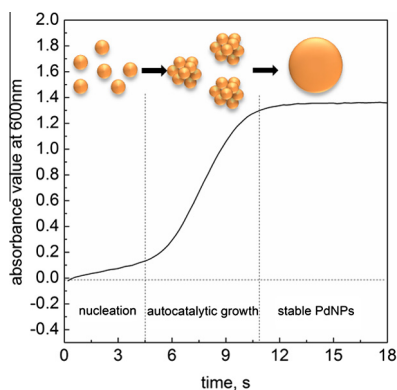


Kinetic studies of nucleation and growth of palladium nanoparticles

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GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, the kinetic studies of nucleation and growth processes of palladium nanoparticles formation are presented. As a palladium precursor the chloride complex of Pd(II) and as a reductant L-ascorbic acid, were used. Kinetic studies were conducted under different experimental conditions such as initial concentration of metal ions, ascorbic acid, chloride ions as well as at different temperature and ionic strength. Using Finke–Watzky model kinetic rate constants were established and discussed. The value of activation enthalpy and entropy have also been determined using Eyring–Polanyi equation. For all obtained colloids, plasmons and values of hydrodynamic radius were registered.

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1. Introduction

Similarly to the other noble metals like gold and platinum, palladium nanoparticles have unique chemical and physical properties, which are different from those of the bulk material. Due to these properties, they are used in catalysis [1–6], in sensors [7–10], hydrogen storage [11–18]. Especially, in catalysis they are

most popular due to their low price in comparison to more noble metals. There are a lot of methods for palladium nanoparticles synthesis such as chemical [19,20], physical [21,22] and biochemical [23,24], which allow for PdNPs synthesis with varied shape and size. Among them, chemical reduction of metal ions is one of the most used due to easiness and simple equipment requirements. In this paper we used chemical reduction method for palladium nanoparticles synthesis using “green” reductant (L-ascorbic acid). The main goal of this study was the kinetics of palladium nanoparticles formation as a key factor for their morphology prediction.

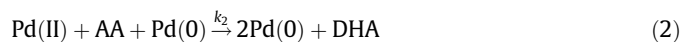
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Besides, there is lack of information about kinetic constants in the literature, which can be useful in the process design. For example obtained data can be used for proper catalysts synthesis, e.g. synthesis of palladium nanoparticles with defined size and shape deposited in microreactor on active carbon fiber. Such continuous palladium nanoparticle synthesis and metal deposition on catalytic carrier requires knowledge about reactions kinetics. Obtained data can be useful for calculation e.g. residence time of reagents in microreactor and thus may help with proper prediction of final product in microsystem. This idea was developed by Luty-Blocho et al. for platinum nanoparticles deposition on active carbon fibers [25].

The process of nanoparticles formation usually includes a few stages, which depend on reaction mechanism. For example, for gold(III) complex ions it includes usually three stages: reduction of Au(III) to Au(I), Au(I) to Au(0) and autocatalytic growth of Au nanoparticles [19,26–28]. However, in the literature, there are also known four and two stage mechanisms [29].

In our study, we use Pd(II) chloride complex ions as palladium precursor, thus we expect, two steps related to reduction of Pd(II) to Pd(0) (nucleation) and autocatalytic growth of palladium nanoparticles:



where AA – ascorbic acid; DHA – dehydroascorbic acid; k_1 – rate constant of cluster nucleation process; k_2 – rate constant of growth.

Such mechanism was first described by Finke and Watzky [30] and then implemented by others [27,28]. Two stage process of nanoparticles synthesis responsible for slow nucleation and fast autocatalytic growth is described very well with sigmoidal kinetic curve, obtained during reactions progress. For such a mechanism represented by Eqs. (1) and (2), analytic solution of differential equation describing the change of Pd(II) ions concentration with time has the following form:

$$A_{\text{Pd(II)},t} = \frac{\frac{k_1}{k_2} + A_{\text{Pd(II)},0}}{1 + \frac{k_1}{k_2 A_{\text{Pd(II)},0}} e^{(k_1 + k_2 A_{\text{Pd(II)},0}) \cdot t}} \quad (3)$$

where $A_{\text{Pd(II)},t}$ and $A_{\text{Pd(II)},0}$ denote palladium absorbance (proportional to ions concentration in accordance with Lambert–Beer Law) changing with time (t) and initial absorbance of palladium (II) ions, respectively. Rate constants k_1 and k_2 are related to observed rate constants $k_{1,\text{obs}}$ and $k_{2,\text{obs}}$. More details about how sigmoidal curve representing of appearance product was recalculated to disappearance of the substrate in a way analogical to Finke and Watzky model. These details includes [Supplementary Materials](#). In our study, we used the Finke and Watzky model in order to determine the rate constants of nucleation and growth of palladium nanoparticles.

