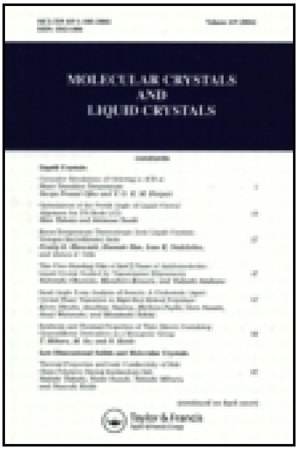

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Metal Nanocatalysts Stabilized in Protective Polymer Matrices

Andrea B. R. Mayer [a] [b] & James E. Mark [a]

[a] Department of Chemistry, University of Cincinnati, Cincinnati, OH, 45221-0172, USA

[b] Department of Chemical Engineering, Chemistry, and Materials Science, Polytechnic University Brooklyn, Six Metro Tech Center, Brooklyn, NY, 11201, USA

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Metal Nanocatalysts Stabilized in Protective Polymer Matrices

ANDREA B. R. MAYER* and JAMES E. MARK

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221–0172, USA

Palladium and platinum nanoparticles were generated in the presence of a variety of protective polymers. The size and size distribution of the metal particles were determined by transmission electron microscopy, and the catalytic activities of the metal-polymer systems were qualitatively tested by the hydrogenation of cyclohexene as a model reaction. Several groups of protective polymers were examined, including water-soluble homopolymers and random copolymers, cationic polyelectrolytes, amphiphilic block copolymers, and latices as carriers. The catalytic properties were found to be significantly influenced by the type of protective polymer used.

Keywords: nanoparticles; colloid; polymer; catalysis; hydrogenation

INTRODUCTION

Due to their nanosize dimensions, transition metal nanoparticles exhibit a number of interesting optical, catalytic, conductive, and magnetic properties[1-6]. Often such colloidal nanoparticles are stabilized by a protective polymeric matrix, which prevents their agglomeration and deactivation.

Colloidal, polymer-protected metal nanocatalysts are especially intriguing since they show a number of significant advantages in comparison to traditional catalyst systems[1-3,5,6]. Due to the small particle sizes, there are large surface areas, resulting in high catalytic activities. Also, the protective function of the polymer facilitates handling and storage of the materials. A further advantage is

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* Present address: Department of Chemical Engineering, Chemistry, and Materials Science, Polytechnic University Brooklyn, Six Metro Tech Center, Brooklyn, NY 11201, USA

the option of tailoring the catalytic properties of the materials, which can result in novel catalytic properties.

Polymer-protected metal nanoparticles can be prepared by a variety of reactions carried out in-situ, that is, in the presence of the protective polymer. Wet-chemistry methods, such as chemical reductions, photoreductions, or thermal decompositions are most frequently employed. Usually, the goal is to obtain small particle sizes and narrow size distributions.

The protective polymer has to fulfill a range of functions, the most important being its ability to act as a good stabilizer of the metal colloids. The protective function of a stabilizing agent can be quantitatively expressed by the "*gold number*", which was first introduced by Zsigmondy[7]. It is defined as the amount of protective colloid in milligrams which just prevents 10 cm^3 of a red gold sol from changing color to violet upon addition of 1 cm^3 of 10 % aqueous solution of NaCl. In addition to this stabilizing effect, the polymer can control nanoparticle features, such as the size, size distribution, shape, and morphology. Finally, it is possible by the selection of the polymeric matrix, to tailor and fine-tune the properties of these materials.

Several types of protective polymers, ranging from water-soluble homopolymers and random copolymers, to cationic polyelectrolytes, amphiphilic block copolymers, and latices as carriers, were investigated for their abilities to stabilize metal nanoparticles, and their utilities as matrices for nanocatalysts[8-15].

