Polymer Bulletin 37, 683–690 (1996)

Polymer Bulletin

Polymer-protected, colloidal platinum nanocatalysts

A. B. R. Mayer*, J. E. Mark

Department of Chemistry and Polymer Research Center, University of Cincinnati,
Cincinnati, OH 45221-0172, USA

Received: 7 June 1996/Accepted: 7 July 1996

Summary

Several stable colloidal platinum nanocatalysts were prepared by in-situ reduction of hexachloroplatinic acid H_2PtCl_6, and were protected by various water-soluble homopolymers and random copolymers as well as cationic polyelectrolytes. The particle sizes, morphologies, and size distributions were determined by transmission electron microscopy (TEM), and the catalytic activity of the platinum nanoparticles was tested by the hydrogenation of cyclohexene. The type of protective polymer and its properties strongly influence the catalytic activity by creating a certain "environment" surrounding the catalytically-active nanometal. Thus, careful selection of the protective polymer plays an important role in the development of tailored metal-polymer catalyst systems.

Introduction

Colloidal noble metals are recently receiving increased attention since they can be especially useful for many technological applications. For instance, colloidal gold and silver nanoparticles exhibit interesting optical properties. Depending on their nanosize, shape, and agglomeration such colloids show different colors and this has been used for coloring glass for a long time (1). Also, colloidal nanosized semiconductive or magnetic materials are of high technological interest (2-5), and very important and promising application of noble metal colloids is in catalysis. For instance, due to their high surface area and special surface properties (amorphous or nanocrystalline), very active and/or selective metal-polymer catalyst systems can be obtained (6,7). It can also be expected that the protective polymer surrounding the catalytically active metal nanoparticle can additionally influence the activity and/or selectivity of various catalytic reactions. For example, Hirai and Toshima (8) have described the importance of the polymer type for polymer-anchored, complex metal catalysts. In the present study, it is suggested that the selection of the polymer type is similarly crucial for polymer-protected, colloidal metal

---

* Corresponding author

nanocatalysts. Therefore, it is necessary to investigate a wide variety of different types of protective polymers and their influence on the catalytic properties of these novel nanocatalysts.

Polymer-protected metal colloids are usually prepared by various in-situ reactions involving suitable metal precursors, such as chemical reductions, photoreductions, or thermal decompositions. The goal is to obtain small particle sizes and narrow size distributions. The choice of the polymer can influence not only the stability of these colloids but also the particle sizes and morphologies.

Generally, the polymers used for such systems should fulfill some or possibly all of the following requirements:

(i) Of course, they should be soluble in the solvents and be thermally stable at the temperatures used during the preparation and technical application of the resulting colloids.

(ii) They should have a good protective function for the stabilization of metal colloids (8) and thus have good interactions with the metal surface.

(ii) Ideally, there should also be the possibility for interaction with the metal precursor, e.g., by ion-pair or complex formation.

Various types of polymers with different "functions", i.e. properties that can influence the outcome of catalytic reactions, should be available and therefore investigated. In this way entire metal-polymer catalyst systems could be tailored for certain applications by having the opportunity to "tune" the catalytic activity and/or selectivity.

For this work several polymer types have been selected for investigation with respect to their influence on the catalytic activity of polymer-protected, colloidal platinum nanoparticles. The idea is that certain properties stemming from the protective polymer can create special "environments" surrounding the catalytic sites of the metal. This, in turn, should have a tremendous effect on the outcome of catalytic reactions:

(i) One group consists of water-soluble homopolymers and random copolymers possessing a hydrophobic backbone to interact with the hydrophobic metal surface, and hydrophilic side-groups to interact with the dispersion medium (8). The stabilization of the metal colloid with such flexible polymers is based on steric effects (9,10). Due to the steric hindrance provided by the polymer to reactants approaching the catalytically active metal surface, selective catalytic reactions can be achieved (9,11-14). Polymers of this type which have usually been used so far are poly(1-vinylpyrrolidone), poly(vinyl alcohol) and amphiphilic block copolymers. In this work, a broader variety of polymers, including e.g. polyacids, have been tested as components for these novel catalytic systems. Also, it can be expected that different degrees of hydrophobicity of the polymers can create different hydrophobic "environments" surrounding the nanocatalyst, and this can again influence the catalytic activity and selectivity of certain reactions involving species with different degrees of hydrophobicities (8).

