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Production of mono- and bimetallic nanoparticles of noble metals by pyrolysis of organic extracts on silicon dioxide

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Abstract. In the present work the influence of the tri-n-octylammonium (Oct₃NH⁺) salt anion (PtCl₆²⁻, PdCl₄²⁻, AuCl₄⁻) nature on the phase composition and mean size of crystallites of the extract pyrolysis products on the SiO₂ nanopowder has been studied. The XRD phase analysis of the composites (metal loading 2.4 wt.%) made under the same conditions, at the pyrolysis of Pt- and Au-containing extracts has shown the formation of nanoparticles of Pt (dₚt = 15 nm) and Au (dₜₚu = 33 nm), respectively. The end-product of the pyrolysis of the Pd-containing extract has an admixture phase of PdO along with the main metal phase (dₚd = 21 nm). At the preparation of bimetallic particles (Pt-Pd, Pt-Au, Pd-Au) on the SiO₂ nanopowder it has been found that the nanoparticles of the PtPd alloy, Pt and Au or Pd and Au nanoparticles are the products of the thermal decomposition of two-component mixtures of extracts. The investigation of catalytic properties of the produced composites in the reaction of glycerol oxidation by molecular oxygen in alkaline aqueous solutions has shown that all bimetallic composites exhibit catalytic activity in contrast to monometallic ones.

1. Introduction
Silicon dioxide is widely used as a carrier at the production of composites, which contain nanoparticles of noble metals, by such methods as sol-gel, ion exchange, impregnation method, deposition-precipitation and others [1]. These composites are used as catalysts in different chemical processes: hydrogenation, CO and alcohol oxidation reactions, manufacture of vinyl acetate, etc.[1, 2].

The promising use of the extractive-pyrolytic method (EPM) for the production of monometallic composites, such as high-dispersed nanoparticles of palladium on α-Al₂O₃ micro granules [3], Al₂O₃, Y₂O₃ nanopowders [4] and platinum on Al₂O₃, γ-AlO(OH),Y₂O₃, CeO₂, SiO₂ nanopowders [5, 6], has been earlier shown. In the reported investigations, solutions of metal-containing tri-n-octylammonium salts ([Oct₃NH⁺]₂PdCl₄, [Oct₃NH⁺]₂AuCl₄) in toluene were used as precursors, which impregnated the carrier and underwent pyrolysis. Alkylammonium salts are known as typical cationic surfactants, and, as the hydration energy of alkylammonium salt anion increases, its absorption ability from the non-aqueous phase at the hydrophilic interfaces increases as well [7]. The conditions of thermal decomposition of palladium- and platinum-containing tri-n-octylammonium salts, which make it possible to completely remove the organic component of the precursor, have been found in [3, 8]. The influence of the composite production conditions (pyrolysis temperature, annealing time, precursor concentration, the carrier specific surface area) on the mean size of metal crystallites was studied [6]. The composites produced by the EPM have been found [4, 5, 9] to exhibit a high catalytic activity in the reactions of glycerol oxidation by molecular oxygen.

In the course of this research, with the synthesis conditions being equal, individual nanoparticles of gold, platinum and palladium on the SiO₂ nanopowder were produced to study the influence of the Oct₃NH⁺ salt anion (PtCl₆²⁻, PdCl₄²⁻, AuCl₄⁻) nature on the phase composition and mean size of crystallites of the extract pyrolysis products. Additionally, the possibility of EPM application for the production of bimetallic particles by thermal decomposition of two-component mixtures of extracts on the carrier was investigated. The catalytic activity of all produced composites has been examined.

2. Experimental
In order to produce composites, Pt-, Pd- and Au-containing extracts were preliminary produced, in which a solution of tri-n-octylamine in toluene was used as an extractant. The method for the
production of metal-containing extracts is described in details in [5, 6]. A weight of a SiO₂ nanopowder (SSA = 190 m²/g) was impregnated by a solution of the extract or two-component mixtures of extracts. The volume of extract (СМе = 0.4 mol/l) corresponded to metal loading in composite 2.4 wt.%. Then, in order to remove the solvent, the sample was dried for 5-10 min at t = 80-105°C. Thermal treatment involved the heating of the sample in the air from room temperature to 300°C at the 100/min rate and the annealing within 5 min.

The phase composition of the extract pyrolysis products on the carrier was defined by an X-ray diffraction method using a diffractometer D8 Advance (Bruker Corporation) with CuKα radiation (λ = 1.5418Å). The mean size of metal crystallites (dₘ) was defined from the (111) peak width by the Scherrer method. SEM measurements were made using the MIRA/TESCAN operating at 15 kV. The specific surface area (SSA) of the composites was measured using the HROM-3 chromatograph by the BET method at the temperature of liquid nitrogen.

Glycerol was oxidized by molecular oxygen in the presence of the produced composites in alkaline aqueous solutions in a thermo-stated slurry bubble column reactor operated in a batch mode. In order to determine the concentration of the reaction products, liquid samples were collected periodically from the reaction mixture. The filtered samples were analyzed by a high performance liquid chromatograph (WATERS 2487).