EXPERIMENTAL

The metal precursors and the reducing agents were obtained from Aldrich. The homopolymers and random copolymers, cationic polyelectrolytes, and latex dispersions in water were purchased from Aldrich, Polysciences, and

Monomer-Polymer & Dajac Laboratories. The block copolymers were obtained from the Polymer Source.

The metal colloids were prepared by refluxing or stirring the alcoholic solutions, reduction with potassium tetrahydroborate, and reduction with sodium hypophosphite, according to the procedures described previously[8-15].

The particle sizes and size distributions of the platinum and palladium nanoparticles were obtained by TEM with a JEOL-100 CX II instrument (operated at an accelerating voltage of 80 kV). 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 with a comparator, and were based on measurements of at least 150 particles.

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 the metal catalysts were added as colloidal dispersions. An amount of catalyst that corresponds to 0.16 wt% platinum or 0.09 wt% palladium (with respect to cyclohexene) was added, and the reaction was performed at a hydrogen pressure of 10 psi for 30 minutes. The reaction mixtures were analyzed by gas chromatography (SE-30 packed column) with a flame ionization detector, and helium as the carrier gas. Test reactions without the addition of any catalyst were performed after each evaluation reaction.

RESULTS AND DISCUSSION

Water-soluble homopolymers and random copolymers

For the stabilization of metal colloids in polar solvents polymers possessing a relatively nonpolar, hydrophobic backbone and hydrophilic side groups have been found to be most effective[2]. The hydrophobic backbone is thought to interact with the metal particle surface, and the hydrophilic side groups provide solubility of the materials by interactions with the polar dispersion medium. Water-soluble vinyl homopolymers, such as poly(N-vinyl-2-pyrrolidone) or poly(vinyl alcohol) have been most thoroughly investigated so far. For such flexible polymers, the stabilization of the metal particles is usually based on steric stabilization. Such materials have been already reported to show high catalytic activities, and selective reactions have been observed as well[1,2,5]. This is mainly due to the steric hindrance provided by the polymer which surrounds the catalytically-active metal, thereby influencing how a reactant can approach approach the catalyst. Thus, it is expected that other polymers can add additional properties and effects for the development of novel tailored catalyst systems.

A variety of water-soluble homopolymers and random copolymers was selected, based on varying degrees of hydrophobicity of their backbones, and based on the nature of their side groups. A general trend with respect to the particle sizes was found, when comparing polymers possessing different hydrophobic character. Some representative examples are summarized in Table I for palladium nanoparticles stabilized by several water-soluble homopolymers and random copolymers. Usually, larger particle sizes were found for protective polymers with a restricted hydrophobic character of the backbone.

The particle size distributions showed a similar trend, that is, larger size distributions were usually found for less hydrophobic polymers. For a range of other water-soluble polymers the particle sizes were more uniform. A typical feature for platinum nanoparticles is the formation of small nanosized "groups", which, however, are colloidally well-stabilized. An example is depicted in Fig. 1 for platinum nanoparticles protected by poly(N-vinyl-2-pyrrolidone-co-acrylic acid) and obtained by refluxing the alcoholic solutions.

TABLE I Palladium nanoparticles stabilized by water-soluble homopolymers and random copolymers

Polymer	Average particle diameter (nm), by TEM
Poly(N-vinyl-2-pyrrolidone-co-acrylic acid)	2.6
Poly(N-vinyl-2-pyrrolidone), av. mol. wt. 40,000	3.9
Poly(2-hydroxypropyl methacrylate)	27.7
Poly(methylvinylether-co-maleic anhydride)	39.7

