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Pd nanoparticles immobilized on PNIPAM– halloysite: highly active and reusable catalyst for Suzuki–Miyaura coupling reactions in water

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Poly(*N*-isopropylacrylamide)-halloysite (PNIPAM-HNT) nanocomposites exhibited inverse temperature solubility with a lower critical solution temperature (LCST) in water. Palladium (Pd) nanoparticles were anchored on PNIPAM-HNT nanocomposites with various amounts of HNT from 5 to 30 wt%. These Pd catalysts exhibited excellent reactivities for Suzuki-Miyaura coupling reactions at 50–70 °C in water. In particular, Pd anchored PNIPAM/HNT (95:5 w/w ratio) nanocomposites showed excellent recyclability up to 10 times in 96% average yield by simple filtration. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: Suzuki-Miyaura reactions; Pd nanoparticles; PNIPAM-halloysite nanocomposite; reusable catalysts; water

Introduction

The Suzuki-Miyaura (SM) reaction is one of the most widely used synthetic protocols for synthesizing biaryl compounds through a palladium (Pd)-catalyzed coupling reaction between an aryl halide and an arylboronic acid.^[1–5] The Suzuki reaction is typically performed with a homogeneous Pd catalyst, phosphorus derivatives as ligands and an inorganic bases (i.e. carbonate, bicarbonate and hydroxide) in aqueous organic solvents.^[5,6] However, a homogeneous Pd-catalyzed SM reaction has several drawbacks if it is to be utilized in industrial applications, such as (i) the difficulty in reusing Pd catalysts, (ii) the need for toxic and expensive ligands and (iii) the difficulty in removing the residual Pd and ligand after the reaction is completed. Recently, enormous efforts have been focused on developing recyclable Pd systems with catalytic activities comparable to those of their homogeneous counterparts. For example, Pd nanoparticles were immobilized on ionic liquids,^[7–9] functionalized polymers,^[10–22] graphene oxide and its derivatives^[23–25] and inorganic substrates such as silica and zeolites.^[26–34] However, there still remains the need to improve their catalytic activities and reaction conditions such as a low reaction temperature and the sole use of water as a solvent system.^[35-45]

It is well known that poly(*N*-isopropylacrylamide) (PNIPAM) microgels exhibit temperature-responsive phase separation (i.e. coil-to-globule transition) from an aqueous solution at the lower critical solution temperature (LCST), typically about 32 °C.^[46–52] The LCST of PNIAPM can also be controlled by employing a clay mineral such as montmorillonite at around 20–46 °C.^[53,54] This indicates that PNIPAM can selectively provide hydrophilic or hydrophobic nano-environments by simply changing the temperature of the reaction medium. Therefore, the SM reaction can likely be carried out with hydrophobic substrates in water without any surfactants or organic solvents if PNIPAM is utilized as a solid support of Pd nanoparticles. Furthermore, PNIPAM can easily be recovered from aqueous solution above its LCST

by simple filtration. These interesting properties have made PNIPAM a promising candidate as a support for recyclable Pd nanoparticle catalysts in SM reactions.^[55–61] However, Pd leaching of Pd-anchored PNIPAM during reactions has limited their wide application in SM reactions.

Halloysite nanotube (HNT) is a two-layered aluminosilicate clay with a hollow tubular structure. It possesses Al—OH groups on the internal surface and Si—OH groups on the external surfaces.^[62-75] Due to these surface functional groups, HNT has been used as a solid support for catalytic particles such as Ru, TiO₂, Ag and Ni.^[71-75] In our previous work, we used PNIPAM-co-4-vinylpyridine (PNIPAM-co-4-VP) as a support for Pd nanoparticles in order to decrease Pd leaching during SM reactions.^[61] As an extension of this study, herein we utilized temperature-responsive PNIPAM/HNT (halloysite nanotube) hydrogel nanocomposites as a support for Pd nanoparticle. PNIPAM/HNT hydrogel nanocomposites were expected to provide both strong anchoring sites for Pd nanoparticles due to

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Scheme 1. Preparation of Pd(0) nanoparticles supported on PNIPAM/HNT hydrogel nanocomposites.

the existence of HNT and temperature-responsive behavior due to the PNIPAM moiety during SM reactions in an aqueous system.