3. Results

The XRD phase analysis of the produced monometallic composites has shown (Fig. 1) that the pyrolysis of [Oct₃NH]₂PtCl₆ and [Oct₃NH]AuCl₄ salts results only in the nanoparticles of platinum (PDF ICDD 00-004-0802) with dₘ = 15 nm (Fig. 1, curve 1) and of gold (PDF ICDD 00-004-0784) with d₉ₙ = 33 nm (Fig. 1, curve 3) on the carrier. Along with the main metal phase (dₘ = 21 nm, PDF ICDD 01-088-2335), the end-product of the thermal decomposition of [Oct₃NH]₂PdCl₄ salt contains also an admixture phase of palladium oxide (PDF ICDD 00-043-1024, fig. 1, curve 2). The PdO formation seemed to be attributed to the thermal treatment performed in the air, not in an inert atmosphere. Hence, d₉ₙ greatly exceeds dₘ and dₘ in the produced composites.

![Figure 1. XRD patterns of the composites:](image)

It is known [7] that the hydration energy of AuCl₄⁻ anion is less than that of PtCl₆²⁻ and PdCl₄²⁻ anions, therefore, the hydrophilic surface of the carrier is worse wetted by the Au-containing extract at the stage of impregnation than by the Pt- and Pd-containing extracts that probably contributes to the formation of larger metal crystallites. The SSA value of the Au-containing composite (165 m²/g) is smaller that those of the Pt- (178 m²/g) and Pd-containing (185 m²/g) composites.

The results obtained by SEM have revealed (Fig. 2) that the gold nanoparticles form larger agglomerates on the carrier surface, which are distributed less uniformly (Fig. 2a) that the agglomerates of palladium (Fig. 2b) and platinum (Fig. 2c).
The phase composition of the pyrolysis products of two-component mixtures of extracts on the carrier was studied at the production of bimetallic composites (Fig. 3). It has been found that the nanoparticles of the PtPd alloy (PDF ICDD 01-072-2838, d_{PtPd} = 20 nm) and of PdO as the admixture phase are the end-products of the thermal decomposition of the mixture of Pt- and Pd-containing extracts (Fig. 3, curve 1); those of the Pd- and Au-containing mixture are the nanoparticles of palladium, gold (d_{Me} = 20 nm) and PdO (Fig. 3, curve 2); those of the Pt-and Au-containing mixture give the nanoparticles of platinum (d_{Pt} = 12 nm) and gold (d_{Au} = 33 nm) (Fig. 3, curve 3).

The catalytic activity of all produced composites was tested in the reaction of glycerol oxidation by molecular oxygen in alkaline aqueous solutions (Table 1). The data in the table evidence that the largest catalytic activity is typical for the platinum-containing composites. Moreover, the bimetallic composites are much more active – the conversion of glycerol is by 26-30% higher if compared with the conversion in the presence of a Pt/SiO\textsubscript{2} monometallic composite. The main product of oxidation is...
glyceric acid, the yield selectivity of which is practically similar in the presence of all platinum-containing composites and varies within 52-57%. Monometallic Pd/SiO₂ and Au/SiO₂ are practically non-active. The disadvantage of the composites under investigation is the partial dissolution of the carrier during the oxidation of glycerol in alkaline aqueous solutions. Therefore, those composites as catalysts should be preferably used in neutral aqueous solutions.

### Table 1. Catalytic activity of mono- and bimetallic catalysts at glycerol oxidation.

| Composite       | Glycerol Conversion | Glyceric acid | Tartronic acid | Lactic acid | Glycolic acid | Oxalic acid | Formic acid |
|-----------------|---------------------|---------------|----------------|-------------|---------------|-------------|-------------|
| Pd/SiO₂         | 1                   | 55            | 0              | 0           | 45            | 0           | 0           |
| Pt/SiO₂         | 62                  | 56            | 4              | 29          | 8             | 1           | 2           |
| Au/SiO₂         | 3                   | 10            | 0              | 32          | 51            | 0           | 7           |
| Pd-Au/SiO₂      | 18                  | 90            | 2              | 2           | 1             | 1           | 1           |
| Pt-Pd/SiO₂      | 92                  | 52            | 8              | 32          | 8             | 1           | 2           |
| Pt-Au/SiO₂      | 88                  | 57            | 12             | 24          | 5             | 2           | 1           |

Reaction conditions: c₀(glycerol) = 0.3 M, c₀(NaOH) = 1.5 M, n(glycerol)/n(Pt) = 300 mol/mol, 60 °C, pO₂ = 1 atm, reaction time 4 h.*Oxidation time 7 h.

### 4. Conclusions

The investigations on the nature of Oct₃NH⁺ salt anion (PtCl₆²⁻, PdCl₄²⁻, AuCl₄⁻) effect on the phase composition and mean size of the crystallites of the pyrolysis extracts’ products on the SiO₂ have shown that the exchange of PtCl₆²⁻ anion by PdCl₄²⁻ one results in the increase of the mean size of metal crystallites from 15 nm to 21 nm and in appearance of the admixture phase of metal oxide (PdO), and the exchange by AuCl₄⁻ results in the increase of the mean size of metal crystallites to 33 nm. It has been found that the use of two-component mixtures of extracts makes it possible to produce bimetallic composites.

The study of the catalytic properties of the produced composites has revealed that the monometallic platinum-containing and all bimetallic composites exhibit catalytic activity in the reaction of glycerol oxidation by molecular oxygen in alkaline aqueous solutions.

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