

Micron-sized membrane reactors: Multicompartment semipermeable polymer particles containing palladium nanoparticles

Douglas R. Robello,* Mark R. Mis, Mridula Nair

Kodak Technology Center, Eastman Kodak Company, Rochester, New York 14650-2109

*Present address: Orthogonal, Inc., 1999 Lake Avenue, Rochester NY 14650

Correspondence to: M. Nair (E-mail: mridula.nair@kodak.com)

ABSTRACT: Multicompartment polymer microparticles are prepared encapsulating palladium nanoparticles within closed-shell compartments, using a double-emulsion ($W_1/O/W_2$), evaporative limited coalescence process. The encapsulation efficiency in some cases is as high as 99%, and very little Pd leaches from the particles. The Pd nanoparticles dispersed in an aqueous environment within the closed-shell compartments of the microparticles catalyze hydrogenation reactions of low molar mass substrates in water at substantial rates. The microparticle walls serve as semipermeable membranes, permitting diffusion of small molecules into the compartments while retaining the larger metal nanoparticles. The microparticles can be reused after simple filtration. The catalytic activity increases on recycling, possibly because of plasticization of polymer walls by the reactant and products, resulting in increased diffusion. In a second demonstration of catalytic activity, the microparticles efficiently decompose hydrogen peroxide. These nanoparticle-containing microparticles serve as convenient, reusable catalyst carriers, and prevent inadvertent human and environmental contact with nanoparticles. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42021.

KEYWORDS: applications; catalysts; colloids; double emulsion; encapsulation; hydrogenation; palladium nanoparticles; polymer microparticles; $W/O/W$; water-in-oil-in-water

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INTRODUCTION

Recently, researchers at Kodak devised a scalable method for producing highly porous uniform polymer microparticles (Figure 1) containing closed-cell pores via water-in-oil-in-water ($W_1/O/W_2$) double emulsions in combination with the evaporative limited coalescence (ELC) process. This method provides simultaneous control of micrometer- and submicrometer-sized features of the microparticles, has been scaled to make kilogram quantities in manufacturing, and is amenable to the incorporation of addenda in closed multicompartment.¹ Although this technology was initially developed to provide tailored electrophotographic toner, such multicompartment microparticles can be useful for a variety of applications. Essentially, the $W_1/O/W_2$ process efficiently entraps one aqueous phase within another, allowing for the encapsulation of water-borne substances useful in medicine, agriculture, foods, personal care products, chemical processes, and so forth. On one hand, such microparticles might enable the confinement of substances within the particles and their release in a controlled manner.² On the other hand, the work described herein focuses on a second class of applications, in which the guest substance is permanently encapsulated in these multicompartment uniform microparticles.

We thought that chemical catalysts might be useful substances to encapsulate permanently. Our research was inspired by a paper by Parthasarathy and Martin,³ who reported a process for confining enzymes and metal nanoparticles in polypyrrole microtubes, and subsequent use of these microtubes to catalyze reactions. Although their encapsulation method was highly impractical, their work did show that the relatively large catalytic substances could be retained in polymer carriers while still allowing for diffusion and reactions of small molecules. Along these lines, we envisioned that multicompartment polymer microparticles with entrapped catalytic substances might act as many small membrane reactors. The walls might be made selectively permeable by optimizing their thickness and selecting an appropriate polymer. The particles might then catalyze reactions of reagents in the external aqueous phase as illustrated in Figure 2. The relatively large catalysts would not diffuse through the walls, and therefore would be retained. However, low molar mass reactants might freely diffuse through the walls, where they would encounter the catalyst in an internal aqueous environment and undergo a chemical reaction. The product of the reaction (also a small molecule) would then diffuse back into the external phase.

This catalyst carrier scheme presents many advantages:

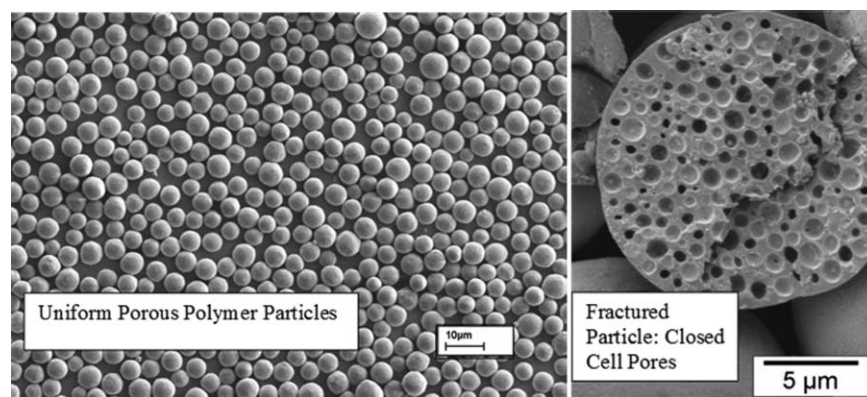


Figure 1. SEM images of spherical porous microparticles made by a double emulsion, ELC process. Photomicrographs taken from Ref. 1, used with permission, © Elsevier 2014.

