J|A|C|S
ARTICLES

Palladium Nanoparticles Captured in Microporous Polymers: A Tailor-Made Catalyst for Heterogeneous Carbon Cross-Coupling Reactions

Shin Ogasawara and Shinji Kato*

Kawamura Institute of Chemical Research, 631 Sakado, Sakura, Chiba 285-0078, Japan

Received July 23, 2009; E-mail: kato@kicr.or.jp

Abstract: A new strategy based on polymerization-induced phase separation (PIPS) techniques was proposed for fabricating palladium nanoparticles (PdNPs) captured in a microporous network polymer. $Pd(OAc)_2$ was premixed with a monomer having a poly(amidoamine)-based dendrimer ligand, and subsequently this was thermally polymerized with an excess amount of ethylene glycol dimethacrylate under PIPS conditions. In this system, the formation of PdNPs occurred concurrently with the polymer synthesis in a one-pot process, even with no additional reducing reagent. The resultant microporous polymer was found to have a mesoporosity; the nitrogen sorption analysis gave a specific-surface area of 511 m^2 g^{-1}, an average pore diameter of 9.9 nm, and a total pore volume of 1.01 mL g^{-1}. The TEM images of the polymer revealed that the created PdNPs were very small with a diameter of mainly ca. 2.0 nm; the high-resolution images were lattice-resolvable, showing the crystalline nature of the PdNPs (Pd(111) facets). Catalytic performances of the PdNP-containing microporous polymers were investigated for a heterogeneous Suzuki−Miyaura reaction of 4′-bromoacetophenone and phenylboronic acid in water. In the presence of 10^{-2} molar equiv of the polymer, the reaction efficiently proceeded at 80 °C and gave the desired product, 4-acetylbiphenyl, in >90% yield after 2 h. On the basis of the ICP-AES analysis, the Pd content released into the solution phase was estimated to be only 0.27% of the initial charge. Thereby, this polymer was successfully recovered by simple filtration and reused with only a minimal loss of activity (yield >90% even at the eighth run). When the catalytic reaction was examined with a low amount of the polymer catalyst, the turnover number (TON) reached 8.5×10^4 while maintaining a good yield. Finally, the dendrimer template effect of the polymer catalyst was discussed by referring to the catalytic performances of a control polymer prepared with nonintegrated ligand monomers.

Introduction

Palladium nanoparticles (PdNPs) supported on insoluble solids are materials of considerable current interest in fundamental scientific fields as well as in environment-friendly recyclable catalytic applications.[1] This is based on the advantages of PdNPs, which includes both the intrinsic versatility of Pd metals as a catalyst[2] and the specific size effect of nanoparticles: that is, a large surface-to-volume ratio.[3] PdNPs so far have been immobilized on a variety of solid supports, such as charcoal,[4] clay,[5] metal oxides, including silica,[6] alumina,[7] and zeolites,[8] and also polymers.[9] However, it is generally pointed out that the heterogeneous PdNP system has a catalytic activity lower than that of its homogeneous counterpart and the Pd atoms often leach out irreversibly from the support, preventing long-lived recyclable use.[1,5,10] Therefore, many studies have been performed aiming to improve the above drawbacks.[11] Among these works, the capture approach for immobilizing PdNPs in solid matrices is fascinating to us, since

---

(1) For reviews, see: (a) Astruc, D. *Inorg. Chem.* **2007**, *46*, 1884. (b) Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852. (c) Kaneda, K.; Ebitani, K.; Mizugaki, T.; Mori, K. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 981. (d) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609. (e) Durand, J.; Teuma, E.; Gómez, M. *Eur. J. Inorg. Chem.* **2008**, 3577.

(2) (a) Tsuji, J. *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*; Wiley: West Sussex, U.K., 2004. (b) *Handbook of Palladium-Catalyzed Organic Reactions*; Malleron, J. L.; Fiaud, J. C., Legros, J. Y., Eds.; Academic Press: London, 2000.

(3) (a) Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A. *Chem. Rev.* **2005**, *105*, 1025, and references therein. (b) Panigrahi, S.; Basu, S.; Praharaj, S.; Pande, S.; Jana, S.; Pal, A.; Ghosh, S. K.; Pal, T. *J. Phys. Chem. C* **2007**, *111*, 4596. (c) Semagina, N.; Renken, A.; Kiwi-Minsker, L. *J. Phys. Chem. C* **2007**, *111*, 13933. (d) Tew, M. W.; Miller, J. T.; van Bokhoven, J. A. *J. Phys. Chem. C* **2009**, *113*, 15140.

(4) Reetz, M. T.; Westermann, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 165.

(5) Mitsudome, T.; Nose, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Jitsukawa, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3288.

(6) (a) Lang, H.-F.; May, R. A.; Iversen, B. L.; Chandler, B. D. *J. Am. Chem. Soc.* **2003**, *125*, 14832. (b) Lang, H.-F.; Maldonado, S.; Stevenson, K. J.; Chandler, B. D. *J. Am. Chem. Soc.* **2004**, *126*, 12949.

(7) Schauermann, S.; Hoffmann, J.; Johanek, V.; Hartmann, J.; Libuda, J.; Freund, H.-J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2532.

(8) Riahi, G.; Guillemot, D.; Polisset-Tfoin, M.; Khodadadi, A. A.; Fraissard, J. *Catal. Today* **2002**, *72*, 115.

