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ORIGINAL CONTRIBUTION

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Nucleation and growth of palladium nanoparticles stabilized by polymers and layer silicates

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Abstract Palladium nanoparticles were synthesized in aqueous medium via reduction by hydrazine using various polymers (polyvinylpyrrolidone and polystyrene sulfonate) and the clay mineral hectorite as stabilizers. The kinetics of homogeneous and heterogeneous nucleation processes was studied by UV-visible spectrophotometry. The effect of the polymer and concentration of the silicate and palladium ions on particle formation rate was investigated. The size of the nanoparticles were determined by transmission electron microscopy. Both polymers and the silicate lamellae were found to be capable of stabilizing the particles. The rate of reduction is decreased by increasing amounts of stabilizing agents and increased by increasing concentrations of precursor ions. The kinetics of heterogeneous nucleation was determined by the adsorption of the palladium species at the clay mineral particles and the viscosity of the hectorite dispersion.

Keywords Palladium nanoparticles · Stabilization by polymer and silicate layers · UV-VIS spectroscopy · TEM

Introduction

Due to the practical significance of precious metal nanoparticles, research on their synthesis and properties has lately gained central importance. The first reproducible procedure was developed by Turkevitch and Kim [1] who prepared 20-nm Au particles by citrate reduction of $[AuCl_4]^-$. At the end of the 1990s, Watzky and Finke [2] proposed a new mechanism for particle formation, i.e., slow, continuous nucleation followed by rapid autocatalytic surface growth, resulting in a nearly monodisperse size distribution. As experimentally proved, a stronger reducing agent brings about the formation of smaller nuclei, which then continue to grow [3]. Growth is interpreted in two different ways: (1) the nuclei formed in the first step then aggregate and (2) their growth is due to collisions with freshly reduced metal atoms. Tauschtreml et al. [4] followed the stepwise growth of silver clusters by spectroscopy. His results demonstrate growth along an autocatalytic reaction pathway, which includes the adsorp-

tion of metal ions followed by their reduction on the surface of the zero-valent metal cluster. It is generally accepted in literature that the final size is determined by the relative rates of nucleation and growth. This is the basis of the presently known most efficient method for the synthesis of nanoparticles, the so-called controlled colloid synthesis, which allows arbitrary control over particle size through varying the ratio of nucleation and growth rates. In the course of particle preparation, an important role played by steric stabilizers that protect the nascent nanoparticles from aggregation, so that very small particles (in the range of a few nanometers) are obtained.

Hoogsteen and Fokkink [5] synthesized polymer-stabilized Pd hydrosols using hypophosphorous acid (H_3PO_2) as reducing agent. The presence of poly(vinyl alcohol) (PVA), a polymer weakly adsorbing to the surface of palladium did not affect the kinetics of particle formation and the particle size could not be controlled. However, polyvinylpyrrolidone (PVP), a polymer strongly bound to the metal surface, influenced the kinetics of particle formation and particle size: Its presence resulted in the formation of smaller particles. Poly(2-vinylpyrrolidone) affects the process of sol formation not only by its high affinity to the metal surface but, owing to its cationic nature, also via complex formation with the precursor salt, $PdCl_4^{2-}$. The authors also established that particle size decreases with increasing concentrations of stabilizer and reducing agent. A similar observation was made later by Ayyappan et al. [6] on other metal sols. Esumi et al. [7] prepared Pd organosols stabilized by PVP by alcohol reduction from various precursor molecules. The size distribution of particles obtained by reduction of palladium acetate was found to be nearly monodisperse, whereas slow reduction of palladium acetylacetonate resulted in a relatively wide range of particle sizes. Hydrazine can reduce all forms of transition metal ions.

Bronstein et al. [8] prepared palladium hydrosols stabilized by a poly(ethylene oxide)-polyethyleneimine diblock copolymer via reduction of $PdCl_4^{2-}$. Seregina et al. [9] synthesized Au, Pd, Pt, and Rh nanoparticles using block copolymers. When comparing the effects of several reducing agents, these authors observed that hydrazine hydrate reduced the precursor ions at a much slower rate than did $NaBH_4$ and phenylhydrazine complexed them but did not reduce metal ions. Wang et al. [10] prepared Pd particles in water/cetyltrimethylammonium bromide and *n*-butanol/isooctane microemulsions. Chen et al. [11] synthesized Pd particles by hydrazine reduction of Pd $(NH_3)Cl_2$ in inverse micellar solution of sodium bis(2-ethylhexyl)sulfosuccinate (AOT)/isooctane. Ingelsten et al. [12] produced platinum nanoparticles in w/o microemulsion by borohydride reduction of H_2PtCl_6. The organic phase was *n*-heptane; alcohol etoxylates and AOT were used as stabilizers. The effect of surfactant type on reaction kinetics was studied.

