

Palladium Nanocatalysts Protected by Polyacids

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ABSTRACT: Several colloidal palladium nanocatalysts prepared by the *in situ* reduction of palladium chloride PdCl₂, ammonium tetrachloropalladate (NH₄)₂PdCl₄, and palladium acetate Pd(CH₃COO)₂ were protected by various water-soluble polymers, with special emphasis on polyacids. The particle sizes, morphologies, and size distributions of the palladium nanoparticles were determined by transmission electron microscopy (TEM), and their catalytic activities were qualitatively tested by the hydrogenation of cyclohexene. The type of the polymer (for example, polyacid versus a nonionic, water-soluble polymer) can influence the nanoparticle sizes and morphologies, as well as colloidal stabilities. For the catalytic activities of these metal-polymer systems, the choice of the protective polymer can be equally important. Lower catalytic activities have been mostly found if polyacids were used as protective matrices for these palladium nanocatalysts. It was found to be important to consider several influences, such as the particle size and morphology, as well as the interaction between the polymer and the catalyst nanoparticle. Thus, the selection of the protective polymer is crucial for the development of tailored metal-polymer catalyst systems. Additional influences may stem from the presence of ions, for example, those from the metal precursor, or the counterions of the polymer side groups. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1209–1219, 1998

Key words: palladium catalysts; protective polymers; polyacids; hydrogenation; cyclohexene

INTRODUCTION

Colloidal metal nanoparticles protected by polymer matrices are receiving considerable attention since they can offer novel options for a variety of technological applications, such as catalysis.^{1–39} Several advantages are expected from such nanocatalyst-polymer systems, as follows: (1) large catalytic activities due to the small particle sizes

(and associated large surface areas); (2) protection and stabilization of the metal nanocatalysts by the polymer, with prevention of agglomeration and deactivation; (3) easy recoverability of the catalysts; and (4) novel possibilities for modifying catalytic properties, such as the activity and selectivity of a system. This can be done by control of the nanosize and special surface properties, as well as modifications of the metal by the selection of the protective polymer surrounding the catalyst.

Common methods to prepare polymer-protected metal colloids are illustrated by a variety of *in situ* reactions, such as chemical reductions, photoreductions, or thermal decompositions of suitable metal precursors. In this way, small par-

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ticle sizes and narrow size distributions of the metal particles can be obtained. In the case of water-soluble, flexible, protective polymers, the stabilization of the metal colloid is usually based on steric effects.^{1,2,40} The polymer is important not only for the stabilization of these metal colloids, but its selection can influence particle sizes, size distributions, and morphologies as well.

For catalytic applications, the protective polymer can play a crucial part in the development of tailored catalyst systems by its influence on catalytic properties. Hirai and Toshima have described the importance of the polymer type for polymer-anchored, complex metal catalysts.¹ Such effects can also apply to polymer-protected metal nanocatalysts. Therefore, it is necessary to investigate a wide variety of polymer types for their usefulness in these catalytic systems and the influence they can have on catalytic properties, such as the activity and/or selectivity. In some of our previous investigations, a strong influence of the polymer matrix on the catalytic activity of palladium and platinum nanoparticles was found.^{31–39} In addition, selective catalytic reactions using polymeric protective matrices were obtained by several other groups.^{3–11} Also, block copolymers turned out to be highly promising matrices for nanoparticles, both for their ability to influence the sizes and morphologies of the nanoparticles^{11–24} and for their ability to exhibit a variety of different morphologies themselves.^{41–45}

The polymer surrounding the metal nanoparticles can influence the catalytic properties in several ways, as follows.

1. It can influence catalytic properties by creation of a certain “environment” surrounding the catalyst and through which the reactant has to pass in order to approach the catalyst surface. Depending on the properties of the polymer, various hydrophobic, electrostatic, or asymmetric environments can be created in this way. This could certainly have a strong influence on the way a reactant can approach and orient towards the catalyst surface.
2. It can influence catalytic properties by making available and polarizing hydrogen sorbed on the catalyst surface, which can be influenced by the polymer. Such influence could also stem, for instance, from the introduction of groups into the polymer (either as side groups or within the backbone)

known to fulfill additional functions, such as hydrogen-transfer catalyses.

3. It can influence catalytic properties by modification of the catalyst surface by the presence of the protective polymer and its special properties, for instance, by the polarization/ionization of the metal nanoparticle surface. Interactions and attachments of the polymer with the metal surface of different strengths, for example, by hydrophobic interactions or complex formations, can additionally influence the catalytic activities and/or selectivities.
4. It can influence catalytic properties by having the protective polymer present during the *in situ* preparation of the nanocatalyst from their respective precursors, which can also influence the particle size and morphology, both of which can also greatly influence catalytic properties.

