C_8H_{17})₃N solution in toluene. After shaking the mixture for 3–5 min, 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 ($c_{\text{Pt}} = 0.4$ mol/L) was the catalyst precursor. The precursor was added to the support. The amount of support was calculated as having a final metal loading of 4.8 wt%. The mixture was thoroughly stirred and dried for 20 min at 85–110 °C to remove the solvent. The dry mixture was heated up at a rate of 10 °C/min and calcined at 300 °C for 5 min in air.

Preparation of platinum catalyst supported on TiO₂ nanofiber (Pt/NF–TiO₂)

TiO₂ nanofiber preparation

The TiO₂ samples were prepared by a microwave method, similar to the hydrothermal method, but with shorter reaction time. For this purpose, a certain amount of TiO₂ anatase nanopowder (Sigma-Aldrich, ≥99.7 wt%, <20 nm particle size) was dissolved in 700 mL of 10 mol/L KOH water solution at room temperature. Then the solution was poured into a microwave vessel made of Teflon. The microwave treatment was performed at 230 °C for 40 min by using Anton Paar Masterwave BTR microwave system. During the reaction, the solution was stirred with a speed of 700 rpm. The as-obtained solution was then cooled to room temperature and left to precipitate TiO₂ particles. Then KOH solution was decanted from the vessel, and the obtained TiO₂ suspension was diluted with a large amount of deionized water to decrease concentration of KOH. Washing and decanting procedures were repeated several times. Finally, a certain amount 1.0 mol/L HCl was added to TiO₂ suspension to reduce pH to 7.0. The obtained suspension was filtered by using a 1.0 μm cellulose nitrate membrane filter. Particles on the filter were washed several times with deionised water and 96 % ethanol. The powder was submitted to drying at 110 °C for 24 h.

TiO₂ nanofiber modification with platinum

TiO₂ nanofiber powder was dispersed in 100 mL ethanol in an ultrasonic bath for 1 h. The amount of support was calculated as having a final Pt loading of 4.8 wt%. The obtained suspension was heated up to 60 °C and stirred for 10 min. The pH was corrected with NH₄OH until it was 5. The surface active substance—hexadecyltrimethylammonium bromide ~1.5 wt% solution in ethanol was added to TiO₂ nanofiber suspension, and the suspension was stirred. The pH was corrected to 7, and a certain mass of H₂PtCl₆·6H₂O was added, the suspension was then stirred for 10 min. Formaldehyde (10 wt%) solution, as a reduction agent, was added, and the obtained mixture was stirred for 1 h at 55–60 °C. After cooling to room temperature, the obtained Pt doped TiO₂ nanofiber suspension was filtered through 1.0 μm membrane filter. The product was washed with deionised water and ethanol. Pt doped TiO₂ nanofibers were dried for 12 h at 80 °C and calcined in air at 500 °C for 2 h.

Catalyst testing

The characterization of morphology, crystallization, chemical content and surface areas was done by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray fluorescence (XRF) and BET surface area analysis method. The phase composition was determined by using XRD analysis with D8 Advance, Bruker AXS system. The Pt crystallite size d_{kr} 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 specific surface areas (SSA) of the catalysts

were measured using HROM-3 chromatograph by BET method at the temperature of liquid nitrogen. Nanofibre morphology characterization was done by SEM TESCAN LYRA3. TEM measurements were carried out by means of transmission electron microscope JEOL JEM 2100 at 200 kV accelerating voltage and at magnifications of $\times 40,000$ – $200,000$. Histograms of Pt particle size distribution were obtained by counting of at least 200 particles from the micrographs, and the mean particle diameter (d_{Pt}) was calculated using the $d_{Pt} = \sum (d_i \cdot n_i) \cdot (\sum n_i)^{-1}$ formula, where n_i is the number of particles of specific diameter.

Glycerol oxidation

Oxidation of glycerol by molecular oxygen in presence of supported platinum catalysts was performed in a thermostated slurry bubble reactor and in an autoclave reactor.