(9) (a) Uozumi, Y.; Nakao, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 194. (b) Price, K. E.; McQuade, D. T. *Chem. Commun.* **2005**, 1714.

(10) Choi, M.; Lee, D.-H.; Na, K.; Yu, B.-W.; Ryoo, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 3673.

(11) For example: (a) Cho, J. K.; Najman, R.; Dean, T. W.; Ichihara, O.; Muller, C.; Bradley, M. *J. Am. Chem. Soc.* **2006**, *128*, 6276. (b) Najman, R.; Cho, J. K.; Coffey, A. F.; Davies, J. W.; Bradley, M. *Chem. Commun.* **2007**, 5031. (c) Shin, J. Y.; Lee, B. S.; Jung, Y.; Kim, S. J.; Lee, S. *Chem. Commun.* **2007**, 5238. (d) Scheuermann, G. M.; Rumi, L.; Steurer, P.; Bannwarth, W.; Mülhaupt, R. *J. Am. Chem. Soc.* **2009**, *131*, 8262.

10.1021/ja9062053

it is favorable to attain the long-term stability of Pd entrapment. For example, Bradley et al. demonstrated that extensive cross-linking of a commercial solid-phase synthesis resin (PS-PEG) was an effective way for PdNP capture to suppress the Pd leaching.[11a] Highly durable catalysts were also obtained by the postcapturing procedure for PdNPs on spherical silica particles, as shown by Lee's group.[11c] These preceding works are interesting, but it should be also pointed out that they are somewhat tedious, due to the stepwise nature for construction of the capture frameworks. In this article, we wish to propose a new capture strategy for PdNPs entrapped in microporous network polymers. An interesting feature of this method is that the PdNP formation concurrently occurs with synthesis of polymer matrices. Consequently, this approach provides a one-pot convenient procedure to prepare captured PdNP systems, which work as high-performance and durable heterogeneous catalysts.

Microporous network polymers are highly designable solid supports and have attracted increasing interest.[12] The *polymerization-induced phase separation* (PIPS) technique is a traditional method for preparing microporous network polymers.[13] PIPS is typically carried out by polymerization of a homogeneous mixture consisting of monomers and solvents, where the solvents are miscible with the monomers but immiscible with the generating polymers, so that a phase-separated state can be obtained in the course of the polymerization. Subsequent removal of the solvents leaves pores inside the network polymers, and the microporous structure thus obtained usually shows a very high surface area. On the basis of such interesting features, the microporous polymers prepared by the PIPS method have been extensively utilized in a variety of application fields. The molecular imprinting technique is a unique example of microporous polymer usage, aiming toward applications in molecular recognition, enzyme-mimic catalytic studies, and medicine.[14] Interestingly, this technique strongly depends on the rigid frameworks of the microporous polymers, which result from the highly cross-linked polymer network structure produced by the PIPS process. Moreover, recently Kanamori et al. clearly proved the designable nature of PIPS. According to their strategy, microporous network polymers with well-defined bicontinuous morphologies were obtained in association with living radical polymerization concepts through the characteristic spinodal decomposition.[12e,15]

On the basis of the aforementioned intriguing structural features, we envisaged that the microporous polymers are powerful tools for the capture of PdNPs as matrices. We also focused on the fact that a radical polymerization process is compatible with precious-metal reduction.[16] According to some precedents, radicals at growing polymer chains are responsible for the metal reductions. For example, when bulk polymerization of methyl methacrylate or acrylonitrile was carried out in the presence of metal salts such as Pd^{2+} and Ag^{+}, the corresponding metal nanoparticles were obtained in polymer solid despite the absence of any specific reducing reagents.[17] Moreover, it is of interest that the radicals of growing polymers seem to be capable of producing highly crystalline metal nanoparticles.[17c] This is important because the crystallinity of metal nanoparticles is a crucial factor for determining its catalytic ability.[18] We therefore hypothesized that, if this reduction system is applied to the PIPS setup of cross-linkable monomer/porogenic solvent mixtures, crystalline PdNPs captured in microporous network polymers would be produced in a convenient one-pot procedure.

In order to verify the hypothesis, a PIPS system of ethylene glycol dimethacrylate (EGDMA) and dimethylformamide (DMF)/diethylene glycol dimethyl ether (diglyme) mixed solvent was arranged in the presence of Pd acetate ($Pd(OAc)_2$) and a radical initiator, 2,2′-azobis(isobutyronitrile) (AIBN). Poly(amidoamine) (PAMAM) dendrimers were selected as a ligand for both Pd^{2+} complexation and stabilization of the created PdNPs. PAMAM and the related dendrimers are widely used for producing size-tuned metal nanoparticles.[19] Unlike the bulk polymerization cases mentioned above, the addition of ligands should be crucial for the present phase-separation system to make the Pd source more distributed to the polymer phase rather than the solvent phase.

