NANO
LETTERS

2001
Vol. 1, No. 12
683−687

Palladium Nanoparticle Catalyst Prepared in Poly(Acrylic Acid)-lined Channels of Diblock Copolymer Microspheres

Zhihua Lu, Guojun Liu,* Heather Phillips, Josephine M. Hill, Jason Chang, and Ronald A. Kydd

Department of Chemistry, University of Calgary, 2500 University Dr., NW, Calgary, Alberta, Canada T2N 1N4

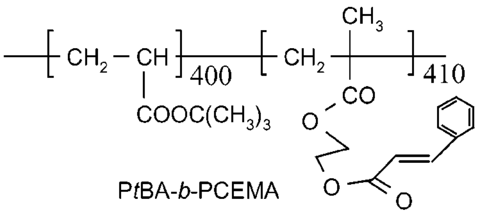
Received August 7, 2001; *Revised Manuscript Received September 27, 2001*

ABSTRACT

Block copolymers self-assemble in bulk, forming a number of intricate block segregation patterns. Such assembled structures can serve as precursors to nano- or microstructures with numerous potential applications. For many applications, such as catalysis, a high surface area to volume ratio is desirable, which requires "breaking up" copolymer solid into dispersed particles. Reported in this letter is the preparation of water-dispersible block copolymer microspheres containing Pd nanoparticles. The Pd nanoparticles are a more efficient catalyst for alkene hydrogenation than is the commercial Pd black catalyst.

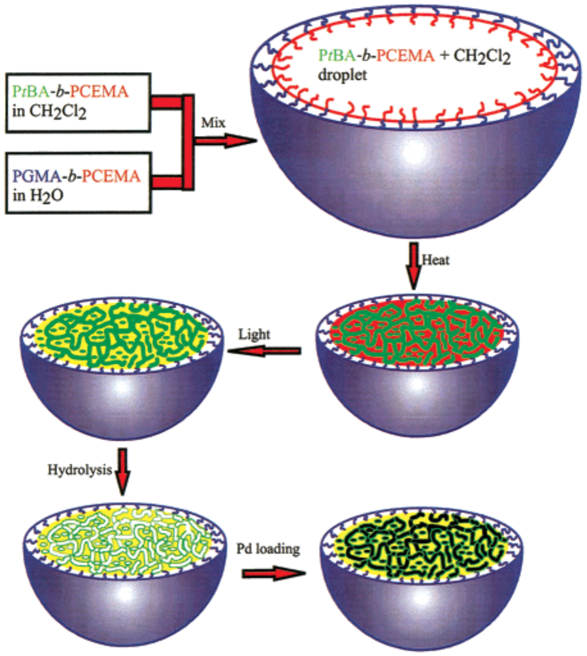
Noble metal catalysts are used in industry mainly as nanoparticles supported on the surfaces of zeolite, silica, alumina, or porous carbon.[1] Various industrial processes exist to prepare such dispersed catalysts.[1] More recent academic endeavors have included their preparation in the cores of diblock copolymer micelles,[2−4] cores of triblock nanospheres,[5] cores of dendrimers,[6−8] hydrophilic domains of diblock copolymer films,[9] matrices of homopolymers,[10] or surfaces of polymer microspheres.[11] More easily, they were prepared from reducing metal salts in solvent using polymer[12−14] or small-molecule ligands[15−18] as dispersing agents. Here we report the preparation of Pd nanoparticles inside a new type of porous polymeric support. The support consists of diblock microspheres containing block-segregated interior domains. Also reported is the performance of the Pd particles in catalyzing the hydrogenation of methyl methacrylate (MMA).

