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Hydrogen in Palladium Nanoparticles: Enhancement of Catalytic Activity in the Reaction of Hexacyanoferrate(III) Ion Reduction in Aqueous Solutions

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Abstract—The catalytic activity of a palladium hydrosol has been studied in the reaction of hexacyanoferrate(III) ion reduction with hydrogen. The reaction rate has been found to increase with the degree of palladium nanoparticle saturation with hydrogen. An equation has been derived to describe the dependence of the reaction rate constant on the time of preliminary saturation of the hydrosol with hydrogen. The observed effect seems to be due to the discharge–ionization of hydrogen dissolved in the nanoparticles and an increase in their electron density, which enhance the catalytic activity of the particles.

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INTRODUCTION

Palladium is one of the most efficient metal catalysts [1, 2], and the study of palladium-based materials is of great and pressing importance. At present, the catalytic activity of this metal in the nanosized state is a subject of rapt attention. Colloidal state and increased surface area markedly affect the rate of catalytic reactions, such as hydrogenation [3, 4], oxidation [5, 6], carbon–carbon-bond formation [7, 8], and electrochemical reactions in fuel cells [9]. In addition, the ability of palladium to adsorb hydrogen has made it possible to use its nanoparticles (NPs) for hydrogen storage [10, 11].

Great attention has been focused on studying the state of hydrogen in metallic palladium and variations in its physical characteristics [12]. However works devoted to studying the effect of molecular hydrogen on the physicochemical and catalytic properties of palladium in the nanosized state are very scarcer. Developed surface must increase catalytic activity. Therefore, the study of the mechanism and main regularities of catalytic reactions involving palladium NPs is a problem of fundamental importance and interest.

The goal of this work was to study the process of palladium NP saturation with hydrogen and determine the effect of this process on palladium catalytic activity.

EXPERIMENTAL

Preparation of Palladium NPs

Palladium nanoparticles were synthesized in aqueous $[Pd(NH_3)_4]Cl_2$ solutions under the action of pulsed UV light by a procedure described previously [13]. Sodium polyacrylate was used as a stabilizer for the obtained Pd NPs. The obtained Pd hydrosol had a monomodal narrow NP size distribution and an average particle size of 2.5 ± 0.3 nm. The ζ potential of the hydrosol had a rather large absolute value (–61.3 mV), which indicated its high aggregative stability.

Hydrogenation of Pd Nanoparticles

Palladium NPs were hydrogenated as follows. The Pd hydrosol was placed into a special unit equipped with a quartz cell having a light path of 1 cm. The design of the unit implied its evacuation and the isolation of its internal space from an environment. After the evacuation, hydrogen was introduced into the unit, and, after the Pd hydrosol was saturated, it was stirred under a low excess pressure for a required time. When it was necessary to remove dissolved hydrogen, the unit with the Pd hydrosol was repeatedly evacuated.

A small change in the ζ potential relative to its initial value (before and after the hydrogenation, $\zeta = -(55.0 \pm 7.0)$ and $-(47.3 \pm 9.0)$ mV, respectively) indicated that some processes occurred on the surface of the metal NPs. However, the retention of its rater large absolute value (larger than 40 mV) suggested that these processes did not deteriorate the high stability of

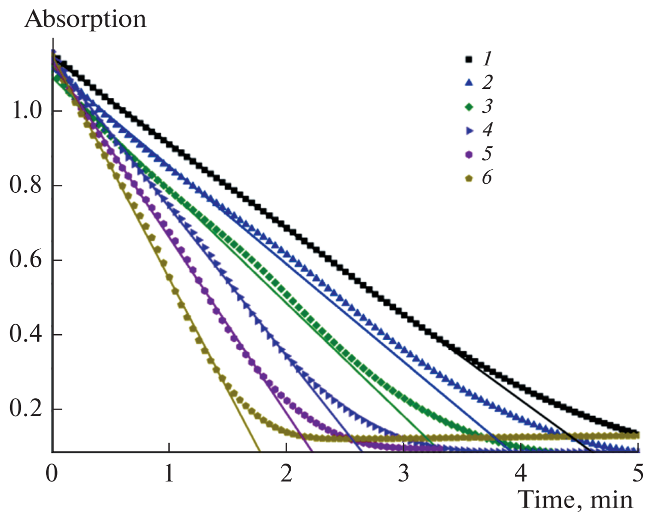

Fig. 1. Kinetic curves for the reduction of hexacyanoferrate(III) ions with hydrogen in palladium hydrosol at different times of its preliminary saturation with hydrogen: (*1*) 0, (*2*) 60, (*3*) 180, (*4*) 420, (*5*) 720, and (*6*) 2400 s. $\left[\mathrm{Fe(CN)}_6^{3-}\right]$ = 1.00 mM, $\left[\mathrm{Pd}^0_{\mathrm{coll}}\right]$ = 0.020 mM, and $[\mathrm{H_2}]$ = 0.80 mM ($p(\mathrm{H_2})$ = 1.025 atm).

