



Size-tuned hydrogel network of palladium-confining polymer particles: a highly active and durable catalyst for Suzuki coupling reactions in water at ambient temperature

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Abstract

Poly(*N*-isopropylacrylamide)-based hydrogel particles (GPs) with different sized hydrogel networks were developed and used to confine a palladium (Pd) catalyst. The size of the gel network was tuned by varying the feed ratio of the cross-linking monomer. Nanosized-Pd(0) was loaded into the GPs, which contain a tertiary-amine ligand, via Pd-ion adsorption and subsequent reduction. The Pd-loaded GPs were used as the catalyst for a Suzuki coupling reaction between phenylboronic acid and 4-bromobenzoic acid in water at 30 °C. Due to the hydrophilic reaction platform provided by the hydrogel matrix of the GPs, the catalytic efficiencies of Pd-loaded GPs were significantly higher than those of commercially available Pd-loaded supports. Notably, the Pd-loaded GPs with the smallest gel networks were highly durable for Suzuki coupling reactions. It is plausible that the smaller network minimized or prevented the enlargement of Pd(0) during the catalytic cycle. The facile synthesis of the GPs, environmentally benign catalytic system, and high catalytic durability and activity of these Pd-loaded GPs are all important factors for the industrial application of these materials.

Introduction

In organic synthesis, carbon–carbon bond formation using palladium (Pd)-catalyzed coupling reactions is well established. In particular, the Suzuki coupling reaction between boronic acids and aryl halide derivatives is an important tool for the synthesis of aromatic compounds, which often constitute pharmaceuticals, agrochemicals, and natural products [1, 2]. The immobilization of Pd catalysts is an attractive methodology that allows for the simple recovery and reuse of a catalyst without the need for scavengers, in

contrast to homogeneous catalysts [3, 4]. The recent and increasing interest in green and sustainable chemistry has driven the development of organic synthesis under mild conditions with low catalyst ratios, water as a solvent, and ambient temperatures [5, 6]. Thus, understanding and developing immobilized Pd catalysts that are highly stable and active in exclusively aqueous media are very important.

Pd catalysts immobilized onto the surfaces of supports are typically on the nano-scale, which contributes to their excellent catalytic activities [3]. However, surface-immobilized Pd catalysts gradually form bulky Pd over many catalytic cycles, which leads to their deactivation [7]. To overcome this problem, Pd catalysts confined within a support material have been designed [8]. Catalysts in which the Pd is confined are highly resistant to leaching and enlargement during repeated catalytic cycles, which results in higher turnover numbers (TONs).

Pd catalysts have been confined within a variety of support materials, including mesoporous silica [9–14], sulfur-modified metals [8, 15, 16], metal organic frameworks [17–21], dendrimers [22–31], covalent organic frameworks [32–36], and microporous organic polymers [37–40], for use in carbon–carbon bond formation. Although these confined catalyst systems have overcome some problems, the ability for the substrate to access the catalyst is often inhibited. Thus, an investigation on the effects of confinement on catalytic

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performance should allow the rational design of immobilized Pd catalysts.

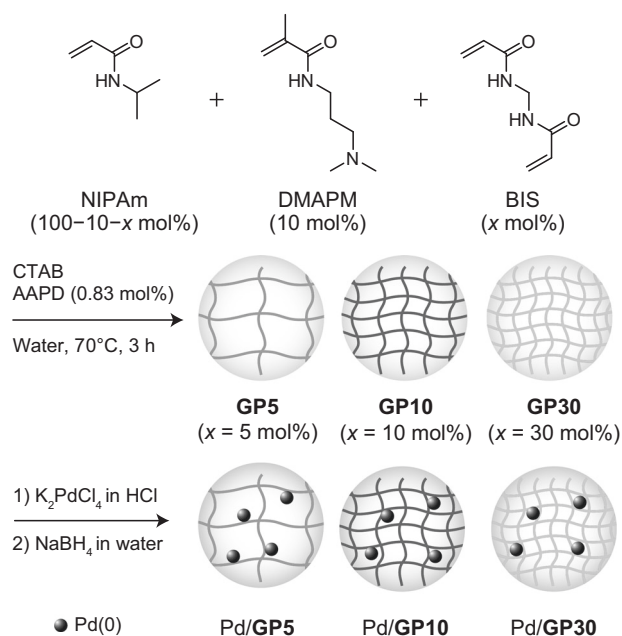
We have previously reported the development of nanosized Pd catalysts confined within poly(*N*-isopropylacrylamide) (PNIPAm)-based hydrogel particles (GPs) via coordination to tertiary-amino groups in the gel network to yield Pd-loaded GPs (Pd/GPs) [41, 42]. The Pd/GPs successfully catalyzed both hydrogenation and Suzuki coupling reactions in an aqueous solution because the GPs were well dispersed in the aqueous media.

