Production of glycolic acid from glycerol using novel fine-disperse platinum catalysts

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Abstract. Using extractive-pyrolytic method fine-disperse Pt containing composites were synthesized and tested in catalytic glycerol oxidation. Catalyst activity and selectivity to glycolic acid was determined oxidizing glycerol in mild conditions. It was concluded that only iron containing platinum catalysts were selective to glycolic acid. Selectivity to glycolic acid reached 53–60% with glycerol conversion 12–56%.

1. Introduction
Selective heterogeneous oxidation of glycerol is one of the most frequently glycerol transformation methods studied today. Fine-disperse composites consisting of noble metal and its support are found their application as effective catalysts in the glycerol oxidation. In the glycerol oxidation number of valuable products can be obtained and one of these products is glycolic acid [1]. Glycolic acid has a broad application field – it is used in textile, food, cosmetic, pharmaceutical and plastics industries [2]. Conventionally glycolic acid is produced from petroleum resources using different hazardous and complicated methods [2, 3]. More eco-friendly glycolic acid preparation methods are enzymatic processes [4]; the main drawback of these methods is low concentration of glycolic acid formed [5]. Selective liquid-phase oxidation of glycerol also is environmentally friendly and it could be used for glycolic acid production. Until now the best selectivity to glycolic acid (52–70% with glycerol conversion of 30–35%) was reached only using supported gold catalysts, besides supported on carbon nanofibers [6, 7].

In this work using extractive-pyrolytic method, we have synthesized several novel fine-disperse platinum catalysts, which contains iron. Their activity and selectivity was studied during liquid-phase glycerol oxidation and compared with already published catalysts [8].

2. Experimental
2.1. Catalyst preparation
Two different types of catalysts were studied – catalysts supported on carriers (Al₂O₃, Y₂O₃, Lu₂O₃, C, Fe₃O₄), which are published in [8], and novel 71wt%Pt+29wt%α-Fe₂O₃ and Pt/Fe composites. For catalyst preparation platinum containing organic extract was used as precursor. The method for the production of metal-containing organic extract is described in [9, 10]. Amounts of extracts were...
calculated based on each metal’s loading in the composite. For the preparation of supported catalysts, the carriers were impregnated with organic extracts and then the mixture was dried at room temperature and calcinated at 300 °C in air for 5 min. For the preparation of Pt/Fe composite a fine-disperse iron powder was added to Pt-containing organic extract and the mixture was calcinated at 600 °C in air for 30 min. Composite with Fe:Pt molar ratio 0.98:0.02 was obtained (Fe$_{0.98}$Pt$_{0.02}$). To produce 71wt%Pt+29wt%α-Fe$_2$O$_3$ composite an equimolar mixture of iron caproate in caproic acid and tri-n-octylammonium hexachloroplatinate in toluene was used as precursor, which was heated from room temperature up to 500 °C and annealed for 5 min in air.

After preparation catalysts were characterized by X-ray diffraction (XRD) using diffractometer D-8 Advance (Bruker AXS) with CuK$_\alpha$ radiation (λ = 1.5418 Å). The average size of Pt crystallites was calculated by line broadening peak (111) using the Scherrer equation. Specific surface area (S.S.A.) of the powders was measured using HROM-3 chromatograph by BET method at temperature of liquid nitrogen. TEM measurements were carried out by means of transmission electron microscope JEOL JEM 2100 at 200 kV accelerating voltage and at magnifications 40 000–200 000x. Histograms of particle size distribution were obtained by counting onto the micrographs, and the mean particle diameter ($d_p$) was calculated using the formula: 

$$d_p = \sum (d_i \cdot n_i) / (\sum n_i)^{1/3},$$

where $n_i$ was the number of particles specific diameter.

### 2.2. Catalyst testing

Novel platinum catalyst activity and selectivity in the glycerol oxidation were tested in thermostatted slurry bubble reactor (50 ml capacity) equipped with gas supply system. Glycerol oxidation process parameters were as follows: c$_o$(glycerol) = 0.3 M, c$_o$(NaOH) = 0.7–1.5 M, n(glycerol)/n(Pt) = 211–300 mol/mol, 60 °C, P(O$_2$) = 1 atm, reaction time 4–7 h. Analysis of the reaction mixture was performed by high-performance chromatograph UFLC Shimadzu Nexera.

### 3. Results

#### 3.1. Catalyst characterisation

In Figure 1 typical TEM microphotograph of synthesized 4.8wt%Pt/Fe$_3$O$_4$ catalyst is presented. The corresponding size distribution histogram of Pt nanoparticles in the 4.8wt%Pt/Fe$_3$O$_4$ catalyst is shown in Figure 2. Electronic microscopy revealed that average size of platinum nanoparticles in this catalyst is 2.4 nm (Table 1). Other catalyst characteristic parameters are shown in Table 1.

