Novel fine-disperse bimetallic Pt-Pd/Al₂O₃ catalysts for glycerol oxidation with molecular oxygen

K Dubencovs¹, S Chornaja¹, E Sproge¹, V Kampars¹, D Markova¹, L Kulikova², V Serga², A Cvetkovs²
¹Institute of Applied Chemistry, Riga Technical University, Latvia
²Institute of Inorganic Chemistry, Riga Technical University, Latvia
E-mail: Konstantins.Dubencovs@rtu.lv

Abstract. Using extractive-pyrolytic method several Pt-Pd bimetallic catalysts supported on plasma-processed alumina nanopowder were synthesized. Pt-Pd loading and glycerol oxidation process parameter influence on catalyst activity and selectivity was determined oxidizing glycerol in mild conditions. Novel bimetallic catalysts in neutral water solutions were practically inactive (glycerol conversion was only 3%) whereas in alkaline solutions they were active and selective to glyceric acid. Using 1.2%Pt-1.2%Pd/Al₂O₃ catalyst glyceric acid was obtained with 65% selectivity (glycerol conversion was 96%). It was shown that novel fine-disperse bimetallic Pt-Pd/Al₂O₃ catalysts were more active compared to analogous monometallic Pt/Al₂O₃ and Pd/Al₂O₃ catalysts.

1. Introduction
Glycerol is the main by-product in the transesterification process of biodiesel production from vegetable oil. Selective glycerol oxidation in presence of supported catalysts is one of the preferable glycerol conversion methods. Many valuable products are obtained in this process – glyceric acid, lactic acid, glycolic acid, tartronic acid etc. [1–3]. Method is environmentally friendly and catalysts can be reused. Generally glyceric acid is selectively produced in glycerol oxidation over monometallic catalysts [3, 4]. Usage of bimetallic catalysts gives opportunity to increase selectivity to glyceric acid [5] and obtain other important glycerol oxidation products like lactic acid or glycolic acid with a good yield [3, 6]. Bimetallic catalysts have some more advantages like higher activity and prolonged catalyst life [7]. In literature only Au-Pt and Au-Pd catalysts are known.

In this work we have synthesized novel fine-disperse Pt-Pd bimetallic catalysts supported on Al₂O₃ prepared by extractive-pyrolytic method described in our earlier papers [8–9]. We have investigated Pt-Pd loading and glycerol oxidation process parameter influence on catalyst activity and selectivity.

2. Experimental
All solutions used were prepared with Millipore superQ water (18 MΩ/cm) and analytical grade reagents. For preparation of catalysts (Pt-Pd nanoparticles on the surface of support) a mixture of platinum and palladium containing organic extracts were used as precursor. The method for the production of metal-containing organic extract is described in [8, 9]. Amounts of extracts were calculated based on each metal’s loading in the composite (0.6, 1.2 and 2.5 wt.%). The support was impregnated with organic extracts. Nanopowder of Al₂O₃ obtained in plasma (SSA 46 m²/g) was used
as the support. The mixture was dried at room temperature and calcinated at 300 °C in air for 5 min. As synthesized nanopowders of catalysts were characterized by X-ray diffraction (XRD) using diffractometer D-8 Advance (Bruker AXS) with CuKα radiation (λ = 1.5418 Å). The average size of Pt-Pd alloy 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 Brunauer–Emmett–Teller (BET) method at temperature of liquid nitrogen.

Powder bimetallic catalyst activity and selectivity in the oxidation of glycerol were tested in thermostatted slurry bubble reactor (50 ml capacity) equipped with gas supply system. Glycerol oxidation process parameters, like NaOH initial concentration c_o(NaOH) = 0–1.5 M, glycerol and platinum molar ratio n(glyc.)/n(Pt-Pd) = 300–500 mol/mol and oxygen partial pressure from 0.2 to 1 atm were varied. Glycerol initial concentration c_o(glyc.) was 0.3 M, reaction temperature was 60 °C. Analysis of the reaction mixture was performed by high-performance chromatograph WATERS 2487.