Herein, a new library of PNIPAm-based GPs with different-sized gel networks was prepared to investigate and understand the catalytic performance of Pd confined within GPs. Gel networks with a defined size were successfully fabricated, and the nanosized Pd was firmly confined within the GPs. Suzuki coupling reactions using the fabricated Pd/GPs were very fast under completely aqueous conditions at ambient temperature (30 °C) compared to commercially available Pd-loaded supports. Importantly, confining the Pd catalysts within the gel networks of defined sizes efficiently prevented deactivation of the Pd catalyst. This work led to the largest reported TON for a Suzuki coupling reaction under completely aqueous conditions at ambient temperature using an immobilized Pd catalyst.

Experimental

Materials

Water with a conductivity of 18.2 MΩ cm (Milli-Q, Millipore Co., Bedford, MA, USA) was used in all experiments. NIPAm (Wako Pure Chemical Industries Ltd., Osaka, Japan), *N*-(3-dimethylaminopropyl) methacrylamide (DMAPM, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), *N,N'*-methylenebisacrylamide (BIS, Tokyo Chemical Industry Co., Ltd.), cetyltrimethylammonium bromide (CTAB, Wako Pure Chemical Industries Ltd.) and 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPD, Wako Pure Chemical Industries Ltd) were used as the gel matrix, tertiary-amine ligand, cross-linker, surfactant, and radical initiator, respectively. NIPAm was purified by recrystallization from benzene/*n*-hexane and dried in vacuo at room temperature. The polymerization inhibitor in DMAPM was removed using an activated alumina column. K₂PdCl₄ (Sigma-Aldrich Co.) and NaBH₄ (Tokyo Chemical Industry Co. Ltd.) were used to prepare the Pd-loaded catalyst. Pd-loaded carbon (Pd/C, Wako Pure Chemical Industries Ltd) and Pd-loaded alumina (Pd/Al₂O₃, Wako Pure Chemical Industries Ltd) were also used as reference Pd catalysts. Phenylboronic acid (Tokyo Chemical Industry Co., Ltd.), 4-bromobenzoic acid (Tokyo Chemical Industry Co., Ltd.), and Na₂CO₃ (Wako Pure Chemical Industries Ltd.) were used to prepare the stock solution of substrates. 4-Phenylbenzoic acid (Tokyo Chemical Industry Co., Ltd) was used to prepare the



Scheme 1 Preparation of Polymer Hydrogel Particles (GPs) Containing Tertiary-Amine Ligands and Loading of Pd Catalyst into the Gel Network of the GPs

standard solution for calibration of the products in the Suzuki coupling reaction.

Preparation and characterization of GPs with different-sized gel networks

PNIPAm-based hydrogel particles (GPs) were used as a support for the Pd catalysts and were synthesized by the copolymerization of NIPAm with a tertiary-amine ligand and a cross-linker above the lower critical solution temperature of PNIPAm (Scheme 1) [41, 42]. NIPAm (100-10-x mol%), DMAPM (10 mol%), BIS (x = 5, 10, and 30 mol%), and CTAB were dissolved in water to adjust the total monomer concentrations (Supplementary Information, Table S1). The monomer solutions were degassed with N₂ gas for more than 1 h, followed by the addition of AAPD as a radical initiator (0.83 mol% of total monomers) to each solution. The mixture was stirred at 70 °C for 3 h. The resulting milky solution was dialyzed (molecular-weight cutoff: 12,000-14,000) against water for 3 days, in which the water was changed 9 times. After freeze-drying a portion of the dialyzed solution, the yield of GPs was determined from the weight of the dry GPs. The hydrodynamic diameter and amount of amine in the GPs were estimated using dynamic light scattering (DLS) and acid-base titration, respectively (see the Supplementary Information). The time course of the monomer (NIPAm, DMAPM, and BIS) conversion was also measured during the copolymerization of GPs in D₂O under similar polymerization conditions (see the Supplementary Information).