By combinations of such options and properties, the polymer can exceed by far its “original” role of merely stabilizing the nanosized particles. It can now take an active part in various technological applications, such as functioning as a “multifunctional protective matrix”.

An additional influence on the catalytic properties can stem from other species, for example, from the polymer side chains, the metal precursor, or the reducing agent—if they are not removed from the colloidal dispersion, for example, by dialysis. Such influences could additionally and purposely be used to control the performance of polymer–metal systems.

In the present investigation, we report the results for palladium colloids prepared from the precursors palladium chloride PdCl₂, ammonium tetrachloropalladate (NH₄)₂PdCl₄, and palladium acetate Pd(CH₃COO)₂ by refluxing the alcoholic solutions in the presence of several water-soluble homopolymers and random copolymers, with special emphasis on various polyacids. The particle sizes and size distributions of the metal nanoparticles were determined by transmission electron microscopy (TEM). The catalytic activities of the metal colloids were qualitatively tested using the hydrogenation of cyclohexene as a model reaction. Depending on the type of protective polymer (for example, polyacid or a nonionic, water-soluble polymer), differences in the catalytic activities were found. Lower catalytic activities have most often been observed for the palladium nanopar-

Table I Origins and Molecular Weights of the Protective Polymers

Polymer	Supplier	Molecular Weight ^a
Poly(1-vinyl pyrrolidone)	Aldrich	$M_w \sim 360,000$
Poly(1-vinyl pyrrolidone-co-vinyl acetate) 60 : 40 (molar)	Aldrich	$M_w \sim 50,000$
Poly(2-ethyl-2-oxazoline)	Aldrich	$M_w \sim 200,000$
Poly(1-vinyl pyrrolidone-co-acrylic acid) 75 : 25 (weight)	Aldrich	$M_w \sim 80,000$
Poly(methacrylic acid)	Polysciences	$M_w \sim 100,000$
Poly(styrene sulfonic acid)	Polysciences	$M_w \sim 70,000$
Poly(2-acrylamido-2-methyl-1-propane sulfonic acid)	Monomer-Polymer & Dajac Laboratories	$M_w \sim 60,000$
Poly(itaconic acid)	Monomer-Polymer & Dajac Laboratories	$M_w \sim 50,000$
Poly(butadiene-co-maleic acid) 1 : 1 (molar)	Polysciences	$M_w \sim 10,000-15,000$
Poly(butylacrylate-co-acrylic acid) 1 : 1 (weight)	Polysciences	not determined
Poly(vinyl phosphonic acid)	Polysciences	high

^a As given by supplier.

ticles when they were protected by polyacids, the exceptions being poly(butadiene-co-maleic acid) and (within the polyacids category) poly(vinyl phosphonic acid). These differences could stem from combined effects of the particle sizes and surface modifications of the palladium nanoparticles by the surrounding protective polymers.

The increased catalytic activities with the use of poly(butadiene-co-maleic acid) and poly(vinyl phosphonic acid) could stem from a promoting effect involving transfer hydrogenation introduced by the butadiene and phosphonic acid parts of the protective polymer.

EXPERIMENTAL

Chemicals

Palladium chloride (PdCl_2) and palladium acetate [$\text{Pd}(\text{CH}_3\text{COO})_2$ and $\text{Pd}(\text{ac})_2$], were obtained from Aldrich (Milwaukee, WI), and ammonium tetrachloropalladate $\{(\text{NH}_4)_2\text{PdCl}_4\}$ was purchased from Strem (Newburyport, MA). The polymers were obtained from Aldrich (Milwaukee, WI), Monomer-Polymer & Dajac Laboratories (Feasterville, PA), and Polysciences (Warrington, PA), as indicated in Table I.

Preparations of Colloids

The palladium colloids were prepared according to the method developed by Hirai et al.^{1,6} The metal precursors [PdCl_2 , $(\text{NH}_4)_2\text{PdCl}_4$, or $\text{Pd}(\text{ac})_2$]

were reduced by refluxing 10 mL of the alcoholic solutions [$6.8 \times 10^{-4}M$, ethanol (EtOH) : water = 1 : 1 (v/v)] containing the polymers in a mass ratio of polymer : palladium = 25 : 1. For the poly(butadiene-co-maleic acid) sample, the EtOH : H_2O ratio was 3 : 1 (v/v). For the PdCl_2 and $(\text{NH}_4)_2\text{PdCl}_4$ precursors, the reflux time was 30 min (oil-bath temperature, 110–120°C), and for the $\text{Pd}(\text{ac})_2$ precursor, 15 min (oil-bath temperature, 80°C). The reduction of the palladium precursors was followed by ultraviolet-visible (UV-vis) spectroscopy for all the samples.

