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Production of High-Dispersed Palladium Particles on α-Al_2O_3 Nanoporous Microgranules by the Extractive-Pyrolytic Method

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Abstract: The extractive-pyrolytic method (EPM) was used for the production of composites based on nanocrystalline palladium. Nanoporous microgranules of α-Al_2O_3 prepared from a plasma-processed nanopowder of Al_2O_3, were used as a carrier. The organic precursor was prepared by extracting palladium from an aqueous solution using n-trioctylammonium chloride ($(C_8H_{17})_3NHCl$) in toluene. The influence of pyrolysis conditions on the phase composition and nanoparticle size of final products has been investigated. X-ray diffraction measurements demonstrated that the heating of samples to 300, 350 and 400 °C (heating rate 14 °/min) resulted in the formation of nanocrystalline palladium on a porous carrier with an average particles size of 15, 23 and 28 nm, accordingly. IR spectra of the above-mentioned samples did not show the presence of organic impurities. Thermal treatment at 250 °C allows to obtain palladium particles with a crystal size of 7 nm, but the complete decomposition of the organic part has not been achieved under such conditions. It has been found that composites produced at pyrolysis temperatures of 250-400 °C (2.5 wt.% Pd content) exhibit catalytic activity at the oxidation of glycerin by molecular oxygen. The study of magnetic properties has shown that the composite produced at 300 ^{0}C exhibits ferromagnetic properties.

Key words: Extractive pyrolytic method, palladium, α-Al_2O_3 nanoporous microgranules.

1. Introduction

Among the technologies for composites production the solution techniques are the most useful and promissing. In recent years, such methods as chemical deposition [1], incipient wetness impregnation [2], sol-gel [3], micro-emulsion [4] and others has been widely used to apply palladium nanoparticles on different carriers.

Homogeneous powders, ceramics and functional film oxide materials of different applications are produced by the EPM [5]. The method involves the extraction of the target component from the aqueous solution followed by pyrolysis. The main advantages of this method are the simplicity and low costs that can do without sophisticated equipment, as well as extractants used; the possibility to use any materials, including unrefined ones, secondary and technological materials and industrial wastes. The refinement, quite exhaustive if necessary, of target components is affected during their extraction. It has been found [6, 7] that the EPM makes it possible to produce cobalt and nickel ferrite ultra disperse powders. Applying the EPM, composites consisting of Pd and silica-based materials with nominal metal loading of 10 wt.% were produced for hydrogen absorption-desorption investigations [8]. This method was also applied for covering powder carriers with fine-disperse platinum [9].

In this work, the EPM was used to produce palladium nanoparticles on porous α-Al_2O_3

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microgranules, and the catalytic and magnetic properties of the produced composites have been studied.

2. Experiments

In order to obtain palladium-containing organic extracts by the liquid extraction method, a trioctylamine ($(C_8H_{17})_3N$) solution in toluene is used. A tetrachloride palladium acid solution in hydrochloric acid (2 M HCl) is added to the trioctylamine solution in toluene. After shaking the mixture for 5 minutes, the organic phase is separated from the aqueous phase and filtered. The obtained organic phase, which is a solution of $[(C_8H_{17})_3NH]_2PdCl_4$ in toluene, is a precursor, which is added to the carrier. Nanoporous microgranules of α-Al_2O_3 (d ≈ 100 μm, porosity 39-40%, average pore diameters 100 nm) produced from the plasma-processed nanopowder of Al_2O_3 [10] were used as a carrier. The carrier was impregnated with a precursor solution, dried and subjected to heat treatment in air at different temperatures.

The produced composites were analyzed by X-ray diffraction (XRD) using a D-8 Advance (Bruker AXS) diffractometer with CuK_α radiation (λ = 1.5418 Å) in a wide range of Bragg angles ($10^o < 2\theta < 75^o$) with a scanning rate of 0.02 ^{o}/s at room temperature. The average crystallite size was calculated from (111) peaks. The infrared transmission spectra were obtained in a Specord 75-IR spectrometer for samples as KBr pellets in the range 400-4,000 cm^{-1}. SEM measurements were made with TM-1000 operating at 15 kV (Hitachi).

Glycerol was oxidized by molecular oxygen in the presence of the produced composites in an alkaline medium in a thermo-stated slurry bubble column reactor operated in batch mode. In order to determine the concentration of reaction products, liquid samples were analyzed using an HPLC chromatograph (WATERS 2487).