Results and Discussion

Synthesis of Composite Microporous Polymers. The outline of this study is depicted in Figure 1. A dendritic monomer (**G3-m**) was initially synthesized by the equimolar reaction between the terminal primary amines of generation-three PAMAM dendrimer and 2-methacryloyloxyethyl isocyanate. **G3-m** contains 30 tertiary amines in the internal region and 32 peripheral methacrylate functions tethered by urea linkages. After premixing with $Pd(OAc)_2$ in DMF, **G3-m** was copolymerized with large excess of EGDMA (9-fold in weight ratio) in a PIPS setup at 70 °C to produce microporous network polymers. In the polymerization mixtures, excess Pd^{2+} ions were introduced against the tertiary amine of **G3-m** (Pd/N ratio 4/3), since the urea linkages are also expected to function as ligands for Pd^{2+} capture.[11c,20] The resulting polymer solids were sized to 75−300 μm and used for subsequent structural analysis and catalytic studies.[6a,21]

Several different amounts of AIBN were added to the polymerization mixtures; the molar ratios to $Pd(OAc)_2$ were 0.046 (**G3-p1**), 0.092 (**G3-p2**), 0.18 (**G3-p3**), 0.55 (**G3-p4**), and 1.1 (**G3-p5**), respectively. From a viewpoint of AIBN/vinyl unit

---

(12) For example: (a) Chen, L.; Phillip, W. A.; Cussler, E. L.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 13786. (b) O'Connor, N. A.; Paisner, D. A.; Huryn, D.; Shea, K. J. *J. Am. Chem. Soc.* **2007**, *129*, 1680. (c) Bhaskarapillai, A.; Sevilimedu, N. V.; Sellergren, B. *Ind. Eng. Chem. Res.* **2009**, *48*, 3730. (d) Takeda, K.; Kuwahara, A.; Ohmori, K.; Takeuchi, T. *J. Am. Chem. Soc.* **2009**, *131*, 8833. (e) Kanamori, K.; Hasegawa, J.; Nakanishi, K.; Hanada, T. *Macromolecules* **2008**, *41*, 7186.

(13) (a) Inoue, T. *Prog. Polym. Sci.* **1995**, *20*, 119. (b) Kiefer, J.; Hedrick, J. L.; Hilborn, J. G. *Adv. Polym. Sci.* **1999**, *147*, 161.

(14) (a) Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1812. (b) *Molecularly Imprinted Polymers: Man Made Mimics of Antibodies and their Applications in Analytical Chemistry*; Sellergren, B., Ed.; Elsevier: Amsterdam, 2001. (c) Alexander, C.; Davidson, L.; Hayes, W. *Tetrahedron* **2003**, *59*, 2025.

(15) (a) Kanamori, K.; Nakanishi, K.; Hanada, T. *Adv. Mater.* **2006**, *18*, 2407. (b) Hasegawa, J.; Kanamori, K.; Nakanishi, K.; Hanada, T.; Yamago, S. *Macromolecules* **2009**, *42*, 1270. (c) Hasegawa, J.; Kanamori, K.; Nakanishi, K.; Hanada, T.; Yamago, S. *Macromol. Rapid Commun.* **2009**, *30*, 986.

(16) (a) Nakao, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 826. (b) Nakao, Y. *J. Colloid Interface Sci.* **1995**, *171*, 386.

(17) (a) Yanagihara, N.; Uchida, K.; Wakabayashi, M.; Hara, T. *Mater. Res. Soc. Symp. Proc.* **1998**, *501*, 227. (b) Yanagihara, N.; Uchida, K.; Wakabayashi, M.; Uetake, Y.; Hara, T. *Langmuir* **1999**, *15*, 3038. (c) Zhang, Z.; Han, M. *J. Mater. Chem.* **2003**, *13*, 641. (d) Aymonier, C.; Bortzmeyer, D.; Thomann, R.; Mülhaupt, R. *Chem. Mater.* **2003**, *15*, 4874.

(18) (a) Gentle, T. M.; Muetterties, E. L. *J. Phys. Chem.* **1983**, *87*, 2469. (b) Rucker, T. G.; Logan, M. A.; Gentle, T. M.; Muetterties, E. L.; Somorjai, G. A. *J. Phys. Chem.* **1986**, *90*, 2703.

(19) For reviews, see: (a) Scott, R. W. J.; Wilson, O. M.; Crooks, R. M. *J. Phys. Chem. B* **2005**, *109*, 692. (b) Astruc, D.; Ornelas, C.; Ruiz, J. *Acc. Chem. Res.* **2008**, *41*, 841. (c) Andrés, R.; de Jesús, E.; Flores, J. C. *New J. Chem.* **2007**, *31*, 1161.

(20) (a) Ramarao, C.; Ley, S. V.; Smith, S. C.; Shirley, I. M.; DeAlmeida, N. *Chem. Commun.* **2002**, 1132. (b) Ley, S. V.; Mitchell, C.; Pears, D.; Ramarao, C.; Yu, J.-Q.; Zhou, W. *Org. Lett.* **2003**, *5*, 4665.

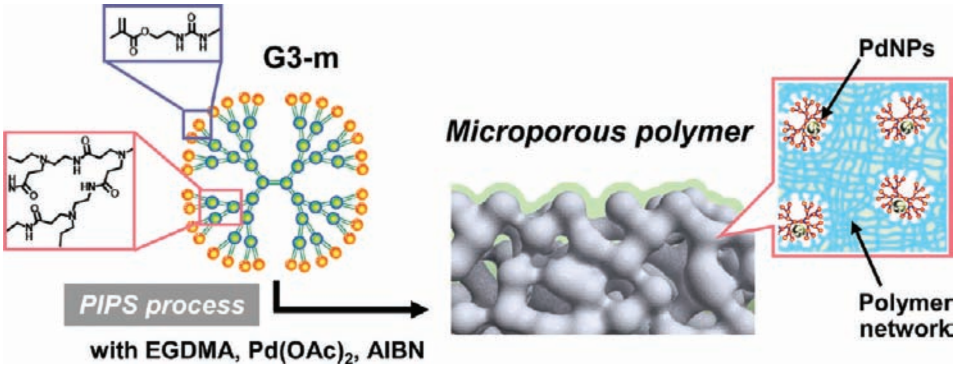


Figure 1. Schematic outline of the preparation of microporous network polymers that contain PdNPs.