Characterization

Transmission electron microscopy with a JEOL-100 CX II instrument (operated at an accelerating voltage of 80 kV) was used to obtain the particle sizes, morphologies, and particle-size distributions for the palladium nanoparticles. The samples were prepared by placing a drop of the colloidal dispersion on a formvar-carbon-coated copper grid and letting the solvent evaporate at room temperature. The particle sizes were determined based on measurements of at least 150 particles.

Catalytic Hydrogenations

The hydrogenations were carried out with a Parr hydrogenation apparatus (shaker type) at room temperature. For the qualitative comparison of the catalytic activities, cyclohexene (0.05 mL) was added to 10 mL of methanol (MeOH), and one of

Table II Properties of Palladium Nanocatalysts Prepared from PdCl₂ Precursor

Polymer	Average Particle Diameter (nm; std dev)	Catalytic Conversion (% cyclohexane)
Poly(1-vinyl pyrrolidone)	1.5 (0.6) ^a	100 ^f /100 ^g
Poly(1-vinyl pyrrolidone-co-vinyl acetate 60/40)	1.5 (3.0) ^b	100 ^f /98.6 ^g
Poly(2-ethyl-2-oxazoline)	1.6 (0.7) ^a	92.3 ^f /89.3 ^g
Poly(1-vinyl pyrrolidone-co-acrylic acid)	1.5 (0.7) ^a	93.8 ^f /91.6 ^g
Poly(methacrylic acid)	6.8 (1.8) ^c	40.6 ^{f,h}
Poly(styrene sulfonic acid)	4.0 (1.6) ^c	31.2 ^f /35.1 ^g
Poly(2-acrylamido-2-methyl-1-propane sulfonic acid)	5.1 (2.3) ^a	48.8 ^f /49.1 ^g
Poly(itaconic acid)	3.1 (4.1) ^b	40.1 ^f
Poly(butadiene-co-maleic acid)	2.7 (0.7) ^a	95.1 ^f /95.0 ^g
Poly(butylacrylate-co-acrylic acid)	^d	14.5 ^f
Poly(vinyl phosphonic acid)	^e	55.5 ^f /55.8 ^g

^a Separate particles.^b Many small separate, spherical particles in coexistence with larger ones (single crystals).^c Spherical and oval particles (some appearing crystalline); incipient agglomeration.^d Agglomerates of particles initially about 7–20 nm; complete precipitation after 1 day.^e Sample not investigated by TEM.^f Catalytic hydrogenation performed within 1 day after colloid preparation.^g Catalytic hydrogenation performed 3 to 5 days after colloid preparation.^h Precipitation after 2 to 3 weeks.

the palladium catalysts was added as a colloidal dispersion. An amount of catalyst that corresponded to 0.09 wt % palladium (with respect to cyclohexene) was added, and the reaction was performed at a hydrogen pressure of 10 psi for 30 min. The reaction mixtures were analyzed by gas chromatography (SE-30 packed column) with a flame ionization detector and helium as the carrier gas. The catalytic hydrogenations were performed within 1 day after the colloid preparation, and further hydrogenations were performed within several days after the colloid preparation as well (as specified in Tables II and III). Test runs without the addition of any catalyst were performed between each evaluation reaction.

RESULTS AND DISCUSSION

Table II gives a listing of the polymer-protected palladium colloids prepared from palladium chloride PdCl₂ by the alcohol reduction method, along with the average particle diameters (and standard deviations), as determined by TEM. The catalytic activities in terms of conversion of cyclohexene to cyclohexane are listed as well. A wide variety of protective polymers are seen to give stabilization of the palladium colloids, and aver-

age particle diameters below 10 nm were usually obtained. In most cases, the colloids were stable in air for several months. Without any protective polymer, precipitation occurs within one day. Usually, the use of polyacids resulted in larger particle sizes, and the formation of clusters or initiation of agglomeration can be seen on the TEM micrographs. An example is shown in Figure 1 for palladium nanoparticles reduced from the PdCl₂ precursor and protected by poly(styrene sulfonic acid). For the copolymers of nonionic polymer and polyacid components, such as poly(1-vinyl pyrrolidone-co-acrylic acid) and poly(butadiene-co-maleic acid), however, well-stabilized palladium colloids were obtained. They exhibited small, spherical, and separated nanoparticles with narrow size distributions. An exception was the copolymer poly(butylacrylate-co-acrylic acid), which gave a poorly stabilized colloid, with complete precipitation occurring after 1 day.