Magnetic measurements were made at room temperature by a vibrating magnetometer (Lake Shore Cryotronic 7404) in magnetic field up to 10 kOe.

3. Results and Discussion

The process of phase formation (Figs. 1 and 2) during the pyrolysis of palladium-containing extracts surfacing the granulated α-Al_2O_3 was investigated by XRD analysis. X-ray diffraction revealed that heating of samples from 200 to 400 °C caused the formation of highly dispersed palladium particles exhibiting the structure of a cubic face-centered lattice (Pd peaks correspond to standard maxima of XRD (PDF ICDD 05-0681). From the data in Fig. 1 (curve 2), it follows that at 400 °C the product of precursor decomposition contains PdO along with Pd.

Fig. 2 illustrates the results of XRD, in particular, the

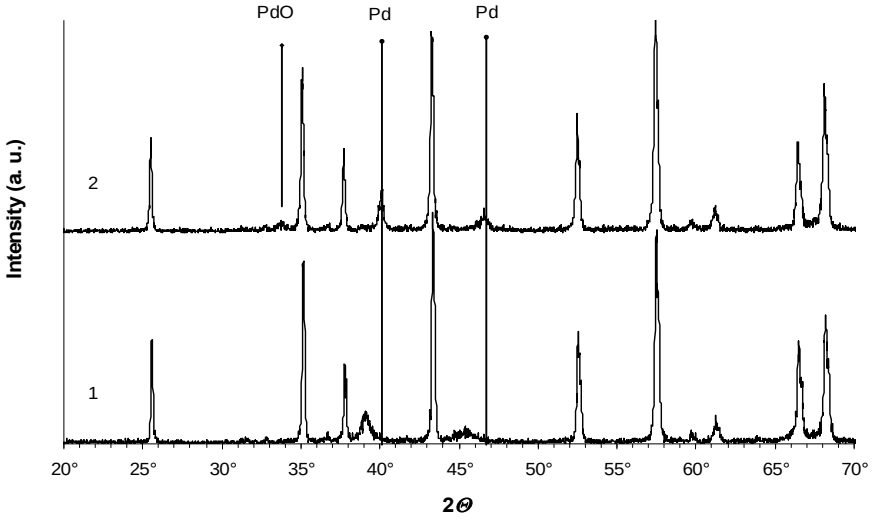


Fig. 1 XRD patterns of Pd/Al_2O_3 composites synthesized at 300 °C (1) and 400 °C (2) Pd content is 2.5 wt.%.

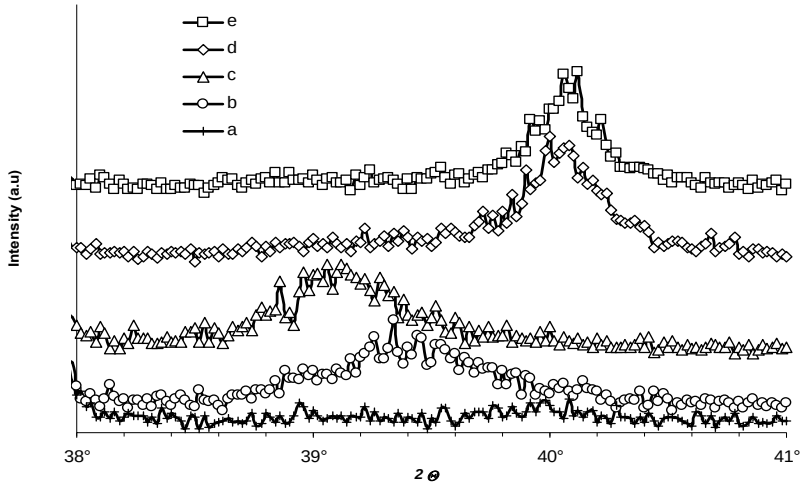


Fig. 2 XRD peak (111) of Pd, (a) sample produced at 200 °C, (b) sample 1, (c) sample 2, (d) sample 3 and (e) sample 4 (Table 1).

peak (111) of palladium nanoparticles produced at different temperatures. From the obtained data, the much wider peak is observed at the lower temperature of thermal treatment of the precursor that is related to the decrease in size of Pd crystallites. Pyrolysis conducted at 250 °C has resulted in Pd particles with a smaller crystallite size if compared to higher (300-400 °C) temperatures (Table 1).