Loading of nanosized Pd(0) into GPs

Pd-loaded GPs (Pd/GPs) were prepared by the adsorption of Pd(II) ions, which were subsequently reduced to Pd(0) (Scheme 1) [41, 42]. After freeze-drying and ion exchange, each of the GPs (100 mg) was mixed with K_2PdCl_4 (0.075 mmol) in an aqueous HCl solution (1.0 mmol L^{-1} , 75 mL). The solutions were shaken at room temperature for 2 days. The solution was dialyzed (molecular-weight cutoff: 10,000) against an aqueous HCl solution (1.0 mmol L^{-1}) for 3 days, in which the HCl solution was changed 5 times. After washing, the GPs, the Pd ions in the GPs were reduced to Pd(0) using an aqueous $NaBH_4$ solution, until the pH reached 8. The solution was then dialyzed (molecular-weight cutoff: 10,000) against water for 3 days, in which the water was changed 5 times. After freeze-drying, the resulting solution, Pd/GPs were obtained as a brown powder. The amount of Pd loaded into the GPs was estimated by immersion in aqua regia and analysis using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ICPS-8100, Shimadzu Corporation, Kyoto, Japan) (see the Supplementary Information). The Pd(0) in the GPs was observed using transmission electron microscopy (TEM, TECNAI 20, Philips FEI, Netherlands). The sizes of the Pd(0) particles loaded into the GPs were measured for 200 particles of Pd(0) using the TEM images (see the Supplementary Information).

Suzuki coupling reaction using Pd-loaded supports

Suzuki coupling reactions between phenylboronic acid and 4-bromobenzoic acid in aqueous media were conducted. Phenylboronic acid (200 mmol L^{-1} , 1.0 eq.), 4-bromobenzoic acid (220 mmol L^{-1} , 1.1 eq.), and Na_2CO_3 (220 mmol L^{-1} , 1.1 eq.) were dissolved in water (15 mL) and stirred at 30°C for 1 h. The catalyzed reaction was initiated by the addition of Pd/GPs, Pd/C, or Pd/ Al_2O_3 ($5 \times 10^{-2} \text{ mol\% Pd}$) to the substrate solution. A small aliquot was taken from the reaction mixture periodically, and the reaction progress was monitored using a high-performance liquid chromatography (HPLC, LC-2000Plus, JASCO Co., Tokyo, Japan) system with a reverse-phase column (Mightysil RP-18 GP 250-4.6, Kanto Chemical Co., Tokyo, Japan) and an ultraviolet detector. A solution of acetonitrile and water (50/50 v/v) including 0.1% trifluoroacetic acid was employed as the mobile phase. The percent conversion of phenylboronic acid was estimated using Eq. 1:

$$\text{Conv.(\%)} = 100 \times \frac{[\text{Phenylboronic acid}]_0 - [\text{Phenylboronic acid}]}{[\text{Phenylboronic acid}]_0}, \quad (1)$$

where the subscript 0 denotes the initial conditions. The apparent reaction rate constants (k) in the Suzuki coupling reaction were estimated by following the second-order reaction model:

$$\ln \frac{\frac{1}{[4\text{-Bromobenzoic acid}]_0 - [\text{Phenylboronic acid}]_0}}{\frac{[4\text{-Bromobenzoic acid}]_0[\text{Phenylboronic acid}]}{[4\text{-Bromobenzoic acid}]_0[\text{Phenylboronic acid}]_0}} = kt, \quad (2)$$

where t is the reaction time. The concentration of 4-bromobenzoic acid was estimated using Eq. 3:

$$[4\text{-Bromobenzoic acid}] = (a - 1)[\text{Phenylboronic acid}]_0 + [\text{Phenylboronic acid}] \quad (3)$$

where a is the feed ratio of 4-bromobenzoic acid to phenylboronic acid. Therefore, Eq. 2 was converted into Eq. 4:

$$\ln \left(\frac{\frac{1}{(a-1)[\text{Phenylboronic acid}]_0}}{\frac{(a-1)[\text{Phenylboronic acid}]_0 + [\text{Phenylboronic acid}]}{a[\text{Phenylboronic acid}]_0}} \right) = kt \quad (4)$$

The turnover numbers (TONs) and initial turnover frequencies (TOFs) of the Pd catalyst were calculated using Eqs. 5 and 6, respectively:

$$\text{TON} = \frac{[\text{Phenylboronic acid}]_0 - [\text{Phenylboronic acid}]}{[\text{Pd}]} \quad (5)$$

$$\text{TOF} = \frac{k[\text{Phenylboronic acid}]_0 [4\text{-phenylbenzoic acid}]_0}{[\text{Pd}]} \quad (6)$$

Evaluation of catalytic durability of Pd/GPs in the Suzuki coupling reaction

Phenylboronic acid (200 mmol L^{-1} , 1.0 eq.), 4-bromobenzoic acid (220 mmol L^{-1} , 1.1 eq.), and Na_2CO_3 (220 mmol L^{-1} , 1.1 eq.) were dissolved in water (15 or 150 mL) and stirred at 30°C for 1 h. The catalyzed reaction was initiated by the addition of Pd/GPs (5×10^{-3} or $5 \times 10^{-4} \text{ mol\% Pd}$) to the substrate solution. A small aliquot was taken from the reaction mixture periodically, and the reaction progress was monitored using an HPLC system. After the reaction, the reaction mixture was dialyzed (molecular-weight cutoff: 20,000) against water for ~1 day, during which the aqueous solution was changed 3 times to recover the spent Pd/GPs. The sizes of the Pd(0) particles loaded into the GPs were measured for 200 Pd(0) particles using TEM images (see the Supplementary Information).

Results and Discussion

Preparation and characterization of GPs with different-sized gel networks

The GPs were synthesized by the pseudo-precipitation copolymerization of NIPAm (100–10– x mol%), DMAPM (10 mol%), and BIS ($x = 5, 10,$ and 30 mol%) [41, 42]. These materials acted as the gel matrix, tertiary-amine ligand, and cross-linker, respectively (Scheme 1). Tuning the feed ratio of BIS gave **GP5** ($x = 5$ mol%), **GP10** ($x = 10$ mol%), and **GP30** ($x = 30$ mol%) with yields of 93, 78, and 78%, respectively (Supplementary Information, Table S1). DLS confirmed that the sizes of the resulting GPs were monomodal with hydrodynamic diameters of 99–175 nm at 30 °C (Supplementary Information, Supplementary Figure S1a). The hydrodynamic diameters changed with the temperature (Supplementary Figure S1b). From the acid–base titrations, the tertiary-amine densities in **GP5**, **GP10**, and **GP30** were determined to be 0.747, 0.696, and 0.612 mmol g⁻¹, respectively (Supplementary Figure S2 and Supplementary Table S2). Monitoring the copolymerization of the GPs in D₂O using ¹H NMR gave the time course of monomer conversion (Supplementary Figure S3).

All the obtained GPs were well dispersed in water media (Figure S1a). Additionally, the hydrodynamic diameters of the GPs were dependent on the temperature, which was attributed to the phase transition of PNIPAm (Figure S1b). The volume-change responsiveness to temperature was suppressed with an increased BIS content. The increase in the cross-linker content in the PNIPAm gel was considered to be proportional to the decrease in the size of the gel network [43]. The network sizes of the PNIPAm gels with BIS contents of 5, 10, and 30 mol% were calculated to be 7.9, 5.2, and 2.8 nm, respectively [44]. The sizes of the GP gel networks were observed to be controlled by their BIS contents. From the results of the acid–base titrations, tertiary-amine ligands were incorporated into the GPs (incorporation ratio, Supplementary Figure S2 and Supplementary Table S2). The monomer consumption was monitored using ¹H NMR, which allowed us to determine the localization of the amine ligands or cross-linkers in the GPs (Supplementary Figure S3). As the incorporation ratios of the NIPAm, DMAPM, and BIS monomers were almost identical to their respective feed ratios during the polymerization, the amine ligands and cross-linker were incorporated relatively uniformly in the resulting GPs.