1. Rapid reactions because the high surface area of the microparticles facilitates diffusion of reactants to and products from the catalysts.
2. Uniform diffusion rates for all particles because of the relatively narrow particle size distribution of the microparticle and their compartments.
3. A primarily aqueous process.
4. Easy recovery and reuse of expensive catalysts.
5. Adaptability to flow reactors.
6. Demonstrated scalability of multicompartiment microparticle synthesis from laboratory to manufacturing scale.¹
7. A simple process using conventional equipment and inexpensive materials (other than the catalysts).
8. Many different polymers can be used as binders.¹
9. More than one kind of catalyst, or functional materials other than catalysts, can be encapsulated in different particles, or even in separate compartments within the same particle.⁴

Among possible catalysts, we decided to investigate metal nanoparticles because these materials have been demonstrated to

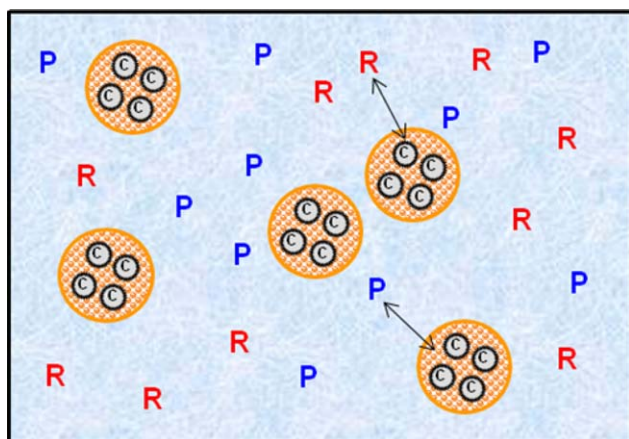


Figure 2. Schematic showing the catalytic reaction system in multicompartiment microparticle-catalyst carriers (not drawn to scale). The semi-permeable membrane material is illustrated in orange, the reactants, products, and encapsulated catalysts are denoted as “R,” “P,” and “C,” respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

promote many industrially important chemical processes. For example, palladium nanoparticles are reported to catalyze Heck and Suzuki reactions in both organic and aqueous media.^{5–11} Of particular relevance to this work are reports showing that palladium nanoparticles catalyze hydrogenations^{12,13} similar to the conventional supported palladium catalysts such as Pd/C.

However, there are significant drawbacks to the use of metal nanoparticles for catalysis. Because precious metals are usually involved, recovery, and reuse are important practical considerations. Unfortunately, the extremely small nanoparticles are difficult to isolate by filtration or centrifugation; therefore, recycling is inconvenient. Perhaps more important, there are serious concerns about health and environmental effects of nanoparticles, particularly in industrial settings.¹⁴ There is an unmet need for a system that allows for convenient recovery and reuse of these expensive catalysts, as well as one that protects people and the environment from their potential adverse effects yet retains high catalytic activity.

Encapsulating the nanoparticles in polymer media seemed to offer a promising approach to such problems, and several previous researchers have attempted to do this. Xu *et al.*¹⁵ described a system in which an emulsion polymerization was performed to form spherical particles (ca. 400 nm diameter) with some inner structure. They subsequently imbibed PdCl₂ into their microparticles, and chemically reduced the metal ions to form Pd nanoparticles within the polymer particles. These Pd containing particles successfully catalyzed the hydrogenation of nitrobenzene in water, and could be recycled by extraction. However, these particles were not made using a standard double emulsion process, and the amount of metal loading was limited by the ion-exchange capacity of their particles and the facility to perform the particle-forming process within the particles themselves. Also, these particles are too small for convenient isolation.

Using a similar process, Crooks *et al.*¹⁶ created and entrapped palladium nanoparticles inside dendrimers, but, of course, these dendrimers are only a few nm in diameter, and cannot be conveniently isolated and recycled.

The double emulsion process discussed here specifically creates uniform particles greater than 1 μm in diameter containing multiple closed-shell compartments; such particles are easily

recoverable by filtration and centrifugation. Furthermore, the process allows for the encapsulation of arbitrary aqueous solutions or dispersions in the compartments. Unlike many previous techniques, the steps of nanoparticle synthesis and encapsulation would be decoupled. Any nanoparticle that can be dispersed in water might be encapsulated. In addition, the flexibility of this process should allow for optimization of the permeability of the microparticles.

Herein, we report successful encapsulation of palladium nanoparticles inside the closed-shell compartments of uniform polymer microparticles made of polycaprolactone, and demonstrate the utility of these microparticles as catalysts for some simple hydrogenation reactions of low molar mass compounds.

EXPERIMENTAL

Materials

Palladium chloride, polycaprolactone (PCL, 45 kDa), and poly(vinyl pyrrolidone) (55 kDa) were obtained from Aldrich Chemical Company. Methoxy(polyethylene oxide)-*b*-polycaprolactone copolymer with a molecular weight of 25 kDa, in which the methoxy(polyethylene oxide) had a molecular weight of 5 kDa, was made via a standard ring opening polymerization of polycaprolactone with methoxy(polyethylene oxide) in the presence of stannous octoate catalyst. Carboxymethyl cellulose (CMC, 250 kDa as the sodium salt) was obtained from Acros Organics. The colloidal silica NALCO 1060™ was obtained from Nalco Chemical Company as a 50 wt % dispersion in water. Poly(methylamino ethanol adipate) oligomer was used to promote the adsorption of silica to the surface of the oil droplet, and was prepared by condensation polymerization of amino ethanol and adipic acid.

Instrumental

Optical and scanning electron microscopy (SEM) were used to characterize the emulsions and the resultant polymer microparticles. The size of the palladium containing multicompart ment microparticles was determined using the Sysmex FPIA-3000 automated particle size analyzer from Malvern Instruments.

The hydrogenation reactions were analyzed using a HP 6890 Gas Chromatographic system equipped with a Rxi®-5ms columns (fused silica) (Restek, Bellefonte, PA) and a flame ionization detector. The method used was a 20 minutes ramp from 40°C to 320°C with the inlet at 170°C and detector at 300°C.

