

REDUCTION OF HEXACYANOFERRATE(III) IONS WITH HYDROGEN CATALYZED BY PALLADIUM NANOPARTICLES

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Abstract

Palladium nanoparticles (5.3 ± 1.4 nm) catalyze the reduction of hexacyanoferrate(III) ions with hydrogen in an aqueous solution. The reaction rate substantially (approximately 5.5-fold) increases if the nanoparticles are pre-saturated with hydrogen. Presumably, the reaction rate is limited by the dissociative adsorption of hydrogen on palladium particles. The difference between the electronic properties of hydrogenated and non-hydrogenated palladium particles determines their activity in dissociation of the hydrogen molecule into atoms.

Keywords: Catalytic reduction, palladium nanoparticles, hydrogen, potassium hexacyanoferrate(III)

1. INTRODUCTION

Nano-sized materials attract a lot of attention in science and technology. They represent a transient form between the atomic state and the condensed material. Therefore, nanomaterials possess a variety of unique properties. In particular, of considerable interest is the applicability of nano-sized transition metal particles in catalysis.

Palladium is one of the most promising catalysts. Palladium nanoparticles have been studied as catalysts of hydrogenation [1,2], oxidation [3-5], carbon-carbon bond formation [6-7], and electrochemical reactions in fuel cells [8]. Palladium nanoparticles of different sizes have been used to catalyze electron transfer reactions [9-12]. Furthermore, palladium nanoparticles can serve as active catalysts for the synthesis of hydrogen peroxide from H₂ and O₂ [13,14].

Palladium is known to absorb up to 850 volumes of hydrogen. The adsorbed H₂ molecules dissociate on the metal surface. It is believed that hydrogen diffuses inside metal and through metallic palladium films in the atomic state [15]. The H atoms are chemically bonded to surface palladium atoms. The interaction of the 1s-electron of hydrogen with palladium electron gas may result in atom ionization and transfer of the electron "into the metal". This mechanism is likely to be inherent in the catalytic processes that involve palladium and molecular hydrogen [16].

Previously, it was shown that saturation of a palladium hydrosol (2 - 3 nm nanoparticles) with hydrogen substantially changes its optical properties. The absorption band of nano-sized metal particles with a peak at 220 nm is converted to a new, broader band with a peak at 265 nm [9]. This change in the optical properties of palladium hydrosol is reversible. When hydrogen is pumped out and the solution is kept under vacuum, the initial absorption band of palladium nanoparticles is gradually restored. Similar results have been reported later in another study [17]. Thus, on saturation of the palladium hydrosol with hydrogen, metal nanoparticles (PdNP) are transformed into hydrogenated palladium nanoparticles (Pd-H₂NP). The considerable difference between the electronic absorption spectra undoubtedly indicates that electronic states of these nano-sized palladium forms are different. Presumably, catalytic characteristics of PdNP and Pd-H₂NP would also noticeably differ. This was confirmed by experiments.

2. EXPERIMENTAL

Preparation of Pd nanoparticles (PdNP)

Palladium nanoparticles PdNP were synthesized by exposure of aqueous solutions of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ to pulsed UV light by following the previously reported procedure [18]. Sodium polyacrylate (PANA) was used as a stabilizer. All solutions were prepared with distilled water, which was additionally deionized.

Preparation of Pd-H₂ nanoparticles (Pd-H₂NP)

Hydrogenated palladium nanoparticles Pd-H₂NP were performed as follows. A PdNP hydrosol was placed into a special cell equipped with a quartz cuvette with a light path of 10.0 mm. The cell design allowed to carry out deaeration of it and to isolate of its internal volume from the environment. Then hydrogen was injected into the cell and saturation of the PdNP hydrosol was followed by stirring the hydrosol under a slight excess pressure for 24 h. After the optical spectrum was measured, hydrogen was removed from the colloidal solution by vacuum pumping.

Catalysis

As a model system for redox catalysis, we used the reduction of hexacyanoferrate(III) ions with hydrogen.

The catalysis was carried out as follows. An aliquot of desire hydrosol was mixed with aqueous solution of hexacyanoferrate(III) ions. The resulting solution was stirred using a magnetic stirrer; then, it was deaerated and saturated with hydrogen.

3. RESULTS AND DISCUSSION

The obtained hydrosol PdNP had a narrow unimodal distribution of spherical nanoparticles with an average size of 5.3 ± 1.4 nm (**Figure 1a**). The ξ -potential was rather high in magnitude (-61.3 mV), which attests to high aggregative stability of the hydrosol. Indeed, the PdNP hydrosol retains stability for a month, and when stored at reduced temperature (5 - 10 °C), for up to six months.

The end of formation of Pd-H₂NP was detected by completion of the transformation of the optical band with a peak at 220 nm into the band with a peak at 265 nm. The Pd-H₂NP hydrosol thus formed also possessed a high aggregative stability (the ξ -potential was about -55.0 mV). The data of TEM and DRS confirm the stability of Pd-H₂NP on air for a long time.