**Figure 1.** TEM microphotograph at magnification 100 000 x of the 4.8wt%Pt/Fe$_3$O$_4$ catalyst.

**Figure 2.** The size distribution histogram of Pt nanoparticles in the 4.8wt%Pt/Fe$_3$O$_4$ catalyst.
3.2. Glycerol oxidation

Prepared platinum catalysts were tested in glycerol oxidation in alkaline water solutions. Method is mild and environmentally friendly, because solvent is water, oxidant is molecular oxygen, experiments are carried out in atmospheric pressure and low temperature (60 °C), but the only by-product of the reaction is also water. The results of research are represented in Table 1. As it can be seen from Table 1, all catalysts were active – glycerol conversion was above 20%. Mostly platinum catalysts were selective to glyceric acid whose selectivity varied from 37 to 55%, except catalysts containing Fe. In [8] glycolic acid was firstly observed as the main product of reaction oxidizing glycerol over Pt/Fe₂O₄ catalysts. From Table 1 it can be seen that also novel 71wt%Pt+29wt%α-Fe₂O₃ and Pt/Fe composites had catalytic activity and these catalysts were selective to glycolic acid, unfortunately their activity wasn’t as good as for catalysts selective to glyceric acid. Selectivity by glycolic for all Fe containing platinum catalysts was similar (53–60%). Selectivity of glycolic acid didn’t depend on glycerol conversion and oxidation time. With increase in glycerol conversion it stayed practically constant. Similar results were reached in [6] – oxidizing glycerol over supported gold catalysts for 1–7 h, selectivity of glycolic acid negligible decreased (for 2%) when glycerol conversion increased from 37 to 100%.

| Catalyst | dₚ (nm) by XRD (or TEM) | S.S.A. of catalyst (m²/g) | Oxidation time, h | Glycerol conv., mol% | Selectivity, mol% |
|----------|--------------------------|--------------------------|-------------------|----------------------|------------------|
|          |                          |                          |                   | GLYA | TART | LACT | GLYC | OXAL |
| 4.8wt%Pt/Al₂O₃ | 20 | 44 | 7 | 73 | 53 | 14 | 19 | 10 | 2 |
| 4.8wt%Pt/Y₂O₃ | 7 | - | 7 | 70 | 50 | 8 | 30 | 8 | 2 |
| 4.8wt%Pt/Lu₂O₃ | 23 | 14 | 7 | 65 | 55 | 11 | 20 | 11 | 2 |
| 4.8wt%Pt/C | 20 | 161 | 7 | 68 | 37 | 18 | 30 | 9 | 4 |
| 2.4wt%Pt/Fe₂O₃ | - | 34 | 7 | 31 | 37 | 2 | 0 | 60 | 1 |
| 4.8wt%Pt/Fe₂O₃ | 2.4* | 30 | 7 | 56 | 36 | 2 | 8 | 53 | 1 |
| 71wt%Pt+29wt%α-Fe₂O₃ | 11-35 | - | 4 | 31 | 31 | 2 | 10 | 54 | 3 |
| Pt/Fe | - | - | 7 | 47 | 30 | 2 | 9 | 55 | 3 |
|          |                          |                          |                   | 4 | 37 | 31 | 2 | 5 | 60 | 3 |
|          |                          |                          |                   | 7 | 48 | 30 | 2 | 4 | 60 | 2 |
|          |                          |                          |                   | 4* | 12 | 31 | 3 | 2 | 55 | 8 |
|          |                          |                          |                   | 7* | 20 | 33 | 2 | 3 | 57 | 5 |

Reaction conditions: cₒ(glycerol) = 0.3 M, cₒ(NaOH) = 1.5 M, cₒ(NaOH)/n(glycerol) = 300 mol/mol (-- 211 mol/mol), P(O₂) = 1 atm, 60 °C. Catalyst calcination temperature: 300 °C (-- 500 °C, b. 600 °C); catalyst calcination time: 5 min (b. 30 min). GLYA – glyceric acid, TART – tartronic acid, LACT – lactic acid, GLYC – glycolic acid, OXAL – oxalic acid.

To determine influence of NaOH/glycerol molar ratio on Pt/Fe catalyst activity and selectivity, oxidation tests with two different initial NaOH concentrations were carried out when other oxidation parameters were kept constant (Table 1). Initial NaOH concentration 1.5 M corresponds to the NaOH/glycerol molar ratio of 5, while 0.7 M corresponds to the NaOH/glycerol molar ratio of 2.3. As it is known formation of glycolic acid is strongly dependent on amount of H₂O₂ which appears in reaction mixture. There is a perception that H₂O₂ is responsible for C–C bond cleavage, thus leading to the formation of glycolic acid [1, 6, 11, 12]. In [6] measures of H₂O₂ amount showed that in the mixture with greater NaOH concentration, H₂O₂ formed less and selectivity to glycolic acid decreased respectively from 37 to 21%. Glycerol conversion wasn’t affected. From Table 1 it can be seen that
decrease of initial NaOH concentration 2 times led to decrease in glycerol conversion 2 times. Selectivity to glycolic acid reduced, contrary to the results of [6], but the decrease of selectivity was small (3–5%).

4. Conclusions
Novel fine-disperse Fe containing platinum catalysts were selective to glycolic acid oxidizing glycerol in alkaline water solutions. Better results were reached when initial NaOH concentration was greater. The best results (selectivity by glycolic acid 60%, with glycerol conversion 48%) was achieved using Pt/Fe catalyst over following oxidation parameters: \(c_o(\text{glycerol}) = 0.3\, \text{M}, c_o(\text{NaOH}) = 1.5\, \text{M}, n(\text{glycerol})/n(\text{Pt}) = 300\, \text{mol/mol}, P(O_2) = 1\, \text{atm}, 60\, ^\circ\text{C}\). Catalyst calcination temperature: 600 °C; catalyst calcination time: 30 min.

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