The diblock microspheres were prepared from an oil-in-water emulsion process used previously to make spheres from preformed homopolymers.[19,20] The diblock utilized here was poly(*t*-butyl acrylate)-*block*-poly(2-cinnamoyloxyethyl methacrylate) or P*t*BA-*b*-PCEMA:



P*t*BA-*b*-PCEMA

Scheme 1. Preparation and Processing of P*t*BA-*b*-PCEMA Microspheres Containing Sponge-like Nanometer-sized P*t*BA Domains



The preparation involved dissolving the diblock in dichloromethane (Scheme 1) first. The oil phase was then dispersed in water using a tailor-made surfactant poly(glyceryl methacrylate)-*block*-poly(2-cinnamoyloxyethyl methacrylate) or PGMA-*b*-PCEMA where PGMA is water-soluble. Solid

10.1021/nl015597a CCC: $20.00
Published on Web 10/12/2001

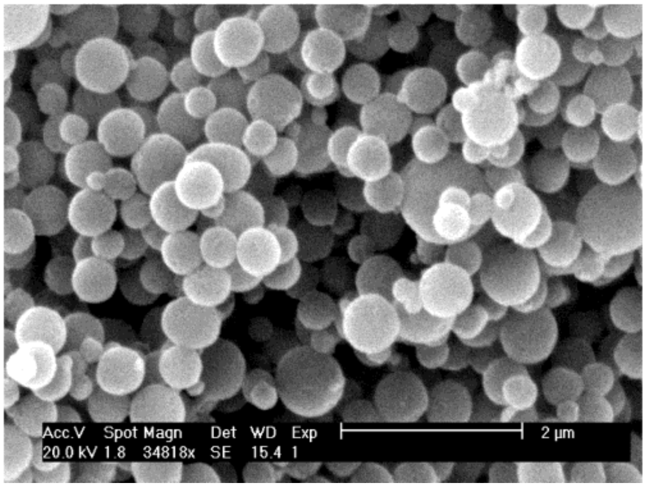
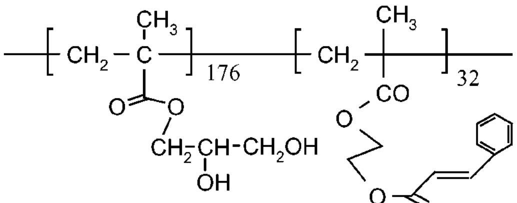


Figure 1. SEM image of P*t*BA-*b*-PCEMA microspheres.

spheres were obtained after CH_2Cl_2 evaporation from the oil droplets at 50 °C. "Permanent" spheres were formed after photocrosslinking the PCEMA blocks of the diblock and the surfactant.



PGMA-*b*-PCEMA

Shown in Figure 1 is a scanning electron microscopic (SEM) image of microspheres thus made at a CEMA double bond conversion of 27%. Most of the particles are spherical with a reasonable diameter distribution around 0.5 μm. Shown in Figure 2a is a transmission electron microscopic (TEM) image of a thin slice of such a microsphere. The projections of the light unstained P*t*BA domains appear in the TEM image as either circles or tortuous strips. These suggest formation of a sponge-like or a gyroid phase, with short-range order, inside the spheres from P*t*BA. While more work is required to establish the exact morphology, evidence to be presented later suggests the continuity of the P*t*BA phase in a sphere. A continuous P*t*BA phase at a volume fraction of 0.37[21] in this case is reasonable, given that some diblocks form the gyroid phase in bulk at the volume fraction of ~38%.[22] A measure for the size of the P*t*BA domains can be obtained from either the width of the strips or the diameter of the circles in Figure 2a. The values fluctuate between 12 and 42 nm with an average ~32 nm. We also performed solid-state nuclear magnetic resonance and infrared (IR) analyses of the microspheres. The results indicated that the spheres consisted mostly of P*t*BA-*b*-PCEMA. The low content of surfactant in the spheres is in agreement with the model of Scheme 1, where PGMA-*b*-PCEMA is depicted to occur at the water/microsphere interface only.