(ii) Another group consists of cationic polyelectrolytes, and these offer the advantage of combining both steric and electrostatic stabilization of the metal colloids (10). A good interaction with the platinum precursor, here the hexachloroplatinic acid anion, by ion-pair formation is provided as well (15). Thus, small particle sizes and narrow size distributions can be expected for this type of protective matrix. It can also be expected that the electrostatic environment created by this type of polymer surrounding the catalytically-active metal nanoparticles can strongly influence the catalytic activity and/or selectivity of the nanocatalyst system (8). This could be especially important for reactions involving polar or charged species.

Several platinum colloids in the presence of these types of polymers described above have been prepared from hexachloroplatinic acid H_2PtCl_6 precursor by refluxing the alcoholic solutions. The particle sizes, morphologies, and size distributions were investigated by transmission electron microscopy (TEM). The catalytic activities of the platinum colloids was tested and compared to one another, using the hydrogenation of cyclohexene as a model reaction. Final conversions of up to 100% could be obtained for these colloidal platinum nanocatalysts. Important differences in the catalytic activity, depending on the type of protective polymer (e.g. cationic polyelectrolyte or polyacid), have been found.

Experimental

Chemicals and reagents: Hexachloroplatinic acid H_2PtCl_6 and platinum on activated carbon (Pt 5 %) were obtained from Aldrich. The polymers and cationic polyelectrolytes were purchased from Aldrich and Polysciences.

Colloid preparation: The platinum colloids were prepared according to the method described by H. Hirai et al. (8,16). The platinum precursor H_2PtCl_6 was reduced by refluxing the alcoholic solutions (6.8×10^{-4} M, ethanol : water = 1 : 1) containing the polymers or polyelectrolytes in a mass ratio of polymer : platinum = 25 : 1.

Characterization: Transmission electron microscopy was used to obtain the particle size, morphology, and particle-size distribution of the metal nanoparticles. The samples were prepared by placing a drop of the colloid on a carbon-coated copper grid and letting the solvent evaporate. The particle sizes were measured with a comparator and the average particle sizes and size distributions were determined based on the measurement of at least 190 particles.

Catalytic hydrogenations: The hydrogenations were carried out with a Parr hydrogenation apparatus at room temperature. For the direct comparison of the catalytic activities, cyclohexene (0.05 ml) was added to 10 ml methanol and the platinum catalysts were added as a colloidal dispersion. In this case an amount of catalyst that corresponds to 0.16 wt% platinum (with respect to cyclohexene) was added (0.5 ml colloidal dispersion) and the reaction was performed at a hydrogen pressure of 10 psi for 30 minutes. For the determination of the final conversions, cyclohexene (0.1 ml) was added to 20 ml methanol, and the platinum catalysts were added either as a colloidal dispersion or as a solid after evaporation of the solvent. In this case an amount of catalyst that corresponds to 0.8 wt% platinum (with respect to cyclohexene) was added (5 ml colloidal dispersion) and the reaction was performed at a hydrogen pressure of 35 psi. Depending on the catalytic activities different reaction times were necessary to obtain conversions up to 100 %. The reaction mixtures were analyzed by gas chromatography (SE-30 packed column) with a flame ionization detector, and helium as the carrier gas.

Results and discussion

A listing of some of the polymers and polyelectrolytes investigated is given in Table 1. Also presented are the average particle diameters (and standard deviations) of the platinum nanoparticles as obtained by TEM, along with results for the catalytic hydrogenations of cyclohexene. As can be seen, a wide variety of protective polymers can be used to obtain stable platinum colloids with particle diameters below 10 nm. A restricted hydrophobic character of the polymer backbone results in less stable platinum colloids, larger particle diameters (20 - 40 nm), and broader size distributions. In the case of several cationic polyelectrolytes based on quaternary ammonium side-groups, very stable platinum colloids with particle diameters below 5 nm and narrow size distributions were obtained. Cationic polyelectrolytes with side groups based on primary ammonium groups or side-groups involving a nitrogen with partial positive charge, as in poly(4-vinylpyridine-N-oxide), were investigated as well. In these cases, however, stronger complexes with the precursor platinum ion are formed so that the reduction to the zerovalent platinum metal cannot be achieved by mild reduction methods (such as refluxing alcoholic solutions) (8).

The catalytic activities listed in Table 1 show that many of the platinum-polymer catalyst systems exhibit activities comparable to commercial platinum on activated carbon (Pt 5 %). In all cases conversions up to 100 % were eventually obtained. This shows that there are no significant poisoning effects, e.g. stemming from the protective polymer, influencing the results.

