High content palladium nanocomposite carbon-palladium films

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Abstract. The results of studies on innovative high content palladium nanocomposite carbonaceous-palladium films (C-Pd film) obtained by Physical Vapor Deposition (PVD) method are presented. The influence of hydrogenation on these films’ structure, morphology and electric properties were investigated. The studies of structure and morphology of such films by SEM, EDS, TEM, XRD, and FTIR methods are presented. Decrease of resistance of these films due to hydrogenation was found.

1. Introduction

Palladium acetate is one of the most popular precursors for preparing active palladium catalysts [1], because of its versatility in catalyzing C–H bond activation [2] and cross-coupling reactions [3] of many different types of organic molecules to make pharmaceuticals [4], various chemical products used in agriculture [5], and electronic materials [6]. Additionally palladium catalysts are used in many processes of the petrochemical and petroleum refining industries, including the hydrogenation of unsaturated compounds, dehydrogenation, isomerization and hydrogenolysis [7÷9].

A conventional way of preparing palladium catalysts consists of loading a support with the initial palladium compound followed by the reduction of this compound [10]. However the reduction mechanisms of the catalysts precursors on support surfaces are still not fully understood.

One of the widespread reductant in the synthesis of supported metal catalysts is hydrogen [11]. Palladium acetate reduction by hydrogen takes place according to the following overall chemical equation:

\[
Pd(OAc)_2 + H_2 \rightarrow Pd + 2HOAc.
\]

Palladium is also used in the preparation of metal complex forming coordination polymers. A polymer–metal complex is composed of synthetic polymer and metal ions bound to the polymer ligand by a coordinate bond [12].

Metal colloids have unique physical properties and high catalytic activity. A common method for obtaining palladium colloids is the reduction of palladium salts in the presence of a stabilizing agent, such as a polymer, which prevents the formation of catalytically inactive “palladium black” due to the existence of a sterile barrier between the nanoparticles. The palladium on the polymer is applied. Their high surface-to-volume ratios make metal colloids very good candidates for active catalysts, but their thermodynamic instability complicates practical applications [13].
Interest in palladium is also related to its hydrogen sorption properties. Palladium is one of the best adsorbents of hydrogen [14]. Molecular hydrogen is dissociated at the palladium surface into two H atoms before absorption. Hydrogen can move in a subsurface layer and diffuse into the metal host lattice as a solid solution (α-phase). As the hydrogen pressure together with its concentration in the metal increases, interactions between hydrogen become locally important, and start a nucleation and growth of the hydride, β-phase of metallic palladium hydride is formed [15÷20]. Palladium is an element which is capable of reversibly absorbing large amounts of hydrogen. Two H atoms can recombine to H₂ in the desorption process.

In the presence of H₂ the resistivity of Pd will change due to the formation of a solid solution of Pd/H [21÷23]. Furthermore, Pd is highly selective to H₂ [24].

In this paper we present new nanocomposite carbonaceous-palladium material (C-Pd film) with high content of palladium (more than 50 wt %) obtained by deposition of palladium acetate and C₆₀ from two separated sources in PVD process. We present results of studies on the structure changes of the C-Pd film due to the hydrogenation of film and on the other hand due to the reduction of the palladium acetate during technological process.

2. Experimental

2.1. Preparation of nanocomposite C-Pd films
Nanocomposite C-Pd films were prepared by Physical Vapor Deposition (PVD) method. These processes were performed from two separate sources, one containing C₆₀ fullerenes (C₆₀, 99.9% Sigma-Aldrich) and other containing palladium acetate (Palladium (II) acetate, 99.98%, Sigma-Aldrich), both in the form of powder. The material is led to the evaporation by resistive heating. PVD process was conducted in a dynamic vacuum 10⁻³ Pa [25÷27]. The duration of the process was 5 min. Films were prepared on quartz glass polished substrates. The thickness of the films was 200÷300 nm.

2.2. Methods for characterization of nanocomposite C-Pd films
The topography and morphology of the prepared C-Pd films were studied by Scanning Electron Microscopy (SEM) method and Energy Dispersive X-ray Spectroscopy (EDS) technique using JEOL JSM-7600F scanning electron microscope with INCA X-Max spectrometer.

Studies of crystalline structure of C-Pd films were performed using Transmission Electron Microscopy (TEM), electron diffraction of selected area (SAED). The Titan Cubed transmission electron microscope operating at 300kV accelerating voltage was used for high-resolution transmission electron microscopy (HRTEM).

X-ray diffraction (XRD) studies were performed with Rigaku SmartLab 3kW diffractometer at room temperature in the 0/20 scanning mode with CuKα radiation and Si:Li semiconductor detector. Diffraction measurements were performed in grazing incidence primary beam geometry (GIXD).