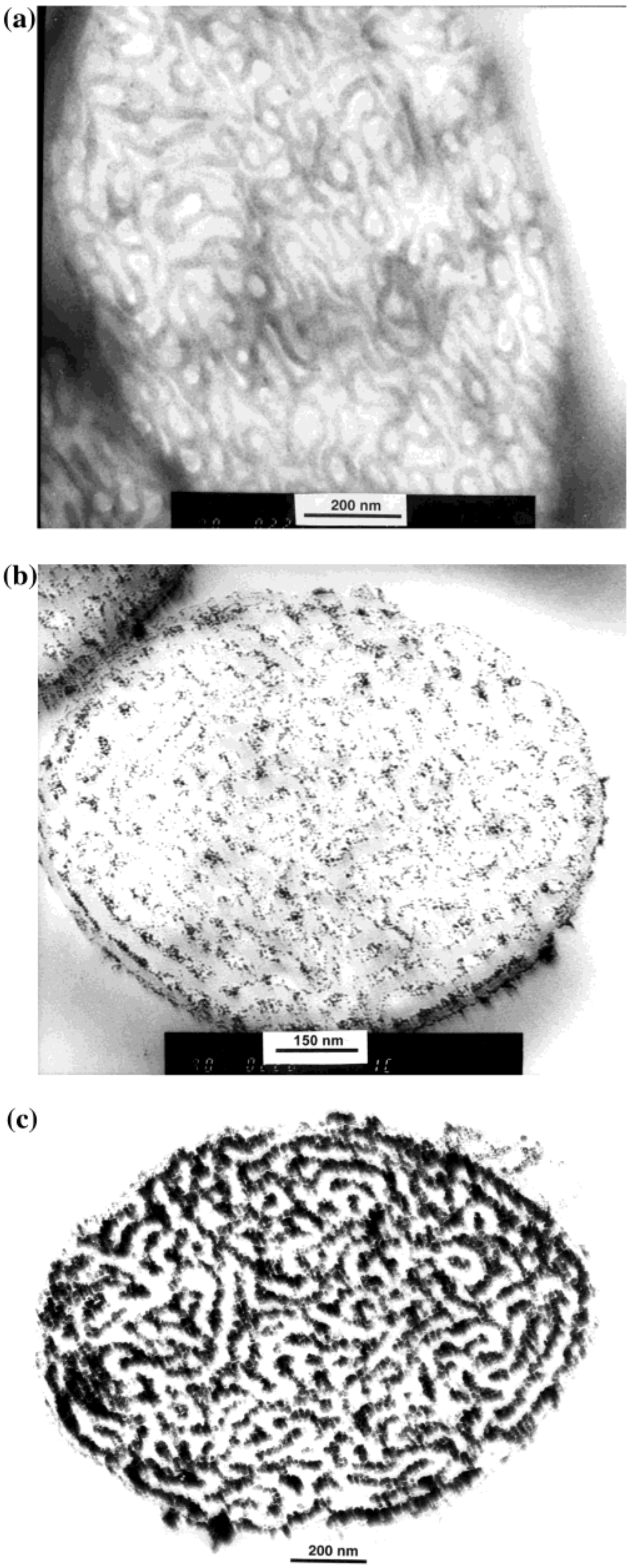


Figure 2. TEM images of thin sections of PCEMA-*b*-P*t*BA microspheres (a) and Pd-loaded PCEMA-*b*-PAA microspheres containing 27% (b) and 63% (c) of Pd.

The *t*-butyl groups were removed quantitatively, as confirmed by IR analysis, from the P*t*BA block (Scheme 1) in the microspheres via acid-catalyzed hydrolysis. Analysis of N_2 adsorption data indicated that the microspheres after *t*-butyl group removal were porous, with a specific surface area of (52.7 ± 1.1) m^2/g and a most probable pore radius

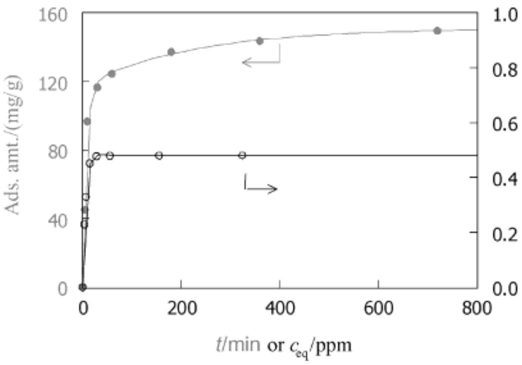


Figure 3. Kinetic (●) and isothermal (○) curves of Pd^{2+} uptake by PCEMA-*b*-PAA microspheres in water.