In this study, PNIPAM/HNT (halloysite nanotube) hydrogels were synthesized in ratios of 95:5, 85:15 and 70:30 (w/w) and then Pd nanoparticles were impregnated on them through Pd²⁺ adsorption and its reduction to Pd(0) species. These catalysts are designated as C1, C2 and C3, respectively. The optimal catalytic system and reaction conditions for SM reactions were thoroughly investigated. The optimized catalytic system was also applied in various substrates. Furthermore, the reusability of the catalyst was examined up to 10 times in recycling tests with two model reactions: (i) bromoacetophenone and phenylboronic acid; and (ii) bromobenzene and 4-methylphenylboronic acid.

Experimental

Materials

All reagents were purchased from commercial sources (Aldrich, TCI). Palladium acetate (Pd(OAc)₂), methanol (MeOH), tetrahydrofuran (THF), ethyl acetate (EA), *N*-isopropylacrylamide (NIPAM; Aldrich, 97%), and *N*,*N'*-methylenebisacrylamide (MBAAm; Aldrich, 99%) were used as received. 2,2'-Azobisisobutyronitrile (AlBN; Junsei Chemicals, 99%), which was used as an initiator, was recrystallized from methanol. Halloysite nanotubes (HNTs; Aldrich) were used without any chemical purification. The HNT has a Brunauer–Emmet–Teller (BET) specific surface area of about $64 \text{ m}^2 \text{ g}^{-1}$, cation exchange capacity of 8 mequiv. g^{-1} and pore volume of 1.25 ml g⁻¹.

Characterization

Transmission electron microscopic (TEM) and energy dispersive X-ray analysis (EDAX) measurements were performed on an HRTEM JEOL transmission electron microscope at an acceleration of 300 kV. X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-2500 X-ray diffractometer (Cu- K_{α} radiation, $\lambda = 1.5418$ Å). The diffraction pattern obtained was compared with that at the International Centre for Diffraction Data (ICDD). The amount of Pd in the catalysts was estimated by inductively coupled plasma (ICP) analysis with a JY Ultima2C. The lower critical solution temperatures (LCSTs) of the synthesized nanocomposites were characterized by differential scanning calorimetry (DSC) measurements (TA Instrument, DSC 2010). All samples were immersed in pH 10 buffer solution at room temperature for 24 h to bring them to equilibrium state before DSC measurements. DSC analyses of the swollen hydrogels were performed from 0 to 50 °C at a heating rate of 2 °C min⁻¹ under nitrogen atmosphere at a flow rate of 40 ml min⁻¹. ¹H NMR spectra were obtained in CDCl₃ with Bruker and Varian spectrometers operating at 400 MHz and 500 MHz, with tetramethylsilane as an internal standard.

Synthesis of PNIPAM/HNT hydrogel nanocomposites

Pd(0) nanoparticles supported on PNIPAM/HNT hydrogel composites were prepared as shown in Scheme 1. PNIPAM/HNT hydrogel nanocomposites were first synthesized by free radical solution polymerization according to the standard procedure, except for the existence of HNT.^[61,76] In this polymerization, HNT content was varied to 5, 10 and 15 wt%. In a typical run for the synthesis of a cross-linked PNIPAM/HNT (95:5, w/w) hydrogel nanocomposites, 1.00 g NIPAM (8.57 mmol, 94 mol%) dissolved in 2 ml methanol, 0.085 g MBAAm (0.55 mmol, 6 mol%) dissolved in 2 ml methanol and 0.05 g HNT in 16 ml toluene were placed in a 100 ml flask. To homogeneously disperse the HNT in the solution, the suspension was stirred for 12 h at room temperature. Polymerization was initiated by adding 3 mol% AIBN (0.045 g, 0.27 mmol) and then the reaction mixture was heated at 80 °C for 4 h. The formed solid polymer was filtered off, washed with methanol, and dried at 20 °C under vacuum for 24 h.