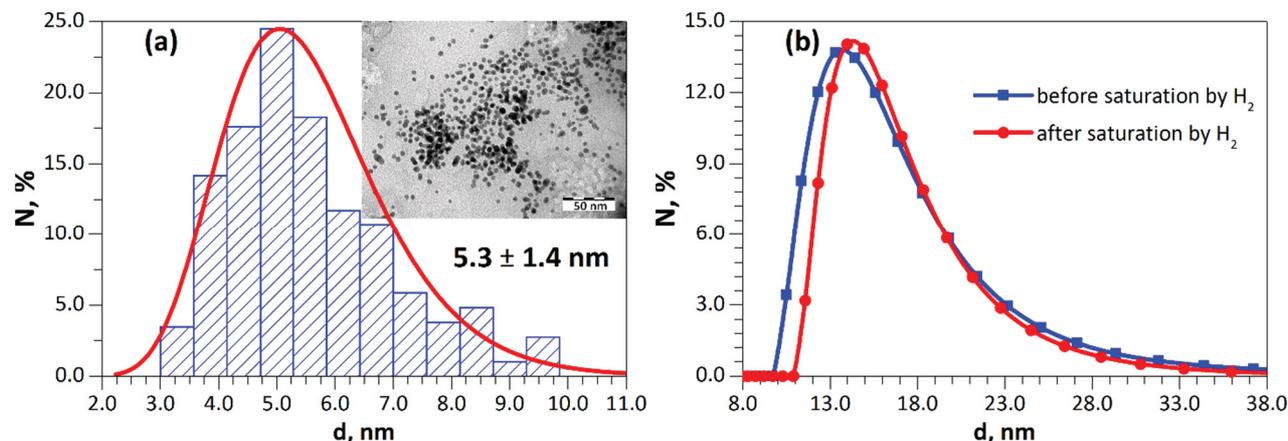


Figure 1 (a) TEM images of PdNP and size distribution. (b) Size distribution of palladium nanoparticles before (PdNP) and after saturation with H₂ (Pd-H₂NP) in aqueous solutions measured by DLS method

The palladium nanoparticle size and distribution after hydrogenation remained the same, according to TEM data. This was also confirmed by DLS used in liquid medium. The average hydrodynamic size and distribution

of palladium colloids proved to be virtually the same for PdNP and Pd-H₂NP hydrosols (**Figure 1b**). That is, palladium hydrogenation in an aqueous solution is not accompanied by any noticeable change in the size of colloidal metal particles. The PdNP and Pd-H₂NP hydrodynamic size (13.8 ± 3.9 nm) is markedly higher than the palladium nanoparticle size determined by TEM (*cf.* **Figures 1a** and **1b**), because the DLS method, unlike TEM, measures the size of the micelle comprising the metal core and the protective solvation shell.

Previously, colloidal gold-catalyzed reduction of hexacyanoferrate(III) ions with borohydride ions in alkaline aqueous solutions has been studied [19].

The ratio of the standard redox potentials of reactants implies that the reaction should proceed spontaneously ($E^0(\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}) = +0.36$ V [20]). However, in the absence of a catalyst, no reduction of $\text{Fe}(\text{CN})_6^{3-}$ with hydrogen in an aqueous solution takes place. The presence of PdNP and Pd-H₂NP aliquots in the solution initiates the process. The reduction was carried out with permanent stirring of the solution. The reaction kinetics was investigated by monitoring the disappearance of the $\text{Fe}(\text{CN})_6^{3-}$ absorption band at 420 nm ($\epsilon_{420} = 1.0 \times 10^3 \text{ M}^{-1} \cdot \text{cm}^{-1}$) [21]. This is exemplified in **Figure 2**, which shows the kinetic curves in the presence of PdNP and Pd-H₂NP with equal palladium concentration (2.0×10^{-5} M Pd⁰). It can be seen that the reaction is much faster with hydrogenated palladium.