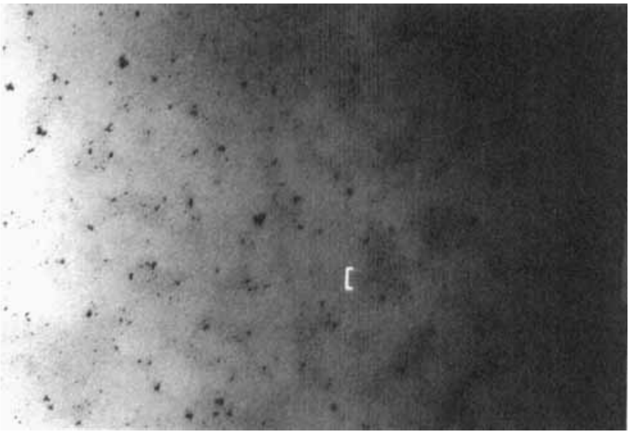

FIGURE 1 TEM micrograph for platinum nanoparticles generated in the presence of poly(N-vinyl-2-pyrrolidone-co-acryliac acid) by refluxing the alcoholic solutions (mass ratio polymer : platinum = 10 : 1) (Bar = 31 nm). The formation of small nanosized "groups" can be observed.

A wide variety of protective polymers are useful for the stabilization of noble metal colloids, and dispersions which were colloidally stable for months and even years could be obtained, with particles exhibiting diameters in the range of 1 – 15 nm. A restricted hydrophobic character of the polymer backbone resulted in less-stable metal colloids, larger particle sizes (20 – 40 nm), and broader size distributions.

The stable palladium and platinum samples were investigated for their catalytic activities, using the hydrogenation of cyclohexene as a model reaction. Table II shows results obtained for platinum catalysts prepared by the alcohol reduction method and protected by nonionic water-soluble polymers and various polyacids (anionic systems). A general trend observed here is the increased catalytic conversion for the samples involving polyacids as protective matrices, in comparison to the ones incorporating the nonionic polymers. No direct influence of the platinum nanoparticle size was observed, indicating that the type of protective polymer is influential as well.

The respective results for palladium nanoparticles prepared by the alcohol reduction method and protected by various water-soluble nonionic homopolymers and polyacids are shown in Table III.

The values for the catalytic conversions generally were higher for the palladium samples than for the platinum ones when nonionic water-soluble polymers were involved. However, a different trend was observed in the use of the polyacids. The effect of polyacids was to increase the catalytic activities of the platinum catalysts, whereas the values for the palladium samples incorporating polyacids were generally lower. While a slight size dependence was observed for the palladium particles (the palladium samples protected by the polyacids in most cases showed somewhat larger particle sizes, and lower catalytic conversions), it is very likely that the decreased catalytic conversion was not caused exclusively by the particle size, but by the presence of the polyacids as well. A reason could be the formation of surface complexes of the acid side groups with the palladium species (palladium is a relatively reactive platinum metal). One exception is the copolymer poly(N-vinyl-2-pyrrolidone-

TABLE II Platinum nanocatalysts protected by water-soluble nonionic polymers and polyacids

Polymer	Av. particle size (nm) (std. dev.)	% Cyclohexane
Poly(N-vinyl-2-pyrrolidone)	2.7 (1.5)	79.9
Poly(N-vinyl-2-pyrrolidone-co-vinyl acetate)	2.2 (0.4)	61.7
Poly(2-hydroxypropyl methacrylate)	~4 (aggl.)	64.5
Poly(N-vinyl-2-pyrrolidone-co-acrylic acid)	2.3 (1.0)	80.1
Poly(methacrylic acid)	1.5 (0.5)	100
Poly(styrene sulfonic acid)	2.3 (0.9)	80.9
Poly(2-acrylamido-2-methyl-1-propane sulfonic acid)	~ 1-4	100
Poly(vinyl phosphonic acid)	1.6 (0.5)	100

co-acrylic acid), where a high catalytic conversion was observed, comparable to that with the nonionic polymer. In this case the copolymer however had an acid content of only 25 wt%, and therefore the main influence stemmed here from the poly(N-vinyl-2-pyrrolidone) units. Increased values were also observed for the polyacids poly(butadiene-co-maleic acid) and (within the polyacid series) also for poly(vinyl phosphonic acid). In this case the reducing character of the butadiene and phosphonic acid components could contribute to hydrogen transfer reactions, resulting in a promoting effect for the catalytic conversion.