the aerosol with respect to aggregation and sedimentation. According to transmission electron microscopy data, the sizes and polydispersity of palladium NPs remained unchanged after hydrogenation. This was also confirmed by dynamic light scattering. Thus, the hydrogenation of the palladium hydrosol in an aqueous solution was not accompanied by noticeable changes in the sizes of colloidal metal particles and/or their aggregation.

Reduction of Hexacyanoferrate(III) Ions with Hydrogen

Hydrogen reduction of hexacyanoferrate(III) ions was used as a model reaction of redox catalysis. The catalysis was realized in the following way. An aliquot of the hydrosol was mixed with an aqueous solution containing potassium hexacyanoferrate(III). The obtained solution was stirred on a magnetic stirrer, deaerated, and saturated with hydrogen.

Investigation Methods

Optical spectra were measured with a Cary 100 Scan spectrophotometer equipped with a thermostated compartment for the cell. The light path was l = 1 cm. All spectra were recorded at 20.0°C.

The hydrodynamic size and ζ potential of the formed colloidal particles were determined by dynamic light scattering with a Delsa Nano C instrument (Beckman Coulter, Inc.) using a laser, which operated at radiation wavelength $\lambda = 658$ nm, and the Delsa Nano software package.

The sizes and shapes of NPs were analyzed using a JEM-2100 transmission electron microscope (TEM) (JEOL). For this purpose, a colloidal solution droplet was applied onto a copper grid (300 mesh) coated with formvar and carbon, and the excess solution was then removed with filter paper.

RESULTS AND DISCUSSION

It was previously found [14] that palladium NPs catalyze hexacyanoferrate(III) reduction with hydrogen in aqueous solutions. As was noted in our previous works [13–16], the catalytic effect of palladium in hydrogen-involving reactions is explained by dissolution of molecular hydrogen in the metal and the dissociative adsorption of $\mathrm{H_2}$ on the metal surface. The "flux" of electrons of hydrogen "into the metal" substantially facilitates the reduction process, which consists in the transfer of electrons from NPs to hexacyanoferrate(III) ions.

It has been found [14] that the optical properties of a Pd hydrosol substantially alter upon its saturation with hydrogen. The absorption band of Pd NPs with a maximum at 215–220 nm is transformed into a new, wider band with a maximum at 265 nm. This change in the optical properties of Pd NPs is reversible. When hydrogen is pumped out and the hydrosol is exposed in vacuum, the initial absorption band of palladium NPs is gradually and slowly restored.

It should be noted that the process of hydrogen removal from NPs in a solution takes times markedly longer than the process of their saturation. The kinetic characteristics of the "direct" process of Pd NP hydrogenation are rather difficult to study; therefore, the relative rate constant method was employed to estimate the process rate. The method consisted in the measurement of the observed rate constants of hexacyanoferrate(III) ion reduction with hydrogen in the presence of Pd NPs saturated with $\mathrm{H_2}$ for different time periods under intense stirring (Fig. 1).

The saturation of a palladium particle with hydrogen followed by the hydrogen discharge on the particle may be represented as follows:

$$\mathrm{H}_{2\,\mathrm{ad}} + 2\mathrm{Pd}^0_{\mathrm{coll}} \xleftrightarrow{K} 2\mathrm{Pd}^0_{\mathrm{coll}}$$
$$-\,\mathrm{H} \xrightarrow{k_{\mathrm{obs}}} 2\mathrm{Pd}^0_{\mathrm{coll}} + 2\mathrm{H}^+ + 2\bar{e},$$

where K is the equilibrium constant of dissociative adsorption and k_{obs} is the observed rate constant of hexacyanoferrate(III) ion reduction.

