Synthesis and properties of magnetic iron oxide/platinum nanocomposites

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Abstract. Iron oxide/platinum nanocomposites have been synthesized by the extractive-pyrolytic method (EPM) involving gradual decomposition of iron capronate and n-trioctylammonium hexachloroplatinate initially produced by solvent extraction. The content of platinum in the composites was 1.2 wt%, 2.4 wt% and 4.8 wt%. Phase composition, morphology and magnetic properties of the produced materials were investigated. XRD analysis and magnetic measurements show that the magnetic phase (magnetite Fe3O4) dominates in a carrier sample produced by the pyrolysis of iron carboxylate, but hematite α-Fe2O3 exists there as an admixture. Referring to the TEM results, the produced composites contain ultra-disperse platinum particles on the carrier, and the mean size of these varies from 3 nm to 9 nm.

1. Introduction

Magnetic composite nanoparticles on the base of ferromagnetic iron oxides combined with platinum are of particular interest for applications in catalysis [1, 2], sensor materials [3], and in biomedicine [4]. Commercial carriers [1, 5] as well as carriers produced by traditional methods, e.g., by coprecipitation of iron salts in an alkali medium [2-4], are used at the production of platinum nanoparticles on magnetic oxides (γ-Fe2O3 or Fe3O4). Platinum nanoparticles are produced by metal vapour synthesis [1], by colloid-deposition route [2], by the reduction of platinum ions from aqueous solutions using NaBH4 as a reducing agent [3] or by γ-ray irradiation [5].

In earlier studies [6-8], platinum-containing composites were produced by the extractive-pyrolytic method (EPM) involving thermal decomposition of platinum-containing n-trioctylammonium salt (n-trioctylammonium hexachloroplatinate [(C8H17)3NH]2PtCl6) on various commercial and plasma processed oxide carriers. Therefore, of certain interest was the use the EPM not only for the covering with metal nanoparticles, but also for the production of oxide carrier.

In the reported study, iron oxide/platinum nanopowders were produced by the EPM, and the phase composition, morphology and magnetic properties of the produced materials were investigated.
2. Experimental
The synthesis of iron oxide/platinum nanocomposites was begun with the production of a carrier. Iron (III) was extracted from a nitrate aqueous solution by caproic acid (HR - C₆H₁₂O₂), with no diluent, by adding a solution of sodium hydroxide in stoichiometric quantities. Sodium ions were removed by 3-fold contact of the extract with a freshly produced aqueous solution of iron nitrate. To prepare iron capronate (FeR₃) as a paste, an excess of the extractant was removed in vacuum. FeR₃ was thermally decomposed by heating until a temperature of 350 °C and annealing during 30 min. Further on, a platinum-containing extract (precursor) was prepared using a solution of n-trioctylamine in toluene as an extractant, following the procedure described in [8].

The platinum-containing composites were produced following the previously developed procedure: the carrier was impregnated by a platinum-containing precursor (C_Pt = 0.4 M at the production of composites with the 2.4 wt% and 4.8 wt% metal content, and C_Pt = 0.03 M at the production of composites with the 1.2 wt% metal content), then drying followed by pyrolysis [6-8].

The phase composition of the produced carrier and Pt-containing composites was characterized by an X-ray diffraction method using a diffractometer D8 Advance (Bruker Corporation) with CuKα radiation (λ = 1.5418Å). The mean size of platinum crystallites was defined from the (111) peak width by the Scherrer method. TEM measurements were made using the JEOL JEM 2100 operating at 200 kV. The specific surface area (SSA) of the carrier was measured by the BET method at the temperature of liquid nitrogen using the HROM-3 chromatograph. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (Lake Shore Cryotronics, Inc., model 7404) with a maximum magnetic field of 1 T. The temperature dependence of sample magnetization was measured within a range of temperatures from room to 680 °C.

3. Results and discussion
The XRD phase analysis of the products of iron capronate pyrolysis has shown (Fig. 1, curve 1) the dominance of the magnetic phase – magnetite Fe₃O₄ and/or maghemite γ-Fe₂O₃ with a non-magnetic admixture of hematite α-Fe₂O₃ (PDF ICDD 01-071-5088).