Elemental Analysis for Palladium

Suspensions of microparticles were thoroughly mixed and aliquots withdrawn promptly to minimize sampling errors. The samples were prepared by digesting them with a mixture of sulfuric, hydrochloric, and nitric acids. The Pd content was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Synthesis of Palladium Nanoparticles: Representative Procedure^{17,18}

All glassware was washed with aqua regia then thoroughly rinsed with deionized water. A 2.0 mM solution of H₂PdCl₄ was prepared by mixing 0.106 g (0.60 mmol) of PdCl₂ and 6 mL of 0.2M aqueous HCl, then diluting with deionized water to a total volume of 250 mL. This procedure was repeated to provide sufficient solution for the next step. A mixture of 300 mL of the H₂PdCl₄

solution, 420 mL of deionized water, 1.334 g poly(vinyl pyrrolidone) (~20 : 1 monomer : Pd), and 80 drops of 1.0M aqueous HCl was heated to reflux. Once reflux began, the mixture was removed from heat and 280 mL of ethanol was added. Immediately the reaction mixture turned brown. The reaction mixture was returned to reflux, held for 3 h, then cooled to ambient, neutralized with NaOH, and most of the water removed at reduced pressure. The resulting nanoparticles were isolated by repeated resuspension in 50% aqueous acetone, followed by centrifugation at 3000 rpm for 30 min. The product was obtained as 0.7332 g of a brown powder.

Preparation of Palladium Containing Multicompart ment Polycaprolactone Microparticles: Representative Procedure

A first water phase (W₁) was prepared using 44.2 g of a 2.3 wt % of a carboxy methyl cellulose sodium salt solution in water along with 8.6 g of a 0.12 wt % Pd nanoparticle solution in water. The oil phase was made using 46.6 g of a 23.6 wt % solution of polycaprolactone in ethyl acetate, 11.6 g of a 23.7 wt % solution of methoxy(polyethylene oxide)-*b*-polycaprolactone copolymer in ethyl acetate, and 113.6 g of ethyl acetate. To this oil phase was added the W₁ phase followed by mixing with a Silverson L4R Mixer fitted with a small holed disintegrating head. The resulting W₁/O phase was further homogenized using a Microfluidizer model 110T from Microfluidics at a pressure of 8000 psi. This W₁/O emulsion was added to a water phase (W₂) comprising 11.7 g of a 50 wt % solution of Nalco 1060 colloidal silica in water, 357.8 g of a pH 4 citrate/phosphate buffer, and 5.8 g of a 10 wt % solution of poly(methyl amino ethanol) adipate in water. The resulting mixture was homogenized with a Silverson L4R Mixer fitted with a large holed disintegrating head followed by an orifice homogenizer at 1500 psi. The ethyl acetate was evaporated using a Buchi ROTA VAPOR RE120 evaporator at 40°C under reduced pressure to yield microparticles containing Pd nanoparticles in discrete compartments within the particles. The microparticles were washed on a glass frit funnel, and stored as a suspension in distilled water. The mode particle size as measured by Sysmex FPIA-3000 was 5.3 μm. Figure 3 is an SEM of these microparticles.

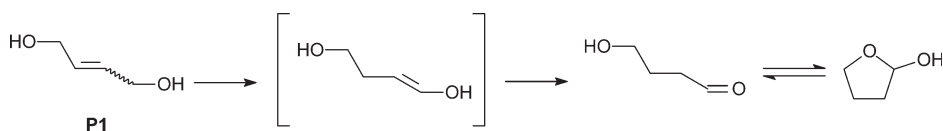
Hydrogenation: Representative Procedure

2-Butyne-1,4-diol (1.0 g, 12 mmol) was dissolved in a mixture of 15 mL water and 10 mL of an aqueous microparticle suspension (3.9% solids, Pd content approximately 26 μg) in a 500 mL heavy-walled glass bottle. The mixture was deaerated by repeatedly pressurizing to 35 psi with nitrogen, then evacuating. Hydrogen was introduced at 48 ± 2 psi, and the mixture shaken continuously at ambient temperature. Note that hydrogen was supplied from a relatively large reserve cylinder, and the pressure did not change noticeably during the course of the reaction. Periodically, small aliquots were removed for GC analysis; afterwards, the mixture was returned to the hydrogenation apparatus following the aforementioned procedure. GC samples were filtered through 0.45 mm PVDF membranes before injection.

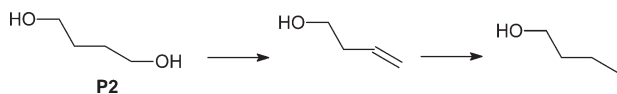
Catalytic Microparticles Recycling Procedure

The reaction mixture after a hydrogenation reaction with Pd-entrapped Pd nanoparticles was centrifuged at 5000 rpm for 10 min to sediment the microparticles. The supernatant was

slower rate. Additionally, the metal apparently catalyzed double bond migration of **P1**, in that a minor amount of the byproduct 2-hydroxytetrahydrofuran was also formed (identity confirmed by GC-MS), but only after a significant amount of **P1** had been produced.



N-Butanol was detected as another byproduct in small amounts after prolonged reaction, possibly via dehydration of **P2** and subsequent hydrogenation.

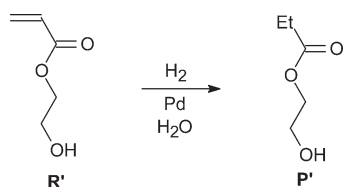


Approximately the same relative amounts of these two byproducts were formed in the hydrogenation of **R** regardless of the Pd catalyst used: Pd containing microparticles as described below, unencapsulated Pd nanoparticles, or a conventional Pd/C catalyst. Apparently, the overall chemistry seems to depend upon the metal itself and not its local environment.

