

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

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[†] Presented at the 1st International Electronic Conference on Processes: Processes System Innovation, 17–31 May 2022; Available online: <https://ecp2022.sciforum.net>.

Abstract: A novel approach for the synthesis of 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 CH₃OH 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 H₂. Evaluation of resistance to carbon monoxide poisoning demonstrated the nanocatalyst's high efficiency. A chronoamperometry confirms the presented catalyst's 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



Citation: Petriev, I.; Pushankina, P.; Glazkova, Y.; Malkov, T.; Andreev, G.; Baryshev, M. Low-Temperature Synthesis of a Nanostructured Palladium-Based Catalyst with Defined Shape and Its Catalytic Characteristics in Methanol Oxidation. *Eng. Proc.* **2022**, *19*, 18. <https://doi.org/10.3390/ECP2022-12662>

Academic Editor: Andrey Yaroslavtsev

Published: 30 May 2022

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1. Introduction

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

2.2. Electrochemical Measurements

The electrochemical measurements were carried out with “Elins” P-40X potentiostat-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 coating 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 $+0.5 \text{ V}$ and chronoamperometry (CA) for 40 min at a constant potential of -0.3 V .

3. Results and Discussions

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

To investigate the morphology of modified palladium-silver film surfaces, 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 sample (Figure 1a) demonstrates characteristic sphere-like nanoparticles with a size range of 90–100 nm. The second sample's 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, the rate of the particle deposition and the amount of surfactant in the working solution, which in turn affected the Cl^- and Br^- ion ratios. The obtained nanoparticles on the palladium-silver film have the characteristic size of 100–150 nm.

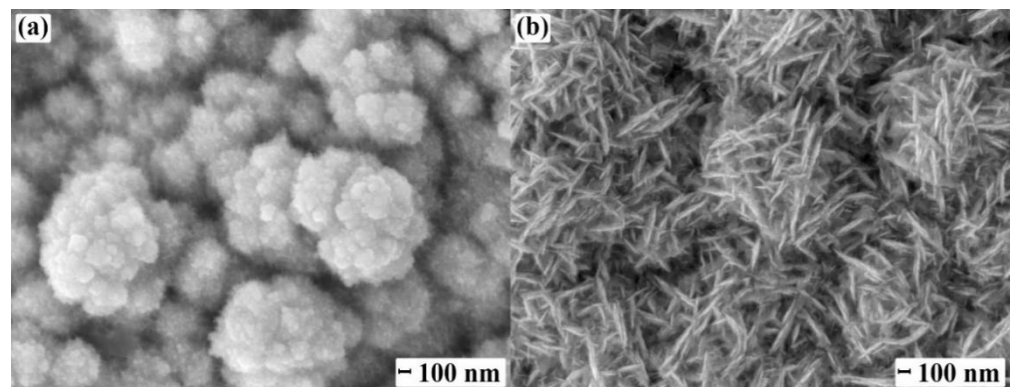


Figure 1. SEM images of the first (a) and second (b) samples' surfaces of Pd23Ag films.

Two prepared samples' CV plots were recorded at a scan rate of 50 mV s^{-1} in the potential range from -0.9 to $+0.5 \text{ V}$ 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 samples, 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, the oxidation reaction becomes possible when the surface of the catalyst is reduced.

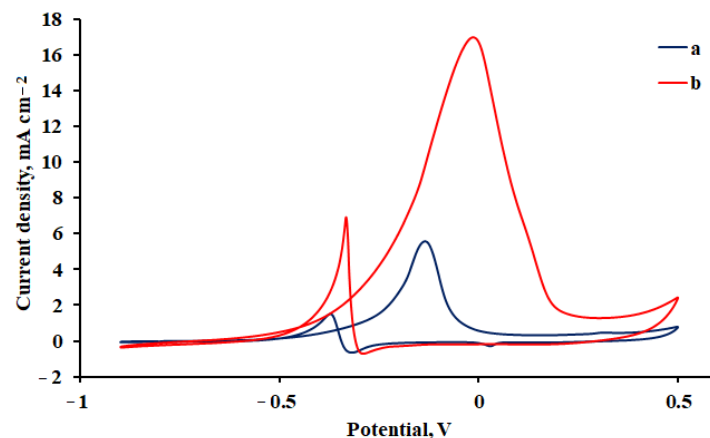


Figure 2. CV plots of steady-state cycles of the first (a) and second (b) samples in the alkaline CH_3OH oxidation reaction.

The current peak ratio (i_F/i_B) corresponds to the catalyst's CO poisoning resistance. Low ratio value indicates the accumulation of an unwanted carbonaceous residual forms on the surface of the catalyst, whereas higher values mean effective carbon monoxide desorption. Thus, the investigated samples have an acceptably high resistance to CO poisoning. However, the first sample demonstrated the highest ratio (i_F/i_B) value of 3.83.

The stability of the two samples was studied by multiscanning during 100 cycles of CV. The highest values of a current density of the samples were achieved on average by the 30th CV-cycle. After this, a slight decrease occurred. The obtained experimental data, in particular, the current density decrease—11.99% by the 100th cycle—were achieved by the second sample, which means it had the best nanocatalyst stability.

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

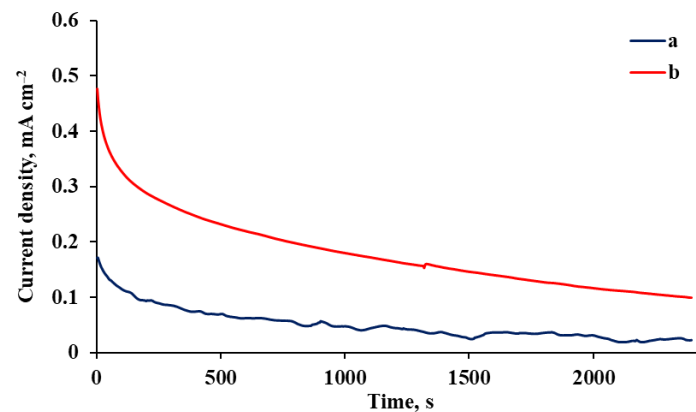


Figure 3. CA plots of the first (a) and second (b) samples in alkaline CH_3OH oxidation.

The indicators of the catalyst quality such as the electrochemically active surface area (ECSA) and the roughness factor (RF) are also quite significant. According to the obtained results, the second sample had the highest ECSA and RF values of 0.19 cm² and 3.8, respectively, which may indicate an increased active center number compared to the first sample.

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 of 17.09 mA cm⁻², CO oxidation resistance and stability of the second sample with a novel catalyst are due to an increase in the surface roughness as well as in the reactive active center number in comparison with ordinary Pd black.

Author Contributions: Conceptualization, I.P. and M.B.; methodology, I.P. and P.P.; formal analysis, T.M.; investigation, I.P., P.P., Y.G. and G.A.; writing—original draft preparation, I.P. and P.P.; writing—review and editing, I.P.; visualization, T.M.; supervision, M.B.; project administration, I.P. and M.B.; funding acquisition, I.P. and M.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Russian Science Foundation, grant number 21-72-00045, <https://rscf.ru/project/21-72-00045/>.

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

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