The need for solid-supported metal catalysts has greatly increased in the recent years. Owing to its simplicity, the preferred method for the preparation of these catalysts is the impregnation technique. However, because impregnation does not allow control over particle size, several novel procedures were developed. Wang et al. [13, 14] adsorbed Pd, Pt, and Rh particles stabilized by PVP and PVA on the surface of silica. Layer silicates, which readily swell in aqueous media and have large internal surfaces, are eminently suitable to serve as supports for the preparation of particles with diameters of a few nanometers not only on their surface but—under appropriate conditions—also in their interlamellar space [15–17]. The metal nuclei are formed in situ on the surface of the support and are stabilized there.

Király et al. [18] grew 2–14 nm Pd particles in an ethanol–toluene binary mixture in situ on organophilized montmorillonite (Hierarchical Direct Access Method). The particles were reduced in the interface enriched in ethanol. Papp et al. [15, 17] prepared Pd and Rh nanoparticles in polymer/clay mineral nanocomposites in aqueous media.

There is ample reading material available on the preparation of nanoparticles, but few publications discuss the kinetics of formation of metal nanoparticles [2–12]. In this study, particle formation on solid surface is investigated by UV-visible (UV-VIS) spectroscopy. Here, we compared heterogeneous and homogeneous formation of palladium particles. Our objective was to study the effect of metal ion concentrations and polymer on the rates of nucleation and particle growth by following the formation of aqueous, polymer-stabilized sols by spectrophotometry. We also studied the effect of hectorite concentration in the case of heterogeneous nucleation.

Materials

The metal precursor $PdCl_2$ (purity 99%) was obtained from Aldrich. Poly(*N*-vinyl-2-pyrrolidone) (K-30, average molecular weight $4{\cdot}10^4$, Fluka) and poly(sodium 4-styrenesulfonate) (PSSNa, average molecular weight $7{\cdot}10^4$, Aldrich) were used to stabilize the Pd nanoparticles. The reducting agent hydrazine hydrate was a 24–26wt% aqueous solution (Fluka).

A synthetic clay mineral (hectorite) (Süd Chemie, optigel SH) was used as a support (ρ=2.5±0.2 g/cm^3, a^S=350± 50 m^2/g, approximate composition $Li_{0,67}[Mg_{5,33}Si_8O_{20}]$.

Methods

The formation of Pd nanoparticles was followed by the Ocean Optics Chem2000-UV-VIS spectrophotometer at wavelengths λ=200–800 nm. The first stage of sol formation was monitored by filling the solution except the reducing agent in a 1-cm cuvette (4.0 ml total volume,

Table 1 Composition of polymer stabilized Pd sols, kinetic parameters, and particle diameter

Stabilizer and concentration (% w/v)		C^0_{Pd2+} (mmol/dm^3)	Polymer/ Pd ratio	k* (s^{-1})	$\tau_{1/2}$ (s)	S[a]	d (nm)
–	–	0.075	–	0.098	7.07	7.7	7.3
PVP	0.5	0.075	4.67×10^4	0.0065	106.64	1.46	3.8
PSSNa	0.5	0.075	2.52×10^4	0.0028	247.55	2.57	2.1

[a] $S=-d \lg A/d \lg \lambda$ where A is the absorbance of sols at λ nm

3.9 ml polymer solution, 50 μl $PdCl_2$ solution; and 50 μl hydrazine hydrate solution). The absorbance spectrum was recorded every 1–2 s within 5 min starting at the moment of the addition of the reducing agent (50 μl of 12.5 mM hydrazine). During the reduction, the reaction mixture was stirred with a micromagnetic stirrer. The rate of reaction was calculated from the increasing absorbance of Pd nanoparticles.

Polymer solutions of adequate concentrations were used as reference. The effect of polymers on the kinetics of particle formation was studied. The concentration of the $PdCl_2$ solution (50 μl) was 3 mmol/dm^3 and the polymer concentration was 0.5% (w/w).