The molecular structure of C-Pd films was investigated by infrared spectroscopy with Fourier transformation (FTIR), FTIR spectra were obtained with ThermoScientific Nicolet iS10 FTIR spectrometer, using ATR (Attenuated Total Reflection) technique, in the spectral range 500 ÷ 4000 cm⁻¹, with a resolution of 4 cm⁻¹.

The hydrogen sensing characteristics of C-Pd films in hydrogen gas presence were measured in a special set-up, designed and built in the Tele and Radio Research Institute [28]. All measurements were performed for the gas mixture of H₂ in nitrogen, with a rate of 50 ml/min. Electrical measurements were carried out in cycles of 10 min. In the first cycle, the gas with hydrogen was introduced to the experimental chamber. After 10 min, the synthetic air was introduced to remove H₂ gas. In the next cycle hydrogen gas was used again. Several hydrogen absorption-desorption cycles were carried out. Measurements were performed at room temperature and at atmospheric pressure.

The scheme of experimental set-up is shown in Fig. 1.
Figure 1. Experimental set-up used for hydrogen sensing measurements (1, 2 - gas bottles, 3, 4 - mass flow controllers, 5 - gas mixer, 6, 11 - valves, 7 - measurement chamber, 8 - voltmeter, 9 - reference resistor, 10 - voltage source)

The response of C-Pd films to hydrogen is defined as the percentage change in film resistance and was calculated using the following equation:

$$\frac{\Delta R}{R_0} = \left(\frac{R - R_0}{R_0}\right) \times 100\%,$$

where $R$ - film resistance after exposure to $H_2$, $R_0$ - film initial resistance in $H_2$ absence.

The electrodes for electrical measurements were prepared of silver paste. Two electrodes were placed on the film surface at a distance of 1 cm from each other. Estimated contact resistance electrode-probe was ~ 0.1 Ω while films resistance was higher than 100 Ω.

3. Results and discussion

3.1. Characterization of nanocomposite C-Pd films
Nanocomposite C-Pd films are composed of palladium nanograins embedded in various carbonaceous matrixes and are characterized by high content of palladium, above even 50 wt %. EDS spectrum of the C-Pd film is show in Fig. 2. Observation of topography by SEM method indicated that nanocomposite C-Pd films have very smooth surface. Exemplary SEM image of C-Pd film surface topography is presented in Fig. 3.

Figure 2. EDS analysis of the C-Pd film
Figure 3. SEM image of the topography of nanocomposite C-Pd film
TEM study revealed that nanocomposite C-Pd films are composed of palladium nanocrystals and carbonaceous matrix. TEM image of the C-Pd film is shown in Fig. 4. Pd nanograins, seen in TEM image as black objects, are very small with diameter of few nm. The Pd nanograins are randomly distributed over the entire carbonaceous matrix. The histogram of C-Pd film is shown in Fig. 4b. The average grain size (rs) of Pd nanograins determined from the histogram in this film is 2.5 nm and all observed objects have diameters smaller than 4 nm.

Figure 4a. TEM image of the nanocomposite C-Pd film; b) histogram of Pd nanograins size of C-Pd film

In Fig. 5 fast Fourier transformation (FFT) diffraction patterns from presented fragment in Fig. 3a of C-Pd film is shown. Visible in Fig. 5 diffused ring could be attributed to \((hkl)\) planes of Pd grains with the structure of \(fcc\) type (marked with yellow circle in Fig. 5). The diffused rings prove the presence of numerous small grains in the C-Pd film.

Figure 5. FFT diffraction patterns from the nanocomposite C-Pd film
3.2. The hydrogen sensing characteristics of C-Pd films

The hydrogen response real time characteristic for nanocomposite C-Pd film is presented in Fig. 6. In the first contact with hydrogen, C-Pd films’ resistance decreases (blue line in Fig. 6). As a result of such activation, the resistance decreased from 31 MΩ to 1.7 kΩ. Then, the experiment of hydrogenation in several cycles was performed. The big decrease of resistance after first hydrogenation can be connected to reduction of palladium acetate to crystalline form of metallic palladium grains by hydrogen. The introduction of synthetic air in every cycle did not cause appreciable return of resistance to the initial value. In the next measurement cycle (red line in Fig. 6) the resistance permanently increases and it stabilizes at a certain level after many cycles realization. It is connected with solution of hydrogen in palladium nanograins and the formation of solid solution of PdHx (resistance increase) and decomposed to Pd nanograin in air (resistance decrease).

![Figure 6. Hydrogen response characteristics for the nanocomposite C-Pd film](image1)

The response of C-Pd film to hydrogen as the percentage change in film resistance is shown in Fig. 7. In this graph we can see that the initial resistance to the reaction with hydrogen increases by 2.7 % in first cycle but in the last by 3.9 %. The ΔR/R0 increase in the subsequent measurement cycles is noticeable. The cause is an incomplete decrease in resistance upon introducing nitrogen into a
measurement chamber. After the first cycle, the resistance decreased below the initial value. The reintroduction of cyclic mixture of hydrogen and synthetic air caused an increase of the resistance when hydrogen gas was introduced and a decrease when synthetic air was introduced. However, resistance did not return to the initial value in the synthetic air within 10 minutes what results in an increased sensitivity in the following cycles of measurement.