Pd(0) nanoparticles anchored on the nanocomposites

As-synthesized PNIPAM/HNT (95:5, w/w) hydrogel nanocomposite (100 mg) was dispersed in MeOH (20 ml) under mechanical shaking. Palladium acetate (Pd(OAc)₂) (10 mg, 0.0445 mmol) was then gradually added to the suspension, followed by sonication for 1 min to thoroughly dissolve the Pd source. The Pd mixture was shaken for 12 h under argon. As the hydrogel reacted with Pd(OAc)₂, the hydrogel color changed to yellow. The mixture was filtered using a 0.20 µm Millipore Nylon membrane filter and washed three times with 20 ml MeOH. The filtered Pd²⁺adsorbed copolymer was then dried in air for 12 h. Black Pd(0) nanoparticles were generated by adding 10 mg (0.264 mmol) NaBH₄ as a reducing reagent to a suspension of the dried copolymers in THF (20 mL) under mechanical shaking for 12 h. 10 ml MeOH was added to remove the residual NaBH₄ and then the Pd(0)-grafted copolymer was separated by filtration. The filtered copolymer was thoroughly washed with 20 ml MeOH and 20 ml THF and then dried in air for 12 h. The other Pd-grafted PNIAPM/HNT nanocomposites, C2 and C3, were also prepared by the same method but with different content of HNT (~15 and 30 wt%), respectively. The loading amounts of Pd(0) nanoparticles in C1, C2, and C3 were estimated by ICP measurements to be 0.494, 4.84 and 1.63 mmol Pd g^{-1} , respectively.

General procedure for the SM reaction

A 10 ml round-bottom flask was charged with 4-bromoacetophenone (**1 h**, 1 mmol, 1 equiv.), phenylboronic acid (**2a**, 1.5 mmol, 1.5 equiv.), K_2CO_3 (414 mg, 3 mmol, 3 equiv.), H_2O (2 ml) and Pd catalyst (1 mol%). The flask was stirred at 70 °C in air. The reaction was monitored by thin-layer chromatography (TLC). After the reaction was complete, the reaction mixture was cooled to room temperature and then simply filtered to recover the catalyst. It was then washed with 10 ml H_2O and ethyl acetate (EtOAc). The organic phase was separated from the aqueous phase, which was extracted three times with 30 ml EtOAc. The organic phases were collected together, dried over $MgSO_4$, and filtered. The solvent was then evaporated under reduced pressure. The pure product was obtained via silica gel column chromatography with an eluent of EtOAc and hexane. The resulting product was analyzed by ¹H NMR spectroscopy.

Recycling the Pd catalyst

Two kinds of SM reactions were carried out. The first five runs were with bromoacetophenone **1 h** and phenylboronic acid **2a**, and the second five runs were with bromobenzene **1a** and 4-methylphenylboronic acid **2b**. The SM reactions were performed as described above. After the first reaction was complete, C1 was recovered by simple filtration and air-dried. The recovered catalyst was successively subjected to the next five runs of the coupling reaction under the same reaction conditions (e.g. concentration of reactants) as the first run. The filtrate (H₂O) was analyzed with ICP measurements to estimate the amount of Pd leaching after each run.



Figure 1. Differential scanning calorimetry (DSC) curves of PNIPAM and PNIPAM/HNT (95:5, w/w).

Results and Discussion

Differential scanning calorimetry (DSC) experiments show the obvious LCST of the PNIPAM at about 31 °C, which is consistent with the previously reported LCST of PNIPAM.^[46–51] The synthesized PNIPAM/HNT (95:5, w/w) nanocomposites, C1, shows a shift of the endothermic peak to about 34 °C (Fig. 1). However, no reproducible thermal responsive behavior was observed for C2 and C3, probably due to the aggregation of HNT inside the matrix of PNIPAM. The temperature ranges of SM reactions were determined on the basis of the DSC measurements.