Loading of nanosized Pd(0) into the GPs and TEM observations

Pd(0) was loaded into **GP5**, **GP10**, and **GP30** via coordination to the tertiary-amine groups [41, 42]. The resulting

GPs turned black after the Pd(0) loading. The amount of Pd loaded into **GP5**, **GP10**, and **GP30** was determined by immersing the material in aqua regia and analyzing it using ICP-AES, which gave values of 0.100, 0.089, and 0.105 mmol g⁻¹, respectively. Using TEM, Pd(0) was observed to be uniformly distributed throughout **GP5**, **GP10**, and **GP30**, with average particle sizes of 2.5 ± 0.3, 2.2 ± 0.4, and 2.5 ± 0.5 nm, respectively (Fig. 1). Because the average size of the Pd(0) loaded into the GPs was smaller than the size of the gel networks (7.9, 5.2, and 2.8 nm for PNIPAm gels with BIS contents of 5, 10, and 30 mol %, respectively) [44], the presence of Pd within the gel networks was assumed.

Suzuki coupling reaction using Pd-loaded supports in aqueous media

To evaluate the catalytic performance of the Pd/GPs, Suzuki coupling reactions between phenylboronic acid and 4-bromobenzoic acid under completely aqueous conditions (Table 1) were conducted. The catalytic reactions were performed using Pd/GPs, Pd/C, or Pd/Al₂O₃ (5 × 10⁻² mol% Pd). After using the catalysts, no Pd leaching in the reaction mixture was detected by ICP-AES (< 10 p.p.b.). Surprisingly, the Pd/GPs converted all the phenylboronic acid into 4-phenylbenzoic acid (conversion percentages of >96%), while the coupling reactions using catalytic Pd/C and Pd/Al₂O₃ had conversions of only 62 and 58%, respectively. Notably, the turnover frequencies (TOFs) of the Pd/GPs were significantly higher (1.28–5.06 × 10³ h⁻¹) than those obtained using Pd/C and Pd/Al₂O₃ (1.30 × 10² and 1.10 × 10² h⁻¹, respectively). The catalytic efficiencies normalized by the surface area of Pd(0) were also estimated using TEM images of Pd/GPs, Pd/C, and Pd/Al₂O₃ (Table 1, Fig. 1a and Supplementary Figure S4).

Using Pd/GPs, the Pd catalytic cycles for the Suzuki coupling reactions were fast enough to give the desired product. It is expected that the diffusivities of both the substrates and the product within the PNIPAm gel network are comparable to those in bulk water [45]. Although the Pd catalysts were effectively confined within the GPs via coordination to the tertiary-amino groups in the gel network, the high flexibility of the PNIPAm chains in aqueous media allowed the substrates to access the catalyst. As a result, the Pd/GPs exhibited TOFs 10 times greater than those of commercially available Pd-loaded supports. Although immobilizing the Pd catalyst on supports often deteriorates the catalytic efficiency due to limited diffusion of the substrates and/or product, using GPs as a reaction platform overcame this disadvantage of immobilized catalysts.