2. Experimental

2.1. Chemicals

2.1.1. Palladium precursor

The stock solution of palladium precursor about 0.1127 M was prepared in accordance with our previous study [19]. Then, appreciable volume of this base solution was diluted in deionized water in order to reach expected concentration. Chloride ions amount in the solution was adjusted with NaCl addition (p.a., POCH). Ionic strength was kept with NaClO₄ (p.a., Koch-Light Laboratories Ltd).

2.1.2. L-ascorbic acid

The aqueous solution of L-ascorbic Acid (Sigma–Aldrich, Germany) was prepared via dissolution of proper amount of reductant in deionized water.

2.2. Methods

The kinetic curves with fivefold iteration were registered by *Spectrophotometer Stopped-flow* (Applied Photophysics, UK). The level of turbidity of obtained solution containing palladium nanoparticles was collected by UV–Vis spectrophotometer (Shimadzu, Japan). Both spectrophotometers are working in the wavelength range 190–900 nm. In order to measure the size and size distribution of obtained palladium particles, Nanozetalyzer Nano-ZS (Malvern, UK), was used.

3. Results and discussion

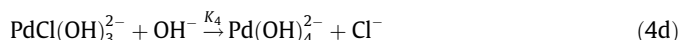
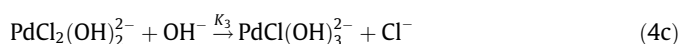
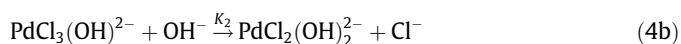
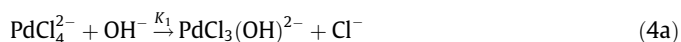
3.1. Experimental conditions

Kinetics of nucleation and growth of palladium nanoparticles was investigated under different conditions of precursor, reductant and chloride ions initial concentration, and also at different temperature and ionic strength (see [Table 1](#)).

3.2. The property of reagents (speciation diagrams)

3.2.1. Palladium(II) chloride complex ions

Palladium(II) chloride complex ions depending on the pH solution and chloride ions concentration, have a different forms. These forms result from complex hydrolysis. The relation between proper hydrolyzed forms of Pd(II) ions are defined by following equilibrium Eqs. (4a)–(4d):



where K_{1-4} denote equilibrium constants for reactions (4a)–(4d), described as follows:

$$K_1 = \frac{[\text{PdCl}_3(\text{OH})^{2-}][\text{Cl}^-]}{[\text{PdCl}_4^{2-}][\text{OH}^-]} = \frac{[\text{PdCl}_3(\text{OH})^{2-}][\text{Cl}^-]}{[\text{PdCl}_4^{2-}] \cdot 10^{\text{pH}-14}}; \quad K_2 = \frac{[\text{PdCl}_2(\text{OH})_2^{2-}][\text{Cl}^-]}{[\text{PdCl}_3(\text{OH})^{2-}] \cdot 10^{\text{pH}-14}}$$

$$K_3 = \frac{[\text{PdCl}(\text{OH})_3^{2-}][\text{Cl}^-]}{[\text{PdCl}_2(\text{OH})_2^{2-}] \cdot 10^{\text{pH}-14}}; \quad K_4 = \frac{[\text{Pd}(\text{OH})_4^{2-}][\text{Cl}^-]}{[\text{PdCl}(\text{OH})_3^{2-}] \cdot 10^{\text{pH}-14}}$$

Values of equilibrium constants are given in our previous paper [19]. From these Eqs. (4a)–(4d) one can conclude that with decreasing pH of the solutions, the hydrolysis process is reversed, and palladium(II) chloride complex ions are more stable, e.g. for pH below 2, in the solution is c.a. 100% of PdCl_4^{2-} (see, [Fig. 1](#)). The chloride ions present in the solution also play an important role in hydrolysis (see equations describing equilibrium constants K_{1-4}) and it can be assumed, that with the increasing amount of Cl^- ions in the solution, the stability of Pd(II) chloride complex is also increasing (the equilibrium is moved to the left). In order to demonstrate these changes, two stability diagrams were calculated and shown in [Fig. 1](#).

Presented diagrams confirm that with increasing initial amount of chloride ions (e.g. ten times), the contribution of individual forms change (see also [Supplementary Materials, Fig. 2S](#)). At fixed

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