General and Inorganic Chemistry

Reversible sorption of hydrogen by colloidal palladium in aqueous solutions

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Colloidal palladium was prepared by γ-irradiation or by H_2 reduction of $Pd(NH_3)_4Cl_2$ in aqueous solutions containing sodium polyacrylate as a stabilizer. The sols contain spherical particles 2—4 nm in diameter. Their optical spectra contain a band at 230 nm ($\varepsilon = 6.1 \cdot 10^3$ L mol^{-1} cm^{-1}) smoothly descending toward the visible range. The sols reversibly absorb chemically from 0.35 to 0.15 g-mol of H_2 per g-atom of Pd. The spectra of ultrafine metal particles saturated with molecular hydrogen exhibit an absorption band at 265 nm ($\varepsilon = 4.5 \cdot 10^3$ L mol^{-1} cm^{-1}). One-electron reduction of methylviologen by hydrogen is catalyzed by the colloidal palladium prepared.

Key words: palladium, reduction; colloidal particles; sorption of hydrogen.

Ultrafine palladium particles in aqueous solutions have been obtained previously upon reduction of its salts in the presence of various stabilizing additives (see, *e.g.*, reviews[1—3]). Particles of an average diameter of ~2.6 nm stabilized by phenanthroline or bipyridyl molecules (L) were obtained upon reduction of Pd^{2+} ions by dihydrogen in AcOH followed by treatment with dioxygen. The idealized composition of such a "giant cluster" can be expressed by the formula $Pd_{561}(AcO)_{180}L_{60}$.[3,4] It is known[5,6] that colloidal metal particles absorb light in the UV and visible spectral ranges. The absorption of surface plasmons depends on the size and especially on the shape of the particles[5—8] as well as on the state of their surface. The latter is widely used in studies of the properties of ultrafine metal particles and peculiarities of their interaction with various compounds.[9—11] The optical absorption of palladium sols has been presented for the first time in our previous publication.[12] The sols were obtained by radiation chemical reduction or by reduction with molecular hydrogen of $Pd(NH_3)_4Cl_2$ in the presence of sodium polyacrylate as a stabilizing additive. The experimental procedure made it possible to obtain the solutions, which were almost completely transparent up to 200 nm. The absorption of the sols is represented by a broad band with a maximum in the UV range smoothly descending toward the visible spectral range. It was also found that colloidal palladium absorbs hydrogen.

This work is devoted to the study of optical properties of colloidal palladium and the peculiarities of its interaction with hydrogen in aqueous solutions.

Experimental

Reagent grade reagents were used. Triply distilled water was used for the preparation of solutions. The concentration of sodium polyacrylate in an aqueous solution is presented in

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moles of monomeric units. γ-Irradiation was carried out on a ^{60}Co source, and the dose rate was 1.8 kGy h^{-1}.

The degree of reduction of methylviologen (MeV^{2+}) with hydrogen was determined by the addition of solutions of MeV^{2+} (2 mL, $1 \cdot 10^{-2}$ mol L^{-1}) and NaOH (1 mL, 0.1 mol L^{-1}) to 20 mL of the solution studied. The concentration of reduced methylviologen was measured spectrophotometrically (λ_{max} = 600 nm, $\varepsilon_{600} = 1.2 \cdot 10^4$ L mol^{-1} cm^{-1}).[13]

Absorption spectra were recorded on Specord UV-VIS or Shimadzu UV-3100 spectrophotometers.

Microscopic studies were carried out on a Philips EM-301 transmission-type electron microscope. Samples were prepared by pouring of a drop of a solution onto a copper-carbon plate and dried in an argon atmosphere.

Results and Discussion

γ-Irradiation of aqueous solutions of $Pd(NH_3)_4Cl_2$ containing isopropanol results in the formation of electrons (e_{aq}) and Me_2COH radicals with high redox potentials (−2.9 and −1.5 V, respectively[14]) in the following reactions:

$$H_2O \rightarrow e_{aq}\ (2.7),\ H\ (0.5),\ OH\ (2.9)$$

$$Me_2CH(OH) + OH(H) \rightarrow Me_2COH + H_2O(H_2)$$

The values of the radiation-chemical yields of the products of radiolysis of water per 100 eV of ionizing radiation are presented in parentheses. The electrons and radicals participate in the subsequent reactions of reduction of Pd^{II} ions, which results eventually in the formation of colloidal palladium particles.[12,15]

