

Ph.D. thesis

**Formation and stabilization of palladium and
rhodium nanocrystallites in polymer solution
and in layered silicates**

Szilvia Papp

Supervisor:

Dr. Imre Dékány

*Nanostructured Materials Research Group
of the Hungarian Academy of Sciences
University of Szeged
Szeged*

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1. Introduction and Objectives

Nanostructured materials are close to the lower limit of the colloid particle size range. These are particles or particle aggregates measuring 1-100 nm, smaller than the wavelength of light - they fall in between molecular dimensions and microscopically visualizable systems. Inorganic colloids and especially metal nanoparticles have been in the focus of interest for a long time. This interest has mainly been due to their aesthetic (ceramic pigments) and technological (catalysts, hydrogen storage) utilization. By virtue of their high activity and selectivity, they have become widely known as catalysts of a novel type. Their valuable characteristics due to their small size, such as their unique electron structure and extremely large specific surface area, however, open the way to yet further possibilities for practical utilization. At the present time nanoparticles are utilized by several academic disciplines, such as polymer chemistry, photochemistry, environmental chemistry, nanoelectronics and optics.

From among the well-known metal colloids, I chose palladium and rhodium as the objects of my studies. Chemical processes catalyzed by these metals have lately become indispensable tools in the hands of organic chemists. I prepared palladium and rhodium particles using routine procedures as well as colloid chemical methods I had developed myself and studied the possibilities of particle size control allowed by the individual procedures.

Polymer-stabilized particles with a diameter of a few nanometers were grown in aqueous medium. The effect of the concentration, the molecular mass and the charge state of the polymer on particle size was studied. The interaction developing between precursor ions and stabilizing polymer molecules has an important role in size control, especially in the case of ionic polymers, because electrolytic interactions affect the rate of the reduction of metal ions and thereby particle size. One of the objectives of the present work was to determine the effect of the stabilizers used on the rate of palladium particle formation. Nucleation and nucleus growth are usually difficult to differentiate. Depending on the method of stabilization, however, the rate of nucleation can be controlled within the appropriately chosen concentration range.

Nanoparticle/support composites were prepared by growing the particles via heterogeneous nucleation on the surface of layered montmorillonite or *in situ* in the interlamellar space. The objective was to control particle size on organophilized montmorillonites with predetermined free interlamellar volumes, by varying the density of interlamellar alkyl chain density. In view of the potent stabilizing effect of polymers, an attempt was made to employ the concerted stabilizing effect of the polymer/clay mineral complex in nanoparticle preparation. Besides montmorillonite, kaolinite, a clay mineral non-swelling in aqueous media was also successfully utilized as support for palladium and rhodium nanoparticles. The effect of the generated nanoparticles on the ordered lamellar structure of clay minerals was studied by X-ray diffraction and small angle X-ray scattering. Parallel with *in situ* synthesis on the surface of montmorillonite, the adsorption of the same polymers on Na-montmorillonite was also investigated. In addition to polymer adsorption, a new method for the investigation of the adsorption of metal nanoparticles on montmorillonite is also presented.

A relationship was sought for between the diverse preparation methods and the oxidation state of the metal particles formed. Finally, the catalytic efficiency of palladium

and rhodium particles immobilized on clay minerals was estimated by a simple hydrogenation test. I wish to emphasize already in the Introduction of my dissertation that the main objective of my work was the preparation of these nanodisperse systems and composites and the investigation of their colloid chemical properties, their stability and the growth of nanocrystalline metals on solid supports. The considerable volume of experimental material compiled did not allow a detailed analysis of the catalytic properties of the nanocrystalline metals obtained using the methods I developed, therefore I can only demonstrate their behavior in a few test reactions. The characterization of their catalytic properties would make further experiments necessary.