Table 1 Suzuki coupling reaction using Pd-loaded catalyst^a

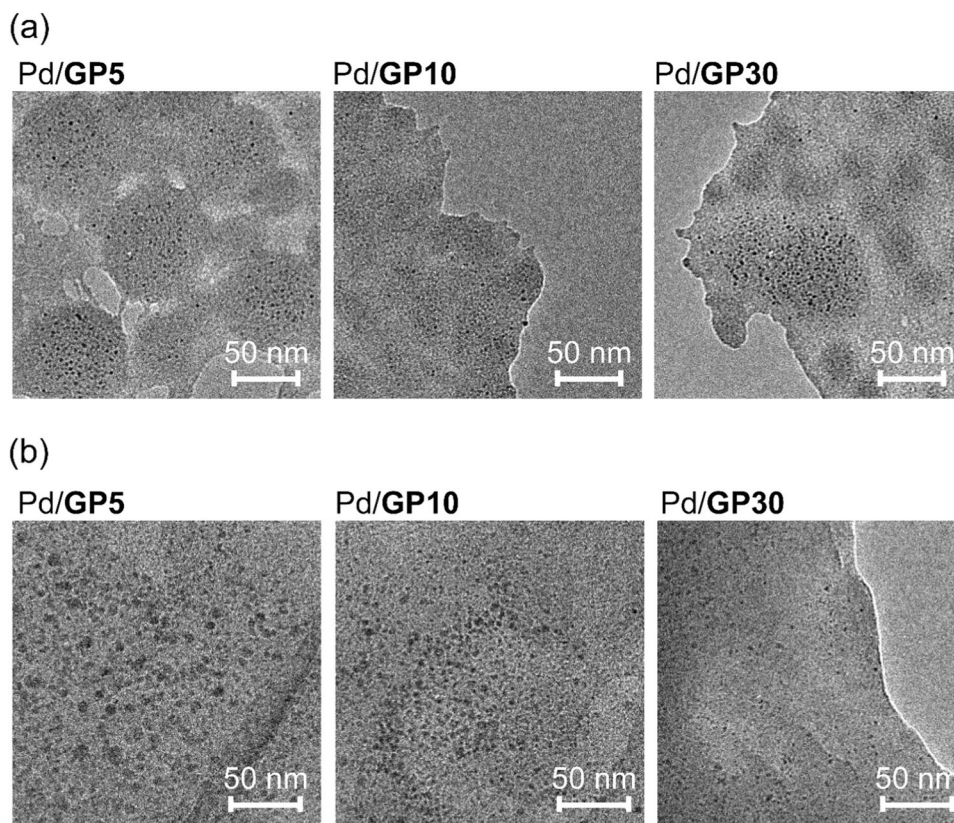
Pd-loaded catalyst	Conv. (%) ^b	TON (-)	TOF (h ⁻¹)	Catalytic efficiency (molecules h ⁻¹ nm ⁻²) ^c
Pd/GP5	96	1.92×10^3	1.28×10^3	3.60×10^4
Pd/GP10	99	1.98×10^3	2.22×10^3	5.51×10^4
Pd/GP30	99	1.98×10^3	5.06×10^3	1.43×10^5
Pd/C	62	1.24×10^3	1.30×10^2	5.26×10^3
Pd/Al ₂ O ₃	58	1.16×10^3	1.10×10^2	4.11×10^3

^aConditions: phenylboronic acid (200 mmol L⁻¹), 4-bromobenzoic acid (220 mmol L⁻¹), Na₂CO₃ (220 mmol L⁻¹), Pd catalyst (5 × 10⁻² mol%), water (15 mL), 30 °C, 1 day

^bDetermined from the concentration of phenylboronic acid after reaction

^cEstimated using the average sizes of Pd(0)

Fig. 1 TEM images of Pd/GP5, Pd/GP10, and Pd/GP30 (a) before and (b) after use in a Suzuki coupling reaction with Pd/GPs at 5 × 10⁻⁴ mol%



Catalytic durability of Pd confined within the GPs

The catalytic durability of Pd/GP5, Pd/GP10, and Pd/GP30 was evaluated in Suzuki coupling reactions. When the amount of Pd added to the reactions was decreased to 5 × 10⁻³ mol%, Pd/GP10 and Pd/GP30 achieved conversions of >99%, while Pd/GP5 no longer catalyzed the reaction

and gave only 68% conversion (Fig. 2a). Surprisingly, when the amount of added Pd was decreased to 5 × 10⁻⁴ mol%, only Pd/GP30 could complete the coupling reaction, with a conversion of 97% (TON of 1.94 × 10⁵), while Pd/GP5 and Pd/GP10 achieved conversions of only 8 and 83% (Fig. 2b). ICP-AES analysis did not detect any leaching of Pd (< 10 ppb) from the GPs after all the catalytic reactions.