The absorption spectrum of the colloidal particles (Fig. 1, curve *3*) was obtained by the subtraction of the absorption spectrum of the solution of compounds that are present or formed during the reduction of palladium (curve *2*) from the spectrum of the solution studied after complete reduction of palladium ions (curve *1*). The optical parameters of colloidal palladium (λ_{max} = 230 nm, $\varepsilon_{230} = 6.1 \cdot 10^3$ L mol^{-1} cm^{-1}) well agree with those determined by the theoretical calculations for particles 10 nm (see Ref. 6) or 5 nm (see Ref. 1) in diameter. The absorption of the solution changes substantially, when hydrogen is added (curve *4*), which can be related to the sorption of the gas with palladium. The spectrum (curve *5*) calculated by the aforementioned procedure is a broader band with λ_{max} = 265 nm and $\varepsilon_{265} = 4.5 \cdot 10^3$ L mol^{-1} cm^{-1}.

Ultrafine particles with the similar optical parameters are formed, when hydrogen is used as the reducing agent for Pd^{II} ions (Fig. 2). In this case, the absorption spectrum of the sols with sorbed hydrogen is observed at the complete reduction, and after evacuation of the solution the spectrum of the "pure" sols is recorded.

It is noteworthy that changes in the contents of the palladium salt in the solution from $2 \cdot 10^{-5}$ to $1 \cdot 10^{-3}$ mol L^{-1} and sodium polyacrylate from $1 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ mol L^{-1} or the replacement of isopropanol by another alcohol in the case of radiation-chemical reduction exerts no effect on the optical parameters of the metal sols obtained.

The sorption of hydrogen by palladium is reversible and can be repeated multiply in the procedure of subse-

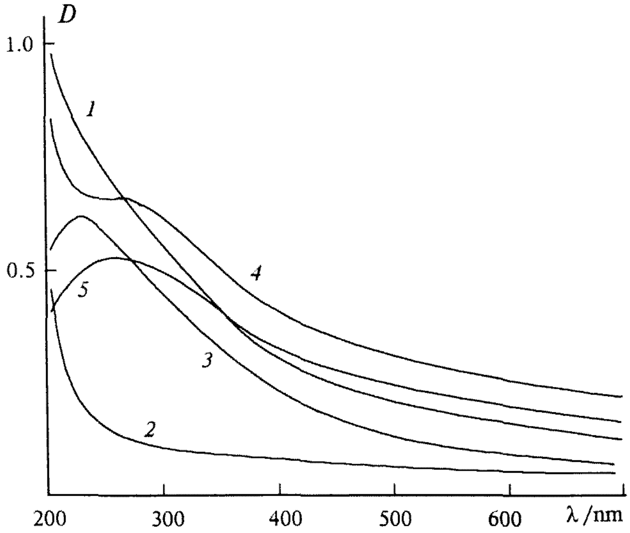

Fig. 1. Absorption spectra of: *1*, evacuated solution of $1 \cdot 10^{-4}$ mol L^{-1} of $Pd(NH_3)_4Cl_2$ containing 0.1 mol L^{-1} of isopropanol and $5 \cdot 10^{-4}$ mol L^{-1} of sodium polyacrylate after complete reduction of palladium, absorbed dose is 0.63 kGy; *2*, solution of 0.1 mol L^{-1} of isopropanol, $5 \cdot 10^{-4}$ mol L^{-1} of sodium polyacrylate, $4 \cdot 10^{-4}$ mol L^{-1} of ammonia, and $2 \cdot 10^{-4}$ mol L^{-1} of NaCl; *3*, obtained by the subtraction of spectrum *2* from spectrum *1*; *4*, after admission of dihydrogen to solution *1*; *5*, obtained by the subtraction of spectrum *2* from spectrum *4*.