Glycerol oxidation in a thermostated slurry bubble reactor was operated in batch mode. The total reactor volume was 50 mL; the total reaction mixture volume was 15 mL. The oxidation was performed as follows: the required quantities of a dry catalyst, distilled water and glycerol aqueous solution were fed into the reactor during thermostating (10 min). The supply of oxygen to the reactor was switched on (oxygen flow = 300 mL/min), and the required volume of sodium hydroxide water solution was added. The oxidation process started at the moment of the addition of sodium hydroxide.

Glycerol oxidation was also carried out in an autoclave ROTH, Model II, connected with a gas burette. The total volume of the reactor was 200 mL; the total volume of the reaction mixture was 30 mL. The experiment of oxidation was performed as follows: the required volumes of distilled water, glycerol water solution and NaOH solution were fed into the reactor. The reactor with reagents and the gas burette were purged, filled with oxygen and thermostated at 60 °C. After thermostating, the required quantity of a dry catalyst was fed into the reactor, the required oxygen pressure was set in the system, and a magnetic mixer was switched on (1100 rpm). Oxidation started after the mixer was switched on.

Oxidation product analysis

In order to determine the concentration of reaction products, liquid samples were collected periodically from the reaction mixture after certain periods of time. Reaction mixture samples were filtered for separation of catalysts. The filtered samples were analyzed by high-performance chromatograph HPLC Shimadzu Nexera equipped with UV–VIS SHIMADZU SPD-20A (UV 210 nm) and ELSD-LTII detectors. A Waters IC–PAC Jon–Exclusion column (300×7.8 mm) (75 °C) was used with aqueous trifluoroacetic acid 0.045 vol% as the eluent. The filtered samples of the reaction mixture (20 μ L) were diluted 50 times with the eluent. The injection volume of 20 μ L, running time of 20 min and eluent flow rate of 0.7 mL/min were adjusted. The identification of the possible products was performed by comparison with the original samples.

Glycerol conversion was calculated according to the following equation:

$$\text{Glycerol conversion (mol\%)} = \frac{n_{\text{initial}} - n_{\text{determined}}}{n_{\text{initial}}} \times 100 \%$$

n_{initial} —amount of starting glycerol, $n_{\text{determined}}$ —amount of remaining glycerol in the reaction sample determined by HPLC.

The selectivity of products was calculated by the following equation:

$$\text{Selectivity (mol\%)} = \frac{n_{\text{product}}}{\text{Glycerol conversion}} \times 100 \%$$

n_{product} —amount of certain product determined by HPLC.

Results

Catalyst characterization

A TEM micrograph of 4.8wt% Pt/NP–TiO₂ catalyst and the corresponding Pt nanoparticle size distribution histogram in Fig. 1 are shown. The morphology of the catalytic material, consisting of support and Pt nanoparticles as an active phase, is visible (Fig. 1). The support with a granular structure with a lower contrast can be seen, while Pt nanoparticles tend to have a higher contrast and spherical-like shape. In some regions of the sample, they are coalesced, thus forming big aggregates. The average size of Pt nanoparticles calculated is 13.3 nm.

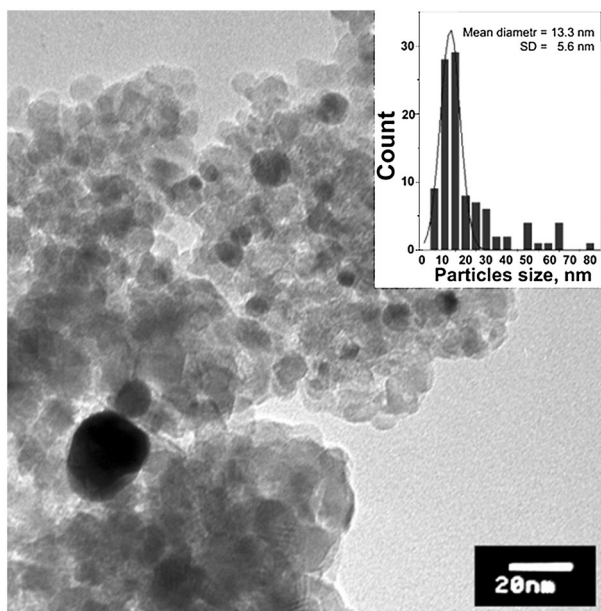


Fig. 1 TEM microphotograph of the 4.8%Pt/NP–TiO₂ catalyst at $\times 200,000$ magnification and corresponding Pt nanoparticle size distribution histogram

