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Low-Temperature Synthesis of a Nanostructured Palladium-Based Catalyst with Defined Shape and its Catalytic Characteristics in Methanol Oxidation †

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Abstract: A novel approach of the synthesis nanostructured catalysts on the surface of Pd23Ag films with high activity is proposed in order to intensify low-temperature (up to 100 °C) hydrogen transport through hydrogen-selective palladium-containing membranes. The developed nanostructured catalyst demonstrates a great increase in catalytic activity of alkaline CH_3OH oxidation reaction, in comparison with palladium black. This is most likely due to an increase in the number of active sites in the material, compared with classical synthesis methods, which enhances the material activity with respect to reactions with H_2. Evaluation of resistance to carbon monoxide poisoning demonstrated the nanocatalysts high efficiency. A chronoamperometry confirms the presented catalyst continuing stability and activity as well as the applicability as catalysts and membranes.

Keywords: nanostructured surface; palladium-containing membranes; catalytic activity; methanol oxidation; hydrogen permeability

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1. Introduction

Noble metals nanoparticles find use in many fields of modern science and industry [1–3]. In particular, there are a big interest of palladium-based functional nanomaterials as hydrogen separation and purification catalysts [4–6]. Such devices must possess such properties as high activity and stability, which requires the presence of a large number of active sites [7]. Therefore, it is necessary to get to the bottom of the influence of nanoparticle morphology on their physical and chemical properties, in particular catalytic activity during the high-yield nanoscale systems development. Now, there are some various ways to synthesize monometallic or bearing synergistic effects from secondary metals nanostructures with need various habitus and shapes [8,9]. The presence of one or several fifth-order axes makes nanoparticles the most advanced [10–12]. Therefore, the aim of the article was to synthesize and investigate novel class of nanostructured palladium-based catalysts demonstrating high efficiency, which increase the material adsorption / desorption activity in reactions with hydrogen, and their catalytic characteristics.

2. Materials and Methods

2.1. Synthesis of Nanostructured Catalysts

In preparation for deposition film of Pd23Ag was washed in 96% ethylene and degreased for 20 min by boiling. Then, the substrate was fixed for later use as an anode in the working cell. The cathode was fixed parallel to the anode for deposition from. After that the film was polarized in 0.05 M H_2SO_4 at a current density of 10 mA cm^{-2}. The deposition was carried out in electrolytic cell with a 2% H_2PdCl_4 solution. A tetrabutylammonium bromide as a surfactant was added in various amounts to the working solution to vary the obtained coating type. The catalytic layer deposition on the film was carried out for 20 min at different current densities for various coatings from 5 to 6 mA cm^{-2}. The electrolytic deposition of a palladium coating with high dispersion was carried out with "Elins" P–40X potentiastat-galvanostat.

2.2. Electrochemical Measurements

The electrochemical measurements was carried out with "Elins" P–40X potentiastat-galvanostat in a regular three-electrode cell containing 1 M NaOH and 0.5 M methanol solution. It consists of working, counter and reference electrodes. The first one was a palladium-silver film with various palladium coatings types. The second one was a Pt foil with similar size. The third one was Ag/AgCl electrode.

The electrocatalytic and stability characteristics study of the samples was carried out by cyclic voltammetry (CV) at a scan rate of 50 mV s^{-1} in the operating potential range from –0.9 V to +0.5 V and chronoamperometry (CA) for 40 min at a constant potential of –0.3 V.

3. Results and Discussions

The electrolytic synthetic approach with several parameters variation was used to synthesize two series of modified films samples. The first samples series was deposited at the current density of 6 mA cm^{-2}. The second series samples synthesis differs in the addition of 0.005 M tetrabutylammonium bromide and in the decreasing of the current density to the value of 5 mA cm^{-2}.

To investigate morphology of modified palladium-silver films surface SEM images were obtained on "JEOL" JSM 7500F. The images of the synthesized Pd nanocatalysts are shown in Figure 1. SEM microphotographs of classical palladium black as the first series samples (Figure 1a) demonstrate a characteristic sphere-like nanoparticles with a size range of 90-100 nm. The second series samples images (Figure 1b) demonstrate filamentary nanoparticles with pointed tips. Most likely, the morphology of the synthesized particles was conditioned by a change in different synthetic parameters, in particular, rate of the particles deposition and the amount of surfactant in working solution, which in their turn affected the Cl^- and Br^- ions ratio. The obtained nanoparticles on palladium-silver film have the characteristic size of 100–150 nm.

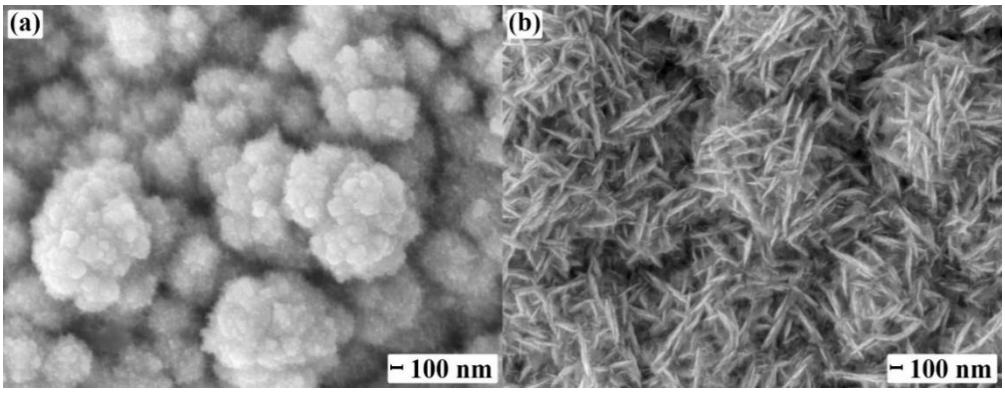

Figure 1. SEM images of the first (a) and second (b) sample series surfaces of Pd23Ag films.