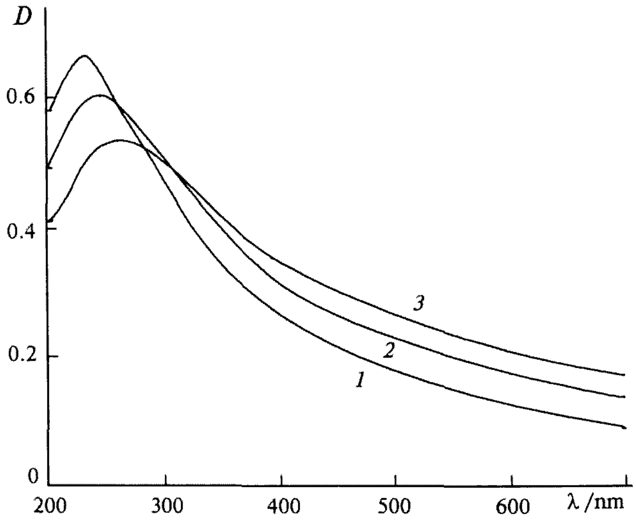

Fig. 2. Absorption spectra of a solution of colloidal palladium ($1 \cdot 10^{-4}$ mol L^{-1} of Pd atoms) saturated by hydrogen (*1*) and at 2 min (*2*) and 30 min after evacuation (*3*). Solution: $1 \cdot 10^{-4}$ mol L^{-1} of $Pd(NH_3)_4Cl_2$ and $5 \cdot 10^{-4}$ mol L^{-1} of sodium polyacrylate.

quent admission and removal of hydrogen without a substantial change in the optical properties of the metal particles. Unfortunately, it is difficult to determine the amount of hydrogen sorbed by the metal sols, because at the optimum concentration of colloids ($(1\div5)\cdot10^{-4}$ mol L^{-1} of Pd) the amount of hydrogen is significantly lower than that of hydrogen in the gas phase. Therefore, the measurements, which take into account a decrease in the gas pressure in the closed volume, are not highly accurate. It has been determined that 1 g-atom of the metal absorbs ~0.35—0.15 g-mol of hydrogen.

The data of the electron microscopic studies show that colloidal palladium particles formed upon the radiation-chemical action or reduction by hydrogen have the mean diameter of 2—4 nm and the shape close to spherical (Fig. 3). The distinguished feature is that they form large aggregates separated from one another by thin (0.2—0.5 nm) partitions. It is likely that the latter are contiguous polymeric shells of sols preventing their coagulation. Sorption and desorption of hydrogen introduce no noticeable changes to the size and spatial distribution of sols.

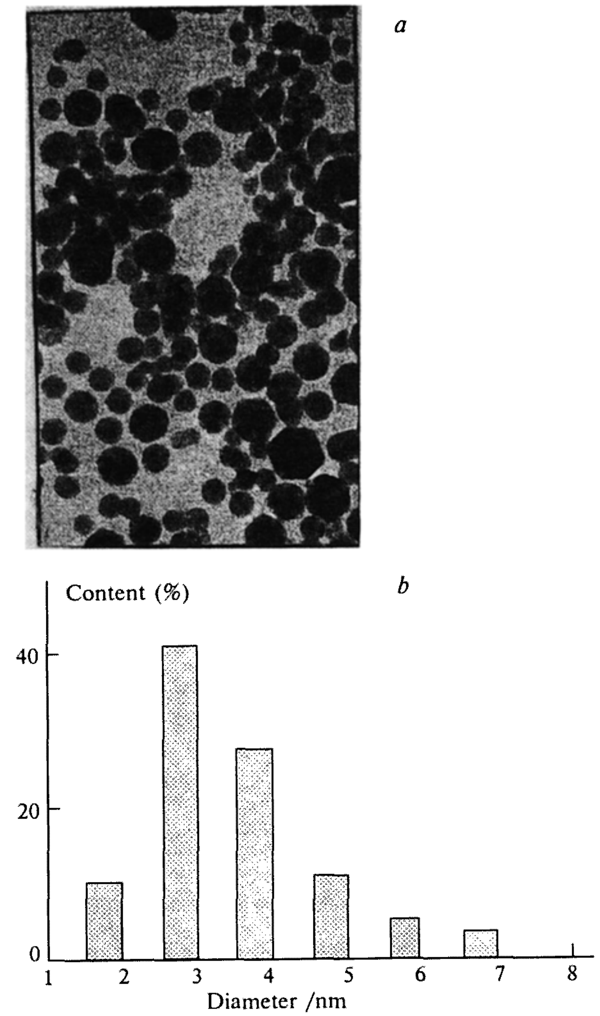

Fig. 3. Electron microscopic photograph of palladium colloids (*a*) and their size distribution (*b*). For description of the solution see Fig. 2.