SEM micrographs show that the obtained 4.8wt% Pt/NF–TiO₂ catalyst consists of macro size fibers (Fig. 2) with total length up to 50 μm . TEM analysis indicates that the macrofibers consist of a large amount of individual nanowires with a diameter in the range of 5–20 nm (Fig. 3). The average size of Pt nanoparticles d_{Pt} calculated is 9 nm.

The phase compositions of 4.8wt% Pt/NP–TiO₂ and 4.8wt% Pt/NF–TiO₂ catalysts were determined by using an XRD analysis (Fig. 4). XRD patterns of catalysts showed anatase and Pt maxima. No other shifts of the diffraction maxima were observed.

Results of the 4.8wt% Pt/NF–TiO₂ and 4.8wt% Pt/NP–TiO₂ catalyst specific surface area, d_{Pt} and d_{kr} measurements are shown in Table 1. The difference between XRD (d_{kr}) and TEM (d_{Pt}) data obtained for Pt/NP–TiO₂ catalyst is probably caused by the presence of a large amount of small-sized particles being amorphous. Also it is well known that XRD data provides information about sizes of the largest particles only.

Glycerol oxidation

Influence of NaOH

The prepared supported platinum catalysts were tested in glycerol oxidation in alkaline water solutions. The method of glycerol oxidation by molecular oxygen is mild and environmentally friendly. A comparison of nanopowder and nanofiber

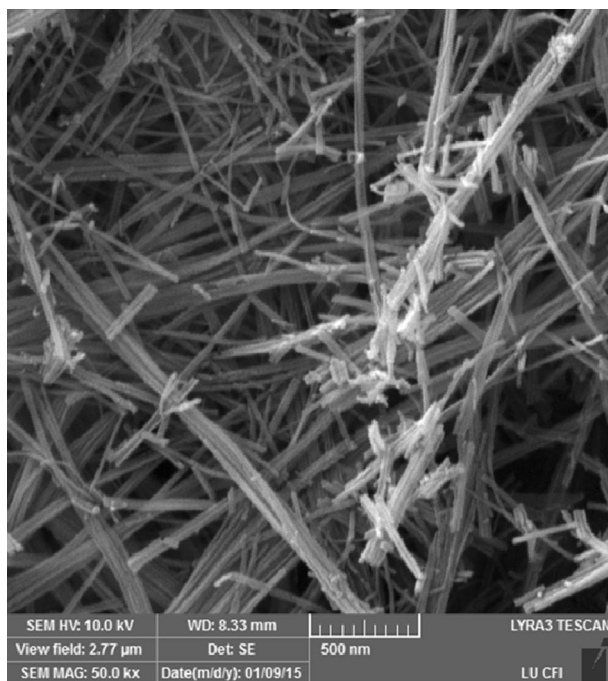


Fig. 2 SEM microphotograph of the 4.8%Pt/NF–TiO₂ catalyst

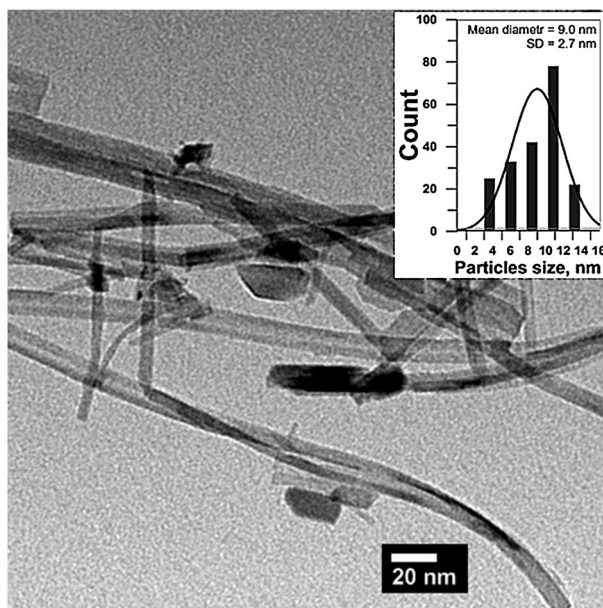


Fig. 3 TEM microphotograph of the 4.8%Pt/NF-TiO₂ catalyst at ×200,000 magnification and corresponding Pt nanoparticle size distribution histogram