Reaction conditions: c_0(glycerol) = 0.3 M, c_0(NaOH) = 1.5 M, n(glycerol)/n(Pd) = 300, T = 60 °C, p(O_2) = 1 atm, reaction time 420 min; GLYA-glyceric acid, LACT-lactic acid, TART-tartronic acid, GLYC-glycolic acid, OXAL-oxalic acid.

However, the IR spectra of the produced materials (Fig. 3) show that at T = 250 °C no complete decomposition of the organic component has been achieved as confirmed by absorption bands at 1,380 cm^{-1}, 1,460 cm^{-1}, 2,830 cm^{-1}, 2,910 cm^{-1} (Fig. 3, curve 1). At the same time, in the samples obtained at 300-400 °C there are no components of the organic precursor (Fig. 3, curve 2).

Thus, the presented results (Figs. 1, 3) show that in order to produce a composite containing only palladium particles on the carrier, the required pyrolysis temperature must be 300 °C.

The effect of the pyrolysis temperature on the catalytic activity and selectivity of the composites has been studied at glycerol oxidation by molecular oxygen. Experimental data show (Table 1) that the decrease of the pyrolysis temperature from 400 to 300 °C practically does not change the catalyst activity, but slightly increases the selectivity of the main product – glyceric acid. Further decrease of the precursor pyrolysis temperature to 250 °C slightly increases the catalyst activity, but decreases the glyceric acid selectivity. So the obtained results indicate that the optimal pyrolysis temperature is 300-350 °C for the production of composites used as catalysts in the

Table 1 Influence of the precursor pyrolysis temperature on the phase composition of final products, the size of Pd crystallites and catalytic properties. (2.5 wt.% Pd content in composites).

Sample No.	T_{pyr} (°C)	Phase composition	d_{Pd} (nm)	Glycerol conv. (%)	Selectivity (mol%)				
					GLYA	LACT	TART	GLYC	OXAL
1	250	Pd, organic impurities	7	45	70	13	6	8	3
2	300	Pd	15	35	74	8	6	8	4
3	350	Pd	23	35	71	7	7	10	5
4	400	Pd, PdO	28	34	69	15	5	8	3

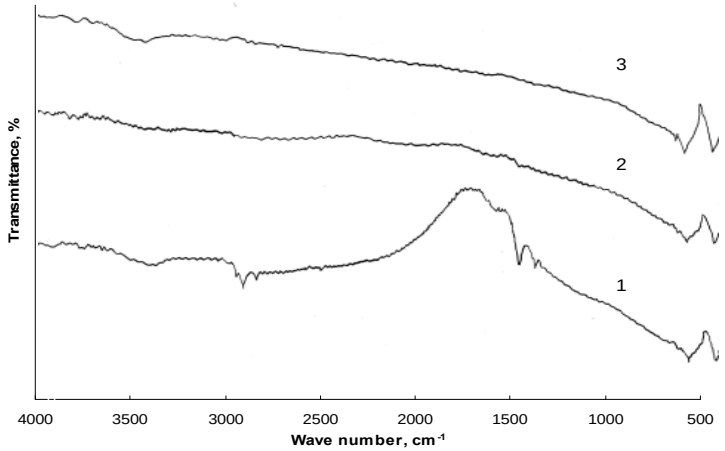


Fig. 3 Infrared spectra of Pd/Al_2O_3 composites synthesized at 250 °C (1) 300 and 350 and 400 °C (2) Al_2O_3 (3) Pd content is 2.5 wt.%.