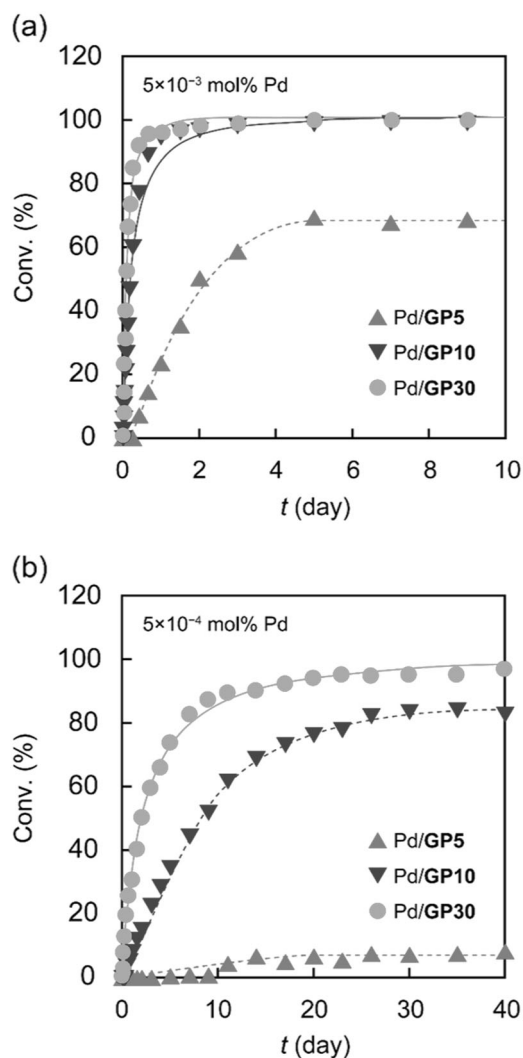


Fig. 2 Evaluation of catalytic durability in a Suzuki coupling reaction using Pd/GP5, Pd/GP10, and Pd/GP30. Conditions: phenylboronic acid (200 mmol L^{-1}), 4-bromobenzoic acid (220 mmol L^{-1}), Na_2CO_3 (220 mmol L^{-1}), Pd catalyst ((a) 5×10^{-3} mol% and (b) 5×10^{-4} mol%), water, 30°C

Pd/GP30, which was composed of a highly cross-linked polymer hydrogel network, exhibited amazing catalytic durability in the Suzuki coupling reaction in water at ambient temperature. The TON (1.94×10^5) for the Suzuki coupling reaction using Pd/GP30 is the largest among those reported when using immobilized Pd catalysts for catalytic reactions under completely aqueous conditions (1.15×10^5 for mesoporous silica [13] and 8.50×10^4 for a dendrimer [29]). Moreover, the catalytic activity of Pd/GP30 in air was stable for a year (Supplementary Information, Supplementary Figure S6). Thus, Pd/GP30 could be used without deoxygenating the reaction mixture, which can be attributed to the hydrophilic reaction platform in the GPs comprising a hydrogel matrix. Tan and coworkers reported that Pd confined within hyper-cross-linked microporous polymers made from aryl networks were highly durable compared with those confined within polymers with less cross-linking [38], which supports the results in our GP systems. The microenvironment around Pd in the GPs likely influenced the catalytic durability in the Suzuki coupling reaction.

Confinement effect of Pd within the GPs on catalytic durability

The size distribution of Pd(0) in the GPs was estimated from TEM images before and after their use in Suzuki coupling reactions (Fig. 1 and Supplementary Figure S5). After use in a Suzuki coupling reaction with 5×10^{-3} and 5×10^{-4} mol% Pd/GPs, aggregates of Pd(0) with sizes ranging from 5–13 nm were observed in the spent GP5 and GP10 (Fig. 3). Interestingly, all the Pd(0) loaded into GP30 had a size of < 5 nm, even after 1.94×10^5 catalytic cycles in the Suzuki coupling reaction.