The analogous results for the palladium colloids reduced from the (NH₄)₂PdCl₄ precursor by refluxing the ethanolic solutions are listed in Table III. The particle sizes and morphologies, as well as the colloidal stabilities, are comparable to the ones obtained from the PdCl₂ precursor; again, separated and spherical particles were observed in many cases. Also, when compared to the

Table III Properties of Palladium Nanocatalysts Prepared from $(\text{NH}_4)_2\text{PdCl}_4$ Precursor

Polymer	Average Particle Diameter (nm; std dev)	Catalytic Conversion (% cyclohexane)
Poly(1-vinyl pyrrolidone)	2.4 (0.6) ^a	98.9 ^f /96.1 ^g
Poly(1-vinyl pyrrolidone- <i>co</i> -vinyl acetate 60/40)	3.0 (0.8) ^a	82.9 ^f /85.2 ^g
Poly(2-ethyl-2-oxazoline)	1.6 (0.4) ^a	64.4 ^f /62.7 ^g
Poly(1-vinyl pyrrolidone- <i>co</i> -acrylic acid)	2.1 (0.7) ^a	92.5 ^f /88.3 ^g
Poly(methacrylic acid)	6.6 (1.8) ^b	31.8 ^f /54.9 ^g /57.2 ^g
Poly(styrene sulfonic acid)	3.9 (1.5) ^a	36.6 ^f /90.1 ^g /87.5 ^g
Poly(2-acrylamido-2-methyl-1-propane sulfonic acid)	4.4 (1.6) ^c	25.1 ^f /65.4 ^g /63.4 ^g
Poly(itaconic acid)	6.6 (2.9) ^d	47.0 ^f
Poly(butadiene- <i>co</i> -maleic acid)	1.9 (0.7) ^a	76.6 ^f /88.9 ^g /91.3 ^g
Poly(butylacrylate- <i>co</i> -acrylic acid)	^e	17.7 ^f

^a Separate particles.

^b Separate, spherical particles, with some appearing crystalline.

^c Separate particles and particles in clusters.

^d Mostly separate, spherical, and oval particles.

^e Agglomerates of particles initially about 10–25 nm, with complete precipitation after 1 day.

^f Catalytic hydrogenation performed within 1 day after colloid preparation.

^g Catalytic hydrogenation performed 3 to 5 days after colloid preparation.

use of polyacids, the particle sizes were smaller for the nonionic polymers, as well as for the poly(1-vinyl pyrrolidone-*co*-acrylic acid) and poly(butadiene-*co*-maleic acid) copolymers. As for the PdCl_2 precursor, the use of the poly(butylacrylate-*co*-acrylic acid) copolymer resulted in a poorly stabilized colloid with complete precipitation occurring within a day. However, in contrast to the colloids prepared from PdCl_2 , these colloids [prepared from $(\text{NH}_4)_2\text{PdCl}_4$] seemed to be somewhat better stabilized, exhibiting a lower ten-

dency to form clusters or agglomerates. For comparison, the TEM micrographs for the most extreme example, palladium nanoparticles in the presence of poly(1-vinyl pyrrolidone-*co*-vinyl acetate), are shown in Figure 2 (preparation from PdCl_2) and in Figure 3 [preparation from $(\text{NH}_4)_2\text{PdCl}_4$]. This is obviously due to the differences in the precursor species used. In contrast to $(\text{NH}_4)_2\text{PdCl}_4$, PdCl_2 is reported to show a tendency to form halogen-bridged complexes.⁴⁶ This



Figure 1 Palladium nanoparticles reduced from PdCl_2 in the presence of poly(styrene sulfonic acid) (bar = 47 nm).

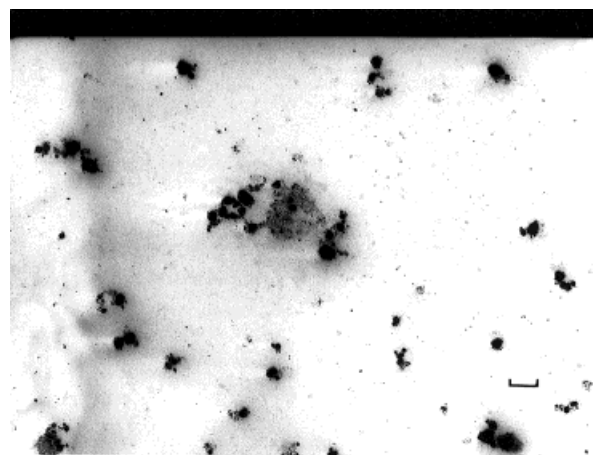


Figure 2 Palladium nanoparticles reduced from PdCl_2 in the presence of poly(1-vinyl pyrrolidone-*co*-vinyl acetate) (bar = 90 nm).