2. Experimental materials and methods

In the course of my experiments the precursor palladium compound was palladium acetate in tetrahydrofuran and palladium(II) chloride in aqueous media; the rhodium precursor was rhodium(III) chloride hydrate in all cases. Salts were reduced by ethanol, hydrazine hydrate ($\text{NH}_2\text{NH}_2(\text{H}_2\text{O})$) or sodium borohydride (NaBH_4). Particles were stabilized by poly(N-vinyl-2-pyrrolidone) (PVP), poly(diallyldimethylammonium chloride) (PDDACl) or poly(sodium-4-styrenesulfonate) (PSSNa). The supports used were Na-montmorillonite and kaolinite. Montmorillonite was organophilized by hexadecylpyridinium chloride (HDPCl) or tetradodecylammonium bromide (TDABr). Kaolinite lamellae were delaminated by the intercalation of dimethyl sulfoxide (DMSO).

UV-VIS studies on palladium and rhodium sols were done in a Uvicon 930 double-beam spectrophotometer. The amount of palladium particles adsorbed on Na-montmorillonite was also determined by the same technique, i.e. based on the adsorption spectra of the supernatants. The kinetics of palladium particle formation was studied in an Ocean Optics Chem 2000 UV-VIS fibre-optic diode-array spectrophotometer in the wavelength range of 200-260 nm.

Size analysis of metal nanoparticles was carried out in a Philips CM-10 transmission electron microscope at an acceleration voltage of 100 kV. Electron micrographs were recorded by a Megaview-II digital camera attached to the instrument. Average particle diameters and size distribution functions were determined using the UTHSCSA Image Tool software.

The effect of stabilizing agents and the incorporation of nanoparticles on the ordered lamellar structure of clay minerals was investigated by X-ray diffraction and small angle X-ray scattering. Changes in basal spacing (001) were studied in the angle range of $1^\circ \leq 2\theta \leq 10^\circ$ in montmorillonite and $1^\circ \leq 2\theta \leq 14^\circ$ in kaolinite. The (111) reflection of crystalline palladium particles was recorded in the angle range of $38^\circ \leq 2\theta \leq 42^\circ$. XRD measurements were carried out in a Philips X-ray diffractometer (PW 1830 generator, PW 1820 goniometer, PW 1711 detector, 40 kV, 35 mA, CuK radiation) and SAXS measurements with a compact Kratky camera, type KCEC/3, built on a PW 1830 generator.

Thermal analysis of composites was done in a Q-1500 D MOM instrument in the range of 25-1000 °C.

Parallel with *in situ* synthesis on the surface of montmorillonite, adsorption of the same polymers on Na-montmorillonite was also studied. Adsorbed amounts were calculated from the total carbon contents of the supernatants of the samples, determined in a Euroglas 1200 instrument.

The surface oxidation state of the particles sitting on the support was determined by XPS measurements in a KRATOS XSAM 800 instrument. The excitation source was AlK radiation. The measurement was controlled and the data were evaluated by VISION 1,3,3, software of KRATOS Ltd.

The activities of a few palladium- and rhodium-containing catalyst samples were tested in liquid-phase hydrogenation of cyclohexene.

3. Theses

1. Kinetic analysis of palladium particle formation

1.1. The kinetics of palladium particle formation was studied in the presence of various stabilizing agents. The role of three polymers, namely PVP, PDDACl and PSSNa was investigated in homogeneous nucleation experiments. All three polymers are capable of stabilizing the metal particles formed. Cationic PDDACl forms a coordination complex with the precursor Pd²⁺ ions, whereas in the case of the neutral PVP and the anionic PSSNa only physical interactions are involved in the stabilizing effect. The rate of reduction is decreased the most by PSSNa, followed by PDDACl and by PVP. Increasing PDDACl concentration was shown to reduce the reaction rate and to cause an increase in particle size. The decrease in reaction rate may be attributed to the increase in the viscosity of the polymer solution, which is accompanied by a drastic decrease in the diffusion constant. Increasing the concentration of Pd²⁺ ions enhanced the rate of nucleation, therefore smaller particles were formed.

1.2. Heterogeneous nucleation was studied on the surface of synthetic layer silicates. The presence of the solid support was shown to significantly decrease the rate of particle formation. Structure building by the lamellae hinders, via the increase in viscosity, the flow of the reducing agent and the formation of particles in the dispersion medium. The fact that the Pd²⁺ species are mostly adsorbed on the surface greatly contributes to the deceleration effect. There is an optimal range of Pd²⁺ concentration range in heterogeneous nucleation, where the rate of nucleation is maximal and the achievable size is minimal. At higher concentrations particles continue to grow due to the availability of precursor; a decrease in concentration, on the other hand, may decelerate the process to an extent favoring particle growth again.