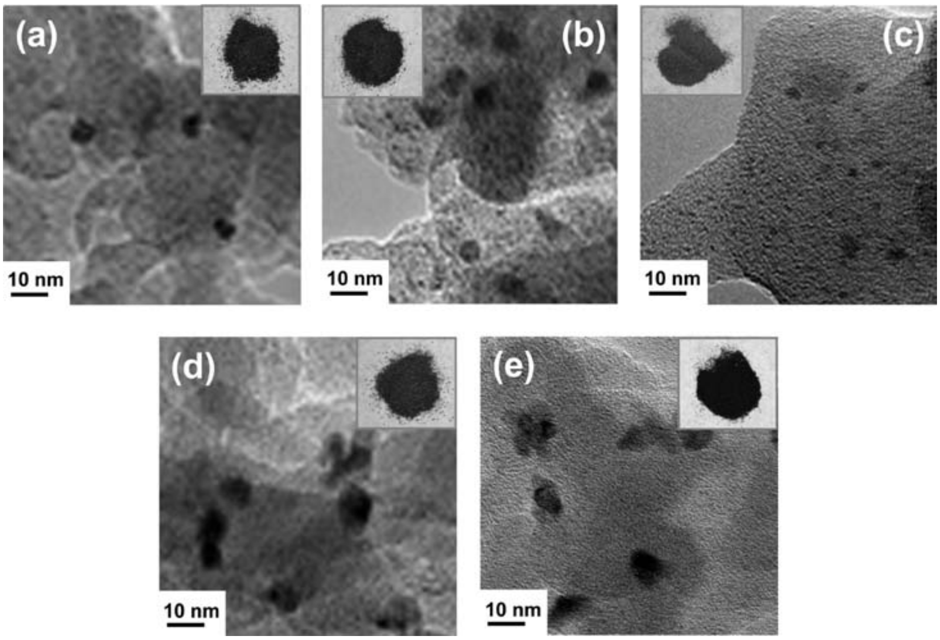


Figure 2. TEM images of created PdNPs in the microporous polymers: (a) **G3-p1**; (b) **G3-p2**; (c) **G3-p3**; (d) **G3-p4**; (e) **G3-p5**. Insets: appearances of each sized polymer.

molar ratio, those correspond to 0.0017, 0.0033, 0.0066, 0.020, and 0.040, respectively. For all of the cases, polymerization reactions proceeded smoothly and finally insoluble polymer solids were obtained through the PIPS process. Figure 2 shows transmission electron microscopy (TEM) images of the polymers, with insets displaying pictures of the sized polymers. It is somewhat surprising that only a slight difference in color was found among the polymers. The color of the polymers should be closely related to the electronic state of the Pd atoms, and therefore the fact that these polymers similarly displayed a dark gray color certainly indicates that the Pd^{2+} ions introduced were reduced to a large extent despite the difference of AIBN contents among the polymers. The TEM analysis supports this presumption: that is, the created PdNPs were clearly found in the images for all the polymer cases.

In the polymerization process, if the Pd reduction takes place only by action of the radicals at growing polymer chains, two radicals are consumed to reduce a Pd^{2+} ion.[17a] An AIBN molecule decomposes and generates two 2-cyano-2-propyl radicals. Therefore, to reduce Pd^{2+} ions stoichiometrically by the growing polymer radicals that are initiated by the AIBN decomposition, at least an equimolar amount of AIBN is required against Pd^{2+} ions. Among the polymerization mixtures, only that having the highest amount of AIBN, **G3-p5**, satisfies this criterion. The thermal spontaneous decomposition temperature of $Pd(OAc)_2$ is 200−260 °C,[22] which is much higher than the polymerization temperature of the present system. It is therefore suggested that there have to be chemicals responsible for Pd reduction in the polymerization process other than the polymer radicals.

Currently, details regarding the present PdNP formation system are still unclear. In addition to the radicals at growing polymer chains mentioned above, an organic radical directly converted from the vinyl groups of EGDMA,[17c] the AIBN initiating radical itself,[23] and the amino groups of **G3-m** can be also listed as possible reducing reagents. However, a very important finding was obtained herein: that is, the PIPS approach was proved to be a convenient and rational method to fabricate a PdNP capture system, which

---

(21) For related composite materials having the dendrimer-stabilized metal nanoparticles, see: (a) Scott, R. W. J.; Wilson, O. M.; Crooks, R. M. *Chem. Mater.* **2004**, *16*, 5682. (b) Knecht, M. R.; Wright, D. W. *Chem. Mater.* **2004**, *16*, 4890. (c) Huang, W.; Kuhn, J. N.; Tsung, C.-K.; Zhang, Y.; Habas, S. E.; Yang, P.; Somorjai, G. A. *Nano Lett.* **2008**, *8*, 2027. (d) Kuhn, J. N.; Huang, W.; Tsung, C.-K.; Zhang, Y.; Somorjai, G. A. *J. Am. Chem. Soc.* **2008**, *130*, 14026.