3. Results
Bimetallic catalysts with Pt-Pd loading from 0.6 to 2.5% for each metal were prepared and tested. The XRD phase analysis of the obtained composites permits to detect formation of Pt-Pd alloy phase on the support (figure 1). As diffraction peaks of the support overlaps with peaks of the catalyst, the average size of Pt-Pd alloy crystallites was determined only for the catalyst with high metal loading (2.5%-Pt 2.5%Pd/Al₂O₃) and was 28 nm (figure 1).

![Figure 1. XRD patterns](image)

Figure 1. XRD patterns: 1 – Al₂O₃; 2 – 0.6%Pt-0.6%Pd/Al₂O₃; 3 – 1.2%Pt-1.2%Pd/Al₂O₃; 4 – 2.5%Pt-2.5%Pd/Al₂O₃.

The prepared catalysts were tested in glycerol oxidation processes. Catalyst activity was estimated by glycerol conversion. Experimentally it was found that catalyst activity is negligible in water solution without NaOH addition. Glycerol conversion was less than 3%. It is known that a basic pH increases the oxidation rate because it favors the deprotonation of the primary hydroxyl group of glycerol or because it favors the product desorption from the catalyst [10]. From table 1 it is visible that all catalysts were very active in the alkaline water solutions. Catalyst activity did not depend on Pt-Pd loading and was similar. Glycerol conversion ranged from 91 to 100%. Catalysts with loading 1.2-2.5% for each metal presented better selectivity to glyceric acid. It was concluded that 1.2%Pt-
1.2%Pd/Al2O3 catalyst is the best for glycerol oxidation to glyceric acid (selectivity to glyceric acid reached 42% with full glycerol conversion).

Also, table 1 data shows that in alkaline solutions novel bimetallic 1.2%Pt-1.2%Pd/Al2O3 catalyst was more active than analogous monometallic 2.5%Pt/Al2O3 and 2.5%Pd/Al2O3 catalysts. At similar glycerol conversion (66–74%) 1.2%Pt-1.2%Pd/Al2O3 catalyst selectivity to glyceric acid was equal to 2.5%Pd/Al2O3 catalyst selectivity and higher than 2.5%Pt/Al2O3 catalyst selectivity.

Table 1. Effect of Pt-Pd loading on the catalyst on glycerol conversion and glycerol oxidation product yield and selectivity.

| Catalyst                  | Oxidation time, h | Glycerol conv., mol% | GLYA | TART | LACT | GLYC | OXAL |
|---------------------------|-------------------|----------------------|------|------|------|------|------|
| 0.6%Pt-0.6%Pd/Al2O3      | 7                 | 97                   | 33   | 37   | 15   | 6    | 9    |
| 1.2%Pt-1.2%Pd/Al2O3      | 3                 | 66                   | 65   | 9    | 20   | 4    | 2    |
|                          | 7                 | 100                  | 42   | 26   | 20   | 6    | 6    |
| 2.5%Pt-2.5%Pd/Al2O3      | 7                 | 91                   | 41   | 26   | 23   | 5    | 5    |
| 2.5%Pt/Al2O3             | 7                 | 69                   | 49   | 9    | 24   | 13   | 2    |
| 2.5%Pd/Al2O3             | 7                 | 74                   | 66   | 8    | 17   | 5    | 4    |

Reaction conditions: \(c_0(\text{NaOH}) = 1.5 \text{ M}, n(\text{glyc.})/n(\text{Me}) = 300 \text{ mol/mol}, P(\text{O}_2) = 1 \text{ atm}, 60 \degree \text{C}. \) GLYA – glyceric acid, TART – tartronic acid, LACT – lactic acid, GLYC – glycolic acid, OXAL – oxalic acid.