Two series prepared samples CV-plots were recorded at a scan rate of 50 mV s^{-1} in the potential range from -0.9 to +0.5 V at room temperature (25 °C) (Figure 2). A distinct

anode peak of all samples in the potential range from -0.3 to -0.05 V during direct scanning is due to electrochemical CH_3OH and H_2O adsorption and carbon monoxide removal of surface-bound Pd. A negative shift of potential peak means enhanced catalytic performance in the methanol oxidation reaction. In the studied sample series the second one had the peak current density value of 17.09 mA cm^{-2} meaning the highest activity. Methanol oxidation resumption causes a cathode peak of lower current density with the reverse potential sweep in the potential range from -0.33 to -0.4 V. Therefore when the surface of the catalyst is reduced the oxidation reaction becomes possible.

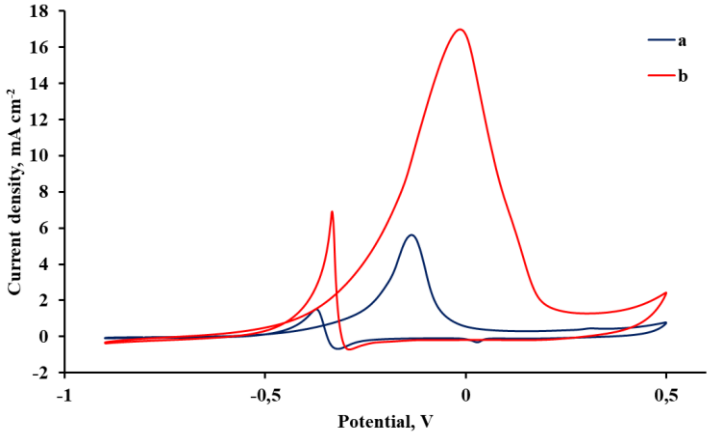

Figure 2. CV-plots of steady-state cycles of the first (a) and second (b) sample series in the alkaline CH_3OH oxidation reaction.

The current peaks ratio (i_F/i_B) corresponds to the catalysts CO poisoning resistance. Low ratio value indicates the accumulation of an unwanted carbonaceous residual forms on surface of the catalyst, whereas higher values means effective carbon monoxide desorption. So the entire investigated sample series have an acceptably high resistance to CO poisoning. However, the first sample series demonstrated the highest ratio (i_F/i_B) value of 3.83.

The two sample series stability was studied by multiscanning during 100 cycles of CV. The highest values of a current density of the sample series were achieved on average by the 30th CV-cycle. After this a slight decrease occured. The obtained experimental data, particulary, the current density decrease – 11.99% by the 100th cycles were achieved by the second sample series, that means the most continuing stability of nanocatalysts.

Further obtained sample series activity and stability was studied by the CA approach (Figure 3). During the experiment, the second sample series demonstrated the highest current density value of 0.099 mA/cm^2 confirming the highest stability in comparison with other samples.

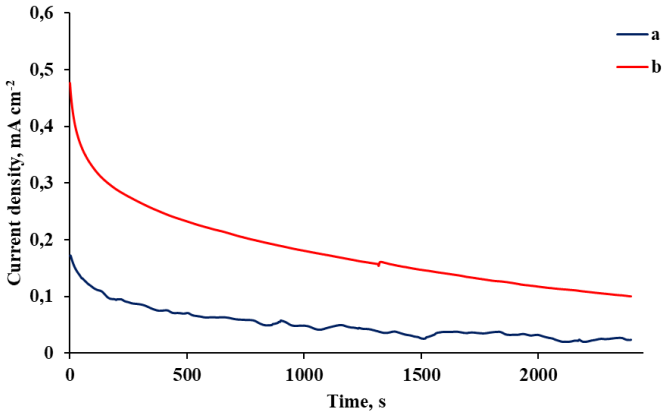

Figure 3. CA-plots of the first (a) and second (b) sample series in alkaline CH_3OH oxidation.

Such indicators of the catalyst quality as the electrochemically active surface area (ECSA) and the roughness factor (RF) are also quite significant. According to the obtained results, the second sample series had the highest ECSA and RF values of 0.19 cm^2 and 3.8 respectively, which may indicate an increased active centers number compared the first sample series.

4. Conclusions

The investigation demonstrated a novel advantageous approach, which solves the problem of manufacturing nanostructured Pd-based catalysts with high efficiency. Such catalysts enhance the adsorption and desorption activity in reactions with hydrogen. The high catalytic activity value up to 17.09 mA cm^{-2}, CO oxidation resistance and stability of the second sample series with a novel catalyst are due to an increase in the surface roughness as well as in the reactive active centers number in comparison with ordinary Pd black.

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Conflicts of Interest: The authors declare no conflict of interest.

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