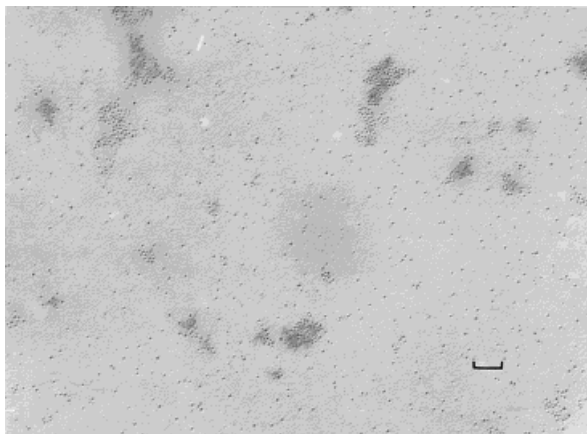


Figure 3 Palladium nanoparticles reduced from $(\text{NH}_4)_2\text{PdCl}_4$ in the presence of poly(1-vinyl pyrrolidone-*co*-vinyl acetate) (bar = 60 nm).

could result in a larger tendency to form agglomerated or “fused” colloid particles, which $(\text{NH}_4)_2\text{PdCl}_4$ does not show. Another difference could stem from the presence of the ammonium counterions in the $(\text{NH}_4)_2\text{PdCl}_4$ precursor species. They could interact with the anionic acid side groups of the protective polymer (in the case of polyacids being at least partially deprotonated), for example, by ion-pair formation, thus changing the interaction of these polyacids with the metal precursor species. Possibly, the repulsion between the anionic tetrachloropalladate ions and the anionic polymer side groups is reduced, allowing better interactions and a more readily protective function of the polymer for the palladium species.

With respect to the nanoparticle size, it is known that usually some interaction of the metal precursor with the polymer (for example, by complex or ion-pair formation) is desired in order to obtain well-stabilized, small particle sizes and narrow size distributions.^{47,48} We have also observed this in some earlier investigations, where the use of cationic polyelectrolytes resulted in very small and well-stabilized palladium, platinum, and gold nanoparticles.^{38,39} This could be partially ascribed to the ion-pair formation of the anionic precursor ions with the cationic polymer side groups.

Polyacids are expected to form complexes with the metal precursor ions.⁴⁹ Therefore, the observed larger particle sizes seem surprising at first, if good interaction of the precursor species with the protective polymer is taken as the only

guarantee for obtaining small particle sizes and well-stabilized metal colloids. However, several other aspects have to be taken into consideration; it is known that slower reduction methods usually result in larger particle sizes.¹¹ This is often achieved by choice of the reducing agent. However, changes are also possible through variation of the precursor species and its interactions (such as complexation strength, possibly enhanced by a chelating effect).

Therefore, even though some precursor–polymer interaction may be desired, the formation of stronger complexes can be expected to result in a more difficult and slower reduction of the metal precursor. In some cases, the reduction is even inhibited for mild reducing agents, such as ethanol at reflux temperatures.¹ For instance, with the presence of amino side groups in a protective polymer, the reduction of various palladium precursors cannot be achieved by this reduction method. The use of stronger reducing agents, such as borohydrides, may result in an initial reduction in some cases; however, the metal colloids are usually reoxidized easily within a short time.⁵⁰

These considerations and observations could be the explanation for the larger particle sizes observed with the use of various polyacids as protective matrices. It is possible that, due to complex formation of the metal precursor ion, the reduction is “slower” for the polyacids (fewer nuclei are initially formed), allowing the growth of somewhat larger nanoparticles.