Effects of NaOH initial concentration and glycerol/metal molar ratio \(n(\text{glyc.})/n(\text{Me})\) are summarized in table 2. Comparing glycerol oxidation in 0.7 M and 1.5 M NaOH solutions, from table 2 data it can be concluded that 1.2%Pt-1.2%Pd/Al2O3 catalyst in the 0.7 M NaOH solution was more active and selective to glyceric acid. While using 1.5 M NaOH water solution full glycerol conversion was reached only after 7 h, in 0.7 M NaOH solution similar glycerol conversion (96%) was reached already after 4 h. Selectivity to glyceric acid in the 0.7 M NaOH was higher by 23% compared to 1.5 M NaOH solution at the same glycerol conversion (96–100%). From table 2 data it is visible that in the 0.7 M NaOH water solutions the selectivity of glycerol oxidation products was not dependent on \(n(\text{glyc.})/n(\text{Me}).\)

Table 2. Glycerol oxidation over 1.2%Pt-1.2%Pd/Al2O3 catalyst. Effect of NaOH initial concentration and \(n(\text{glyc.})/n(\text{Me}).\)

| \(c_0(\text{NaOH}), \text{M}\) | Oxidation time, h | Glycerol conv., mol% | Selectivity, % |
|------------------------------|-------------------|----------------------|----------------|
| 0.7                          | 4                 | 96                   | GLYA | TART | LACT | GLYC | OXAL |
|                              | 7                 | 91                   | 65   | 11   | 14   | 6    | 4    |
| 1.5                          | 7                 | 100                  | 42   | 26   | 20   | 6    | 6    |

Reaction conditions: \(n(\text{glyc.})/n(\text{Me}) = 300 \text{ mol/mol}, P(\text{O}_2) = 1 \text{ atm}, 60 \degree \text{C}. \) \(^*n(\text{glyc.})/n(\text{Me}) = 500 \text{ mol/mol}\)

From Fig. 2 it can be seen that oxygen partial pressure significantly influences rate of glycerol oxidation. In oxidation with molecular oxygen \((P(\text{O}_2) = 1 \text{ atm})\) after 7 h glycerol conversion was 90%, but reduction of oxygen partial pressure to 0.2 atm resulted in glycerol conversion of only 35%. At the same time selectivity to glyceric acid also dependent on \(P(\text{O}_2).\) At similar glycerol conversion (till 35%) selectivity to glyceric acid at \(P(\text{O}_2) = 1 \text{ atm}\) was higher by 10% in comparison with selectivity at \(P(\text{O}_2) = 0.2 \text{ atm}.\) Fig. 2 show that the process selectivity to the main oxidation product, glyceric acid, slightly reduces. Selectivity to glyceric acid reduces due to glyceric acid oxidation to tartronic acid when the glycerol conversion degree increases.
Summarizing all the data it can be concluded that the best result (65% selectivity to glyceric acid with 96% glycerol conversion) was achieved using 1.2%Pt-1.2%Pd/Al₂O₃ catalyst when glycerol oxidation conditions were as follows: cₒ(glyc.) = 0.3 M, cₒ(NaOH) = 0.7 M, n(glyc.)/n(Me) = 300 mol/mol, t = 60 °C, P(O₂) = 1 atm, oxidation time 4 hours.

Figure 2. Influence of oxygen partial pressure on 2.5%Pt-2.5%Pd/Al₂O₃ catalyst activity and selectivity to glyceric acid.

4. Conclusions
Novel bimetallic Pt-Pd/Al₂O₃ catalysts with nanosized Pt-Pd alloy particles prepared by extractive-pyrolytic method were very active in the glycerol oxidation processes when alkaline solutions were used. Optimal conditions for obtaining glyceric acid from glycerol were determined. Fine-disperse bimetallic Pt-Pd/Al₂O₃ catalysts were more active compared to analogous monometallic Pt/Al₂O₃ and Pd/Al₂O₃ catalysts.

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