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Synthesis of Palladium Nanoparticles by the Thermal Destruction of Pd(II) Solvate Complexes in Alcohols

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The composition and structure of Pd(II) solvate complexes in alcohols within the temperature range of 20–150°C are investigated by spectroscopic methods. As revealed, the Pd(II) solvate complexes of square-planar structure of D_{4h} symmetry are formed in alcohols: in ethanol, $[\text{Pd}(\text{C}_2\text{H}_6\text{O})_4]^{2+}$; in ethylene glycol, $[\text{Pd}(\text{C}_2\text{H}_6\text{O}_2)_2]^{2+}$; in glycerol, $[\text{Pd}(\text{C}_3\text{H}_8\text{O}_3)_2]^{2+}$. Synthesis of Pd nanoparticles (of 4–30 nm) is carried out by the thermal destruction of Pd(II) solvate complexes. As shown, the Pd nanoparticles (of 8–10 nm) can be stabilized by introducing fine-dispersed SiO_2 oxide in systems.

Досліджено спектроскопічними методами склад та будову сольватокмплексів Pd(II) в спиртах в інтервалі температур 20–150°C. Встановлено, що в спиртах утворюються сольватокмплекси Pd(II) в етанолі $[\text{Pd}(\text{C}_2\text{H}_6\text{O})_4]^{2+}$, в етиленгліколі $[\text{Pd}(\text{C}_2\text{H}_6\text{O}_2)_2]^{2+}$, у гліцерині $[\text{Pd}(\text{C}_3\text{H}_8\text{O}_3)_2]^{2+}$ пласкоквадратної будови симетрії D_{4h} . Синтезу металевих наночастинок Pd (4–30 нм) виконано термодеструкцією сольватокмплексів Pd(II). Показано можливість стабілізації наночастинок Pd (8–10 нм) шляхом введення в системи дрібнодисперсного оксиду SiO_2 .

Исследованы спектроскопическими методами состав и строение сольватокмплесов Pd(II) в спиртах при температуре 20–150°C. Установлено, что в спиртах образуются сольватокмплесы Pd(II) в этаноле $[\text{Pd}(\text{C}_2\text{H}_6\text{O})_4]^{2+}$, в этиленгликоле $[\text{Pd}(\text{C}_2\text{H}_6\text{O}_2)_2]^{2+}$, в глицерине $[\text{Pd}(\text{C}_3\text{H}_8\text{O}_3)_2]^{2+}$ плоскоквадратного строения симметрии D_{4h} . Произведён синтез металлических наночастиц Pd (4–30 нм) термодеструкцией сольватокмплесов Pd(II). Показана возможность стабилизации наночастиц Pd (8–10 нм) при введении мелкодисперсного оксида SiO_2 .

Key words: palladium, solvate complexes, spectroscopy, synthesis, metal nanoparticles.

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1. INTRODUCTION

Complex compounds of palladium are finding increasing use in various branches of science and technology [1, 2]. In spite of the fact that the works on the formation of metal nanoparticles have been carried out for a long time, the problem of creation and stabilization of nanoclusters in liquid phase remains topical because of low yield. The main reason of this is a high activity of the particles formed, which cannot be stabilized in this state, *i.e.* they aggregate into large structures. Complex compounds of Pd(II) in nonaqueous media play a special role since such systems can be used to produce palladium nanoparticles [1, 3, 4].

An analysis of nanoparticle synthesis carried out by us indicates that high-temperature processes of atomization of compounds are used with their subsequent condensation to clusters of different size and shape, which are of trustworthy character, which is due to geometrical and design features of devices [1, 3–6]. The methods for the synthesis of nanoparticles from different complex compounds of metals allow one to control the processes and can afford thereby highly efficient technologies for the development of novel nanomaterials. In view of this, production of palladium nanoparticles in organic solvents by the low-temperature destruction of palladium solvate complexes formed in them has good prospects. Methods for the chemical reduction of complex compounds of metals are of prime importance in the solution of this problem. This makes it possible to control the processes of the synthesis of nanoparticles from complex compounds of metals in liquid phase and to create by virtue of these novel nanomaterials.

The aim of this work was to obtain palladium nanoparticles in alcoholic solvents by the thermal destruction of palladium solvate complexes formed in them.