The hydrogenations were performed in aqueous solutions containing suspensions of microparticles. Progress was monitored by periodically analyzing the reaction mixture by GC. For example, Figure 4 shows GC data for the stepwise hydrogenation of **R** → **P1** → **P2**.

As expected, the microparticles containing the larger concentration of catalyst led to faster hydrogenation (Figure 5). The estimated initial turnover frequencies for the two batches were 2400 and 2900 h⁻¹, respectively, in this case. A control experiment using similar PCL microparticles but without palladium showed no hydrogenation of **R** at all.

To demonstrate the generality of the catalytic activity of the Pd containing microparticles, a different hydrogenation reaction was performed using 2-hydroxyethyl acrylate (**R'**).



The same two batches of microparticles were tested, and results similar to the previous experiments were obtained (Figure 6). The microparticles with the higher level of Pd were very effective catalysts; the reaction was complete within 1 h. Those carrying less Pd catalyzed this hydrogenation at a slower but still substantial rate. The estimated initial turnover frequencies for the two batches were >5900 and 8100 h⁻¹, respectively. The first value represents a lower limit, because the reaction was complete by the time the first data point was taken, therefore the initial slope is not known.

Comparison of Catalytic Activity of Palladium Containing Microparticles with Free Palladium Nanoparticles. Comparisons were made to the same reactions using free (i.e., untrapped) Pd nanoparticles (Figure 7). Judging from the initial turnover frequencies (TOF, Table I), the rate of hydrogenation

using the Pd-entrapped microparticles was about 20% that of a reaction carried out with the same amount of freely suspended (i.e., unencapsulated) palladium nanoparticles. This result suggests that the diffusion of the reactants into the compartments of the particles slows the overall conversion, but the reaction still proceeds at a substantial rate.

Catalytic Activity of Palladium Containing Microparticles on Storage and Recycling. The above hydrogenation reaction with the microparticles containing 48 μg Pd/g of dry microparticle was repeated with the same materials at the same concentrations 3 months later, and virtually identical results were obtained (Table I). The microparticles had been stored between reactions suspended in water in a closed bottle at room temperature. This result indicates that the catalytic activity of the entrapped Pd nanoparticles is preserved for long periods of time within the PCL microparticles. Also, the observation that the reaction rate did not increase on storage in water suggests that the Pd nanoparticles did not escape in significant amounts from the microparticles, because free nanoparticles are significantly more active catalysts than entrapped nanoparticles (see above). These results are in agreement with elemental analysis of the external aqueous phase after storage, as mentioned above.

The facility for recycling the catalytic Pd containing microparticles was demonstrated in a series of hydrogenations in which the microparticles were isolated, washed, and reused. Surprisingly, the rate of reaction increased substantially on each cycle

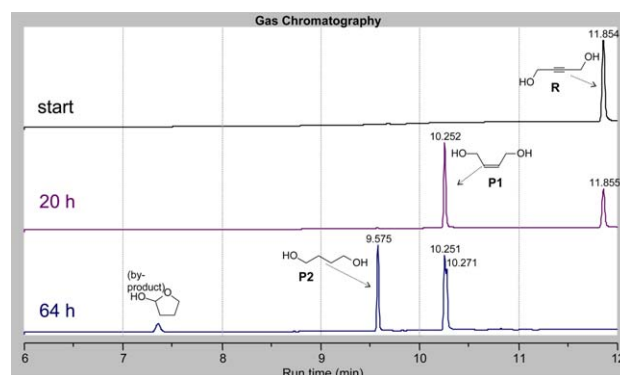


Figure 4. Gas chromatograms from the hydrogenation of 2-butyn-1,4-diol in water catalyzed by Pd nanoparticles entrapped in multicompartment PCL microparticles. Assignments of the product peaks were made by comparing retention times with authentic samples, and confirmed by GC/MS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

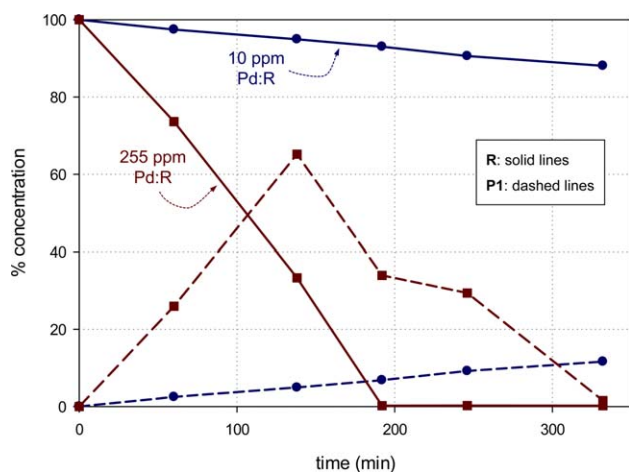


Figure 5. Hydrogenation at 48 ± 2 psi of 2-butyne-1,4-diol (R) in water at room temperature catalyzed by Pd nanoparticles entrapped in multi-compartment PCL microparticles. Two different batches of microparticles were used, containing 48 (circles) and 1300 (squares) μg Pd/g of microparticle. The graph shows concentrations (measured by GC) of R (solid lines) and the first hydrogenation product, 2-butene-1,4-diol (P1, dotted lines) as a function of time. The plots are labeled with the initial Pd : R concentrations. The weight ratio of microparticles to R was 1 : 4 in both cases. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(Figure 8). (Note: these sequential reactions were adjusted each time for a constant R : microparticles weight ratio and initial [R].)