In the studies on heterogeneous nucleation, stabilization was attained by the addition of a synthetic hectorite (Optigel SH), which forms optically transparent dispersion. Because the aqueous dispersion of Optigel SH is highly alkaline (pH=10–11), the optigel was treated with 1 M hydrochloric acid for 24 h, washed with distilled water to pH=7.5, centrifuged, dried at room temperature, and ground. The solid support obtained was swollen in water before use. The volumes added were identical with those indicated for homogeneous nucleation. The concentrations of the dispersion were varied between 0.01 and 0.5% (w/v) and of the precursor ions between 0.019 and 0.075 mmol/dm^3 (Tables 1 and 2).

$PdCl_2$ solution was added to the hectorite suspension instead of the polymer solution, followed by the reducing agent then hydrazine hydrate solution under constant stirring. In part of the experiments, hectorite concentration was varied in the range of 0.5–0.001% (w/v), while Pd^{2+} ion concentration was kept constant ($c^0_{Pd2+} = 0.075 \mathrm{mmol/dm^3}$).

The adsorption experiment was performed in 1% (w/v) dispersion; adsorption time was 24 h. The amount of palladium ions adsorbed on hectorite was determined on the basis of the UV-VIS absorption spectra of the supernatant.

Transmission electron micrographs (TEM) from the samples were made in Philips CM-10 transmission electron microscope with an accelerating voltage of 100 kV. The microscope was equipped with a Megaview II digital camera. The size distribution of the particles was determined by using the UTHSCSA Image Tool 2.00 software.

Results and discussion

It is known from Elding's work that Pd^{2+} ions occur in the form of coordination complexes of various compositions depending on pH and Cl^- ion concentration: $[PdCl_n(H_2O)_{4-n}]^{2-n}$ where n=0, 1, 2, 3, and 4 [19]. The spectrum of the aqueous palladium chloride solution (pH=3.6) used in kinetic measurements displays a peak at 212 nm and a shoulder at 237 nm (Fig. 1). These suggest the presence of two different chloro complexes: According to data in the literature, they are characteristic of the $[PdCl_3(H_2O)]^-$ and $[PdCl_2(H_2O)_2]$ complexes. After the addition of polymer solution, pH of palladium chloride solutions increased to 3.8–4.0. In our experiments, the spectrum of the palladium chloride solutions, i.e., the composition of chloro complexes, remained unchanged between pH=3.6 and 4.0. PVP and PSSNa solutions have significant absorbance in the UV range; therefore, the corresponding initial spectra do not contain bands at wavelengths below 220 and 235 nm.

Formation of palladium particles by homogeneous nucleation in polymer solutions

Figure 1 shows temporal changes in the spectrum of palladium ions reduced in the absence of stabilizers. Reduction is instantaneous and the spectrum subsequently remains nearly unchanged. The baseline of the spectrum

Table 2 Composition of Pd° nanoparticles stabilized by hectorite, kinetic parameters, and particle diameter

Stabilizer and concentration (% w/v)		C^0_{Pd2+}(mmol/dm^3)	Pd content (wt%)	Pd content (mmol/g)	k* (s^{-1})	$\tau_{1/2}$ (s)	S	d (nm)
hectorite	0.5	0.075	0.16	0.015	0.0013	533.19	2.80	2.0
	0.1	0.075	0.79	0.075	0.0059	117.48	2.54	2.2
	0.02	0.075	3.84	0.375	0.0102	67.95	2.00	2.8
	0.02	0.056	2.89	0.280	0.0075	92.42	2.57	2.1
	0.02	0.038	1.98	0.190	0.0048	144.41	2.23	2.5
	0.02	0.019	1.00	0.095	0.0028	247.55	1.84	3.0
	0.001	0.075	44.39	7.500	0.022	31.51	1.61	3.4

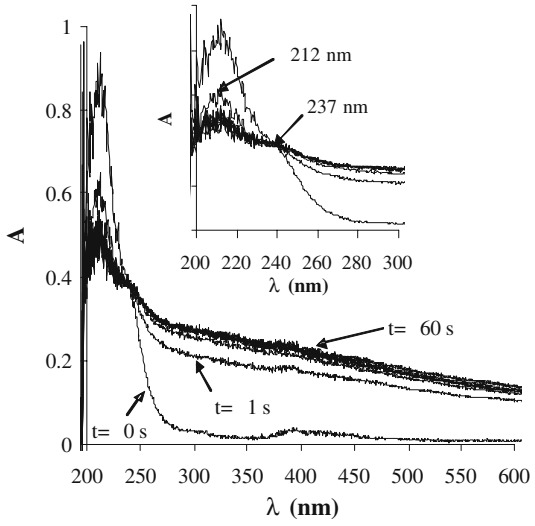

Fig. 1 Reduction of $PdCl_2$ solution (without any stabilizer) followed up by UV-VIS spectroscopy

rises significantly, indicating the formation of larger palladium particles and aggregates.