(22) (a) Gross, M. E.; Appelbaum, A.; Gallagher, P. K. *J. Appl. Phys.* **1987**, *61*, 1628. (b) Esumi, K.; Tano, T.; Meguro, K. *Langmuir* **1989**, *5*, 268. (c) Tano, T.; Esumi, K.; Meguro, K. *J. Colloid Interface Sci.* **1989**, *133*, 530.

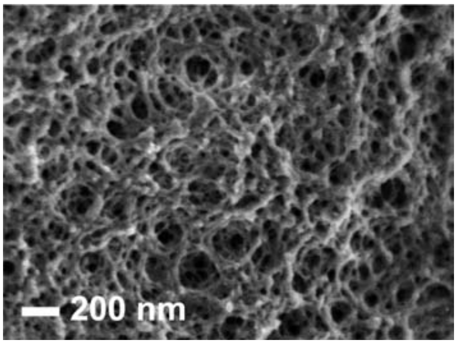


Figure 3. FE-SEM image of the microporous polymer **G3-p3**.

involves the polymer synthesis and Pd reduction in one pot. Work is now in progress to get a detailed insight into chemical events occurring in the present approach.

Finally in this section, it is worthwhile to compare the present system to that prepared with additional reducing reagents. When tetrabutylammonium borohydride (TBABH$_4$), a typical reagent for metal reduction, was added to the PIPS process, the polymerization was accompanied by the formation of Pd black out of the microporous polymer. Additionally, the Pd^0 species in the polymer appear to be considerably large according to the TEM observations (Figure S1). This apparently comes from rapid Pd reduction with TBABH$_4$, probably due to the fact that Pd reduction by additional reagents proceeds independently of the polymerization reaction. In contrast, the Pd reduction without TBABH$_4$ proceeds competitively and cooperatively with the polymer propagation, since all the possible reducing reagents are inherent components for the PIPS process.

Characterization of a Composite Microporous Polymer (G3-p3). This section begins with a comparison among the TEM images shown in Figure 2. It is of interest to note that **G3-p3** prepared under the condition of a 0.18 AIBN/Pd ratio gave the smallest PdNPs. The PdNPs in this polymer mainly consist of small particles <2 and 3−5 nm in diameter, while other polymers contain relatively large PdNPs of around 10 nm. To define the reason why **G3-p3** gave this specific result is not straightforward, but a possible speculation can be made that the amount of AIBN radicals generated in **G3-p3** at an early stage might suit the controlled growth of PdNPs inside the dendrimers under the competitive conditions between the polymer propagation and Pd reduction. With reference to these results, **G3-p3** was used for the following studies.

Thermogravimetry/differential thermal analysis (TG/DTA) for **G3-p3** revealed that its Pd loading was 0.31 mmol g^{-1}, which indicates that 98% of the feed Pd^{2+} ions are incorporated in the polymer. This is in good accord with the result that no Pd species was released to the solvent phase during the PIPS process.

Figure 3 shows a scanning electron microscopy (SEM) image of **G3-p3**. This clearly exhibits a 3D bicontinuous structure that consists of an interpenetrating network of polymer skeletons and pores. On the basis of the nitrogen adsorption−desorption analysis, the BET surface area of **G3-p3** was very large, which was estimated to be 511 m^2 g^{-1}. Moreover, **G3-p3** was found to have a mesoporosity; BJH analysis gave a peak pore diameter of 22.2 nm, an average pore diameter of 9.9 nm, and a total pore volume of 1.01 mL g^{-1} (Figure 4). When **G3-p3** is used in catalytic studies, all these characteristics should benefit it in making reaction substrate access to the Pd sites easier.

To get an insight into more detailed structure of the PdNPs, high-resolution (HR) TEM analysis was carried out for **G3-p3**.

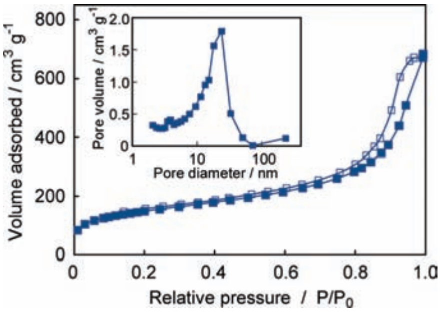


Figure 4. Nitrogen adsorption (filled squares)−desorption (open squares) isotherms of **G3-p3**. The inset shows the pore size distribution from the desorption data.

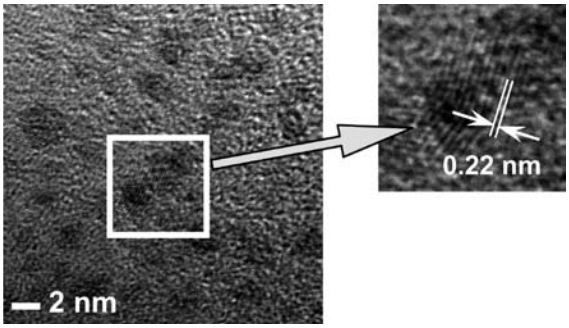


Figure 5. HR-TEM image of **G3-p3**: crystalline PdNPs with resolvable atomic lattice.