One explanation for this observed increase in catalytic activity on recycling is plasticization of the crystalline PCL microparticle walls by the reactants and products during the first hydrogenation

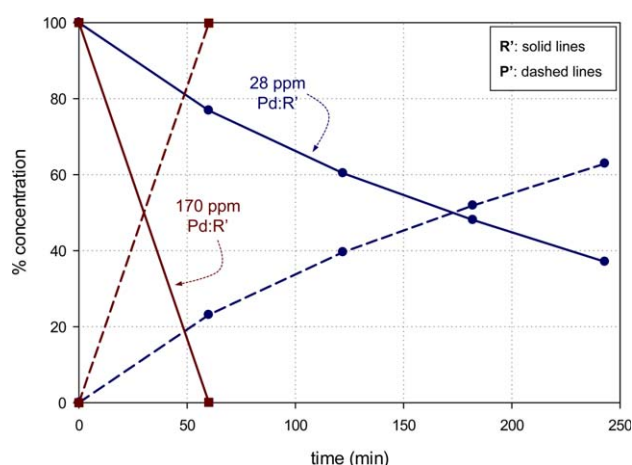


Figure 6. Hydrogenation at 48 ± 2 psi of 2-hydroxyethyl acrylate (R') in water at room temperature catalyzed by Pd nanoparticles entrapped in multi-compartment PCL microparticles. Two different batches of microparticles were used, containing 48 (circles) and 1300 (squares) μg Pd/g of microparticle. The graph shows relative concentrations (measured by GC) of R' (solid lines) and the product, 2-hydroxyethyl propionate (P', dotted lines) as a function of time. The plots are labeled with the initial Pd : R' concentrations. The initial [R'] was approximately 0.33M. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

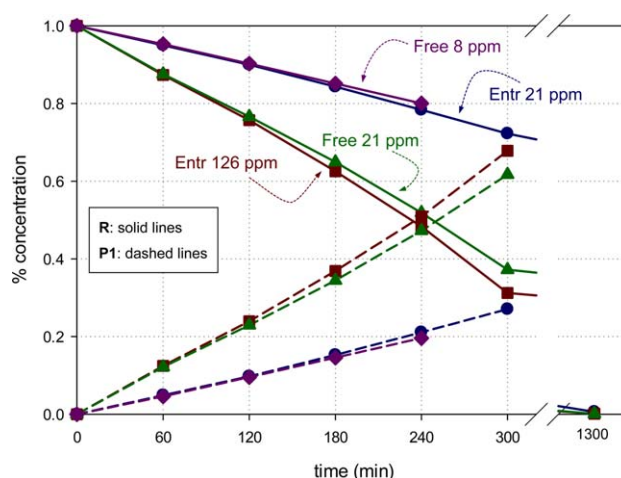


Figure 7. Hydrogenation at 48 ± 2 psi of 2-butyne-1,4-diol (R) in water at room temperature using Pd nanoparticles entrapped in multi-compartment PCL microparticles or free Pd nanoparticles. Two different batches of microparticles were used, containing 48 (circles) and 1300 (squares) μg Pd/g of dry microparticle. Similarly, two different concentrations of free nanoparticles were used (triangles and diamonds). The graph shows concentrations (measured by GC) of R (solid lines) and the first hydrogenation product, 2-butene-1,4-diol (P1, dotted lines) as a function of time. The plots are labeled with the initial Pd : R concentrations. Note that nearly all of R is consumed after prolonged reaction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tion cycle. This hypothesis was probed by taking a sample of Pd-loaded microparticles through a dummy reaction process. The same steps as used in the hydrogenation reactions were followed; the reaction vessel was charged with a mixture of R, P1, and P2 as well as the microparticles and water, but, instead of hydrogen, the vessel was pressurized with nitrogen. After shaking the mixture for 20 h, the microparticles were isolated by filtration, washed with water, resuspended in water, and then used in an actual hydrogenation. The rate of hydrogenation using these pretreated microparticles was compared to that of a control reaction using a fresh sample of the original microparticles (Figure 9). (Note: the amount and concentration of R were

Table I. Rate Data for Hydrogenation of 2-Butyne-1,4-diol (R) Using Entrapped and Unentrapped Pd Nanoparticles

Catalyst type	μg Pd/g Microparticle	Pd : R mol ratio (ppm)	$-d[R]/dt$ (initial, mol/h)	TOF (h^{-1})
Entrapped	48	26	$5.80\text{E-}04$	2400
Entrapped ^a	48	26	$5.47\text{E-}04$	2200
Entrapped	1300	156	$1.47\text{E-}03$	1000
Free	-	0.34	$3.56\text{E-}05$	11,000
Free	-	8.0	$5.47\text{E-}04$	5800
Free	-	26	$1.46\text{E-}03$	6000

Hydrogenations were performed in aqueous media using a shaker apparatus at room temperature and 48 ± 2 psi of H_2 . The initial concentration of R was 0.46M.

^a Repeat reaction 3 months later with same materials and concentrations (see text).