2. The effect of the magnitude of nanoreactor volume on palladium particle formation on organophilized montmorillonite

Pd⁰ nanoparticles were prepared in the interlamellar volume of montmorillonite modified with hexadecylpyridinium chloride and tetradodecylammonium bromide. It was shown that both hydrophobic montmorillonites swell readily in tetrahydrofuran/ethanol mixtures and the internal surfaces (interlamellar space) can be used as nanoreactors for the synthesis of Pd particles. In HDP-montmorillonite a larger interlamellar space is available.

A new peak appears in the smaller angle range of X-ray diffraction pattern ($d_L = 4.24$ nm) of HDP-montmorillonite, in the course of formation of Pd⁰ nanoparticles. This indicates that particles were also formed in the interlamellar space and a considerable fraction of these were retained between the lamellae of the support even after desiccation. Since the surface density of the alkyl chains in TDA-montmorillonites is 4 times higher and, consequently, the free volume is smaller, Pd⁰ nanocrystals migrate from among the internal

surfaces onto the external surface. In this case hydrophobic montmorillonite mainly acts as a template to promote the size-controlled synthesis of Pd⁰ particles and its role as support is secondary. This method allows size control of palladium particles in the range of 2.4-4.1 nm. When palladium content is increased at the lower alkyl chain density, larger particles may be obtained.

3. Synthesis and stabilization of palladium nanoparticles in polymer solutions and polymer/montmorillonite composites: the role of macromolecules in the surface fixation of nanoparticles

3.1. Aqueous solutions of polymers (PVP, PDDACl) and Na-montmorillonite were used for the stabilization of Pd⁰ nanoparticles. Interlamellar incorporation of nanoparticles into the clay mineral was proved by X-ray diffraction. TEM measurements show that, depending on the method of stabilization and the concentration of precursor Pd²⁺ ions, average particle size can be controlled within the range of 1.1-6.8 nm. The smallest particles were obtained by polymer stabilization in aqueous medium. The size of particles generated on the surface of montmorillonite by heterogeneous nucleation increased with increasing metal concentration. When polymer is added to this system, particle size can be decreased by increasing polymer concentration. In this case the particles are stabilized by the concerted action of the support and the macromolecule.

3.2. Adsorption of the polymer-stabilized palladium particles on the surface of the montmorillonite support was investigated. It was found that at low polymer concentrations the polymer-protected palladium sol particles not only adhere to the external surfaces but are also capable of incorporation between the lamellae of the clay mineral. As polymer concentration is increased, the number of incorporable particles decreases. At high polymer/particle ratios polymer adsorption hinders particle adsorption. At low polymer/particle ratios attraction due to the surface-particle interaction prevails and, as a consequence, more Pd particles are adsorbed on the surface.

4. Synthesis and stabilization of palladium nanoparticles on kaolinite

Highly crystalline kaolinite may also serve as an excellent support for metal nanoparticles, if the tightly interlinked layers are first delaminated. Metal particles were prepared on the surface of untreated, polymer-treated (PVP, PDDACl) and surfactant-treated (octylamine) kaolinite. Interlamellar presence of particles was demonstrated by the appearance of a peak in the smaller angle range ($dL = 4.13-6.87$ nm). As verified by TEM, each method enabled the preparation of nanometer-size Pd particles. Electron micrographs usually display completely amorphous particles, with crystalline palladium found only in the samples controlled by kaolinite lamellae. Average particle size increased with increasing precursor ion concentration. Both octylamine and non-ionic as well as cationic polymers and octylamine proved to be suitable for the reduction and control of particle size. The use of sodium borohydride, a more potent reducing agent than hydrazine hydrate, increased the rate of nucleation, resulting in the formation of a higher number of smaller particles.