The reaction of sorbed hydrogen with methylviologen, which forms the MeV^+ ion in the reaction of one-electron reduction, was also studied. It is established that the addition of methylviologen to an aqueous solution of colloidal palladium after removal of hydrogen does not result in the formation of the MeV^+ ions (Fig. 4), *i.e.*, the complete desorption of the gas from the colloidal particles is achieved upon evacuation. The consequent admission of the gas into the solution immediately results in the appearance of an absorption band at 600 nm, whose intensity increases rapidly. The rate of formation of MeV^+ is limited by the transition of hydrogen from the gas phase to the solution. It is noteworthy that the reaction $2MeV^{2+} + H_2 \rightarrow 2MeV^+ + 2H^+$ does not occur in the absence of palladium. The MeV^+ ions are oxidized to MeV^{2+} by oxygen. The optical absorption of colloidal palladium is almost unchanged in this spectral range ($\lambda >$ 320 nm), which does not overlap with the absorption inherent for MeV^{2+}. Electron microscopic studies confirm the retention of the initial colloidal particles. Thus, the latter act as a catalyst of the redox reaction of MeV^{2+} with H_2.

The "red" shift of the band of plasmon absorption of the ultrafine palladium particles observed upon the sorption of hydrogen indicates[5,6] to the partial binding of electrons by the sorbed hydrogen. One can speak about some "demetallization" of the electrons and the appear-

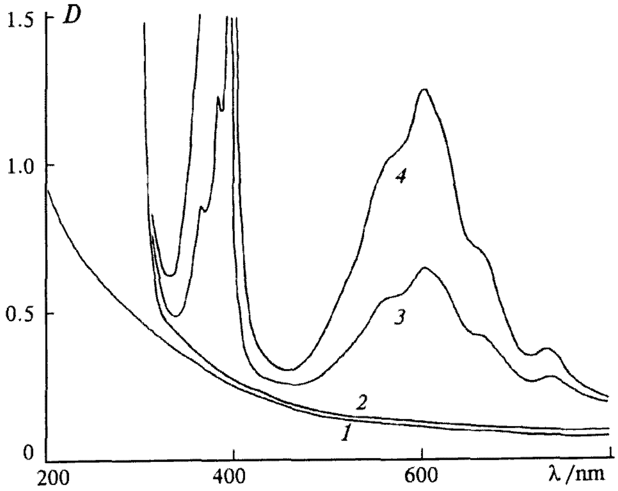

Fig. 4. Absorption spectra of an evacuated solution of colloidal palladium ($1\cdot10^{-4}$ mol L^{-1} of Pd atoms) (*1*) and after the addition of methylviologen (*2*) and at 2 min (*3*) and 15 min (*4*) after admission dihydrogen. For description of the solution see Fig. 2.

ance of the covalent bond on the surface of the metal particles, *i.e.*, about the chemisorption of hydrogen. The electronic properties of ultrafine metal particles of colloidal silver have been studied previously.[9,10] In particular, it has been shown that the accumulation of excessive electrons in a particle results in a "blue" shift, while the accumulation of positive holes or chemisorption of nucleophilic molecules results in a red shift of the plasmon absorption band.

The capability of palladium to sorb efficiently hydrogen is well known (see, *e.g.*, Ref. 16). Therefore, it could be *a priori* expected that ultrafine metal particles with a huge free surface energy would interact with hydrogen rapidly and quantitatively.

According to the common views,[16] the interaction of molecular hydrogen with palladium results in its dissociation, and hydrogen atoms occupy octahedral sites in the lattice. At normal pressures, only a portion of octahedral sites (~60 %) are accessible to H atoms, *i.e.*, 0.3 of a hydrogen molecule is sorbed per Pd atom. It is established[17] that the energy of electron emission increases as the hydrogen coverage enlarges, which testifies to the efficient electron transfer from the metal to the chemisorbed H atoms. There is a certain quantitative correspondence with the red shift of the absorption band of colloids observed upon sorption of hydrogen in this work, which testifies to a decrease in the density of free electrons in the metal. The catalytic effect of the metal on the reduction of methylviologen is caused by the activation of hydrogen upon its dissolution in the palladium sols. The amount of hydrogen sorbed by colloids and measured in our experiments (0.35—0.15 g-mol of H_2 per g-atom of Pd) most likely confirms the assumption that the gas is sorbed by the whole bulk particle to the accessible sites in its lattice. However, it is noteworthy that "surface" atoms comprise a considerable fraction of all atoms in a particle (60—30 % of atoms are present on the surface of particles 2—4 nm in diameter), and the layers adjacent to the surface also retain the high activity. Therefore, the separation of the volume and surface in the ultrafine particle, as in the case of the compact metal, to a great extent is of no sense.

The results obtained show that the optical absorption of colloidal palladium in an aqueous solution is the sensitive factor of the chemical state of the metal and, in particular, makes it possible to establish the chemical nature of sorption of hydrogen. This allows one to use absorption spectra of sols for the study of mechanism of sol-catalyzed reactions.

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