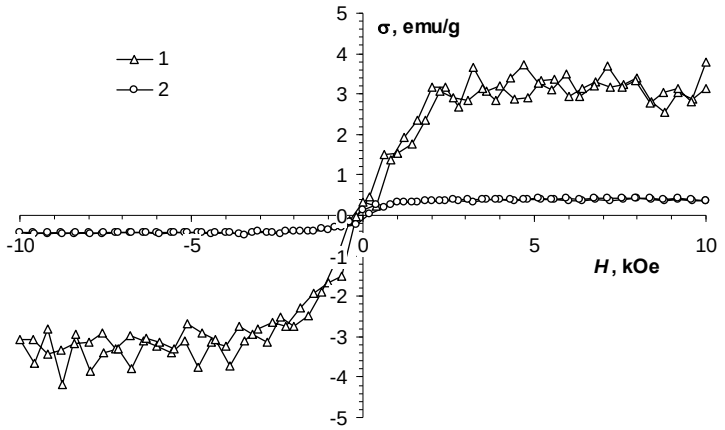


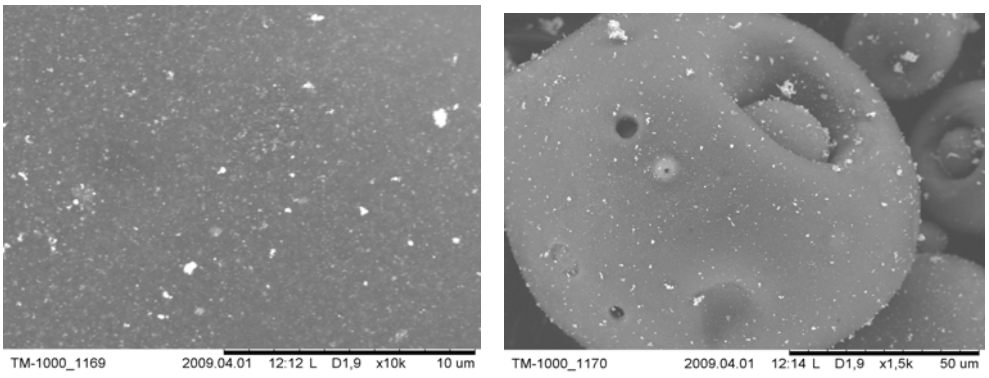
Fig. 4 Ferromagnetic magnetization of samples produced under different conditions at room temperature: (1) pyrolysis of extract at 300 °C, Pd content 2.5 wt.%; (2) pyrolysis of extract at 400 °C, Pd content 0.1 wt.%.

glycerol oxidation process.

Bulk crystalline palladium has no ferromagnetic properties. With reference to theoretical studies [11], palladium particles of smaller sizes are expected to exhibit ferromagnetic properties. The ferromagnetic properties of experimentally produced palladium clusters (average size 23 nm) are discussed in Ref. [12].

Though the possibility of magnetic structuring under such conditions was unpredictable, the made magnetic measurements showed that due to the production condition, some composites demonstrated ferromagnetism. Since the base of the composites (α-Al_2O_3) is diamagnetic, the appearance of ferromagnetic properties in the samples under investigation can be ascribed only to the products of pyrolysis. It has been found (Fig. 4, curve 2) that a composite having 0.1 wt.% of Pd exhibits weak ferromagnetic properties (ferromagnetic magnetization 0.42 memu/g). The magnetic properties of samples produced at pyrolysis of a relevant amount of the reagent ($(C_8H_{17})_3NHCl$) on the carrier were also investigated. It has been found that the samples also exhibit ferromagnetic properties, which are not so pronounced (0.28 memu/g). Among the samples presented in Table 1, only sample 3 has ferromagnetic properties (3.21 memu/g) (Fig. 4, curve 1). It should be emphasized that palladium produced by the pyrolysis of the precursor with no carrier also exhibits ferromagnetic properties (2.06 memu/g).

SEM micrographs of Pd/α-Al_2O_3 composite are



(a) (b)

Fig. 5 SEM micrographs of (a) Al_2O_3 granules with Pd nanoparticles surfacing and (b) the Al_2O_3 granule surface fragment with Pd nanoparticles surfacing. Pd content is 1 wt.%, pyrolysis at 400 °C.

presented in Fig. 5. The lighter particles on the external surface of microgranules (Fig. 5a) are likely Pd particles or agglomerates. Yet, even the large magnification does not allow unambiguous conclusions due to the indistinct image (Fig. 5b).

4. Conclusions

The extractive pyrolytic method has made it possible to produce palladium on the carrier, granulated Al_2O_3, with an ultra disperse structure. The phase composition of the final product and the size of palladium crystallites vary from 7 to 28 nm depending on the conditions of thermal treatment. The produced composites exhibit catalytic activity at oxidation of glycerin by molecular oxygen. Under certain conditions of synthesis, palladium nanoparticles exhibit ferromagnetic properties.

Acknowledgments

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