Because there is no characteristic absorption peak associated with the presence of palladium nanoparticles, their formation can be monitored by following either the decrease in precursor ion concentration or, at higher wavelengths, the rise of the baseline. The rise of the baseline is indicative of the increase in the number and size of the particles formed [20]. In the present case, it was more accurate to follow the latter method because of the noise at the maximum. Particle growth was therefore characterized by the temporal increase in absorbance at λ=600 nm.

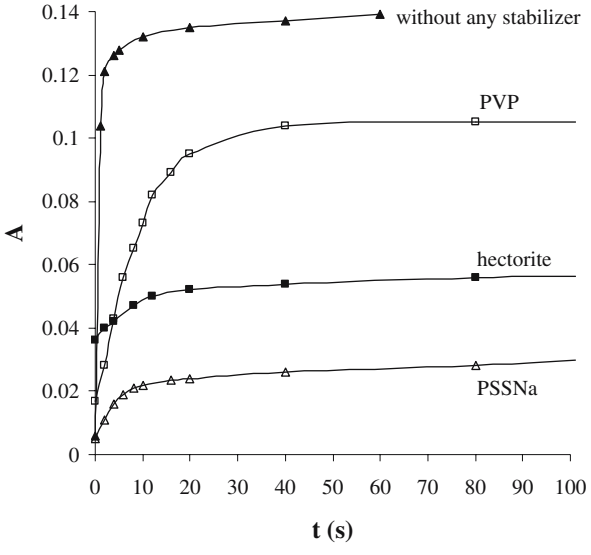

Fig. 2 Absorbance (λ=600 nm) vs time curves of Pd nanoparticles stabilized by hectorite and polymers [$c_{stabilizer}$=0.5% (w/v) and c_{Pd2+}=0.038 mmol/dm^3]

The kinetic curves of this system do not allow differentiation of nucleation and nucleus growth. The rate of the entire process was characterized by the slope of the initial section of the absorbance vs time curve, termed as apparent rate constant (k*). The apparent rate constant of particle formation for reduction in the absence of stabilizers is k*=0.098 s^{-1}.

Our experience showed that the slope of straight lines obtained by linearization of UV-VIS absorption spectra decreases with increasing particle size. According to data on Pt sols reported by Furlong et al. [20], the absolute values of slopes (S) corresponding to particles with diameters of d=4, 3, 2, and 1.4 nm are 1.4, 1.8, 2.8, and 3.6, respectively (diameters were determined by TEM). After fitting a power function to the data reported, we determined the possible sizes of the particles formed in the systems with various compositions using the equation d (nm)=5.574·S$^{1.017}$. The absorbance values of the spectra were normalized to λ=450 nm, lg I was plotted against lg A and the slope of the straight line obtained was inserted into the above equation (Tables 1 and 2). Sixty seconds after reduction, the size of particles generated without stabilizers was 7.3 nm. TEM showed 6–20 nm aggregates consisting of individual particles with d_{ave}=2.1 nm.

When PVP was used as stabilizer [0.5% (w/v) PVP] at an initial Pd^{2+} concentration of 0.075 mmol/dm^3, the spectrum shown in Fig. 3 was obtained. Absorbance was read at λ=600 nm on the descending branch and plotted against time (Fig. 2).