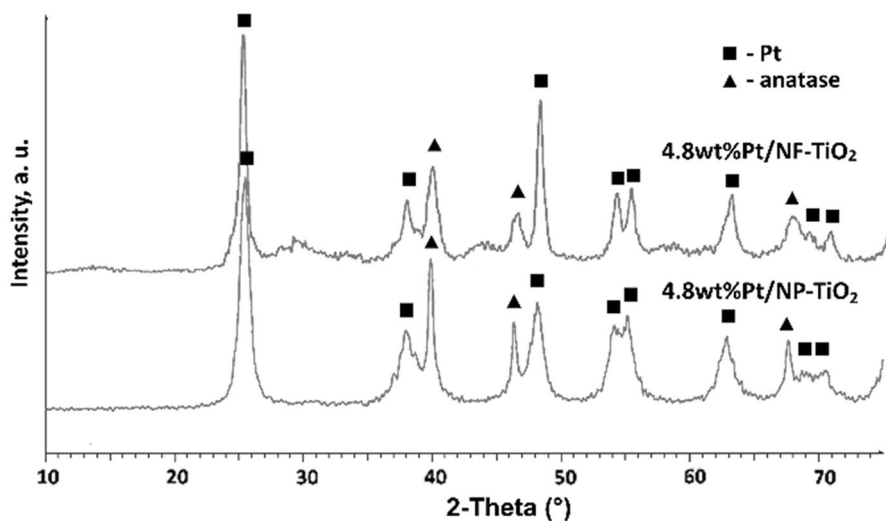


Fig. 4 XRD of the 4.8wt% Pt/NF-TiO₂ and 4.8wt% Pt/NP-TiO₂ catalysts

supported catalyst activity and selectivity in glycerol oxidation, as well as initial NaOH concentration influence on both catalyst activity and product distribution, is summarized in Table 1.

Table 1 Glycerol oxidation over platinum catalysts

Catalyst	$C_0(\text{NaOH})$ (mol/L)	Oxidation time, (h)	Glycerol conv., (mol%)	Selectivity (mol%)				
				GLYA	TART	LACT	GLYC	OXAL
4.8wt% Pt/NF-TiO ₂	–	7	0	0	0	0	0	0
$d_{kr} = 11$ nm	0.6	4	69	56	5	26	9	2
$d_{pt} = 9$ nm; SD = 2.7 nm	0.6	7	90	51	10	26	9	2
SSA = 72 m ² /g	1.5	4	64	53	6	30	8	1
	1.5	7	95	45	15	28	8	2
4.8wt% Pt/NP-TiO ₂	–	7	0	0	0	0	0	0
$d_{kr} = 25$ nm	0.6	4	69	64	3	15	15	1
$d_{pt} = 13.3$ nm; SD = 5.6 nm	0.6	7	85	60	7	15	16	2
SSA = 66 m ² /g	1.5	4	62	66	5	18	10	1
	1.5	7	94	59	11	17	10	1

Reaction conditions: $c_0(\text{glycerol}) = 0.3$ mol/L, $n(\text{glycerol})/n(\text{Pt}) = 300$ mol/mol, $P(\text{O}_2) = 1$ atm, 60 °C

GLYA glyceric acid, TART tartaric acid, LACT lactic acid, GLYC glycolic acid, OXAL oxalic acid, FORM formic acid

First, it was verified that supports NP-TiO₂ and NF-TiO₂ are inactive in glycerol oxidation experiments on their own. Then experiments with 4.8wt% Pt/NP-TiO₂ were done without base addition, at 1 atm pressure. It was found that catalyst activity is very low (glycerol conversion was above 1 %) [5]. Analogous results were achieved when 4.8wt% Pt/NF-TiO₂ was used. So it was concluded that base plays a significant role, if Pt/TiO₂ catalysts are used, however M. Zhang et al. reported that carbon nanofibers supported Pt catalysts can be even very active in base-free glycerol oxidation processes; glycerol conversion reached 90 % there [26].