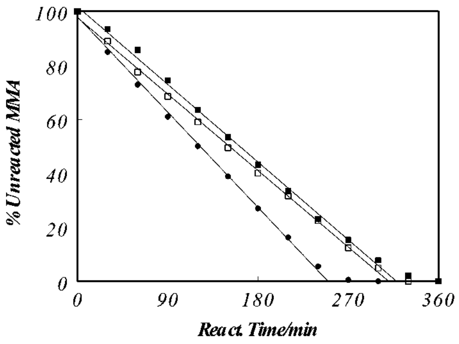


Figure 4. MMA conversion as a function of time using Pd black (■) and our micorspheres containing 27% (●) and 63% (Y) Pd as the catalyst.

of 15 nm, i.e., the pore size at its distribution function maximum. The pore size distribution width at half peak height was ~8 nm. This pore radius of 15 nm is in agreement with the P*t*BA domain radius of ~16 nm as determined from Figure 2a and suggests the collapsing of PAA chains on the channel walls of the dry microspheres.

The PAA chains in the porous microspheres should be swollen in water and have affinity for inorganic metal ions. Illustrated in Figure 3 are the thermodynamic and kinetic data of Pd^{2+} uptake by the spheres. Approximately 10 h were required to establish Pd^{2+} adsorption equilibrium, which is tens of times faster than the rate of metal ion uptake by thin films of poly(methyl tetracyclododecene)-*block*-poly(2-norbornene-5,6-dicarboxylic acid) containing poly(2-norbornene-5,6-dicarboxylic acid) cylindrical domains.[23] The faster kinetics here is most probably due to the low polymer chain segmental density in the PAA-lined channels and due to the high specific surface area of the microspheres. At adsorption equilibrium, Pd^{2+} uptake at sufficiently high equilibrium Pd^{2+} concentrations, c_{eq}, is ~151 mg per gram of microspheres. Assuming 100% *t*-butyl removal, the isotherm data obtained could also be presented in moles of Pd^{2+} taken up per mole of carboxyl groups (Figure 3). The binding capacity is 0.48 Pd^{2+} ions per carboxyl group, which is again much higher than that observed by Clay and Cohen[23] for Pd^{2+} adsorption by their thin films. The stoichiometric binding of Pd^{2+} by the carboxyl groups here suggests the continuity of the PAA-lined channels and thus the original P*t*BA domains.

Reduction of Pd^{2+} in the PAA-lined channels was achieved using hydrazine following a literature method.[3] Pd formation was confirmed from an electron diffraction study.[5] Thermogravimetric analysis of such microspheres gave a Pd mass fraction of 14.5% or a Pd loading of 156 mg per gram of microspheres, which is in good agreement with 151 mg of Pd^{2+} per gram of microspheres as obtained from Figure 3.