2. MATERIALS AND EXPERIMENTAL METHODS

Since PdCl₂ is practically insoluble in the solvents under investigation, we made a search for Pd(II) compounds, which would be soluble in nonaqueous media. Such a soluble compound is [(NH₄)₂PdCl₄], which was synthesized by us by the method reported in [7].

The following methods were employed in the investigations: electron absorption spectroscopy (Specord UV-VIS), IR spectroscopy (Specord M-80), gas chromatography (LKhM-80), x-ray phase analysis (DRON-3M), transmission electron microscopy (TEM) (JEOL-100). The electron absorption spectra (EAS) of the Pd(II) solvate complexes formed were examined after introducing the salt [(NH₄)₂PtCl₄] (0.001–0.01 mol/l) in ethanol, ethylene glycol and glycerol in a range of 40000–12000 cm⁻¹ in a temperature range of 20–150°C. The measure-

ments were made in quartz cells with an absorbing layer thickness of 5 mm.

3. RESULTS AND DISCUSSION

When dissolving $[(\text{NH}_4)_2\text{PdCl}_4]$ in ethanol, absorption bands at 30000, 25800, and 20000 cm^{-1} were found in EAS (Fig. 1, *a*). According to [8, 9], the appearance of the spectra and the absorption frequencies are typical of Pd(II) complexes with formation of the central coordination unit $[\text{PdO}_4]$ of square-planar structure. This is possible in the case of formation of solvate complexes $[\text{Pd}(\text{C}_2\text{H}_6\text{O})_4]^{2+}$ of square-planar structure in ethanol. In accordance with the energy level diagram for d^8 electron configuration, three absorption bands for solvate complexes $[\text{Pd}(\text{C}_2\text{H}_6\text{O})_4]^{2+}$ of D_{4h} symmetry may be assigned to the ${}^1A_{1g} \rightarrow {}^1E_g$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^3A_{2g}$ transitions.

The EAS obtained on the dissolution of $[(\text{NH}_4)_2\text{PdCl}_4]$ in ethylene glycol is also characterized by three bands: 30200 cm^{-1} , 25300 cm^{-1} , 20200 cm^{-1} (Fig. 1, *b*). According to literature data [8, 9], the appearance of the spectrum and the frequency range of the absorption bands are typical of Pd(II) complexes with formation of $[\text{PdO}_4]$ chromophores of square-planar structure, and the absorption bands may be assigned to the transitions ${}^1A_{1g} \rightarrow {}^1E_g$; ${}^1A_{1g} \rightarrow {}^1A_{2g}$; ${}^1A_{1g} \rightarrow {}^3A_{2g}$ respectively. The possibility of coordination of ethylene glycol molecules in a bidentate manner [10] must lead to the formation of Pd(II) solvate complexes of the most probable composition $[\text{Pd}(\text{C}_2\text{H}_6\text{O}_2)_2]^{2+}$ of D_{4h} symmetry.