For the well stabilized colloidal platinum catalysts, e.g. with poly(1-vinyl pyrrolidone), poly(1-vinyl pyrrolidone-co-vinyl acetate), or poly(2-ethyl-2-oxazoline), the catalytic activities are maintained after storage of the colloids in air for several weeks. Polymers possessing a less hydrophobic backbone, such as poly(2-hydroxypropyl methacrylate) or poly(methylvinylether-co-maleic anhydride), result in larger particle sizes and less stable colloids. In these cases the particle sizes change during storage and after longer times partial precipitation of the platinum metal can occur. This, of course, has an influence on the catalytic activity, which therefore underlies fluctuations to a much larger extent. In these cases of poorer stabilization stemming from poorer attachment and

Table 1: Particle Sizes and Catalytic Activities of Polymer-Protected Platinum Nanocatalysts

Polymer/ Polyelectrolyte	Average Particle Size (Standard Deviation)	Catalytic Activity % Cyclohexane [a)]	Final Conversion % Cyclohexane [b)]
5% Platinum on activated carbon	-	65.4	100
Poly(1-vinyl pyrrolidone) Av. mol. wt. 360,000	2.7 nm (1.5)	73.0	100
Poly(2-ethyl-2-oxazoline) Av. mol. wt. 200,000	2.6 nm (0.81)	55.8	100
Poly(1-vinylpyrrolidone-co-vinyl acetate)	2.2 nm (0.41)	61.7	100
Poly(2-hydroxypropyl-methacrylate)	~ 30 nm [c)]	64.5 [d)]	100
Poly(methylvinylether-co-maleic anhydride)	~ 40 nm	42.7 [d)]	100
Poly(methacrylic acid)	1.5 nm (0.45)	100	100
Poly(1-vinylpyrrolidone-co-acrylic acid)	2.4 nm (0.84)	80.1	100
Poly(styrene sulfonic acid)	2.3 nm (0.89)	80.9	100
Poly(2-acrylamido-2-methyl-1-propane sulfonic acid)	2.0 nm (0.97)	100	100
Poly(vinyl phosphonic acid)	1.6 nm (0.43)	100	100

Table 1, Cont.: Particle Sizes and Catalytic Activities of Polymer-Protected Platinum Nanocatalysts

Polymer/ Polyelectrolyte	Average Particle Size (Standard Deviation)	Catalytic Activity % Cyclohexane [a]	Final Conversion % Cyclohexane [b]
Poly(diallyldimethyl ammonium chloride)	1.8 nm (0.68)	22.4	100
Poly(methacrylamido-propyltrimethyl ammonium chloride)	1.4 nm (0.40)	22.7	100
Poly(3-chloro-2-hydroxy-propyl-2-methacryloxy-ethyldimethyl ammonium chloride)	1.7 nm (0.84)	27.3	100

[a] Hydrogenation conditions: 10 ml methanol, hydrogen pressure 10 psi, 0.16 wt% platinum, hydrogenation time 30 min, room temperature

[b] Hydrogenation conditions: 20 ml methanol, hydrogen pressure 35 psi, 0.8 wt% platinum, room temperature

[c] Agglomerates of about 30 nm diameter containing particles of initial ~ 4 nm diameter

[d] Value for freshly prepared platinum colloid

interaction of the protective polymer with the catalytically-active metal surface, the particle size seems to play a role with respect to catalytic activities. It can be assumed that the formation of larger agglomerates due to the poor stabilization by such polymers eventually leads to a decrease of the catalytic activity of these systems. In the case of poly(methylvinylether-co-maleic anhydride), for instance, the catalytic activity drops from 42.7 % for the freshly prepared colloid to about 30 % after storage for approximately 3 weeks. Therefore, such polymers with a lower protective function for the stabilization of metal colloids are less suitable for obtaining catalyst systems with constant activities.

The catalytic activities in Table 1 furthermore show the very high catalytic activities of platinum-polymer systems incorporating polyacids. The activities even exceed the one exhibited by the commercial platinum on activated carbon (Pt 5 %). In the case of stable colloids, e.g., for poly(vinyl phosphonic acid) as protective matrix, the catalytic activity is maintained even after storage for several months. It is suggested that the formation of weak complexes involving the acid-groups is responsible for the high activities in these cases.