3.3. Characterization of nanocomposite C-Pd films after activation

SEM image of the topography of the surface of nanocomposite C-Pd film after hydrogen measurement is presented in Fig. 8. Comparing these results with the SEM image before the hydrogen sensing measurement (Fig. 3), no changes were observed.

![SEM image of the nanocomposite C-Pd film after hydrogen measurement](image)

**Figure 8.** SEM image of the nanocomposite C-Pd film after hydrogen measurement

However, changes in the crystalline structure of nanocomposite C-Pd films were noticed. In TEM images of the C-Pd film after hydrogen measurement (Fig. 9), we observed increase in grain’s diameter while comparing with Pd grains observed in Fig. 4. Additionally a large dispersion of the distribution of the size of nanograins of C-Pd films is visible. In Fig. 9a Pd grains with different diameters are found. Many small nanograins with diameters to 10 nm are visible, but the hydrogen measurement caused also migration and agglomeration of palladium to big palladium particles. In the volume of the C-Pd film, the joined chain forming particles are observed. These chains can create current conduction paths. That could explain the reason of the C-Pd film’s resistance decrease after the hydrogen measurement.

The histogram of nanograins diameter distribution for sample after hydrogen measurement (Fig. 9b) included only smaller grains because it is difficult to distinguish individual grains in the agglomerate. The histogram shows that the average grain size (rs) of Pd nanograins is 6 nm. This means that due to the hydrogen measurement, the grain’s diameter increased twice. There were also differences in Fast Fourier Transformation (FFT) diffraction patterns from C-Pd before and after hydrogen measurement (Fig. 10).
Large dispersion of the size distribution of Pd nanograins reflects in the electron diffraction patterns (Fig. 10) where both diffuse diffraction rings (for small crystallites) and bright spots (for large crystallites) are visible. The first two inner rings, corresponding to distances between \{111\} and \{002\} palladium crystal are found.

X-ray diffraction studies have shown a change in the structure of the C-Pd film due to hydrogenation. In XRD pattern for initial C-Pd film (obtained by PVD process) we observe palladium acetate (Fig. 11 black line) while crystalline form of metallic palladium grains is no visible. XRD spectrum of C-Pd film (red line) after hydrogenation demonstrates that peaks of metallic palladium are observed. The Pd peak’s intensity indicates a small size of these grains. XRD results suggest a formation of Pd nanograins after hydrogenation of films and disappearing of palladium acetate crystalline form.

**Figure 9a.** TEM image of the nanocomposite C-Pd film after hydrogen measurement  
**Figure 9b.** Histogram of Pd nanograins size of C-Pd film after hydrogen measurement

**Figure 10.** Fast Fourier Transformation (FFT) diffraction pattern from the nanocomposite C-Pd film
Figure 11. XRD spectra of the C-Pd film after PVD process – black line and after hydrogen measurement – red line

The absorption spectra for infrared region for nanocomposite C-Pd film are presented in Fig. 12 (black line). In the region $400 \div 2000 \text{ cm}^{-1}$ the characteristic band for $\text{C}_{60}$ molecule vibration (1182 cm$^{-1}$) and characteristic bands of some characteristic groups for palladium acetate Pd(CH$_3$COO)$_2$ are found. The bands attributed to vibrations of palladium acetate are as follows: asymmetric stretching vibrations of COO at 1605 cm$^{-1}$; band attributed to a symmetric stretching vibrations COO at 1432 cm$^{-1}$ and band characteristic for CH$_3$ bending vibrations - 1335 and 695 cm$^{-1}$ [29:32]. FTIR spectrum for hydrogenated film does not exhibit characteristic bands of palladium acetate (red line on Fig. 12). This result confirm conclusion from XRD studies about decomposition of palladium acetate and modification of Pd crystalline structure to the metallic.

Figure 12. FTIR spectra of the C-Pd film after PVD process – black line and after hydrogen measurement – red line

4. Conclusions
Concluding, the results of XRD, FTIR and hydrogenation experiments show that C-Pd films with high content of palladium after first hydrogenation process change their form (palladium acetate disappears while Pd nanograins are formed). Due to this reorganisation of the film structure, the stable film containing palladium nanograins with average diameter of 6 nm is formed.
During many cycles of the gassing/degassing process the resistance of C-Pd films permanently changes. The effect can be connected to the hydrogen adsorption/desorption and the formation of PdH nanograins during the adsorption process. During the desorption process PdH grains turn into Pd grains, but not completely. Due to the big size (6nm in diameter) of Pd nanograins, hydrogen desorption is not total and the resistance of film increases. On the other hand the formation of conductivity paths consisted of Pd nanograins is observed.

These structural changes in the C-Pd films are stable.

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