The Pd particles formed catalyzed further Pd deposition during electroless plating.[24] By varying the relative amounts of microspheres and Pd^{2+} used, we obtained the Pd loadings of 0.37 and 1.71 g per gram of microspheres for two samples. These corresponded to the Pd mass fractions of 27% and 63% in the Pd-loaded spheres. Shown in Figure 2b is a TEM image of a thin slice of such a sphere with 27% Pd. Since the sample was not stained, the dark regions correspond to the presence of Pd. The Pd particles produced are small and discontinuous and are concentrated primarily in the PAA-lined channels. Shown in Figure 2c is a TEM image of a thin slice containing 63% Pd. The diameters of the Pd particles of Figure 2c are larger than those found in Figure 2b, as expected, but are smaller than 30 nm, the diameter for the PAA-lined channels in the porous microspheres. Figure 2c also reveals that the Pd particles are distributed throughout the spheres. Since the transport of Pd^{2+} via PCEMA matrix should be slow, this ubiquitous Pd production inside the spheres suggests again the connectivity of the PAA-lined channels. The specific surface area and most probable pore diameter are (29.8 ± 2.6) $m^2\ g^{-1}$ and 0.9 nm, respectively, for the sample. The decrease in pore diameter is consistent with pore filling by Pd. Caution, however, is required in interpreting the specific surface area due to the presence of accessible surfaces from both Pd and PAA in this case. The Pd-loaded microspheres catalyzed the clean hydrogenation of methyl methacrylate (MMA) to methyl 2-methylpropionate. Since MMA was used in much excess relative to Pd and the amount of MMA adsorbed by the microspheres should be negligible relative to that reacted at sufficiently high conversions, we equated the disappearance of MMA from the supernatant to MMA conversion. Plotted in Figure 4 are the MMA disappearance data as a function of time using microspheres containing 27% and 63% Pd as catalysts. Also plotted for comparison are the kinetic data of MMA hydrogenation using commercial Pd black (specific surface area as determined by us was 48 $m^2\ g^{-1}$, which is slightly higher than 40 $m^2\ g^{-1}$ provided by Aldrich) as the catalyst. At an equal initial MMA to Pd molar ratio of 94, the Pd-loaded spheres catalyzed hydrogenation faster than did Pd black. The faster catalysis may have derived from the improved dispersion of the catalyst in the microspheres. In addition, the reaction environment in the channels may be more favorable in the channels of the spheres.

We have also tested the activities of the recycled catalysts. Figure 5 shows MMA hydrogenation data obtained using recycled microspheres containing 27% Pd or recycled Pd black as the catalyst. Our catalyst performs consistently better than Pd black, regardless of the catalyst usage time. The disappointing feature was that the activity of our catalyst, like Pd black, decreased with usage, which is in contrast to behavior observed by Chen et al.[11b] for Pt nanoparticles immobilized at microsphere surfaces. Since our SEM and

Table 1: Characteristics of the Diblock and Surfactant

sample	dn_r/dc (mL/g)	LS $\bar{M}_w$ (g/mol)	GPC $\bar{M}_w/\bar{M}_n$	NMR n/m	n	m
P*t*BA-*b*-PCEMA	0.095 (in $CHCl_3$)	1.59×10^5	1.18	0.98	400	410
PGMA-*b*-PCEMA	0.100 (in DMF)	0.36×10^5	1.15[a]	5.5	176	32

[a] Measured in THF in the PSMA-*b*-PCEMA form, where PSMA denotes poly(solketal methacrylate).

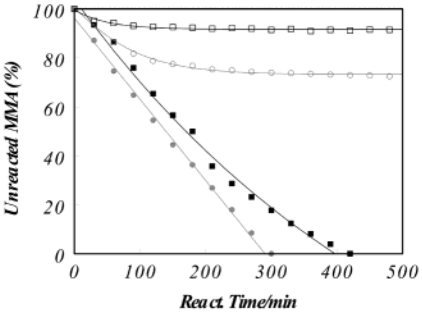


Figure 5. MMA conversion as a function of time using recycled Pd black and our microspheres containing 27% Pd as the catalyst. Data denoted by (■) and (□) were obtained using the same batch of Pd black the second and third time, respectively. Data denoted by (●) and (○) were obtained using the same batch of microspheres the second and third time, respectively.

TEM results did not reveal any structural change for the microspheres after repeated usage, the decreased activity might be associated with the gradual blockage of the PAA channels by unknown impurities. Similar results were obtained using recycled microspheres containing 63% Pd as the catalyst.