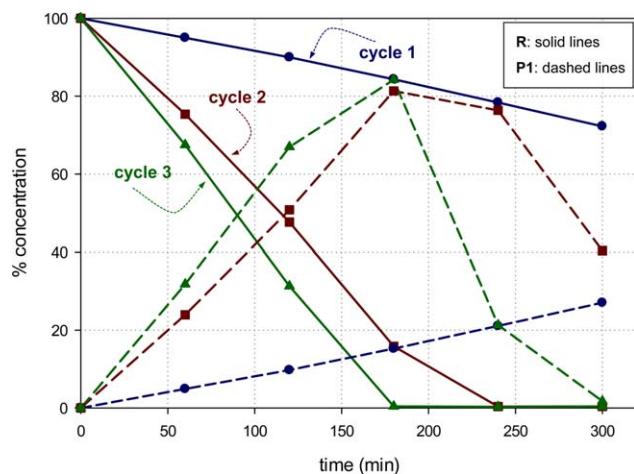


Figure 8. Hydrogenation at 48 ± 2 psi of 2-butyne-1,4-diol (**R**) in water at room temperature using Pd nanoparticles entrapped in multicompartment PCL microparticles. The graph shows concentrations (measured by GC) of **R** (solid lines) and the first hydrogenation product, 2-butene-1,4-diol (**P1**, dotted lines) as a function of time. The initial ratio of Pd : **R** was 21 ppm, and the initial concentration of **R** was 0.46M. The three plots show data for the initial reaction (circles), then data for subsequent reactions in which the microparticles were recovered from the previous reaction and re-used successively once (squares) and twice (triangles). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

adjusted to be identical in the two reactions.) The pretreated microparticles appeared to be significantly more active as catalysts compared to the original material.

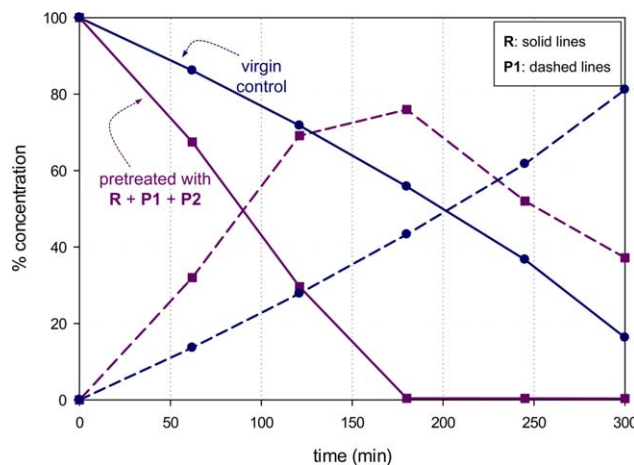


Figure 9. Hydrogenation at 48 ± 2 psi of 2-butyne-1,4-diol (**R**) in water at room temperature using two samples of multicompartment PCL microparticles with entrapped Pd nanoparticles. The graph shows concentrations (measured by GC) of **R** (solid lines) and the first hydrogenation product, 2-butene-1,4-diol (**P1**, dotted lines) as a function of time. The initial ratio of Pd : **R** was 125 ppm, and the initial concentration of **R** was 0.46M. Results using microparticles that were pretreated with a mixture of reactant and products (squares) is compared to those of the initial unmodified microparticles (circles). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The observations of increased reaction rates on recycling and on pretreatment with the reactant and products suggests that the organic materials change either the inherent catalytic activity of the Pd nanoparticles, or increase the diffusion rate into the PLC microparticles, or both. This effect must occur on a timescale of many hours. If the effect occurred within the first few minutes on exposure to **R**, no subsequent changes in activity would have been observed. If the effect occurred within just a few hours, then a rate acceleration would have taken place during the course of the reaction, and no increase in catalytic activity would have been observed upon recycling. If the effect took many days, then the increase upon recycling and pretreatment would not have occurred at all.

The most likely explanation for this behavior is the original hypothesis of plasticization of PCL, and that, over about 10 h, the organic compounds change the morphology of the PLC microparticle wall material, rendering it more permeable. This effect may occur via plasticization of the polymer by the small molecules, possibly reducing its degree of crystallinity. (PCL is a semicrystalline polymer.) The retention of the nanoparticles is apparently preserved, however. Otherwise, substantial amounts of Pd would have been removed during the washing steps, and the catalytic activity would have fallen, not increased.

It is significant that the rate of reaction after recycling or pretreatment rivals that of the previously mentioned control reactions using unencapsulated Pd nanoparticles at the same relative metal concentration. This finding suggests that, in optimized systems, the rate of catalyzed reactions need not be limited by diffusion through the walls of the microparticle carrier.

Location of the Palladium Nanoparticles within the Microparticles. One remaining question about this catalyst carrier system is the actual location of the Pd nanoparticles within the polymer microparticles. It is conceivable that the high catalytic activity of the microparticles may be caused by surface-bound Pd nanoparticles, possibly adsorbed on the colloidal silica.

To address this question, the catalytic activity of Pd containing microparticles was tested using a sample that had been treated with KOH (pH = 10) for 1 h, isolated, and washed with water. These conditions are known from previous research to remove a large fraction of the surface silica. Two control samples of the same original microparticles were used for comparison. One was washed only with water but otherwise handled in the same way as the KOH treated microparticles. The second control was the original batch of microparticles, with the initial weight ratio of microparticle : **R** and [**R**] adjusted to match those of the other two samples. As can be seen in Figure 10, water washing did not change the apparent catalytic activity of the Pd containing microparticles, while washing with KOH led to a significant increase.

The Pd content of these three samples was measured. The control and water-washed samples were identical, while the Pd content of the KOH treated particles decreased only very slightly (Table II).