The TEM observations revealed that the Pd(0) within the spent GP5 and GP10 was enlarged compared with the fresh catalysts, which was caused by aggregation and Ostwald ripening (Fig. 3) [46]. It is noteworthy that the enlargement

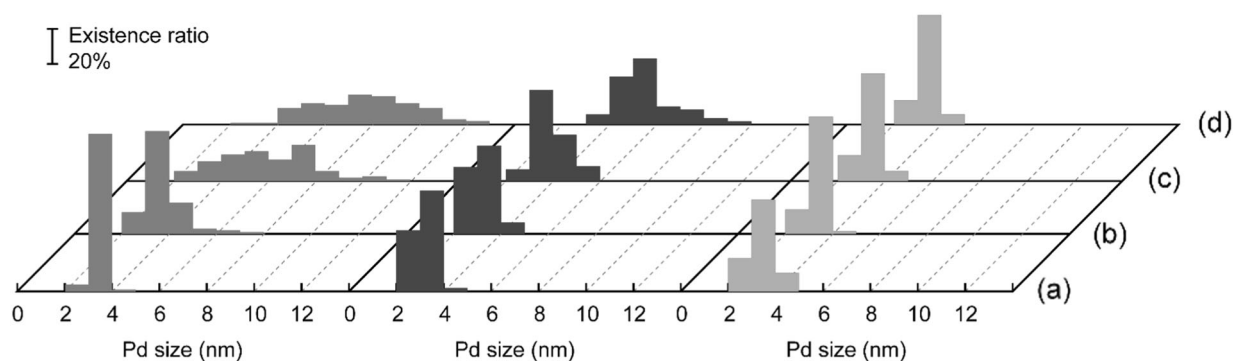


Fig. 3 Size distributions of Pd(0) loaded into GP5 (left, red bars), GP10 (center, blue bars), and GP30 (right, green bars) (a) before and after use in a Suzuki coupling reaction with Pd/GPs at (b) 5×10^{-2} mol%, (c) 5×10^{-3} mol%, and (d) 5×10^{-4} mol%

of Pd(0) within the **GP30** was successfully prevented to achieve the highest TON for the Suzuki coupling reaction. Thus, confinement of the Pd catalyst within the GPs imparted catalytic durability to this Suzuki coupling reaction. The TON for the Pd catalyst in GPs improved as the size of the gel network in the GPs decreased. Using GPs with different-sized gel networks, we determined that confining a Pd catalyst within a highly cross-linked polymer prevented aggregation of the Pd during the catalytic cycle. Moreover, because the hydrophilic reaction platform in the GPs was composed of a hydrogel matrix, Pd catalyst loaded in **GP30** gave the highest TON (1.94×10^5) for the Suzuki coupling reaction in exclusively aqueous media at ambient temperature among those for immobilized Pd catalysts that have been reported under similar conditions.

Conclusions

Pd was confined within PNIPAm-based hydrogel particles for use as a catalyst in a Suzuki coupling reaction between phenylboronic acid and 4-bromobenzoic acid in completely aqueous media at ambient temperature. The GPs were synthesized by copolymerization of a gel matrix, a tertiary-amine ligand, and cross-linking monomers. The size of the gel networks was tuned by varying the feed ratio of the cross-linking monomer. Pd catalysts were loaded into the GPs by Pd-ion adsorption and subsequent reduction, which yielded Pd/GPs that contained Pd(0) with an average particle size of several nanometers. The flexible polymer chains allowed the substrates to easily access the Pd catalysts confined within the GPs. The catalytic performance of the Pd/GPs was significantly better than those of commercially available Pd-loaded supports. Notably, Pd/GP with the smallest gel network (**Pd/GP30**) was highly durable. It is plausible that the smaller network minimized or prevented the enlargement of Pd(0) during the catalytic cycles. The facile synthesis of the GPs, environmentally benign catalytic system (completely aqueous at ambient temperature (30°C)), and high catalytic durability and activity of Pd/GPs are all important factors for their industrial application. We expect that this confined catalyst system will have significant impacts on reactions catalyzed by immobilized metals using green and sustainable chemistry.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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