As evinced by Fig. 2, the initial rate was considerably lower than that for the reduction in the absence of the stabilizers. After 40 s, the baseline did not rise any more (A=0.104) and remained below the value measured without stabilizer (A=0.137). The average particle diameter calcu-

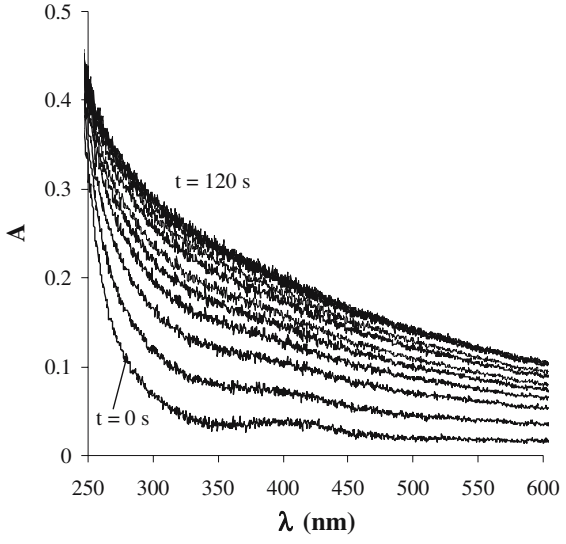

Fig. 3 UV-VIS spectra of the sols stabilized by PVP during formation of nanoparticles

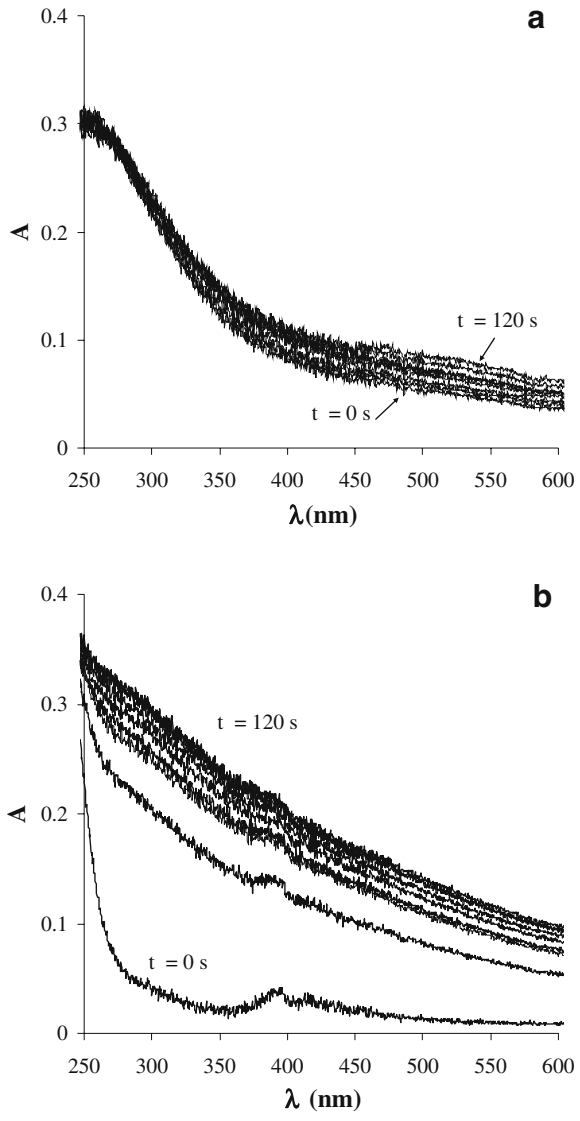

Fig. 4 UV-VIS spectra of Pd° nanoparticles formation on hectorite **a** $c_{hektorit}$=0.5% (w/v), c_{Pd2+}=0.075 mmol/dm^3 and **b** $c_{hektorit}$= 0.001% (w/v), c_{Pd2+}=0.075 mmol/dm^3

lated from the spectrum is 3.8 nm. It can be assumed that the PVP molecules are able to bind strongly to the metal surface and thereby to influence particle size and the kinetics of particle formation (Fig. 3). By nearly immediately encasing the rapidly forming particles, PVP prevents their growth by collision.

The effect of the negatively charged PSS^- molecules on the kinetics of particle formation was also assessed. The initial spectrum was similar to that obtained with PVP, but reduction was much slower. The value of the apparent rate constant was considerably lower (k^*=0.0065→0.0028 s^{-1}). The rise of the baseline was less pronounced, i.e., fewer and smaller particles were formed. The yellowish hue of the sol also indicated that there remained unreduced Pd^{2+} in the system.

Palladium particle formation by heterogeneous nucleation in the presence of hectorite

When a $PdCl_2$ solution was added to the hectorite dispersion, the pH was 5.8. The spectrum recorded (Fig. 4) resembled that of the hydrolyzed salt solution.