A further test has been carried out for PdCl_2 . Often, this precursor can be already reduced at room temperature with the use of an ethanol : water solvent system, due to the formation of the $\text{Pd}(\text{OH})_2$ species in this solvent system.⁵ Thus, PdCl_2 can be slowly reduced already at room temperature in the presence of various nonionic, water-soluble polymers, such as poly(1-vinyl pyrrolidone), poly(2-ethyl-2-oxazoline), and poly(1-vinyl pyrrolidone-*co*-vinylacetate), upon the addition of water to an ethanolic solution of PdCl_2 and the respective polymer. The reduction process could be easily followed by the change in color from yellow to brown, as well as UV-vis spectroscopy. With the use of poly(1-vinyl pyrrolidone-*co*-acrylic acid) copolymer, however, an elevated temperature was necessary for achieving the reduction under the same conditions. This can be ascribed to complex formation between the acid units and the PdCl_2 precursor, therefore inhibit-

ing the reduction under very mild conditions (that is, at room temperature). Similarly, the use of various polyacids required elevated temperatures for the reduction of the PdCl₂ precursor in the respective solvent system. In comparison, the systems containing the sulfonic acid units were more stable at room temperature than the ones containing carboxylic acid units. This is in agreement with the higher affinity of Pd(II) towards sulfur-containing ligands than towards oxygen-containing ones.⁵¹ The sample containing poly(vinylphosphonic acid), however, was easily reduced at room temperature, probably due to the reducing character of the phosphonic acid units.

Thus, an optimum has to be found between the interaction of the metal precursor with the protective polymer on the one hand, in order to achieve well-stabilized metal colloids exhibiting small particle sizes and narrow size distributions. On the other hand, these interactions should not be such as to slow down the reduction under certain reduction conditions (unless the preparation of somewhat larger particle sizes is desired), or to even inhibit the metal colloid formation.

The catalytic activities in terms of conversion of cyclohexene are listed in Tables II and III as well. For the well-stabilized colloidal palladium nanocatalysts protected by the nonionic polymers, high catalytic activities were found. When comparing the nonionic protective polymers poly(1-vinyl pyrrolidone) and poly(1-vinyl pyrrolidone-*co*-vinyl acetate) for the 2 different palladium precursors, it seems that for the same protective polymer, somewhat larger average particle sizes give slightly lower catalytic activities. This is to be expected since larger particles have lower surface areas, which, in turn, should cause lowered catalytic activities. Such comparisons, however, should be made only for the same polymer type (also including the same molecular weight) since the interactions of the polymer with the catalyst surface are highly influential as well and should not be neglected. Therefore, the direct investigation of the dependency of the catalytic activity on particle size is not possible if different polymer types are used.

One exception for the nonionic polymers is found for poly(2-ethyl-2-oxazoline), where a lower value has been found for the catalytic activity if (NH₄)₂PdCl₄ is used as a precursor, even though the particle sizes and morphologies are similar. For both precursors separate, spherical particles have been found. A reason for the differences in

the catalytic activity could be the influence of the ammonium ions being present from the palladium precursor. It was found by us earlier that the presence of ammonium species can lower the catalytic activities for palladium catalysts.³⁸ Especially for poly(2-ethyl-2-oxazoline) as the protective polymer, a large difference was found if tetraethylammonium chloride was added to the hydrogenation mixture, resulting in a significant decrease of the catalytic activity for the respective palladium-polymer system. For poly(1-vinyl pyrrolidone-*co*-acrylic acid), no such decreasing effect from the use of (NH₄)₂PdCl₄ is observed, since the ammonium ion might act as a counterion for the carboxylate units, thus interacting more with the polymer and to a lesser extent with the catalyst surface. Equally, poly(1-vinyl pyrrolidone) is reported to be surrounded by a negative cloud, therefore involving electrostatic stabilization and offering stronger interactions of the ammonium ion rather with the polymer than with the palladium surface.⁵²

A somewhat reduced catalytic activity is observed for poly(1-vinyl pyrrolidone-*co*-acrylic acid) for both palladium precursors [PdCl₂ and (NH₄)₂PdCl₄] when compared to the poly(1-vinyl pyrrolidone) homopolymer. Even though the particle sizes and morphologies are comparable for the copolymer and the homopolymer, the catalytic activities are reduced to some extent for the copolymer containing the acidic units. This could obviously be due to the presence of these acidic units and their effects on the polymer-palladium colloid interaction.