In summary, we have prepared microspheres containing PAA-lined channels that are probably continuous. The microspheres can be used as catalyst supports. While Pd supported in the microspheres is a more active catalyst than Pd black, our catalyst is not competitive in production cost for such an application. Porous microspheres can also be produced more cheaply from traditional methods used for macroporous resin preparation.[25] The advantage of preparing porous microspheres from block copolymers using this approach lies in the potential for more precise pore size and geometry control,[26] because block segregation is a thermodynamically driven process and block segregation patterns can be tuned by changing the copolymer composition and structure.[22] Such precise catalyst positioning may be of critical importance in, for instance, fuel cell design, where a catalytic site becomes active only if there is facilitated electron, proton, and reagent transfer to and from the site.[27]

Procedures. The precursors to P*t*BA-*b*-PCEMA[28] and PGMA-*b*-PCEMA[29] were prepared by anionic polymerization. The preparation and purification procedures are similar to those used previously[28,29] and are thus not repeated here. Light scattering, NMR, and gel permeation chromatography (GPC) were used to characterize P*t*BA-*b*-PCEMA and PSMA-*b*-PCEMA, where PSMA denotes poly(solketal methacrylate) that hydrolyzes readily in slightly acidic medium to yield PGMA. The characterization results for the polymers are given in Table 1.

To prepare the microspheres, 250 mg of PGMA-*b*-PCEMA was dissolved in 2.0 mL of methanol and then added to 48 mL of water. P*t*BA-*b*-PCEMA, 250 mg, dissolved in 10 mL of CH_2Cl_2 was mixed with the surfactant solution under magnetic stirring to yield a cloudy mixture. The mixture was sonicated (Branson 1200) for 5 min to yield an emulsion. The emulsion was added over 45 min into 100 mL of water stirred at 500 rpm at 45 °C in a three-neck round-bottomed Pyrex flask. Organic-solvent-free diblock spheres were obtained after evaporating CH_2Cl_2 at 50 °C for 1 h. The microspheres were cross-linked using UV light from a 500-W mercury lamp. PCEMA double bond conversion obtained from CEMA absorbance decreases at 274 nm was typically ~27%. The microspheres were separated from the supernatant by centrifugation and rinsed with distilled water and then methanol thrice to remove surfactant that was not attached to the microspheres but existed probably as cross-linked micelles. After vacuum drying, 241 mg of microspheres was obtained with a yield of 96% with respect to P*t*BA-*b*-PCEMA, suggesting a low degree of surfactant incorporation into the spheres.

To obtain SEM images of the microspheres, the powder was spread on a conductive carbon adhesive tape. The spheres were sputter-coated with a ~6 nm thick Au−Pt layer and scanned using a SEI XL30 ESEM instrument operated at 20 kV. To obtain the internal structures of the microspheres using TEM, the microspheres, 5 mg, were mixed with 0.05 mL of a 20 wt % polystyrene (Aldrich, $\bar{M}_w = 20000$ g mol^{-1}, $\bar{M}_W/\bar{M}_n = 5$) solution in THF. The mixture was spread on a glass plate and dried in air overnight to obtain a film that was ~300 μm thick. The film was further dried at 70 °C for 48 h and then sandwiched between two polystyrene plates heated to 110 °C, ~3 mm thick, for microtoming (Ultracut-E, Reichert-Jung) into 50-nm-thick slices. The slices were picked up with Formvar-coated copper grids and stained with OsO_4 vapor for 12 h before viewing under a Hitachi-700 electron microscope operated at 75 kV. The Pd-loaded spheres were not stained.

We hydrolyzed the *t*-butyl groups of P*t*BA by stirring the microspheres, 50 mg, with 4 mL of trifluoroacetic acid (CF_3COOH) in 20 mL of dichloromethane at room temperature for 1 h. The quantitative removal of the *t*-butyl groups was confirmed by the disappearance of the *t*-butyl rocking peak at 846 cm^{-1}. To obtain the kinetic data of Pd^{2+} uptake by the *t*-butyl-removed microspheres, the microspheres, 10.0 mg, were mixed with 10.0 mL of a 100-ppm aqueous Pd^{2+} solution derived from $Pd(NO_3)_2$. At different times, the microspheres were separated from the supernatant by centrifugation followed by filtration through 0.45-μm filters. The resultant solution was analyzed spectrophotometrically for Pd^{2+} concentration at 250 nm. The final and initial Pd^{2+} concentrations were compared to calculate the amount of Pd^{2+} uptake by the microspheres. To obtain the Pd^{2+} uptake isotherm, the microspheres, 10 mg, were equilibrated with $Pd(NO_3)_2$ solutions at different initial concentrations for 24 h and the supernatants were then analyzed for Pd^{2+} final concentrations (c_{eq}).