![Figure 1. XRD patterns of samples: 1 – iron oxide carrier; 2 – iron oxide/1.2 wt% Pt and iron oxide/2.4 wt% Pt composites; 3 – iron oxide/4.8 wt% Pt composite.](image-url)
The similarity of the crystal lattices of Fe₃O₄ and γ-Fe₂O₃ does not allow to conclude on which magnetic phase is present in the sample. Both oxides have the structure of spinel and similar crystal lattice parameter values: for Fe₃O₄ a₀ = 8.378 Å (PDF ICDD 01-071-6336) and for γ-Fe₂O₃ a₀ = 8.361 Å (PDF ICDD 00-071-6450).

The produced iron oxide powder (SSA = 39 m²/g) was later used as a carrier for the production of platinum-containing composites. When preparing a sample with the 4.8 wt% Pt-content, during the pyrolysis of a platinum-containing precursor, platinum particles (PDF ICDD 00-004-0802) of a mean size of 8 nm (Fig. 1, curve 3) were found to form on the carrier; but with the 1.2 wt% and 2.4 wt% Pt-content in the samples, amorphous metal particles were found (Fig. 1, curve 2).

With reference to the results of the magnetic measurements, the iron oxide powder (the carrier) exhibited ferromagnetic properties and had the coercivity Hₐ = 11 kA/m and the spontaneous magnetization σ ≈ 60 A·m²/kg (Fig. 2).

**Figure 2.** Magnetization loop of the carrier.

The temperature dependence of the sample magnetization showed (Fig. 3) that the Curie temperature of the magnetic material under study was 580 °C that corresponds to the Curie temperature of bulk magnetite (the Curie temperature of bulk maghemite is 675°C) [9]. This fact gives grounds to suggest that the basic magnetic phase of the sample is magnetite, which can include only a small amount of maghemite admixture.

**Figure 3.** Temperature dependence of the carrier magnetization under the 1 T magnetic field.
With reference to the XRD data (Fig. 1), after covering with platinum, the phase composition of the carrier remained the same. This was also confirmed by the results of magnetic measurements: the \( H_c \) value did not practically change, \( \sigma \) decreased a little to 50 A\( \cdot \)m\(^2\)/kg, which seems to be determined by the presence of platinum in the sample. The temperature dependence of the sample composite magnetization (the platinum content 4.8 wt%) was similar to the dependence plotted for the carrier (Fig. 3).

TEM investigations have revealed (Fig. 4) that the Pt-nanoparticles in the produced composites have a spherical shape and are immobilized on the carrier surface.

![TEM images and size distribution of platinum nanoparticles in composites](image)

**Figure 4.** TEM images and size distribution of platinum nanoparticles in composites: 

- a – iron oxide/4.8 wt% Pt;
- b – iron oxide/2.4 wt% Pt;
- c – iron oxide/1.2 wt% Pt.

A comparative analysis of the data listed in Table 1 evidences that the mean size of the particles in sample 1 (TEM data, Fig. 4a) is smaller that the mean size of the crystallites (XRD data). The X-ray amorphous platinum particles in sample composites 2 and 3 (TEM data, Figs. 4 b, c) have a mean diameter of 4 and 9
nm, respectively. The difference of the XRD and TEM data obtained for samples 1 and 3 is probably caused by the presence of a large amount of small-sized particles being amorphous (Figs. 4a, c).

| Sample No. | Pt content in composite, wt% | Pt crystallite mean size from XRD, nm | Pt particle mean diameter from TEM, nm |
|------------|-----------------------------|-------------------------------------|--------------------------------------|
| 1          | 4.8                         | 8                                   | 3                                    |
| 2          | 2.4                         | amorphous                           | 4                                    |
| 3          | 1.2                         | amorphous                           | 9                                    |

The catalytic properties of the produced composites with the 2.4 wt% and 4.8 wt% platinum content were studied in the reaction of glycerol oxidation by molecular oxygen in alkaline aqueous solutions and it has been shown that composites exhibit catalytic activity [10].

4. Conclusions
The performed investigations have demonstrated the dominance of the magnetic phase – magnetite Fe₃O₄ – in the sample carrier produced by iron carboxylate pyrolysis, but hematite α-Fe₂O₃ is present there as an admixture. During the production of metal-containing composites by the EPM, the phase composition of the carrier does not practically change, and the mean size of the platinum particles in the composites varies from 3 nm to 9 nm.

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