This is consistent with the observation that the catalytic activities are mostly lower for the palladium-polymer systems involving polyacids, with the exception being the poly(butadiene-*co*-maleic acid) copolymer and (within the polyacids) poly(vinyl phosphonic acid). In most cases, the particle sizes are larger for these polyacid systems, so particle size effects could certainly be responsible to some extent for the lower catalytic activities. However, it seems unlikely that this alone should have such a large effect. This view is supported by the somewhat reduced catalytic activity for the poly(1-vinyl pyrrolidone-*co*-acrylic acid) copolymer in comparison to the poly(1-vinyl pyrrolidone) homopolymer, as already mentioned above. Therefore, it is suggested that an additional effect could play a role as well. This could be surface modifications of the palladium catalyst surface by the polymer, which would lead to an additional

Table IV Properties of Palladium Nanocatalysts Prepared from Palladium Acetate Precursor

Polymer	Average Particle Diameter (nm; std dev)	Catalytic Conversion (% cyclohexane) ^e
Poly(1-vinyl pyrrolidone)	1.7 (0.8) ^a	73.8
Poly(1-vinyl pyrrolidone-co-vinyl acetate 60/40)	~ 2–5 ^b	49.9
Poly(1-vinyl pyrrolidone-co-acrylic acid)	~ 2 ^c	25.5
Poly(styrene sulfonic acid)	3.3 (3.3) ^d	11.9

^a Separate particles.

^b Particles clustered into small agglomerates.

^c Particles coexisting with agglomerates of about 55 nm (consisting of particles of about 8 nm)

^d Very small spherical particles of about 1 nm diameter coexisting with larger crystalline particles.

^e Catalytic hydrogenations performed within 1 day after colloid preparation.

decrease of the catalytic activity. Palladium as the chemically most active platinum metal is more prone to surface modifications, up to partial reoxidation, stronger polarization/ionization of the palladium nanoparticle surface, and/or complex formation with the outer nanoparticle layer.⁵³ With the presence of polyacids (which are at least, to some extent, deprotonated), surface-complex formation (probably enhanced by a chelating effect) or the mere polarization of the catalyst surface by the surrounding negative charge might occur to some extent. Such a surrounding negative charge can be expected to lead to a decrease of the catalytic activity for the hydrogenation of cyclohexene. For poly(1-vinyl pyrrolidone-co-acrylic acid) 75 : 25 with its lower acid content, a less significant decrease in catalytic activity was found.

The reduction of the samples was followed by UV-vis spectroscopy, and UV-vis spectra were taken as well after storing the samples in air at room temperature for 1 week. The spectra remained unchanged; therefore, excessive reoxidation (possibly by air) of the palladium species during this period (and catalytic evaluation) could be excluded.

Some further experiments were conducted for some selected examples in order to investigate the influence of acidic units on the catalytic activity of such palladium-polymer systems. Instead of adding an additional organic acid, such as acetic acid, to the reaction mixture, a further palladium precursor, namely, palladium acetate Pd(ac)₂ was used. As the corresponding base of a weak acid, its effect is expected to be comparable to the acid, without adding an additional agent and without having additional effects from different precursor

counterions. The results, that is, the average particle diameters (and standard deviations) and the catalytic activities for these systems, are listed in Table IV. It can be seen that the catalytic activities are significantly reduced.

The lower catalytic activities thus might stem from surface modifications, such as charge transfer, polarization, or surface-complex formation. These results show that the counterions from the metal precursors, when left in the colloidal dispersion, have to be considered as well and could even be used to control the reaction in some ways.

The presence of ammonium counterions could explain the higher catalytic activities for the palladium-polyacid systems, when prepared from the (NH₄)₂PdCl₄ precursor. The presence of ammonium ions seems to be the only pronounced difference between the 2 systems with respect to their preparations. While the presence of such ammonium species can lead to a decrease of catalytic activity if purely nonionic protective polymers are used (due to interaction with the catalyst surface), their effects could be different for the cases of anionic polyelectrolytes and polyacids. The ammonium ions stemming from this precursor could partially neutralize the deprotonated polymeric acid groups, which could then interact to a lesser extent (for example, by a less-polarizing or complexing effect) with the palladium nanocatalyst. In this way, the palladium surface would be less modified and more available for the catalytic reaction to occur, which seems to be confirmed by the higher catalytic activities observed. Another finding seems to point in this direction; for poly(methacrylic acid), poly(styrene sulfonic acid), and poly(2-acrylamido-2-methyl-1-propane sulfonic acid), a lower catalytic activity (compara-

ble to the samples prepared from PdCl_2) was found for the catalytic reaction being performed within a few hours after the preparation of the palladium colloids. After 2 to 3 days, the catalytic activities become larger and then stay at this elevated value. This is not the case for the samples prepared from the PdCl_2 precursor, which keep their lower values. The following reasons for these observations are suggested here: initially stronger interactions between the acidic units and the palladium species might be initially present, thus influencing the catalytic activity. In the case of the $(\text{NH}_4)_2\text{PdCl}_4$ precursor, the ammonium ions can interact with and neutralize the anionic acid units as counter cations. This would, in turn, result in a less-pronounced interaction of the acid units with the palladium surface, thus resulting in the observed change (that is, increase) in catalytic activity. A similar effect has been observed by Bronstein et al., where the protonation of pyridine units within a protective block polymer resulted in less interaction and higher catalytic activities of palladium nanocatalysts.¹³

Such observations might provide interesting options for conducting catalytic reactions using polyacid systems. The course of the catalytic reaction could be changed during the reaction by adding certain counterions or simply by changing the pH of the reaction mixture. The prerequisite, of course, is a well-stabilized metal colloid that remains stabilized during these additions. Poorly stabilized palladium colloids lead to a significant decrease of the catalytic activity, as can be seen for the poly(butylacrylate-acrylic acid) samples.