According to Table 1, in alkaline solutions, both TiO₂ nanofiber and TiO₂ nanopowder supported catalysts show similar activity. Increasing NaOH concentration from 0.6 to 1.5 mol/L, glycerol maximum conversion increases by 5–9 %. It can also be seen from Table 1 that glyceric acid as the main product is obtained in all cases, but tartronic, lactic, glycolic, oxalic and formic acids are by-products. Nanopowder supported Pt catalysts are obviously more selective to glyceric acid than Pt catalysts with nanofibers. 4.8wt% Pt/NP-TiO₂ catalyst selectivity varies from 59–66 %, while 4.8wt% Pt/NF-TiO₂ catalyst selectivity is in the range of 45–56 %. In [33] it was reported that platinum supported catalysts with bigger particles are more selective to glyceric acid compared to finer particles. It is in accordance with our results, as the 4.8wt% Pt/NP-TiO₂ catalyst is characterized by bigger particles than the 4.8wt% Pt/NF-TiO₂ catalyst (Table 1). At the same time, Pt particle size practically does not influence catalyst activity, as glycerol conversion achieved in the presence of Pt/NP-TiO₂ catalyst is similar to glycerol conversion obtained in the presence of Pt/NP-TiO₂ catalyst.

4.8wt% Pt/NF-TiO₂ and 4.8wt% Pt/NP-TiO₂ catalyst selectivity to glyceric acid does not depend on the initial NaOH concentration in solutions (Table 1). 4.8wt% Pt/NP-TiO₂ catalyst selectivity varies from 64 to 66 % at glycerol conversion 62–69 % ($c_0(\text{NaOH}) = 0.6$ or 1.5 mol/L), but with extended reaction time and increase in glycerol conversion from 62 to 94 % ($c_0(\text{NaOH}) = 1.5$ mol/L), the selectivity to glyceric acid decreases from 66 to 59 %. 4.8wt% Pt/NF-TiO₂ catalyst selectivity is in the range of 53 to 56 % at glycerol conversion 64–69 % ($c_0(\text{NaOH}) = 0.6$ or 1.5 mol/L), but with extended reaction time and increase in glycerol conversion from 64 to 95 % ($c_0(\text{NaOH}) = 1.5$ mol/L), the selectivity to glyceric acid for this catalyst also decreases (from 53 to 45 %). However, M. Zhang et al. [24] reported that 2.5 % Pt/S-CNFs catalysts selectivity to glyceric acid isn't influenced by reaction time.

Testing three nanofiber supported catalysts with different Pt loading, it was found that only the catalyst with the greatest Pt content (4.8 wt%) shows good activity in basic solution. The catalyst with Pt loading of 1.14 wt% did not show any catalytic activity, but 1.54 wt% Pt catalyst had very low activity (glycerol conversion 5 %, $c_0(\text{NaOH}) = 1.5$ mol/L, reaction time 5 h). From the literature, it is known that catalyst activity increases with increase in Pt loading [27, 53, 54] until a certain limit.

Influence of oxygen pressure

Some time ago, as the main drawback of Pt supported catalysts, authors considered their poisoning and deactivation at elevated pressure; therefore, it was suggested to use atmospheric pressure oxidizing glycerol over monometallic Pt supported catalysts [6, 24, 54]. Nowadays, it is proven that these catalysts can be also used in oxidation processes in autoclaves at 3 and 5 atm pressure without evidence of poisoning [13, 18, 29]. However, no one has studied the influence of oxygen pressure elevation.