The Pd nanoparticles were grafted on to the PNIPAM/HNT nanocomposites by dispersing Pd(OAc)₂ in the solution of the nanocomposites and then reducing adsorbed Pd²⁺ to Pd(0) with NaBH₄. The formation of Pd nanoparticles was visually observed with the mixture's change in color to black, and it was characterized by TEM, EDAX and XRD measurements. Figure 2(a)-(b) show TEM images of the Pd nanoparticles on PNIPAM/HNT (95:5 wt/wt ratio) as a representative sample (Note that TEM images of the other Pd catalysts (C2 and C3) are not shown here because they did not show satisfactory activities in the SM reactions (see Table 1).). According to the TEM images, C1 had rod-shaped HNT particles with a diameter of about $0.15 \,\mu m$ and a length of about 0.6 µm. The Pd nanoparticles were mainly anchored on the surface and inside the pores of the HNT particles, having spherical morphologies with diameters of less than about 15 nm inside the pores. The particle sizes were increased to approximately 50-70 nm on the surface probably due to the aggregations of the smaller Pd nanoparticles. The synthesized C1 sample was further characterized by EDAX and XRD measurements as shown in Figs S1 and S2, respectively (supporting information). The EDAX spectrum of C1 confirms the presence



Figure 2. Transmission electron microscope (TEM) images of Pd nanoparticles grafted on to PNIPAM/HNT (95:5, w/w) (a, b) before and (c, d) after SM reactions.

Table 1. Suzuki coupling reactions of 4-bromoacetophenone 1h and phenylboronic acid 2a with C1–C3 as a function of temperature and the amount of C1^a



by ¹H NMR).

of palladium, aluminum and silicon in C1 (Fig. S1). The powder XRD pattern of C1 shows the diffraction peaks at about 40°, 46.6° and 68°, which were unambiguously indexed as (111), (200) and (220) reflections, respectively, on the basis of ICDD file 46–1043 for crystalline metallic Pd(0) (Fig. S2). The broad peaks at about 20° and 11° were attributed to amorphous PNIPAM and HNT, respectively.^[77,78]

The catalytic activities of as-prepared C1-C3 were estimated via a coupling reaction between 4-bromoacetophenone 1h and phenylboronic acid 2a (Table 1). First, C1–C3 were applied for the reaction under the conditions of 5 mmol% Pd catalysts and K₂CO₃ (3 equiv.) as a base at 60 °C in water, respectively (entries 1-3, Table 1). C1 and C2 afforded 98-99% yields of 4-acetylbiphenyl 3h. However, reaction time with C1 was shorter than that of C2 (1.5 h vs. 2 h). The coupling reaction with C3 showed a moderate conversion yield of 55% even in 2 h. Based on these results, we chose C1 as the optimum catalyst for the SM reaction. To optimize reaction conditions such as reaction temperature and amount of palladium catalysts, we performed several test reactions with C1 (Table 1, entries 1 and 4-7). First, in order to optimize reaction temperatures using C1, we investigated conversion yields with 5 mmol% Pd catalyst as a function of temperature from 50 to 70° C (Table 1, entries 1 and 4-6). As the reaction temperature increased, the reaction time was significantly decreased from 1.5 to 0.5 h, affording similar conversion yields of about 98–99%. Furthermore, the reaction was quantitatively completed within 0.8 h at 70° C (entry 6, Table 1). To estimate the effects of the amount of Pd catalysts on the conversion reaction, we performed an additional reaction with 1 mmol% Pd catalysts (Table 1, entry 7), resulting in quantitative conversion within a slightly longer reaction time of 1 h compared to that of 5 mmol% Pd catalysts. Considering the amount of catalysts used in the reaction, 1 mmol% Pd catalyst is more effective than 5 mmol% Pd. Thus the reaction condition was

optimized as C1, 70 $^\circ C$ and 1 mmol% Pd, which was applied to the conversion reactions of a variety of substrates as below.

The reactions of a variety of aryl bromides 1 with arylboronic acids 2 are listed in Table 2, under the optimized reaction conditions (i.e. 1 mmol% C1, at 70 °C, in water). The coupling reactions of phenylboronic acid 2a with a wide range of aryl bromides with electron-donating groups (entries 1-3) provided excellent conversions above 95%. However, 4-methylaryl bromide 1d afforded only a moderate yield of the corresponding product (82%, entry 4). In addition, aryl bromides with electron-withdrawing groups also showed excellent conversion yields (>94%) (entries 5-10). Bromobenzene 1a and 4-methylphenylboronic acids **2b** were converted to the corresponding biaryl product with a high yield of 95% (entry 11). On the other hand, 4-methoxy and 4-chlorophenylboronic acids gave moderate yields of 80% and 74%, respectively (entries 12 and 13). Furthermore, C1 shows an excellent reactivity even in the conversion reaction between 4-bromoacetophenone 1 h and various arylboronic acids with electron-donating and withdrawing groups (yields > 94%, entries 14-17).