Cationic polyelectrolytes

Cationic polyelectrolytes are of interest as stabilizing matrices for metal colloids since they can provide a combination of steric and electrostatic stabilization. In addition, the metal precursor ions can interact with the charged polymer components by ion pair formation. This should result in small particle diameters and narrow size distributions. Due to the electrostatic environment created by the polyelectrolyte matrix, selective catalytic reactions are expected, especially if charged or polar reactants are involved.

TABLE III Palladium nanocatalysts protected by water-soluble nonionic polymers and polyacids

Polymer	Av. particle size (nm) (std. dev.)	% Cyclohexane
Poly(N-vinyl-2-pyrrolidone)	1.5 (0.6)	100
Poly(N-vinyl-2-pyrrolidone-co-vinyl acetate)	1.5 (3.0)	100
Poly(2-ethyl-2-oxazoline)	1.6 (0.7)	92.3
Poly(N-vinyl-2-pyrrolidone-co-acrylic acid)	1.5 (0.7)	93.8
Poly(methacrylic acid)	6.8 (1.8)	40.6
Poly(styrene sulfonic acid)	4.0 (1.6)	31.2
Poly(2-acrylamido-2-methyl-1-propane sulfonic acid)	5.1 (2.3)	48.8
Poly(vinyl phosphonic acid)	- [a]	55.5
Poly(itaconic acid)	3.1 (4.1)	40.1
Poly(butadiene-co-maleic acid)	2.7 (0.7)	95.1

[a] No TEM pictures taken.

A typical example for palladium nanoparticles obtained in the presence of poly(2-hydroxy-3-methacryloxypropyltrimethyl ammonium chloride) by the alcohol reduction method is shown in Fig. 2, demonstrating small particle sizes and narrow size distribution.

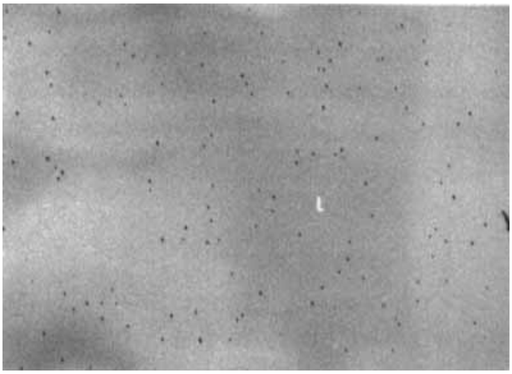

FIGURE 2 TEM micrograph for palladium nanoparticles generated in the presence of poly(2-hydroxy-3-methacryloxypropyltrimethyl ammonium chloride) by refluxing an alcoholic solution (Bar = 50 nm). Homogeneously distributed particles exhibiting a narrow size distribution are in evidence.

The results for the catalytic activities for several platinum samples obtained by the alcohol reduction method and protected by cationic polyelectrolytes are summarized in Table IV, in comparison to samples protected by nonionic polymers. The catalytic activities were drastically reduced for the samples involving the cationic polyelectrolytes, even though the particle sizes were very small. These reduced activities can stem from the electrostatic environment created by the polyelectrolytes around the catalytically-active platinum nanoparticles, which influences the diffusion of the hydrophobic reactant cyclohexene to the catalyst surface. In the case of the respective palladium nanocatalysts the catalytic conversions were reduced even further if cationic polyelectrolytes were employed. It is proposed that in these cases an additional surface modification of the palladium nanocatalysts was involved (for instance, by the formation of surface complexes or the polarization of the catalyst surface), in addition to the electrostatic environment around the nanoparticles. These results demonstrate clearly the strong dependence of the catalytic properties on the protective polymer matrix, which can superimpose on the expected size dependence of the catalytic activities.