In contrast, the catalytic activities are lower for platinum-polymer systems involving cationic polyelectrolytes, even though the platinum nanoparticles have very small particle sizes. It has to be pointed out that also in these cases conversions up to 100 % can be obtained, suggesting the absence of poisoning effects (possibly stemming from the polyelectrolyte). An explanation is that the electrostatic "environment" created by the polyelectrolytes surrounding the catalytically-active metal has a crucial effect on the catalytic activity of these systems. Here, the hydrophobic reactant cyclohexene has to pass through this electrostatic "environment" in order to approach the platinum surface for the catalytic reaction to occur. In addition, the positively charged polyelectrolyte surrounding the catalysts surface can further modify the catalytic activity and selectivity, e.g., by causing the polarization/ionization of hydrogen sorbed by the metal catalyst.

These examples show clearly that the catalytic activities of such polymer-protected, colloidal nanoparticles are not entirely ruled by their particle sizes and morphologies. The selection of the protective matrix with its special "functions" and properties is at least of equal importance for the tailoring of such catalyst systems. Thus, different protective polymers allow the introduction of various properties into the catalytic systems, depending on the function the polymer needs to fulfill in combination with the catalytically-active metal. Polymer-protected, colloidal metal nanocatalysts can be regarded as metal-polymer systems that can offer options to "tune" the catalyst activities and/or selectivities for a variety of applications.

Conclusions

Various homopolymers, copolymers and cationic polyelectrolytes are suitable for the preparation of stable platinum colloids which are catalytically active for the hydrogenation of cyclohexene. Conversions up to 100 % can readily be obtained. In many cases the catalytic activities are comparable to commercial platinum on activated carbon (Pt 5 %) catalyst. In addition, the selection of the protective polymer can not only influence the metal particle size and morphology (in combination with the reduction method chosen) but can also have a tremendous influence on the catalytic activities of the metal-polymer systems. Therefore, with the selection of protective polymers carrying certain "functions", a huge variability can be achieved for the "tuning" and development of tailored metal-polymer nanocatalysts.

In this context, the investigation of chiral polymers should be highly interesting. The asymmetric "environment" created by such polymers surrounding the nanocatalyst could have a large influence on enantioselective catalytic reactions.

Acknowledgments

We would like to thank Professor R. Morris, Department of Cell Biology, Neurobiology and Anatomy, University of Cincinnati, for his support in performing the transmission electron microscopy, and Professor A. Pinhas, Department of Chemistry, University of Cincinnati, for his help in analyzing the hydrogenation mixtures by gas chromatography. The financial support for this research was provided by the National Science Foundation (Grant DMR-9422223, Polymers Program, Division of Materials Research).

References

1. Puddephatt RJ (1978) The Chemistry of Gold. Elsevier Scientific Publishing Company, Amsterdam
2. Moffitt M, Eisenberg A (1995) Chem Mater 7: 1178
3. Moffitt M, McMahon L, Pessel V, Eisenberg A (1995) Chem Mater 7: 1185
4. Cummins CC, Schrock RR, Cohen RE (1992) Chem Mater 4: 27
5. Yue J, Sankaran V, Cohen RE, Schrock RR (1993) J Am Chem Soc 115: 4409
6. Bönnemann H, Brijoux W, Joussen T (1990) Angew Chem Int Ed Engl 29: 273
7. Bönnemann H, Brijoux W, Brinkmann R, Fretzen R, Joussen T, Köppler R, Korall B, Neiteler P, Richter J (1994) J Mol Cat 86: 129
8. Hirai H, Toshima N (1986) In: Iwasawa Y (ed) Catalysis by Metal Complexes, Tailored Metal Catalysts. D. Reidel Publishing Company, Dordrecht
9. Bradley JS (1994) In: G. Schmid (ed) Clusters and Colloids. From Theory to Applications. VCH, Weinheim
10. Napper DH (1983) Polymeric Stabilization of Colloidal Dispersions. Academic Press, London
11. Hirai H, Chawanya H, Toshima N (1981) Makromol Chem, Rapid Commun 2: 99
12. Toshima N, Yonezawa T, Kushihashi K (1993) J Chem Soc, Faraday Trans 89: 2537
13. Hirai H, Chawanya H, Toshima N (1985) Reactive Polymers 3: 127
14. Antonietti M, Wenz E, Bronstein L, Seregina M (1995) PMSE Preprints 73: 283
15. Warshawsky A, Upson DA (1989) J Pol Sci: Part A: Pol Chem 27: 2963
16. Hirai H, Nakao Y, Toshima N (1979) J Macromol Sci A13: 727