As mentioned above, **G3-p3** possesses very small PdNPs with a diameter of around 2.0 nm, which was easily detected in the image of Figure 5. The high-resolution image is lattice-resolvable, showing the crystalline nature of the PdNPs. The interplanar spacing of the 1D fringes is 0.22 nm, which agrees well with the (111) lattice spacing of face-centered cubic (fcc) Pd.[24] The Pd(111) facets are generally acknowledged as the best surface for catalytic usage.[18]

These morphological features were consistent with the X-ray scattering data of **G3-p3**. On the basis of the small-angle X-ray scattering (SAXS) data of this polymer (Figure S2), the PdNPs were calculated to consist of small particles with diameters of 1.3 and 5.1 nm, where the ratios of numbers of particles were 0.96 and 0.04, respectively. It is of interest that these values for the particle size are very close to those evaluated from the TEM results. Likewise, a peak that is assigned to the Pd(111) facets was clearly observed in the wide-angle X-ray scattering (WAXS) pattern of **G3-p3** (Figure S3), which supports the crystalline nature of the created PdNPs.

Also of interest is the result of electron energy loss spectroscopy (EELS), in which elemental maps collected from **G3-p3** (Figure 6) reveal that Pd and N elements are located at nearly same positions. Thus, this result supports that the PdNPs were created in the dendrimer sites. In relation to this finding, when a control polymer was prepared by the PIPS process in the absence of **G3-m**, 48.8% of the added Pd^{2+} was detected in the porogenic solvent phase (ICP-AES). This strongly suggests the crucial role of the dendrimer ligand in Pd^{2+} capture.

Catalytic Performances of G3-p3. Catalytic performances of **G3-p3** were investigated for a heterogeneous Suzuki−Miyaura

---

(23) (a) Chen, C.-W.; Chen, M.-Q.; Serizawa, T.; Akashi, M. *Adv. Mater.* **1998**, *10*, 1122. (b) Chen, C.-W.; Serizawa, T.; Akashi, M. *Langmuir* **1999**, *15*, 7998. (c) Chen, C.-W.; Serizawa, T.; Akashi, M. *Chem. Mater.* **2002**, *14*, 2232. (d) Kong, H.; Jang, J. *Chem. Commun.* **2006**, 3010.

(24) Liu, Q.; Bauer, J. C.; Schaak, R. E.; Lunsford, J. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 6221.

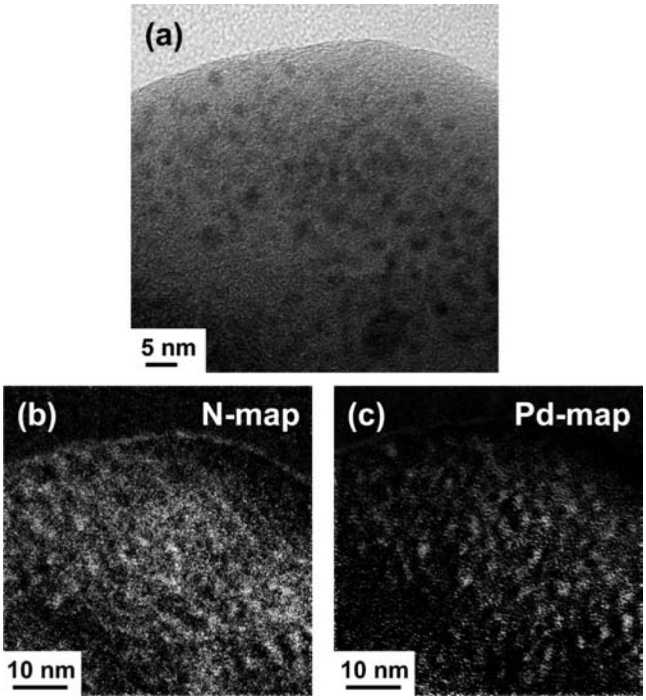


Figure 6. Spatially resolved elemental EELS maps of **G3-p3**: (a) zero-energy loss image; (b) nitrogen element mapping; (c) palladium element mapping. Note that the images given are not in identical positions due to sample fluctuation but definitely present the information from the same area.

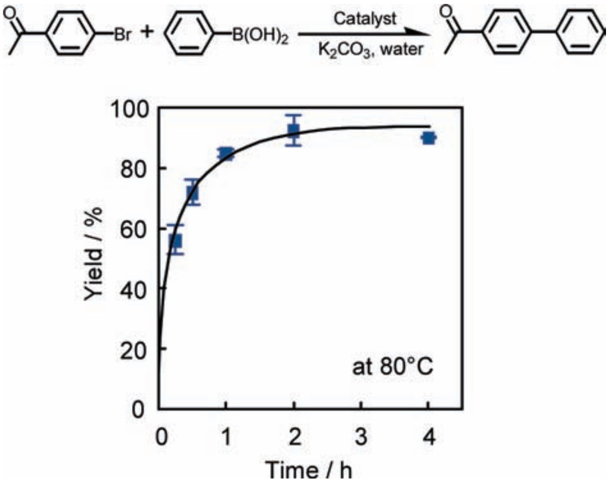


Figure 7. Kinetic profile of the **G3-p3** catalyzed Suzuki−Miyaura reaction in water. Reaction conditions: 4′-bromoacetophenone (0.65 mmol), phenylboronic acid (0.86 mmol), potassium carbonate (2.0 mmol), **G3-p3** (10^{-2} molar equiv), water (12 mL), 80 °C. The reaction yield was evaluated as an average value from at least three independent experiments.