TABLE IV Platinum nanocatalysts protected by cationic polyelectrolytes

Polymer / polyelectrolyte	Av. particle size (nm) (std. dev.)	% Cyclohexane
Poly(N-vinyl-2-pyrrolidone)	2.7 (1.5)	73.0
Poly(2-ethyl-2-oxazoline)	2.6 (0.8)	55.8
Poly(N-vinyl pyrrolidone-co-vinyl acetate)	2.2 (0.4)	61.7
Poly(diallyldimethyl ammonium chloride)	1.8 (0.7)	22.4
Poly(methacrylamidopropyl trimethyl ammonium chloride)	1.4 (0.4)	22.7
Poly((3-chloro-2-hydroxypropyl-2-methacryloxyethyldimethyl ammonium chloride)	1.7 (0.8)	27.3

Amphiphilic block copolymers

Amphiphilic block copolymers, containing one hydrophilic and one hydrophobic block are known to be efficient steric stabilizers for metal colloids. In addition, the formation of spherical micelles in selective solvents for one of the polymer block components has been used for the control of the particle growth[3]. Several catalytically-active systems based on block copolymer-metal composites have been reported, and often the catalytic activity and selectivity could be additionally controlled by the selection of the block copolymer parameters[3].

For these investigations two amphiphilic block copolymers, namely polystyrene-*block*-poly(methacrylic acid) (PS-b-PMAA) and polystyrene-*block*-poly(ethylene oxide) (PS-b-PEO), were selected. Polar solvent systems were employed, resulting in the formation of micelles possessing a hydrophobic polystyrene core and a hydrophilic corona. Furthermore both the metal precursors and the reduction methods were varied[7]. Some results for the samples, including catalytic results, are given in Table V for palladium nanoparticles protected by PS-b-PMAA.

No direct dependence of the catalytic activities on the particle sizes was found. However, when comparing the results, several general trends were recognized. When comparing the samples obtained from the more hydrophobic precursors palladium acetate and palladium acetylacetonate with samples generated from palladium chloride by the same reduction methods (especially the alcohol reduction method), lower catalytic conversions were found for the more hydrophobic precursors. When comparing the sterically hindered precursor palladium acetylacetonate (in combination with the reduction by KBH_4) with the respective sample obtained from palladium chloride, an increased value for the catalytic conversion was observed for the sterically-hindered palladium precursor. Finally, when comparing the results for palladium acetylacetonate for samples where the reaction mixtures have been stirred for two days before performing the reduction, the stirred samples showed reduced catalytic conversions. These findings lead to the conclusion that full or partial embedding of the resulting palladium nanoparticles could be responsible for the variations in catalytic conversions. Catalyst nanoparticles which are embedded in a hydrophobic polystyrene matrix should show a higher blocking of the catalytically active sites, than particles which are embedded in a hydrophilic matrix which is less-strongly interacting with the catalyst surface.

Similar results pointing in the same direction were also found for the palladium nanocatalysts protected by the PS-b-PEO polymer[7].

TABLE V Palladium nanocatalysts protected by PS-b-PMAA

Precursor	Reduction Method	Conversion % cyclohexane	Av. particle diam.(nm) (std. dev.)	Micelle diam.(nm)
$PdCl_2$	Refluxing	23.1	7.9 (6.3)	~ 15
$PdCl_2$	KBH_4	33.5	2.1 (1.2)	-
$Pd(ac)_2$	Refluxing	13.8	3.4 (0.8)	~ 15
$Pd(ac)_2$	KBH_4	14.6	1.3 (0.5)	~ 15
$Pd(ac)_2$	RT	6.1	1.0 (0.9)	~ 15
$Pd(ac)_2$	60°C	8.2	1.3 (1.2)	~ 15
$Pd(ac)_2$	NaH_2PO_2	52.3	2.5 (1.6)	~ 15
$Pd(F_3ac)_2$	RT	6.2	3.5 (1.5)	~ 15
$Pd(F_3ac)_2$	60(C	8.3	2.7 (1.0)	~ 15
$Pd(F_3ac)_2$	NaH_2PO_2	34.2[a)]	1.8 (0.4)	~ 15-22
$Pd(acac)_2$	Refluxing	11.8	6.3 (3.8)	~ 14-20
$Pd(acac)_2$	Stirred/Refl.	15.8	5.4 (2.6)	~ 15
$Pd(acac)_2$	KBH_4	80.7	2.0 (0.7)	~ 15, loose
$Pd(acac)_2$	Stirred/KBH_4	54.6	2.1 (0.9)	~ 35