In glycerol, the EAS of Pd(II) chromophores is similar to that in eth-

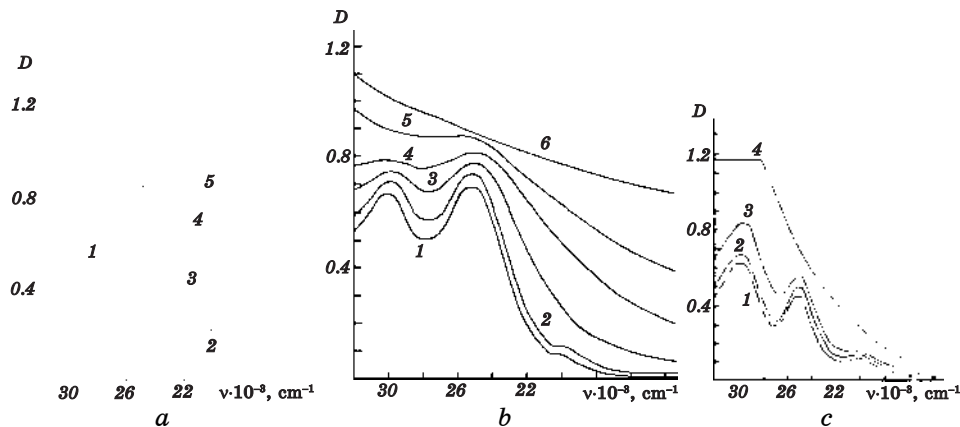


Fig. 1. Electron absorption spectra of palladium(II) in ethanol (*a*), ethylene glycol (*b*) and glycerol (*c*) at a temperature of: (*a*) (1) 20°C, (2) 30°C, (3) 50°C, (4) 60°C, (5) 70°C; (*b*) (1) 20°C, (2) 40°C, (3) 60°C, (4) 80°C, (5) 100°C, (6) 110°C; (*c*) (1) 20°C, (2) 60°C, (3) 80°C, (4) 100°C.

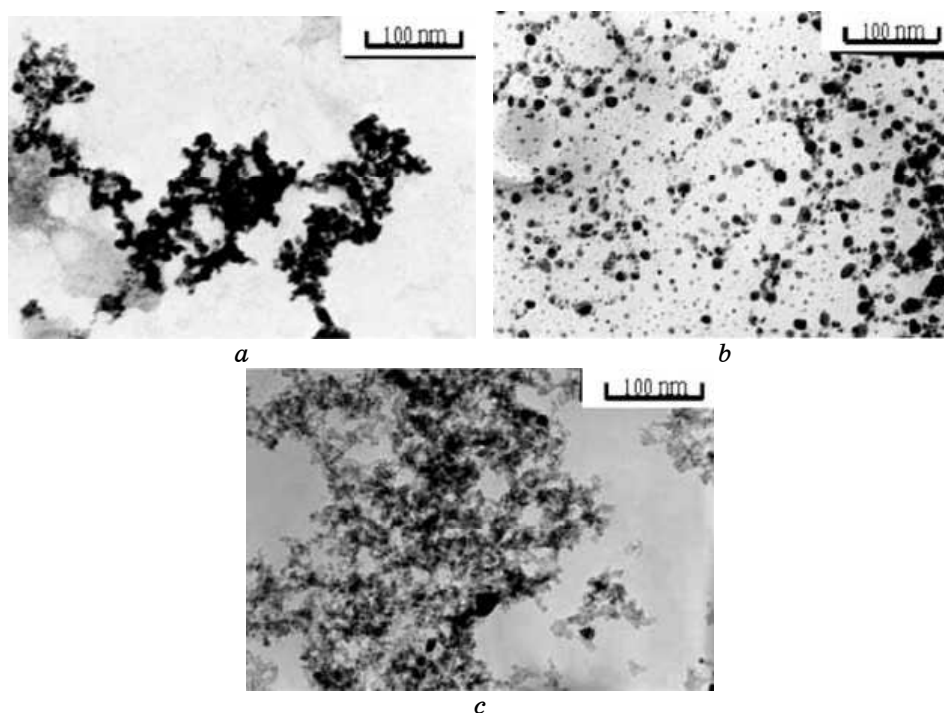


Fig. 2. Transmission electron microscopy of palladium nanoparticles after thermal destruction of the solvate complexes $[\text{Pd}(\text{C}_2\text{H}_6\text{O})_4]^{2+}$ in ethanol (7–30 nm) (a), $[\text{Pd}(\text{C}_2\text{H}_6\text{O}_2)_2]^{2+}$ in ethylene glycol (4–20 nm) (b), and $[\text{Pd}(\text{C}_3\text{H}_8\text{O}_3)_2]^{2+}$ in glycerol (5–30 nm) (c).

ylene glycol and is also characterized by three absorption bands: 30000 cm^{-1} , 24400 cm^{-1} , 19800 cm^{-1} (Fig. 1, c). In glycerol, by analogy with ethylene glycol, $[\text{PdO}_4]$ chromophores of square-planar structure are formed. Pd(II) is most probably coordinated by glycerol molecules in a bidentate manner to form solvate complexes $[\text{Pd}(\text{C}_3\text{H}_8\text{O}_3)_2]^{2+}$ of D_{4h} symmetry.

Thus, $[\text{PdO}_4]$ chromophores are formed in alcohols via the presence of the $[\text{Pd}(\text{C}_2\text{H}_6\text{O})_4]^{2+}$, $[\text{Pd}(\text{C}_2\text{H}_6\text{O}_2)_2]^{2+}$, and $[\text{Pd}(\text{C}_3\text{H}_8\text{O}_3)_2]^{2+}$ solvate complexes of square-planar structure of D_{4h} symmetry.