In this work, we have investigated oxygen pressure influence on catalyst activity and selectivity in the range of 1 to 9 atm (Figs. 5 and 6). At first the results of oxidation at atmospheric and elevated pressure choosing the $n(\text{glycerol})/n(\text{Pt})$ ratio = 300 mol/mol were analyzed (Fig. 5). At the glycerol/Pt molar ratio of 300 mol/mol, mass transfer limitation is possible at 1 atm pressure. As it can be seen from Fig. 5, both catalysts become more active when pressure is elevated from 1 to 6 atm. Applying 1 atm pressure, it takes seven or more hours to complete glycerol oxidation, but when the pressure of 6 atm is used, oxidation is completed already after 4 h (glycerol conversion reaches 95–100 %). At 1 atm, the two catalyst activities were similar (Table 1, Fig. 5), but a difference between catalyst activities arises at 6 atm, and the catalyst with nanofibers becomes slightly more active. After identical oxidation time in the presence of the 4.8wt% Pt/NF-TiO₂ catalyst, glycerol conversion at 6 atm is by 5–14 % greater than in the presence of the 4.8wt% Pt/NP-TiO₂ catalyst. So it can be considered that nanofiber supported catalyst is more resistant against its surface overoxidation and deactivates slightly less at 6 atm oxygen pressure.

The catalyst selectivities to glyceric acid (Fig. 5a) at similar glycerol conversion significantly rise with increasing pressure. The difference between selectivity at 1 and 6 atm reaches 19 %. For example in the presence of the 4.8wt% Pt/NP-TiO₂ catalyst at 94–95 % glycerol conversion, the selectivity to glyceric acid reaches

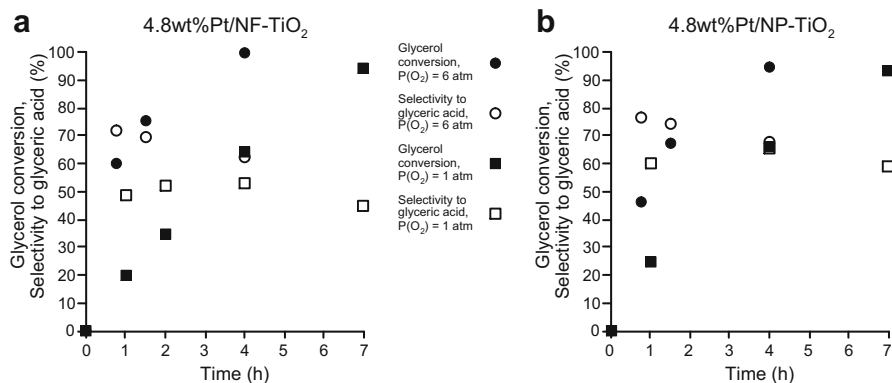


Fig. 5 Glycerol oxidation using 4.8 wt% Pt/NF-TiO₂ and 4.8 wt% Pt/NP-TiO₂ catalysts. Effect of oxygen pressure on glycerol conversion and selectivity to glyceric acid at $n(\text{glycerol})/n(\text{Pt}) = 300$ mol/mol. Reaction conditions: $c_0(\text{glycerol}) = 0.3$ mol/L, $c_0(\text{NaOH}) = 1.5$ mol/L, 60 °C