[a)] Hydrogenation conditions the same as for the other reactions, but with one third of the amounts.

An example of a sample is shown in Fig. 3. It is for palladium nanoparticles generated in the presence of PS-b-PEO by stirring the solution at room temperature using a solvent mixture tetrahydrofuran : ethanol = 1 : 2 (v/v).

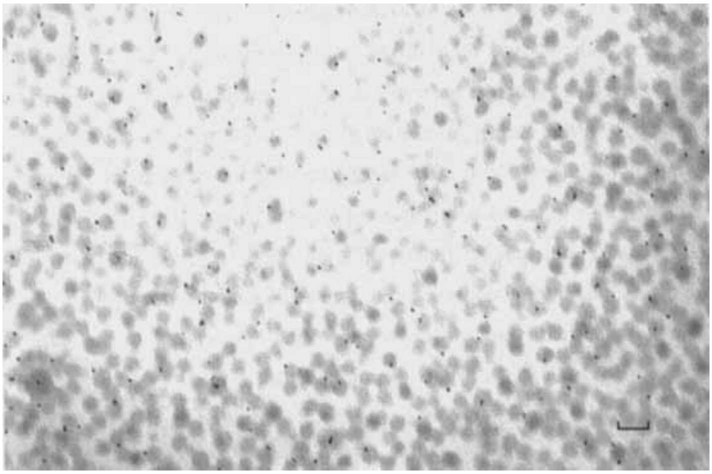

FIGURE 3 TEM micrograph for palladium nanoparticles generated in the presence of PS-b-PEO by stirring the solution at room temperature using a solvent mixture tetrahydrofuran : ethanol = 1 : 2 (v/v) (Bar = 53 nm). The gray areas stem from the polymer micelles, whereas the black dots depict the palladium nanoparticles.

Further results also underscore the importance and influence of side products, stemming, for instance, from the reducing agent. The samples reduced by sodium hypophosphite, for example, showed increased values for the catalytic conversion. In the literature it is reported that systems combining NaH_2PO_2 or phosphinic or phosphorous acid with palladium are efficient catalysts for hydrogenations at mild conditions[16-18]. Therefore, it is likely that the side products stemming from the reducing agent here have a similar promoting effect on the catalytic activities.

Latices as carriers

Various latex dispersions have been investigated for their ability to immobilize metal nanocatalysts, and their utility as components in catalytically-active systems. Several advantages are expected from the use of latex carriers: (i) the carrier could prevent the agglomeration of the nanoparticles during storage and application, (ii) it could also offer an opportunity to combine the properties stemming from supported and polymer-protected nanocatalysts, (iii) it could allow a broader selection of "functional" polymers, and (iv) the latex surface could offer an additional option to influence and tune the catalyst properties.

The latex carriers can be incorporated into a three-component catalyst system, which contains the following components[11]:

(i) the latex as the carrier which prevents agglomeration of the nanoparticles and can influence the catalytic properties of the system,

(ii) the metal nanoparticles as the catalytically-active parts which are immobilized,

(iii) a protective polymer which controls the catalytic properties and stabilizes the dispersion.