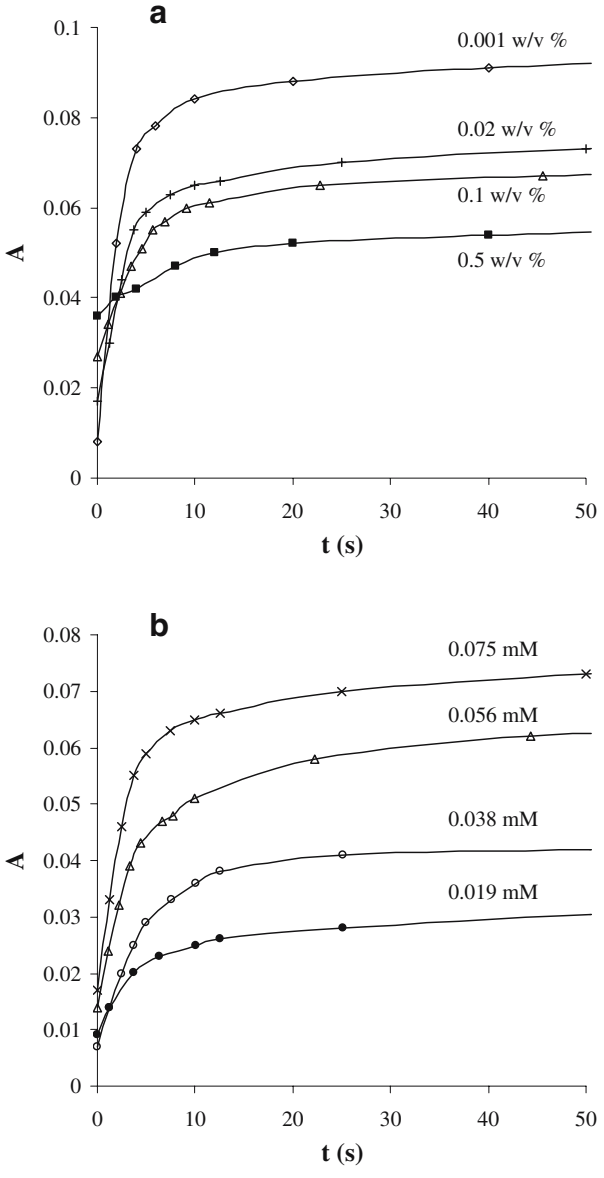

Fig. 5 Absorbance (λ=600 nm) vs time curves of Pd nanoparticles stabilized by **a** hectorite at constant Pd^{2+} ion and varying hectorite concentration and **b** at constant hectorite and varying Pd^{2+} ion concentration

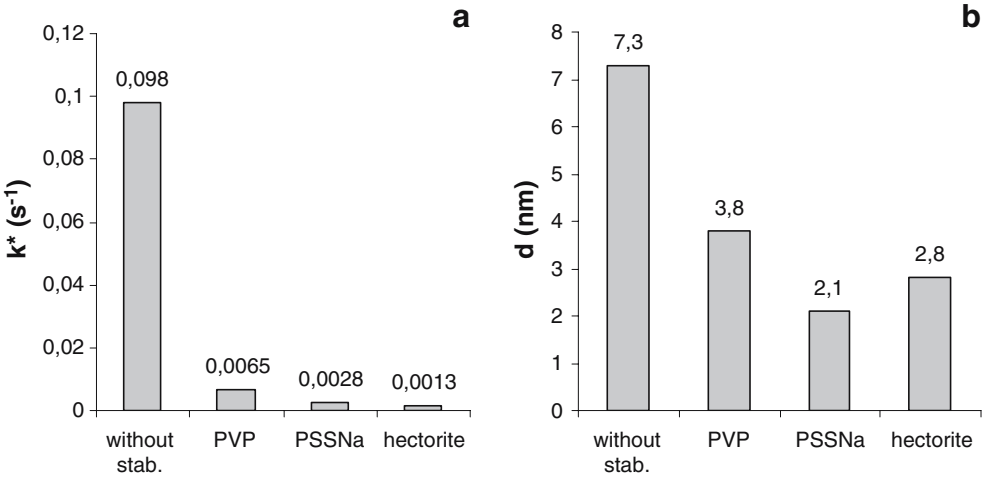

Fig. 6 **a** Apparent rate constants and **b** particle diameters obtained with different stabilizers

The spectra recorded in the course of measurements on the most highly concentrated dispersion [0.5% (w/v)] are presented in Fig. 4a. During reduction, the initial spectrum did not change considerably, apart form a slight upward shift. Absorbances were determined at λ=600 nm and plotted against time (Fig. 5).