The adsorbed Pd^{2+} was reduced inside the PAA-lined channels using hydrazine under N_2 atmosphere. To reduce Pd^{2+} in 100 mg of microspheres dispersed in 100 mL of water, the microsphere dispersion was mixed with 5.0 mL of an aqueous hydrazine solution, 0.50 mg/mL, and then stirred for 3 h. Microspheres were separated from the supernatant by centrifugation, rinsed with water thrice, and dried under reduced pressure. More Pd was incorporated into the microspheres by electroless plating. To obtain 27% Pd, 100 mg of microspheres with 13.5% Pd were dispersed in 5.0 mL of a solution of $PdCl_2$ (3.9 gL^{-1}), Na_2EDTA (67.2 gL^{-1}), and NH_4OH (350 gL^{-1}) in water. Then 0.030 mL of hydrazine in 2.0 mL of water was added over 0.5 h under stirring. The mixture was further stirred for 1.5 h before the microspheres were separated by centrifugation, rinsed with water thrice, and dried in a vacuum. A quantity of 111 mg of microspheres was obtained. Spheres with 63% Pd were obtained after plating 50 mg of microspheres containing 13.5% Pd with 25.0 mL of the plating solution.

The setup and procedure used for MMA hydrogenation have been described previously.[5] For all reactions, the initial MMA concentration, stirring speed, and hydrogen bubbling rate were kept constant, as was the initial MMA to Pd molar ratio of 94:1. As an example, 23.4 mg of microspheres containing 27% Pd were dispersed in 20 mL of methanol. Hydrogen was bubbled through the solution for 1.5 h at a rate of 0.50 mL min^{-1} to reduce oxides formed on Pd surfaces. MMA, 0.60 mL and density at 0.936 g mL^{-1}, was then added with a syringe. The sample was centrifuged at different times to settle the microspheres, and 0.10 mL was taken from the supernatant for composition analysis by gas chromatography. Pd black was purchased from Aldrich.

Catalysts were recovered after hydrogenation experiments by centrifugation. The catalyst recovered was then rinsed with methanol and separated from methanol again by centrifugation. Methanol rinsing was repeated thrice. The catalysts were then dried under vacuum before testing for activity. Within the error of gravimetric analysis, the recovery efficiency of Pd black and Pd-containing microspheres was 100%.

The procedure and formula used to obtain the Pd content by thermogravimetric analysis are reported previously.[5] Pore parameters and surface areas were determined from N_2 adsorption isotherms at 77 K on an Advanced Scientific Designs RXM 100 instrument. The samples were pretreated for 1−2 h at 323 K under vacuum to remove adsorbed gases. The surface areas were determined using the BET (Brunauer−Emmett−Teller) method. Mesopore size distribution was determined using the method of BJH (Barrett, Joyner, and Halenda).[30]

Acknowledgment. The Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged for sponsoring this research.