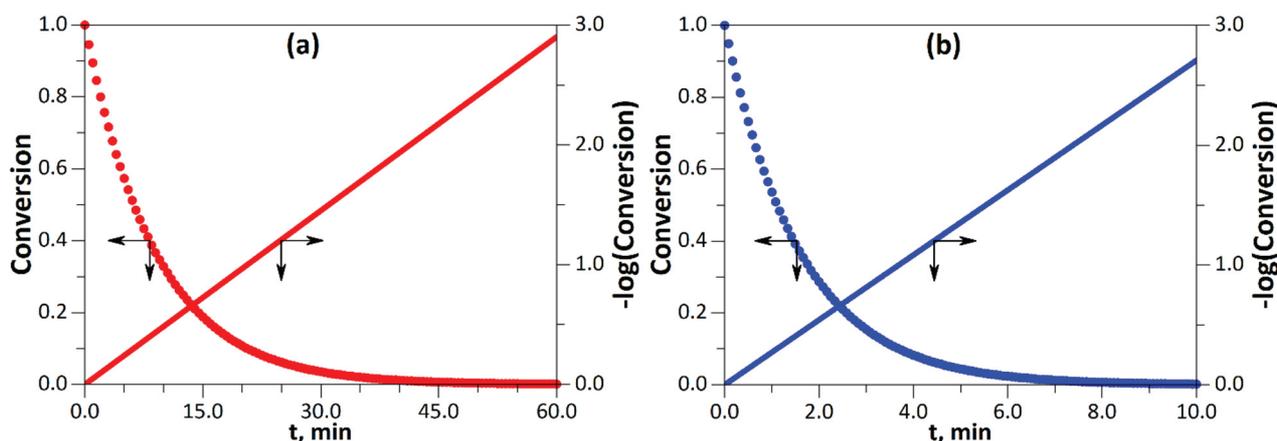


Figure 2 Kinetic curves for the reduction of hexacyanoferrate(III) ions with hydrogen in the presence of palladium nanoparticles: **(a)** - PdNP and **(b)** - Pd-H₂NP.

Solution: $[\text{Pd}^0] = 2.0 \times 10^{-5}$ M; $C_0(\text{Fe}(\text{CN})_6^{3-}) = 1.0 \times 10^{-3}$ M; $p(\text{H}_2) = 1.0$ atm

It was found that during the catalytic reaction, the hydrosols retained stability and no nanoparticle aggregation took place. The nanoparticle size and distribution checked by TEM and DLS-method did not change noticeably. Note also that 24 h after the reaction conducted in air, a weak light-blue color appeared in solutions. Apparently, this was due to partial dissolution of palladium and formation of the Pd²⁺ ferrocyanide complex. However, in PdNP and Pd-H₂NP hydrosols in the presence of hydrogen, no palladium corrosion was observed even on long-term storage (24 h). The kinetics of $\text{Fe}(\text{CN})_6^{3-}$ reduction in the presence of PdNP and Pd-H₂NP is described by first-order equations (**Figure 2**). Kinetic experiments were repeated at least 3 times. They were reproduced with an error of $\pm 5\%$. The rate constants for the palladium content of 2.0×10^{-5} M are $1.11 \times 10^{-1} \text{ s}^{-1}$ and $6.24 \times 10^{-1} \text{ s}^{-1}$ for PdNP and Pd-H₂NP, respectively. That is, the rate of one-electron reduction of the hexacyanoferrate(III) ions with hydrogen is ~ 6 times lower with the PdNP catalyst than with the Pd-H₂NP catalyst. Results of our experiments confirm the fact that the catalytic activity of PdNP and Pd-H₂NP is not changed for a long time (2 - 3 days).

The rate of this reaction is proportional to the concentration of nanoparticles in solution, i.e., to the catalyst surface area. The concentration of hydrogen accumulated in Pd-H₂NP itself is too low to affect the process by itself. For the Pd⁰ concentration used (2.0×10^{-5} M) and the known ratio $\text{H}_2/\text{Pd}^0 \approx 0.35 \div 0.65$ [9], the content of the dissolved H₂ in the Pd-H₂NP hydrosol is only about 1×10^{-5} M. This is incomparably less than the electron

equivalent needed to reduce 1.0×10^{-3} M of $\text{Fe}(\text{CN})_6^{3-}$. The processes of hydrogen saturation of palladium nanoparticles and, conversely, hydrogen withdrawal from hydrogenated palladium by evacuation of the solution are rather slow and may last for tens of minutes. This implies that the $\text{Fe}(\text{CN})_6^{3-}$ reduction with hydrogen over a short period of time from several to ten minutes involves, most likely, palladium nanoparticles in the initial chemical form: PdNP or Pd-H₂NP.

The dissociative adsorption of H₂ molecules on palladium nanoparticles is apparently the rate-limiting step of the reduction under these conditions. The dissociative adsorption and the related electron transfer, is also the rate-limiting step in the Au(III) reduction with hydrogen on gold nanoparticles in aqueous solution²². The catalytic activity of the "hydrogenated" palladium proves to be substantially higher than that of "non-hydrogenated" palladium. Hydrogen accumulated in palladium results in a considerable rearrangement of the electron subsystem of the nanoparticles [9, 17]. As follows from experiments, it activates the atomization of hydrogen. It has been previously [23, 24] found that platinum nanoparticles in aqueous solution prepared by various methods also differ noticeably in catalytic activity.

4. CONCLUSION

Thus, our results demonstrate that palladium nanoparticles efficiently catalyze the reduction of the hexacyanoferrate(III) ions by hydrogen. The hydrogenated palladium particles possess a considerably (approximately 6-fold) higher catalytic activity. Palladium hydrosols are convenient systems for investigating reactions involving hydrogen. Palladium is highly promising for catalysis and, therefore, our results can be useful for understanding of the mechanism of hydrogenation of organic compounds. Studies of the effect of composition of aqueous solutions (concentrations of reactants: Pd⁰, $\text{Fe}(\text{CN})_6^{3-}$, H₂ and pH value), temperature, and palladium nanoparticle size and structure on the kinetics and mechanism of the catalytic reduction of the hexacyanoferrate(III) ion with hydrogen are currently underway and will be reported elsewhere.

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