5. Preparation and stabilization of rhodium nanoparticles in polymer solutions and on layer silicates

5.1. The effect of the charge state, the molecular mass and the concentration of polymers (PVP, PDDACl and PSSNa) on the size of the particles formed was studied. In

sols stabilized by PDDACl, increasing the molecular mass resulted in smaller particle size, since due to steric reasons, the primary particles cannot aggregate. Increasing PVP concentration did not significantly increase particle size. Nearly identical particle sizes were obtained in sols stabilized with PVP and PDDACl. The largest particles were obtained in sols stabilized by PSSNa: the particles assemble to form bulky strings. The negatively charged polymer chains cannot get strongly bound to the surface of the metal particles, which leads to more extensive aggregation. When rhodium ion concentration is increased at low polymer concentrations, primary particles link up to form secondary particles, resulting in the increase of average particle size.

5.2. Rhodium/montmorillonite and rhodium/kaolinite composites were prepared in aqueous medium. The particles formed were stabilized by polymers and by the lamellae of clay minerals. The interlamellar incorporation of nanoparticles was proved by X-ray diffraction. The polymers promoted intercalation of rhodium nanoparticles into the clay mineral. In the absence of nanoparticles, the intercalation of polymers was significantly less extensive. These studies revealed that, depending on the method of stabilization and the concentration of precursor Rh^{3+} ions, average particle size is 1-3 nm on montmorillonite and 1-2 nm on kaolinite, because the interlamellar adhesion force in kaolinite is higher. The extremely small particles size is not decreased further by the polymer added. The resulting particle size can be explained by polymer/support interactions. When the reaction medium contains layered silicates and a readily adsorbable polymer (PVP, PDDACl), average particle size will exceed that obtained by homogeneous nucleation. In the absence of polymers, the majority of the particles grew on the external surfaces, leaving the original basal spacing of the support unchanged. Comparison of the syntheses of palladium and rhodium particles shows that, under identical conditions, RhCl_3 gives rise to smaller particles than does PdCl_2 .

6. Structural studies on metal nanoparticles / layer silicate composites by small angle X-ray scattering

In order to obtain more detailed information on the nanostructure of the composites prepared, some characteristic samples were also studied by small-angle X-ray scattering. The incorporation of metal particles of high electron density considerably increased the scattering intensity of the samples, their specific surface areas increased several-fold and the surface of the support became coarsened. When the number of metal particles is higher, the increase is more extensive.

When present at identical percentage (w/w) concentrations, rhodium particles increased the value of S_p to a much higher extent than did palladium particles. This observation is in agreement with average particle sizes determined by electron microscopy, which shows that the distribution of rhodium is more disperse on the surface of both supports. The structural transformation brought about by disaggregation results in the decrease of correlation length.

7. Studies on the valence state of palladium and rhodium particles

The surface oxidation state of the particles sitting on the support in the metal-containing catalysts was determined by XPS. The surface of the particles was found to be partially oxidized in each catalyst studied. Palladium is accompanied by PdO_2 and rhodium by Rh_2O_3 . These results suggest that either only part of the metal ions added to the support

was reduced in the course of synthesis, or all were reduced but were later partially reoxidized on the surface by oxygen in the air. The possibility of the presence of species with higher oxidation states being a result of a metal-support interaction taking place on the surface cannot be excluded either.

The amount of oxidized palladium on the surface ($\text{Pd}^0/\text{Pd}^{4+}=2.3$) did not change with particle size. This observation allows to conclude that the geometry of the particles is not spherical: they rise above the plane defined by the support to a distance much smaller than the particle diameter obtained by TEM. In the presence of PDDACl relatively more PdO_2 was formed on the surface, whereas surface oxidation was inhibited by octylamine. In the case of rhodium particles the proportion of oxidized metal was higher, which is probably due to the extremely small particle size. No difference was observed between different reducing agents and supports.

8. *The activity of supported metal catalysts*

The catalytic activity of the samples was tested in the liquid phase hydrogenation of cyclohexene. The TOF values obtained are close to those published in the literature for similar Pd-montmorillonites. In our experience, in the case of smaller particles the same efficiency can be achieved with less palladium. In polymer-containing samples efficiency was found to decrease in spite of the smaller particle size, especially in the case of PDDACl. Kaolinite as support has a negative effect on the catalytic activity of rhodium. In contrast, palladium proved to be more active on the surface of kaolinite.

4. Publications in connection with the Ph.D. thesis

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