Electron transfer to hexacyanoferrate(III) ions is a fast process. The experimentally obtained dependences have led us to state that the rate-limiting step is the dissociative adsorption of $\mathrm{H_2}$ on the NP surface. In this case, the observed reaction constant of hexacyanoferrate(III) ion reduction is proportional to the

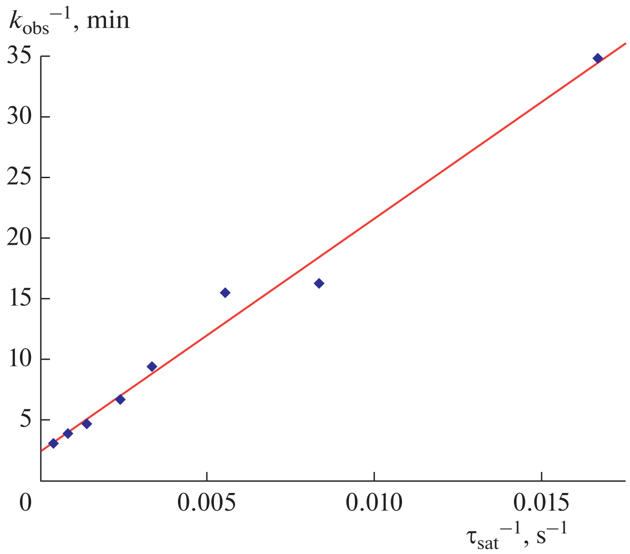

Fig. 2. Linear anamorphosis for the dependence of the rate constant of hexacyanoferrate(III) ion reduction with hydrogen in Pd hydrosol on the time of its preliminary saturation with hydrogen. $[Fe(CN)_6^{3-}]$ = 1.00 mM, $[Pd^0_{coll}]$ = 0.020 mM, and $[H_2]$ = 0.80 mM ($p(H_2)$ = 1.025 atm).

degree of NP surface coverage with hydrogen atoms θ_H (the degree of dissociative adsorption) with certain proportionality coefficient α. The degree of coverage may, in turn, be expressed on the basis of the phenomenological consideration of the adsorption–desorption equilibrium as follows:

$$\theta_H = \frac{K[H_{2\,ad}]}{1 + K[H_{2\,ad}]}.$$

Adsorbed hydrogen concentration $[H_{2\,ad}]$ on the NP surface is proportional to the time of hydrosol saturation with hydrogen (τ_{sat}). Then, the equation for the observed reaction rate constant k_{obs} and the degree of dissociative adsorption θ_H may be transformed into the following form:

$$k_{obs} = \alpha\theta_H = \alpha\frac{K[H_{2\,ad}]}{1 + K[H_{2\,ad}]} = \alpha\frac{K\beta\tau_{sat}}{1 + K\beta\tau_{sat}}.$$

To linearize this equation and calculate constant parameters α and $K\beta$, it should be represented as follows:

$$\frac{1}{k_{obs}} = \frac{\alpha}{K\beta}\frac{1}{\tau_{sat}} + \alpha. \qquad (1)$$

Equation (1) adequately describes the experimental data. Figure 2 presents the dependence of the rate constant of hexacyanoferrate(III) ion reduction with hydrogen in the Pd hydrosol on the time of its preliminary saturation with hydrogen in the rectifying coordinates. It should be noted that Eq. (1) has been derived under the assumption of Langmuir monomolecular adsorption. In reality, this process is, in this case, complicated by its polymolecular character, a nonequivalence of adsorption sites (NPs have an anisotropic surface), and hydrogen diffusion from the surface deeper inside of the Pd NPs.

To confirm that it is hydrogen dissolved in the metal that affects the catalytic properties of Pd NPs, we studied the influence of the time of the saturation with hydrogen of a solution containing hexacyanoferrate(III) ions but free of the catalyst on the reduction rate. This scenario of the experiment excluded the effect of the time of the preliminary saturation of Pd NPs with hydrogen, but showed only the influence of H_2 concentration in the solution on the process kinetics. Therewith, the reduction process itself was realized in the presence of “hydrogenated” Pd NPs. It is seen (Fig. 3) that the amount of hydrogen sufficient for the reduction of all hexacyanoferrate(III) ions is accumulated over nearly 15 s of solution saturation with it. Moreover, the kinetic parameters of the reduction process itself, i.e., the rate constant and the reaction order with respect to hydrogen, remain unchanged at all values of τ_{sat}. At τ_{sat} shorter than 15 s, the kinetic curves exhibit an inflection and the passage to the linear regime corresponding to the pseudozero order of the reaction. That is, the amount of H_2 in the solution appears to be insufficient for the reduction of all hexacyanoferrate(III) ions, and, after it is completely consumed, the process is limited by the dissolution of H_2 in the reaction mixture (Fig. 3a, linear regions of the kinetic curves at τ_{sat} = 0, 2, 5, and 10 s).