These results are inconsistent with the Pd nanoparticles being associated primarily with the surface silica on the

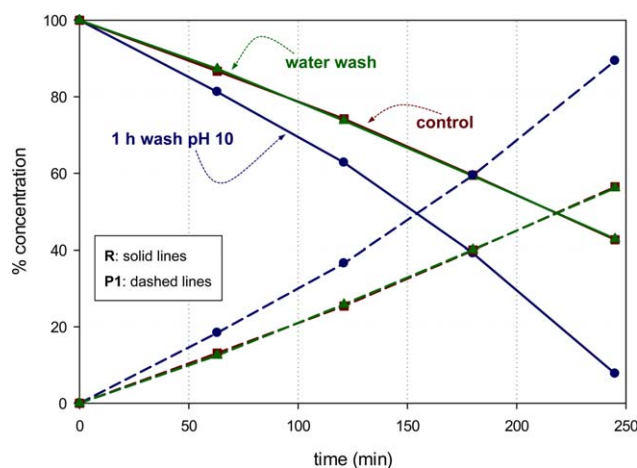


Figure 10. Hydrogenation at 48 ± 2 psi of 2-butyne-1,4-diol (R) in water at room temperature using three samples of multicompartiment PCL microparticles with entrapped Pd nanoparticles. The graph shows concentrations (measured by GC) of R (solid lines) and the first hydrogenation product, 2-butene-1,4-diol (P1, dotted lines) as a function of time. The initial ratio of Pd : R was 124 ± 4 ppm, and the initial concentration of R was $0.46M$. One sample of microparticles had been pretreated with KOH at pH = 10 (circles), and a second simply washed with water (triangles). The control sample (squares) consisted of the original Pd containing microparticles, with concentrations adjusted to match those of the other two samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

microparticles. The base pretreatment should have removed much of the silica, presumably taking the Pd nanoparticles with it. Not only was the Pd content barely changed, but the catalytic activity of the base-treated microparticles increased. This increase may be caused by enhanced permeability of the microparticles once the surface silica coating is partially removed or due to a reduction in molecular weight of the PCL upon contact with the pH 10 solution.

To test the ability of microparticles to adsorb Pd nanoparticles, a sample of empty PCL microparticles (with colloidal silica on the surface) was stirred with an aliquot of free nanoparticles equivalent to the concentration of metal in the above-mentioned batch of Pd containing microparticles with $48 \mu\text{g Pd/g}$ microparticle. The sample was filtered, and the isolated microparticles were thoroughly washed with water to remove any unbound Pd. When tested as catalyst for the hydrogenation of 2-butyne-1,4-diol, these Pd-adsorbed microparticles showed small but noticeable activity (Figure 11). This activity was preserved even in a second

Table II. Pd Content of PCL Microparticles, Measured by Inductively Coupled Plasma Atomic Emission Spectroscopy on Samples that Had Been Acid-Digested

Sample	$\mu\text{g Pd/g}$ microparticle ^a
Control	1300
Water-washed	1330
Base-washed	1240

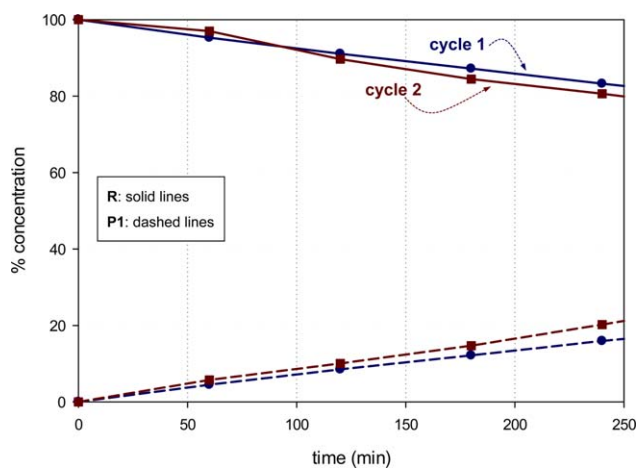


Figure 11. Hydrogenation at 48 ± 2 psi of 2-butyne-1,4-diol (R) in water at room temperature using empty multicompartiment PCL microparticles that had been exposed to free Pd nanoparticles. The graph shows concentrations (measured by GC) of R (solid lines) and the first hydrogenation product, 2-butene-1,4-diol (P1, dotted lines) as a function of time. The initial concentration of R was $0.46M$. The two plots show data for the initial reaction (circles), then data for a subsequent reaction in which the microparticles were recovered from the previous reaction and re-used (squares). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cycle after the microparticles were isolated, washed, and reused for the same reaction.

It is significant that the catalytic activity of these microparticles with apparently adsorbed Pd was constant upon recycling. This observation contrasts with similar recycling experiments using microparticles containing encapsulated Pd in which the activity increased (cf. Figures 8 and 11).

To probe further the apparent adsorption of Pd, the same microparticles were treated with base. Specifically, one sample of empty PCL microparticles was stirred with KOH at pH = 10 for 1 h, isolated by filtration, and washed with water, then exposed to free Pd nanoparticles in the same way as the experiment described above. A second sample was treated in the same way, but the order of KOH and Pd nanoparticle treatments was reversed. A control sample was simply isolated by filtration and washed with water. All three samples were used to catalyze the hydrogenation of 2-butyne-1,4-diol, and those that had been exposed to base showed diminished catalytic activity (Figure 12).

The above results together suggest that free Pd nanoparticles can be adsorbed to the colloidal silica on the surface of the particle. Base treatment strips some of the silica, leading to lowered Pd concentration on the surface and decreased catalytic activity. Alternatively, pretreatment with base removes some of the silica from the surface, decreasing the available sites for adsorption, thereby lowering Pd concentration on the surface and decreasing catalytic activity.