Immobilized metal nanoparticles can be prepared in-situ in a simple way, by absorption from solution. Two trends can be observed from these results. More hydrophobic latex types resulted in a higher tendency of immobilization of the platinum nanoparticles. Also, the more rapid reduction by potassium tetrahydroborate resulted in a lower tendency for immobilization of the particles. All samples exhibited high catalytic activity for the conversion of cyclohexene. As an example, Fig. 4 depicts a TEM micrograph for platinum nanoparticles immobilized on poly(N-vinyl-2-pyrrolidone-styrene) latex, reduced from H_2PtCl_6 precursor by refluxing an alcoholic solution. The immobilization of the platinum nanoparticles (black dots) on the latex particles can be clearly recognized.

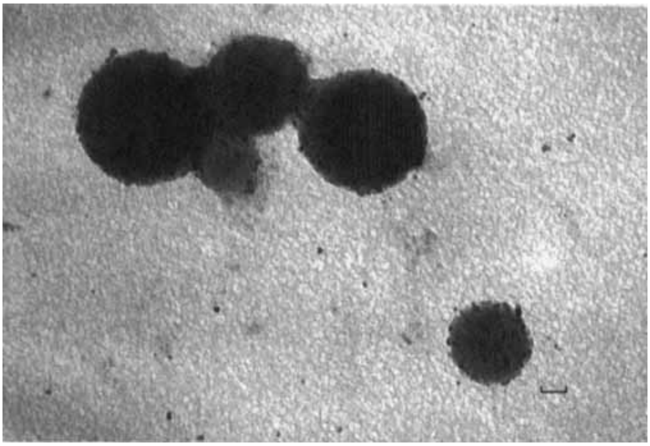

FIGURE 4 TEM micrograph for platinum nanoparticles generated from H_2PtCl_6 in the presence of poly(N-vinyl-2-pyrrolidone-styrene) latex by refluxing an alcoholic solution (Bar = 19 nm).

An additional polymer was added to several samples which contained immobilized metal particles, and the resulting three-component systems were tested as hydrogenation catalysts as well. Even after these steps the immobilization of the metal particles remained preserved. Several additional polymer types were used, specifically one representative of a water-soluble, nonionic homopolymer [poly(N-vinyl-2-pyrrolidone)], of a cationic polyelectrolyte [poly(diallyldimethyl ammonium chloride)], and of a polyacid [poly(styrene sulfonic acid)]. These polymers were added in different amounts, and the results for the catalytic investigations for a representative series are given in Table VI for platinum nanoparticles prepared by the alcohol reduction method.

TABLE VI Platinum nanoparticles immobilized on poly(vinyldene chloride) latex, in the presence of additional polymers: catalytic hydrogenation of cyclohexene

	% Cyclohexane		
Protective polymer Mass ratios:	10:1	25:1	50:1
None	85.3	-	-
Poly(N-vinyl-2-pyrrolidone)	74.6	70.7	71.8
Poly(diallyldimethyl ammonium chloride)	46.0	36.5	25.3
Poly(styrene sulfonic acid)	89.9	99.9	100

The same trends were found as for the non-immobilized, colloidal platinum nanocatalysts which are protected by these types of polymers, that is, increased catalytic conversion for the use of a polyacid, and decreased catalytic conversion for the use of a cationic polyelectroyte. In addition, these trends seem to be increased with the use of larger portions of the polymers.

This demonstrates that such three-component catalyst systems involving latex carriers can offer intriguing routes for tuning catalyst properties. Such properties can be varied by a number of factors, including the type of the protective polymer, the type of the latex carrier, and the mass ratio of protective polymer : platinum nanocatalyst.

SUMMARY

Polymer-protected noble metal nanocatalysts are highly promising for the design of novel catalyst systems, exhibiting a number of advantages. The nanoparticle features and colloidal stability can be controlled by several parameters, such as the choice of the protective polymer, the preparation methods, and the metal precursors. The catalytic properties can be tuned in a similar way, for instance, by variation of the protective polymer, the support material or various by-products. Such high versatility of these polymer-metal composite materials is intriguing, and seems promising for further developments of tailored and selective catalysts.

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