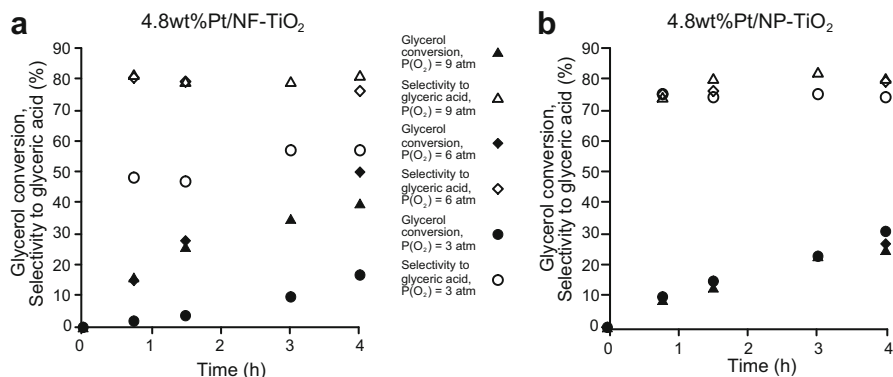


Fig. 6 Glycerol oxidation using 4.8wt% Pt/NF-TiO₂ and 4.8wt% Pt/NP-TiO₂ catalysts. Effect of oxygen pressure on glycerol conversion and selectivity to glyceric acid at $n(\text{glycerol})/n(\text{Pt}) = 6000$ mol/mol. Reaction conditions: $c_0(\text{glycerol}) = 0.3$ mol/L, $c_0(\text{NaOH}) = 1.5$ mol/L, 60 °C

68 % when 6 atm oxygen pressure is used and only 59 % at 1 atm. In comparison, the 4.8wt% Pt/NP-TiO₂ catalyst shows better selectivity to glyceric acid than the 4.8wt% Pt/NF-TiO₂ catalyst, regardless of the applied oxygen pressure, when $n(\text{glycerol})/n(\text{Pt})$ ratio = 300 mol/mol.

Investigating Pt supported catalyst poisoning at elevated pressure, experiments at 3–9 atm oxygen pressure were done using reduced catalyst content in the reaction mixture ($n(\text{glycerol})/n(\text{Pt})$ ratio = 6000 mol/mol) (Fig. 6). For the 4.8wt% Pt/NP-TiO₂ catalyst, pressure elevation negligibly affected activity and selectivity to glyceric acid. So it can be concluded that the 4.8wt% Pt/NP-TiO₂ catalyst slightly deactivates at a higher pressure. A more pronounced influence of pressure elevation was experienced for the nanofiber supported Pt catalyst. By increasing oxygen pressure from 3 to 6 atm, catalysts activity was raised about three times—glycerol conversion increased from 17 to 50 %, but with further increase in pressure to 9 atm, 4.8wt% Pt/NF-TiO₂ catalyst activity reduced, and glycerol conversion drop to 40 % evidenced that the catalyst faced poisoning. At 6 atm, the 4.8wt% Pt/NF-TiO₂ catalysts showed the best results—the highest activity and also the highest yield to glyceric acid. Comparing both nanopowder and nanofiber supported catalysts, it is seen in Fig. 5 that 4.8wt% Pt/NP-TiO₂ and 4.8wt% Pt/NF-TiO₂ catalyst activities were similar at atmospheric pressure, but according to Fig. 6 data, upon increasing the pressure to 6 atm, the 4.8wt% Pt/NF-TiO₂ catalyst became more active than the 4.8wt% Pt/NP-TiO₂ catalyst. A further increase in pressure from 6 to 9 atm (Fig. 6) caused the nanofiber supported catalyst activity to rise more, while the nanopowder supported catalyst's activity was no longer influenced by oxygen pressure. At 6 atm oxygen pressure and ($n(\text{glycerol})/n(\text{Pt})$ ratio = 6000 mol/mol), the process of oxidation flows in a kinetic regime. Thus, as it follows from the data of Fig. 6, it can be concluded that in these conditions the 4.8wt% Pt/NF-TiO₂ catalyst is more active compared to the 4.8wt% Pt/NP-TiO₂ catalyst and demonstrates better resistance against overoxidation at elevated oxygen pressure.