Figure 6a is a summary of the rate constants determined in the presence of the stabilizers. Hectorite decelerated the reduction more effectively than did the polymers. Structure building by the clay mineral lamellae probably hinders the flow of reducing agent by an increase in viscosity. To prove this assumption, the relative viscosity (i.e., relative to water) of the hectorite dispersion was determined at several concentrations in an Ostwald capillary viscometer. Increasing the concentration of the dispersion clearly increased the viscosity. It is therefore possible that the presence of hectorite lamellae inhibits the reduction by hindering the diffusion. Naturally, in addition to the increase in viscosity, the fact that the bulk of the Pd^{2+} species are adsorbed on the clay, mineral surface also contributes to the delaying effect. The adsorption of Pd^{2+} ions on hectorite was examined in a separate experiment. The data clearly show that in the concentration range tested, all added ions were bound to the support, which means that nucleation takes place on the surface.

When the reaction was studied at a lower hectorite content [0.001% (w/v)], the spectrum was modified as shown in Fig. 4b. The reaction rate increased with decreasing hectorite concentration. The apparent rate constants determined are listed in Table 2 and absorbance vs time functions are shown in Fig. 5. Due to the 500-fold dilution, the apparent rate constant (k*) is significantly increased (0.0013→0.022 s^{-1}). The spectrum was highly similar to that recorded in water (Fig. 1), but the rise of the baseline and the initial slope of the A vs t curve were much less pronounced. This means that the stabilizing effect of silicate lamellae prevails even at this low hectorite concentration. Figure 7b reveals that when hectorite concentration is reduced, larger particles are formed. This is not surprising considering the significant change in palladium concentration per unit mass of hectorite (Table 2).

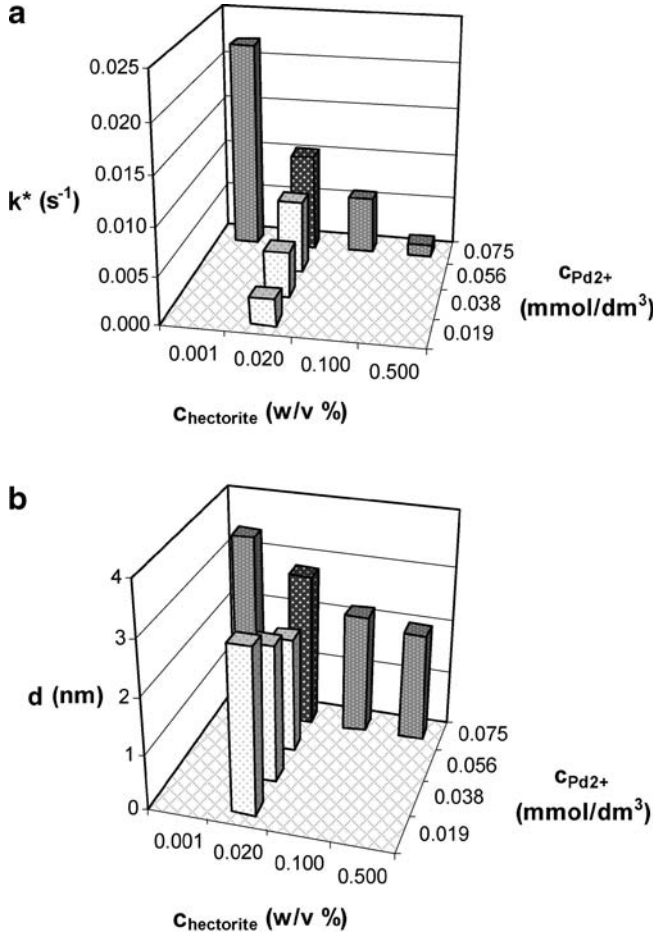

Fig. 7 **a** Apparent rate constants and **b** particle diameters at different precursor and hectorite concentrations