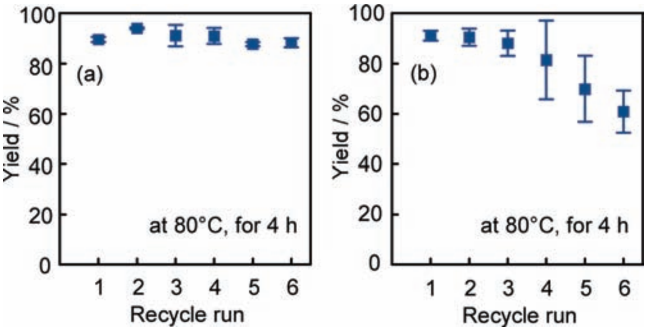


Figure 8. Recycle performances of the polymer catalysts: (a) **G3-p3**; (b) **Cont-p**. Reaction conditions selected were identical with those shown in Figure 7. The reaction yield was evaluated as an average value from at least three independent experiments.

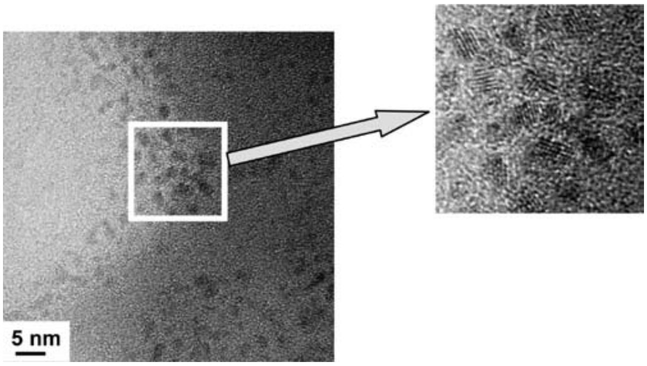
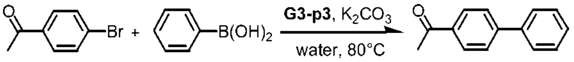


Figure 9. HR-TEM image of **G3-p3** after recycle use for catalytic Suzuki−Miyaura reactions: crystalline PdNPs with resolvable atomic lattice.

Table 1. **G3-p3** Catalyzed Suzuki-Miyaura Reactions



G3-p3/mol equiv	time/h	yield/%	TON[a]
0.01	4	96	96
0.0001	20	100	10000
0.00001	40	85	85000

[a] Turnover number.

reaction of 4′-bromoacetophenone and phenylboronic acid in water. The fabrication of water-compatible catalysts is a highly challenging subject in the field of green sustainable chemistry.[25] Figure 7 shows a kinetic profile of the catalytic reaction. Under the presence of 10^{-2} molar equiv of **G3-p3**, the reaction efficiently proceeded and gave the desired product, 4-acetylbiphenyl, in >90% yield after 2 h. **G3-p3** was successfully recovered by simple filtration and reused with only a minimal loss of activity. Interestingly, it has been proved that the Pd content in the reaction mixture after filtration corresponds to only 0.27% of the initial charge on the basis of the ICP-AES analysis. Thus, **G3-p3** was demonstrated to be a durable catalyst working under the successive recycle runs, which revealed a high yield greater than 90% even at the eighth run (Figure 8a). No noticeable change of the TEM image in size and lattice pattern (Figure 9) and of the WAXS pattern (Figure S3) was observed for the PdNPs after recycling. When the catalytic reaction was examined with a low amount of **G3-p3**, the turnover number (TON) reached 8.5×10^4 while a good yield was maintained (Table 1).

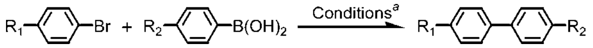
With regard to the catalytic high efficiency and recyclability of **G3-p3**, the recent study of Astruc's group is worthy of note.[26] They demonstrated that the very high catalytic activity of their dendrimer-stabilized PdNPs system originated from the action of detached Pd atoms in the solution phase, where the PdNP

---

(25) For recent remarkable studies, see: (a) Ornelas, C.; Ruiz, J.; Salmon, L.; Astruc, D. *Adv. Synth. Catal.* **2008**, *350*, 837. (b) Uozumi, Y.; Yamada, Y. M. A. *Chem. Rec.* **2009**, *9*, 51. (c) Han, J.; Liu, Y.; Guo, R. *J. Am. Chem. Soc.* **2009**, *131*, 2060.

(26) Diallo, A. K.; Ornelas, C.; Salmon, L.; Ruiz Aranzaes, J.; Astruc, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8644. For related papers, see: Davies, I. W.; Matty, L.; Hughes, D. L.; Reider, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 10139. de Vries, J. G. *Dalton Trans.* **2006**, 421.