In all cases, the catalytic activity of the microparticles with entrapped Pd-nanoparticles is much greater than that of the samples with only apparently adsorbed Pd. Also, the catalytic

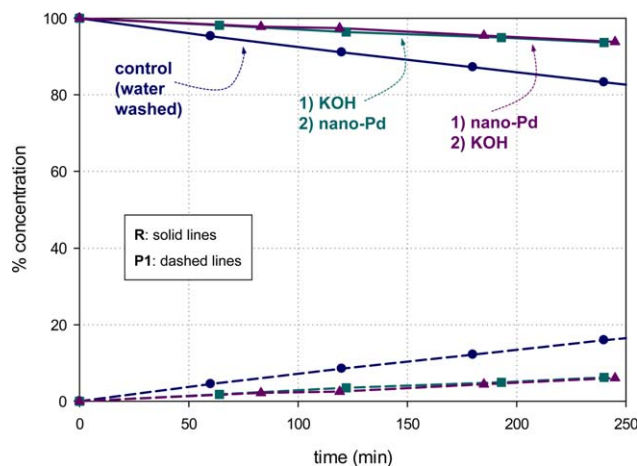


Figure 12. Hydrogenation at 48 ± 2 psi of 2-butyne-1,4-diol (R) in water at room temperature using empty multicompartment PCL microparticles that had been exposed to free Pd nanoparticles. The graph shows concentrations (measured by GC) of R (solid lines) and the first hydrogenation product, 2-butene-1,4-diol (P1, dotted lines) as a function of time. The initial concentration of R was 0.46M. The plots show the effect of base-washing microparticles with adsorbed Pd nanoparticles (see text). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

activity of the former is increased by base treatment, while that of the latter decreases. These observations are consistent with the Pd nanoparticles being present inside the compartments of the microparticle rather than on the surface.

Decomposition of Hydrogen Peroxide Catalyzed by Palladium Containing Microparticles

Another example of the catalytic properties of the palladium containing microparticles was also investigated. The catalytic decomposition of hydrogen peroxide over transition metal

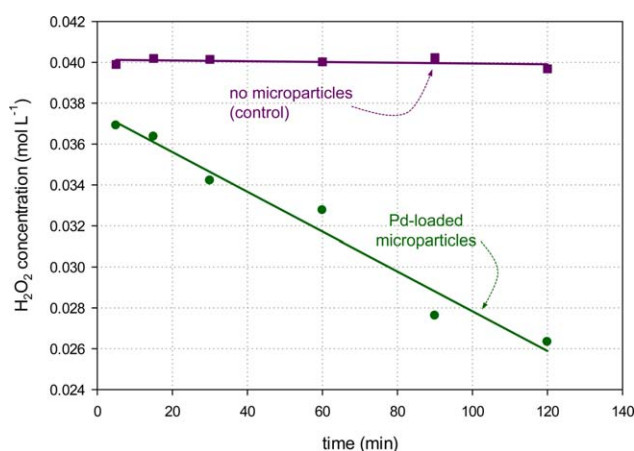
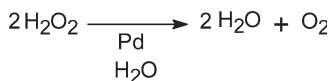


Figure 13. Concentration of H_2O_2 determined by absorption at 240 nm for solutions stirred at room temperature with (circles) and without (squares) palladium-loaded microparticles. Samples containing microparticles were filtered before analysis to remove interferences caused by light scattering. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surfaces is widely known and also included in the previously mentioned paper by Parthasarathy and Martin.³



Given the hydrogenation results, it was expected that the diffusion of hydrogen peroxide through the microparticle to the catalytic palladium nanoparticles would be facile. Suspensions of palladium containing microparticles in dilute H_2O_2 were prepared and stirred for varying amounts of time. The microparticles were easily separated from the solution via simple filtration. The H_2O_2 concentration was monitored by measuring the absorbance of the solution at 240 nm. The data presented in Figure 13 show that the palladium containing microparticles do catalyze the disproportionation of hydrogen peroxide. Because hydrogen peroxide is known to decompose slowly even in the absence of any catalyst, a control experiment was performed with the same H_2O_2 solution but without the palladium-loaded microparticles. It is clear that on the time scale of these experiments that no significant decomposition of hydrogen peroxide occurs without the catalytic microparticles.

CONCLUSIONS

We were able to entrap varying concentrations of palladium nanoparticles within multicompartment polycaprolactone microparticles with high efficiency. The metal nanoparticles are retained essentially indefinitely under ambient conditions. Despite entrapment of the palladium within the compartments, these microparticles successfully catalyzed the hydrogenation of unsaturated organic compounds and also the decomposition of hydrogen peroxide in aqueous media. The results suggest that the reactants were able to diffuse through the polymer walls of the microparticles into the compartments in which the catalyst was present, and undergo reaction. For hydrogenations, the microparticle-encapsulated catalyst was initially less active as an equivalent amount of unencapsulated catalyst, but the activity of the microparticles increased markedly when the samples were isolated and reused. This increase in activity on recycling was attributed to plasticization of the polymer walls by the organic reactants and products, with concomitant increase in permeability. However, further research is required to test this hypothesis. Removal of the surface silica from the microparticles led to a moderate increase in catalytic activity, possibly also through enhanced diffusion. Control experiments were consistent with the metal nanoparticles being contained within the inner compartments of the polymer microparticles rather than adsorbed onto the surface. This entrapped system offers an expeditious means for separating and reusing the catalytic nanoparticles, while minimizing potential human contact with and environmental contamination by the metal.

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