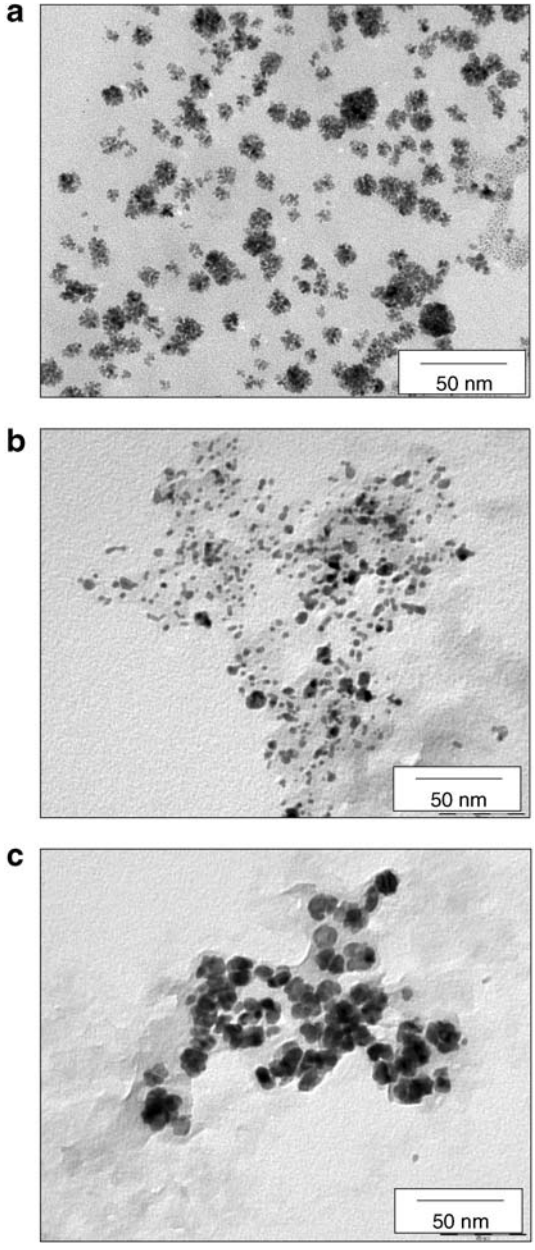

Fig. 8 TEM pictures of Pd° nanoparticles prepared **a** without any stabilizer and **b**, **c** on hectorite lamellae [**a**: $d_{ave.}$=2.1 nm, **b**: $d_{ave.}$=2.8 nm, and **c**: $d_{ave.}$=6.2 nm, $c_{hektorit}$=0.001% (w/v), c_{Pd2+}=0.075 mmol/dm^3]

The rate-limiting role of precursor ions was studied at a constant hectorite concentration [0.02% (w/v)] (Fig. 5b). The concentration of the $PdCl_2$ solution was varied between 0.019 mmol/dm^3 and 0.075 mmol/dm^3. The initial slope of A vs t curves gradually decreased with decreasing concentration, as quantified by a significant increase in half-time (67.95→247.5 s^{-1}) (Table 2 and Fig. 7a). The particle size (Fig. 7b) first decreased and then increased, which may indicate aggregation of primary particles. Thus, there exists an optimal concentration range within which the rate of nucleation is maximal and which lead to a minimum of the particle size. At higher concentrations, the particle diameter increases due to supply of material, whereas a decrease in concentration may decelerate the process to an extent already favoring particle growth.

We attempted to determine the size of the palladium particles generated in our experiments by TEM. Electron micrographs were taken at 180,000-fold magnification (Fig. 8a–c). Evaluable electron micrographs were obtained for two samples. The TEM image of palladium particles prepared in absence of a stabilizer are presented in the Fig. 8a. The TEM shows small, nearly monodisperse, aggredated particles. Figure 8b,c shows a sample, which was prepared at the lowest hectorite concentration. Palladium particles formed on the surface of hectorite lamellae with polydisperse size distribution are partially aggregated; the sample was not homogeneous. At higher dispersion concentrations and in the case of polymer stabilization, the shielding effect of hectorite or macromolecules interfered with the photography.

Summary

The kinetics of the formation of palladium particles in the presence of two different types of stabilizers was investigated. PVP and PSSNa stabilized the nascent metal particles. PSSNa was more effective in decreasing the rate of reduction. Heterogeneous nucleation was studied in the presence of hectorite. Higher concentrations of hectorite decreased the reaction rate significantly, probably due to the increase in viscosity and to the adsorption of the palladium ions.

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