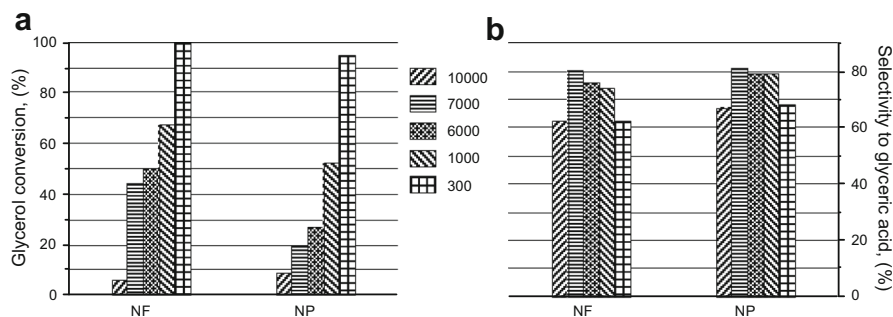


Fig. 7 Glycerol oxidation using 4.8wt% Pt/NF–TiO₂ (NF) and 4.8wt% Pt/NP–TiO₂ (NP) catalysts. Effect of $n(\text{glycerol})/n(\text{Pt})$ ratio on glycerol conversion (a) and selectivity to glyceric acid (b). Reaction conditions: $c_0(\text{glycerol}) = 0.3 \text{ mol/L}$, $c_0(\text{NaOH}) = 1.5 \text{ mol/L}$, $P(\text{O}_2) = 6 \text{ atm}$, 60°C , oxidation time 4 h

The 4.8wt% Pt/NF–TiO₂ catalyst at elevated pressures becomes superior to the 4.8wt% Pt/NP–TiO₂ catalyst.

Influence of $n(\text{glycerol})/n(\text{Pt})$

The influence of $n(\text{glycerol})/n(\text{Pt})$ ratio on catalyst activity and selectivity is represented in Fig. 7. Decreasing the $n(\text{glycerol})/n(\text{Pt})$ ratio from 10,000 to 300 mol/mol or increasing the catalyst content in the reaction mixture results in glycerol conversion gradual increase from 5 to 100 % in the case of the 4.8wt% Pt/NF–TiO₂ catalyst and from 6 to 95 % in the case of the 4.8wt% Pt/NP–TiO₂ catalyst (Fig. 7a). These results are in accordance with other results [22, 24, 55]. All the time at elevated pressure (6 atm) starting from ratio $n(\text{glycerol})/n(\text{Pt}) = 1000 \text{ mol/mol}$, the 4.8wt% Pt/NF–TiO₂ catalyst showed better activity than the 4.8wt% Pt/NP–TiO₂ catalyst. Meanwhile, the influence of this parameter on catalyst selectivity was not so significant (Fig. 7b). At different $n(\text{glycerol})/n(\text{Pt})$ ratios, the selectivity to glyceric acid fluctuated, but overall its yield increased from 3 to 62 % and from 3 to 65 % for the 4.8wt% Pt/NF–TiO₂ catalyst and the 4.8wt% Pt/NP–TiO₂ catalyst accordingly.

Conclusion

Novel TiO₂ nanofiber supported platinum catalysts as well as TiO₂ nanopowder supported Pt catalysts are active in alkaline water solutions. The main product of glycerol oxidation processes is glyceric acid. The increase of $n(\text{glycerol})/n(\text{Pt})$ ratio leads to significant decrease in glycerol conversion, while the rise of oxygen pressure from 1 to 6 atm promotes activity for both catalysts and selectivity of novel nanofiber supported Pt catalyst. If the glycerol oxidation process takes place under mass transfer limitation, 4.8wt% Pt/NP–TiO₂ and 4.8wt% Pt/NF–TiO₂ catalysts show similar activity. The best results were achieved over the following oxidation parameters: $c_0(\text{glycerol}) = 0.3 \text{ mol/L}$, $c_0(\text{NaOH}) = 1.5 \text{ mol/L}$, $n(\text{glycerol})/n(\text{Pt}) = 300 \text{ mol/mol}$, $P(\text{O}_2) = 6 \text{ atm}$, 60°C . Using the 4.8wt% Pt/NF–TiO₂

catalyst selectivity by glyceric acid was 63 % with glycerol conversion of 100 %, while using 4.8wt% Pt/NP–TiO₂ catalyst selectivity by glyceric acid reached 68 % with glycerol conversion of 95 %. However, if the oxidation takes place in a kinetic regime at 3–9 atm oxygen pressure and n(glycerol)/n(Pt) ratio = 1000–10,000 - mol/mol, novel TiO₂ nanofiber supported Pt catalyst becomes more active than TiO₂ nanopowder supported Pt catalyst. It was observed that the 4.8wt% Pt/NF–TiO₂ catalyst demonstrates better resistance against overoxidation at elevated oxygen pressure.

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