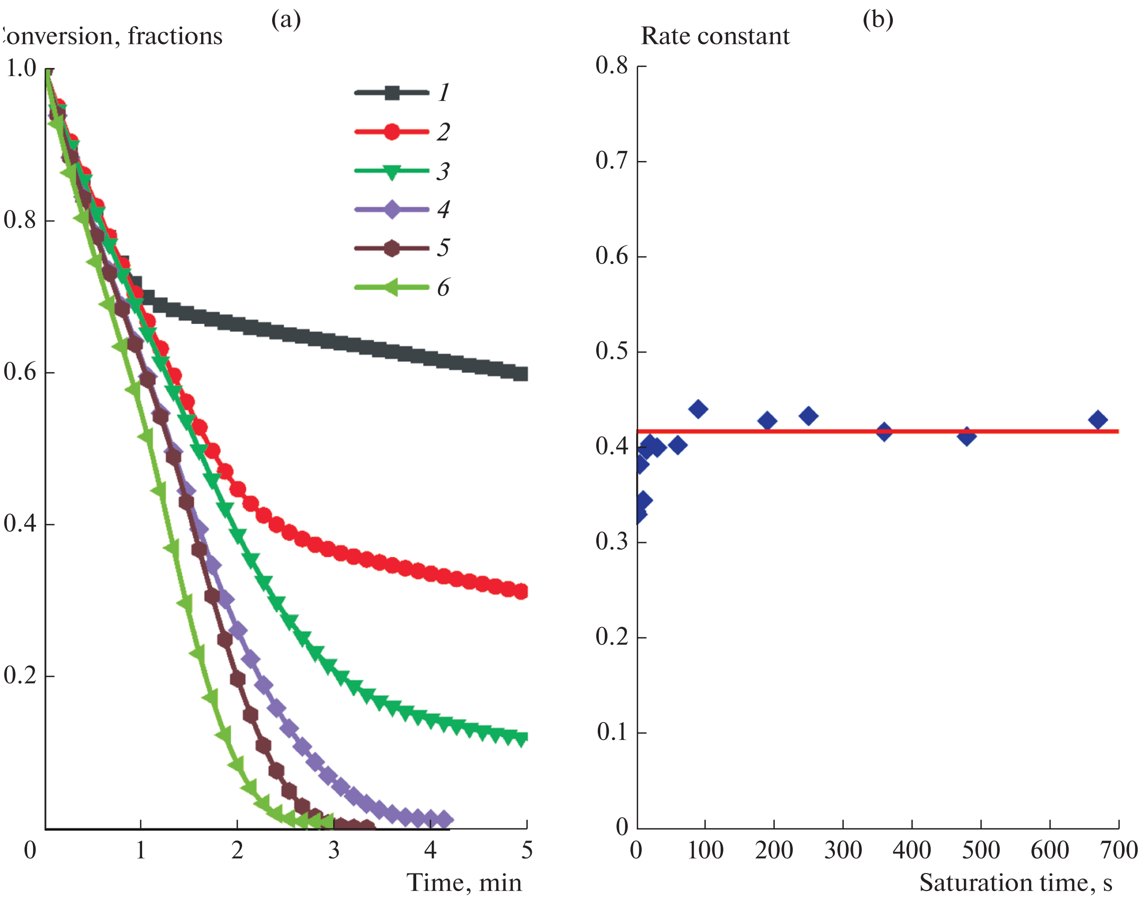

Fig. 3. Panel (a): Kinetic curves for the reduction of hexacyanoferrate(III) ions with hydrogen in the presence of Pd hydrosol at different times of saturation of potassium hexacyanoferrate(III) solution with hydrogen: (*1*) 0, (*2*) 2, (*3*) 10, (*4*) 15, (*5*) 60, and (*6*) 670 s. Panel (b): Rate constant of this process as depending on the time of solution saturation. $\left[\mathrm{Fe(CN)}_6^{3-}\right] = 1.00$ mM, $\left[\mathrm{Pd}^0_{\mathrm{coll}}\right] = 0.020$ mM, and $[\mathrm{H_2}] = 0.80$ mM ($p(\mathrm{H_2}) = 1.025$ atm).

As has been shown previously [14], hydrogen dissolved in the metal changes its catalytic and optical characteristics. Therefore, we relate the increase observed in the catalytic properties of Pd NPs with the discharge–ionization of hydrogen dissolved in the metal and the appearance of an excess electron density in the NPs. This induces the transition of catalytic Pd NPs to a new, "hydrogenated," state. The excess electron density in the metal leads to an enhancement of the catalytic properties. All these facts indicate a fundamental difference between a usual Pd hydrosol and a "hydrogenated" Pd hydrosol. Moreover, this result is in good agreement with the accepted assumption that the entire process is limited by the rate of $\mathrm{H_2}$ dissociative adsorption on the surface of palladium NPs.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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