As the temperature rises, an increase in the intensity of absorption bands and their shift towards the long-wavelength region of the spectrum take place in the EAS of Pd(II) solvate complexes in ethanol, ethylene glycol and glycerol (Fig. 1). This behaviour in the EAS of Pd(II) solvate complexes in alcohols is due to the ligand-field reduction with rising temperature and to the filling of higher vibrational sublevels, which leads to a decrease in electron transition energy.

At a temperature of over 60°C in ethanol and 100°C in ethylene gly-

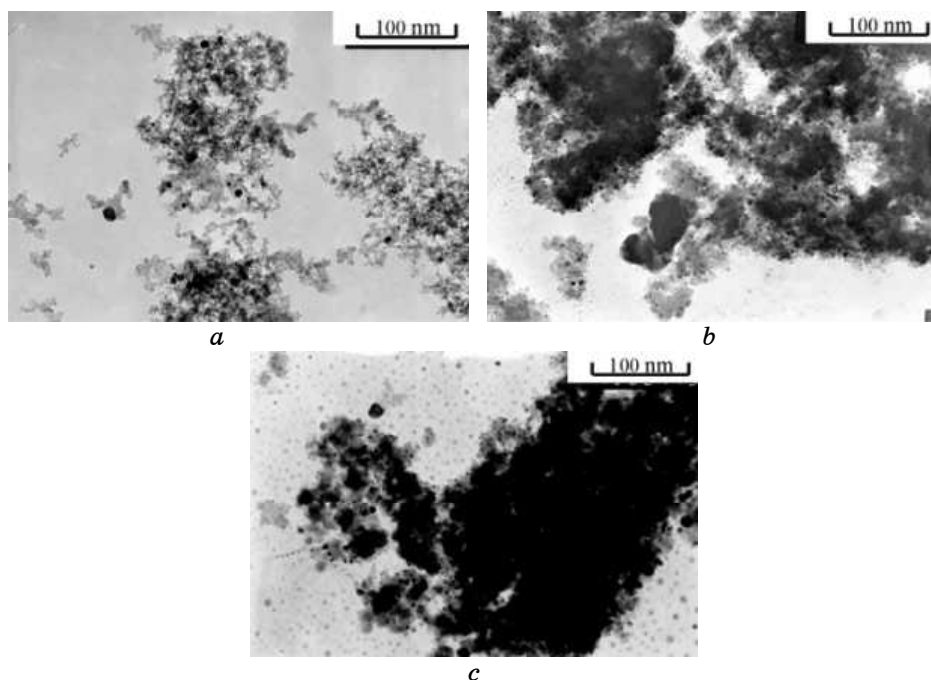
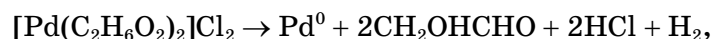
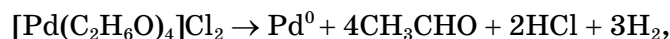


Fig. 3. Transmission electron microscopy of palladium nanoparticles (8–14 nm) in the SiO₂ surface in ethanol (a), ethylene glycol (b), glycerol (c).

col and glycerol, the spectra of Pd(II) solvate complexes change: the characteristic absorption bands of Pd(II) solvate complexes disappear, and complete absorption is observed (Fig. 1). This is brought about by the thermal destruction of the solvate complexes $[\text{Pd}(\text{C}_2\text{H}_6\text{O})_4]^{2+}$, $[\text{Pd}(\text{C}_2\text{H}_6\text{O}_2)_2]^{2+}$, $[\text{Pd}(\text{C}_3\text{H}_8\text{O}_3)_2]^{2+}$ formed, reduction of Pd(II) to Pd⁰, and oxidation of alcohols to corresponding aldehydes [11]. The reduction of Pd(II) solvate complexes to Pd⁰ in alcohols proceeds according to the proposed reactions:



The reaction products obtained by us corroborate the proposed schemes of the processes that occur in alcohols during the reduction of Pd(II) to Pd⁰. It has been found that along with the reduction of Pd(II) to Pd⁰, oxidation of alcohols to corresponding aldehydes: ethyl aldehyde CH₃CHO, glycolaldehyde CH₂OHCHO and glyceraldehyde CH₂OHCHOHCHO takes place. The formation of the aldehydes is sup-

ported by the presence of a characteristic stretching vibration band of aldehyde carbonyl group in the IR absorption spectra of the systems under investigation: at 1730 cm^{-1} for ethyl aldehyde, 1685 cm^{-1} for glycolaldehyde, 1700 cm^{-1} for glyceraldehyde [12]. Moreover, according to gas-chromatographic data, the reaction products HCl and H_2 have been found in gaseous samples in the case of reducing Pd(II) to Pd^0 .

An x-ray phase analysis of precipitates separated as ultrafine particles from the solvents under investigation showed formation of metallic palladium.

According to transmission electron microscopy data (Fig. 2), the size of the Pd particles obtained is 7–30 nm in ethanol, 4–20 nm in ethylene glycol, 5–30 nm in glycerol. The methods for the synthesis of Pd particles from different Pd(II) solvate complexes permit one to control the processes and can afford thereby highly efficient technologies for the development of novel nanomaterials.

To prevent aggregation and to find out whether stabilization of the palladium nanoparticle size is possible, we employed a method of introducing fine (10–12 nm) SiO_2 oxide into the system to sorb the palladium nanoparticles on it. The SiO_2 –palladium nanoparticles ratio was 10:1 and 5:1.

According to TEM data, the size of the obtained palladium nanoparticles adsorbed on the SiO_2 surface is 8–14 nm (Fig. 3) in the systems under investigation.

A confirmation of the formation of metallic palladium and its sorption on the SiO_2 surface was given by the XPS method. This method was employed by us to study the state of palladium and silicon after thermal destruction of palladium(II) solvate complexes. The energy distribution of photoelectrons knocked out by x-rays on interaction with sample gives direct information on the electronic state of the inner level or valence orbitals from which electron was liberated, and this is very sensitive to the changes, which occur during some interactions or others. From XPS of samples under investigation, where palladium was sorbed on the SiO_2 surface in ethanol, ethylene glycol and glycerol, the electronic state of the palladium levels $3d_{3/2}$ (M_{IV} -shell) and $3d_{5/2}$ (M_{V} -shell) and silicon level $2P_{1/2}$ (L_{II} -shell) on the SiO_2 surface has been obtained. For the M -shells of palladium adsorbed on the SiO_2 surface, a chemical shift ($M_{\text{IV}} = 339.8\text{ eV}$, $M_{\text{V}} = 334.8\text{ eV}$) relative to free metallic palladium ($M_{\text{IV}} = 340\text{ eV}$, $M_{\text{V}} = 335\text{ eV}$) takes place [13]. Similar changes occur for the L_{II} -shell of silicon atoms in SiO_2 . For instance, for silicon atoms in SiO_2 , the value of the L_{II} -shell is 103 eV [14], whereas there is a chemical shift of the L_{II} -shell to 103.4 eV on interaction with palladium. The changes in inner-electron binding energy for palladium and silicon may be accounted for by the electric charge redistribution of outer shells on chemical bond formation. As the chemical shift for the shells of palladium and silicon atoms is

small, the bond is very weak and does not give rise to changes in the valent state of palladium and silicon from the initial one.

The observed changes may be interpreted in terms of ionic interaction between palladium and silicon in SiO₂. The valence electrons do not penetrate into the middle of atomic cores, and the chemical shifts must therefore be the same for all inner electrons [13]. This picture is observed in our experiments for the *M*-shells of palladium, where the distance between the *M*_{IV}- and *M*_V-shells retains the value of 5 eV for both free and sorbed metal.

The methods developed by us for the synthesis of Pd nanoparticles by the thermal destruction of various Pd(II) solvate complexes in ethanol, ethylene glycol and glycerol will allow one to control the processes of formation of palladium nanoparticles different in size (4–30 nm). It has been shown that the size of Pd nanoparticles can be stabilized to 8–14 nm by introducing fine SiO₂ oxide in the systems under investigation.

The results of studies on the production of palladium nanoparticles and coating of nanomaterials with them can be utilized in the development of novel catalysts, selective adsorbents, medicinal preparations *etc.*

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