A special case seems to be the use of poly(butadiene-*co*-maleic acid), for which high catalytic activities have been found. For both palladium precursors [PdCl_2 and $(\text{NH}_4)_2\text{PdCl}_4$], the colloids are very well-stabilized, showing separate, spherical particles. Palladium particles prepared from PdCl_2 in the presence of poly(butadiene-*co*-maleic acid) are shown in Figure 4. In this case, the hydrophobic butadiene unit is responsible for the increased colloid stability [the poly(maleic acid) homopolymer being only a poor stabilizer for metal colloids]. Also, the formation of palladium-butadiene complexes by dative π -bonds is known^{49,51} and could be influential here as well, both for the colloid stabilization and for the formation of small spherical particles exhibiting a narrow size distribution. In addition, the presence of the butadiene unit could have a promoting

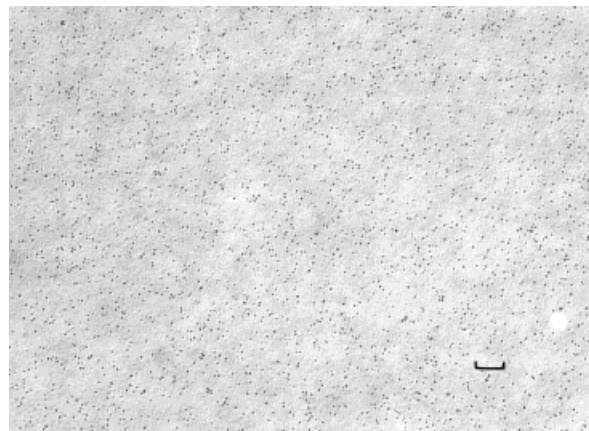


Figure 4 Palladium nanoparticles reduced from PdCl_2 in the presence of poly(butadiene-*co*-maleic acid) (bar = 60 nm).

effect on the catalytic activity due to a hydrogen transfer effect provided by the double bonds of the butadiene units.

Poly(vinyl phosphonic acid) as a protective matrix resulted in higher catalytic activities with the polyacid homopolymers, in the case of the PdCl_2 precursor. It has been reported that phosphinic and phosphorous acids lead to mild hydrogenation conditions for palladium catalysts due to hydrogen transfer catalysis.^{54–56} The phosphonic acid side groups might similarly lead to some promoting effects in this case.

These 2 cases are examples of adding such hydrogen transfer agents not separately, but in combination with the protective polymer, attached either as a side group [as for poly(vinyl phosphonic acid)] or within the polymer backbone [as for poly(butadiene-*co*-maleic acid)]. Thus, the polymer used in such systems can perform “multifunctional” tasks, thereby providing an elegant option for the design of novel polymer-metal catalyst systems.

CONCLUSIONS

The reported results show that the catalytic activity of a metal-polymer system can be modified and adjusted by the selection of the protective polymer, in combination with choices of the metal precursor and reduction method. This is especially important since variations in catalytic activities are often accompanied by variations in

catalytic selectivities.⁵⁷ The combination of adjustment of particle sizes and morphologies, and the selection of the protective polymer, which can take an active part in such systems, can lead to catalysts that can be tailored for special needs.

Additional ions could be used to "tune" the course of the catalytic reaction. A change of the rate of a catalytic reaction might thus be achieved by the addition of certain ions or by changing the pH of the reaction mixture. Effects would be due to interactions of these species with, for example, the polymer matrix surrounding the catalytically active metal surface.

A further interesting option is the incorporation of additional functions, such as hydrogen transfer units, into the protective polymer. Also of interest would be development of polymer units (either attached as side groups or within the backbone) that could control the course of a catalytic reaction or terminate it at a certain desired point. This could be achieved by incorporation of units that, for instance, can be hydrogenated themselves (in order to avoid "overhydrogenation" of the product) or that can disproportionate with a reaction product (in order to obtain a desired intermediate product).

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