References

(1) Campbell, I. M. *Catalysis at Surfaces*; Chapman and Hall: London, 1988.
(2) Spatz, J. P.; Roescher, A.; Sheiko, S.; Krausch, G.; Möller, M. *Adv. Mater.* **1995**, *7*, 1000.
(3) (a) Antonietti, M.; Wenz, M.; Bronstein, L.; Seregina, M. V. *Adv. Mater*. **1995**, *7*, 1000. (b) Klingelhofer, S.; Heitz, W.; Greiner, A.; Oestreich, S.; Förster, S.; Antonietti, M. *J. Am. Chem. Soc. 119*, **1997**, 10116. (b) Seregina, M. V.; Bronstein, L. M.; Platonova, O. A.; Chernyshov, D. M.; Valetsky, P. M.; Hartmann, J.; Wenz, E.; Antonietti, M. *Chem. Mater.* **1997**, *9*, 932. (d) Förster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195.
(4) Watson, K. J.; Zhu, J.; Nguyen, S. T.; Mirkin, C. A. *J. Am. Chem. Soc. 121*, **1999**, 462.
(5) Underhill, R. S.; Liu, G. J. *Chem. Mater.* **2000**, *12*, 3633.
(6) Balogh, L.; Tomalia, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 7355.
(7) (a) Zhao, M.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877. (b) Zhao, M.; Crooks, R. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 364.
(8) Vassilev, K.; Kreider, J.; Miller, P. D.; Ford, W. T. *React. Funct. Polym.* **1999**, *41*, 205.
(9) (a) Ciebien, J. F.; Cohen, R. E.; Duran, A. *Supramolec. Sci.* **1998**, *5*, 31. (b) Ciebien, J. F.; Cohen, R. E.; Duran, A. *Mater. Sci. Eng.* **1999**, *7*, 45.
(10) Vorontsov, P. S.; Gerasimov, G. N.; Golubeva, E. N.; Grigor'ev, E. I.; Zav'yalov, S. A.; Zav'yalova, L. M.; Trakhtenberg, L. I. *Russ. J. Phys. Chem.* **1998**, *72*, 1742.
(11) (a) Pathak, S.; Greci, M. T.; Kwong, R. C.; Mercado; K.; Prakash, G. K. S.; Olah, G. A.; Thompson, M. E. *Chem. Mater.* **2000**, *12*, 1985. (b) Chen, C.-W.; Serizawa, T.; Akashi, M. *Chem. Mater.* **1999**, *11*, 1381.
(12) Hirai, H.; Yakura, N.; Seta, N.; Hodoshima, S. *React. Funct. Polym.* **1998**, *37*, 121.
(13) Mayer, A. B. R.; Mark, J. E. *Macromol. Rep.* **1996**, *A33*, 451.
(14) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.
(15) Jana, N. R.; Wang, Z. L.; Pal, T. *Langmuir* **2000**, *16*, 2457.
(16) Reetz, M. T.; Lohmer, G. *Chem. Commun.* **1996**, 1921.
(17) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709.
(18) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.
(19) Nakache, E.; Poulain, N.; Candau, F.; Orecchioni, A.-M.; Irache, J. M. In *Handbook of Nanostructured Materials and Nanotechnology*; Nalwa, H. S., Ed.; Academic Press: San Diego, 2000; Vol. 5, pp 577−635, and references therein.
(20) Ouchi, T.; Hamada, A.; Ohya, Y. *Makromol. Chem. Phys.* **1999**, *200*, 436.
(21) Liu, G. J.; Ding, J.; Hashimoto, T.; Saijo, K.; Winnik, F. M.; Nigam, S. *Chem. Mater.* **1999**, *11*, 2233. The densities of PCEMA and P*t*BA as reported in this paper are 1.25 and 1.02 g/mL, respectively.
(22) Bates, F. S.; Fredrickson, G. H. *Phys. Today* **1999**, February issue, 32.
(23) Clay, R. T.; Cohen, R. E. *Supramolec. Sci.* **1997**, *4*, 113.
(24) (a) Uemiya, S.; Kude, Y.; Sugino, K.; Sato, N.; Satsuda, T.; Kikuchi, E. *Chem. Lett.* **1988**, 1687. (b) Zaman, J.; Chakma, A. *J. Membr. Sci.* **1994**, *92*, 1.
(25) See, for example, Horak, D.; Benes, M. In *Polymeric Materials Encyclopedia*−*Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 3934.
(26) Lu, Z.; Liu, G. J.; Liu. F. *Macromolecules*, in press.
(27) See, for example, Arico, A. S.; Creti, P.; Kim, H.; Mantegna, R.; Giordano, N.; Antonucci, V. *J. Electrochem. Soc.* **1996**, *143*, 3950.
(28) Henselwood, F.; Liu, G. J. *Macromolecules* **1997**, *30*, 488.
(29) Liu, F.; Liu, G. J. *Macromolecules* **2001**, *34*, 1302.
(30) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373.

NL015597A