Table 2. **G3-p3** Catalyzed Suzuki−Miyaura Reactions of Various Substrates



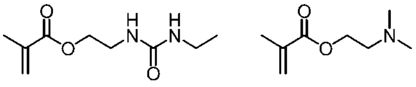
entry	R_1	R_2	time/h	yield/%
1	CH_3CO	H	4	96
2	CN	H	4	83
3	OH	H	4	86
4	CH_3O	H	8	82
5	CH_3O	CH_3O	8	81

[a] Conditions: aryl bromide (0.65 mmol), arylboronic acid (0.86 mmol), potassium carbonate (2.0 mmol), **G3-p3** (10^{-2} molar equiv of aryl bromide), water (12 mL), 80 °C.

functions as a reservoir for delivering catalytically active Pd atoms to the reaction field. On this basis, it is certainly suggested that the catalytic high efficiency and recyclability of PdNPs are compatible with the Pd leaching phenomena. In our system, the loss of Pd was very small as mentioned above, thus probably indicating that this is predominantly not the case for the solution-phase catalysis. A possible explanation can be made that the isolated Pd atom remains coordinated to the dendrimer ligands to a large extent,[27] so that the Pd could subsequently return to the mother PdNPs after the catalytic cycle. Alternatively, a heterogeneous pathway that entirely operates the catalytic events at the surface of PdNPs[28] is also a possible reason for explaining the small loss of Pd during the reaction. At any rate, our capture approach should have an advantage in suppressing the Pd leaching, because of the plausible solidly built framework structure that guards the PdNPs by the adjacent dendrimer templates and the surrounding solid matrices of network polymers. However, it should be noted that even a small loss of the released Pd could contribute to some extent to the entire catalytic performance of the polymer.[29]

The catalytic activity of **G3-p3** was then examined for the aqueous Suzuki−Miyaura reactions with a range of aryl bromides and arylboronic acids. Using both electron-rich and electron-deficient reactants, the desired coupling products were obtained in good yields. The results are summarized in Table 2.

Finally, it is of interest to refer to a preliminary study investigating the dendrimer template effect of **G3-p3**. A control polymer containing PdNPs (**Cont-p**) was prepared with both tertiary amine bearing (**TA-m**) and urea linkage containing (**UR-m**) methacrylate monomers under identical PIPS conditions (Figure 10). **Cont-p** that contains amounts of the ligand sites (tertiary amines and urea linkages) identical with those in **G3-p3** was found to be highly porous and showed a large BET surface area of 345 $m^2\ g^{-1}$. The porosity of **Cont-p** was comparable with that of **G3-p3**, revealing that the 3D mesoporous structures of these two polymers are nearly equal (Figure S4). However, **Cont-p** apparently gave different catalytic durability regarding Suzuki−Miyaura reactions. In the early runs with **Cont-p**, the desired biphenyl product was obtained in high yield (ca. 90%). However, the reaction yield gradually decreased with successive recycle runs and was only 60% at the sixth run (Figure 8b). The TEM analysis (Figure S5) indicates that the catalytic use of **Cont-p** is likely to induce the size increase and/or agglomeration of PdNPs. This is probably due to the lack of an integrated coordination environment in **Cont-p**, which should lead to Pd agglomeration under the provided dynamic equilibrium mechanism between PdNPs and isolated Pd species.[26,27] Studies are now in progress to further investigate the dendrimer template effect for the present PdNP system supported on microporous polymers.



UR-m **TA-m**

Figure 10. Chemical structures of the methacrylate monomers used for the **Cont-p** synthesis.

Conclusions

In the present study, we have demonstrated that the PIPS technique is a convenient and useful tool to prepare microporous polymer supports for PdNPs capture. In this system, the PIPS plays two important roles: one is in producing microporous platforms and the other in converting Pd ions to zerovalent nanoparticles. Under the competitive conditions of the Pd reduction and polymer propagation, the controlled growth of PdNPs was achieved with the aid of the dendrimer ligands. The resultant polymer was proved to have a mesoporosity with a very high specific surface area, and the created PdNPs were highly crystalline and very small with a diameter of mainly around 2.0 nm. On the basis of the solidly built framework structure, the loss of Pd was greatly suppressed during the catalytic cycles. Thereby, the PdNP-containing microporous polymer can function as an excellent catalyst for heterogeneous aqueous carbon cross-coupling reactions, with the fascinating nature of both high activity and durability.

The next important issue of our study is to elucidate the detailed mechanism of the PIPS process involving Pd reduction to lead to PdNP formation. Work is currently underway to get a detailed insight into the present system and also to extend this technique to other metals, ligands, and catalytic reactions.

Acknowledgment. Parts of the TEM images were obtained at the Graduate School of Materials Science, Nara Institute of Science and Technology, with the support of Kyoto-Advanced Nanotechnology Network. We thank Dr. Masafumi Uota for helpful discussions and technical support. We also thank the Analysis Center and Physics & Characterization Science Group, Corporate R&D Department of DIC Corp., for analytical support.

Supporting Information Available: Text and figures giving experimental details, SAXS and WAXS profiles for the microporous polymers, and FE-SEM and TEM micrographs for the control polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

JA9062053

---

(27) Bernechea, M.; de Jesús, E.; López-Mardomingo, C.; Terreros, P. *Inorg. Chem.* **2009**, *48*, 4491.

(28) (a) Narayanan, R.; El-Sayed, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 8340. (b) Mori, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2004**, *126*, 10657.

(29) For a reference, brief filtration tests were performed for **G3-p3**. The polymer was placed in water at 80 °C with shaking for 4 h and then filtered off. When the filtrate was used for a Suzuki−Miyaura reaction (for the conditions, see Figures 7 and 8), the catalytic yield obtained was 3.1%, where the Pd content in the filtrate was estimated to be 0.35% of the initial charge (ICP-AES).