Lastly, we estimated recyclability of C1 by performing two model reactions at 70 °C in water: (i) 4-bromoacetophenone **1 h** and phenylboronic acid **2a** for the first five runs; and (ii) bromobenzene **1a** and 4-methylphenylboronic acid **2b** for the next five runs, respectively (Table 3). It was found that C1 showed

Table 2. Suzuki coupling reactions of various aryl bromides 1 and arylboronic acids 2 with C1 at 70 $^{\circ}$ C in water^a

$ \begin{array}{c} $				
Entry	1 (R ¹)	2 (R ²)	Time (h)	Yield (%) ^b
1	1a (—H)	2a (—H)	1.5	97
2	1b (—NH ₂)	2a	3	97
3	1c (—OH)	2a	1	Quant.
4	1d (—CH ₃)	2a	4	82
5	1e (—NO ₂)	2a	1	95
6	1f (—CN)	2a	0.5	Quant.
7	1 g (—CO ₂ CH ₃)	2a	4	94
8	1 h (—COCH ₃)	2a	1	Quant.
9	1i (—CHO)	2a	3	99
10	1j (—CF ₃)	2a	2	95
11	1a	2b (—CH ₃)	1	95
12	1a	2c (—OCH ₃)	1	80
13	1a	2d (—Cl)	4	74
14	1 h	2b	0.5	94
15	1 h	2c	1	97
16	1 h	2d	2	98
17	1 h	2e (—F)	3	98

^aReaction conditions: aryl bromide (**1**, 1 mmol), arylboronic acid (**2**, 1.5 mmol, 1.5 equiv.), K_2CO_3 (3 mmol, 3 equiv.), H_2O (2 ml) and 1 mmol% Pd catalyst (C1).

^bIsolated yield (the purity of the isolated product was confirmed by ¹H NMR).

Yield (%)^a

90



 TOF^b
 196
 194
 182
 196
 180

 Reaction conditions: bromobenzene (**1a**, 1 mmol), 4-methylphenylboronic acid (**2b**, 1.5 mmol, 1.5 equiv.), K₂CO₃ (3 mmol, 3 equiv.), H₂O (2 ml), 1 mmol % Pd catalyst (C1) and a reaction time of 30 min.
 1

^alsolated yield (the purity of the isolated product was confirmed by ¹H NMR).

98

^bTurnover frequency defined as moles of 4-bromoacetophenone or bromobenzene consumed per mole of total metal per hour.

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excellent recyclability for the first five runs, resulting in high yields above 94–99% in 40 min (turnover frequency (TOF) of above $188 h^{-1}$). The high catalytic activity was preserved for the following five runs, affording 90–98% conversion (TOF of above $180 h^{-1}$). After each run, the amount of Pd leaching from C1 was estimated by performing ICP measurements on the supernatant solutions. The solutions were collected by filtering the catalyst from the reaction mixture after the reactions were complete. No significant Pd leaching (<1 ppm) was observed. In addition, there was no significant agglomeration of Pd nanoparticles after SM reactions on the basis of the TEM images (Fig. 1c, d). This suggests that the excellent recyclability is attributed to the existence of HNT as a solid support of Pd nanoparticles in the network of PNIPAM.

In conclusion, Pd nanoparticles were successfully anchored on PNIPAM/HNT hydrogel nanocomposites. The Pd-anchored PNIPAM/HNT catalysts demonstrated excellent catalytic activities for various SM reactions even under mild reaction conditions, such as with water as sole solvent at 70 °C. In particular, catalyst C1 showed superior recyclability to that of the Pd-grafted PNIPAM system. Although various supports such as carbon, polymers and modified SiO₂ have been utilized to develop heterogeneous Pd catalytic systems, most of them needed either a higher reaction temperature, above 80 °C,^[21] or an aqueous solvent mixed with ethanol^[23,30,79,80] or DMF^[26,81] to achieve comparable catalytic activities to our system. We therefore believe that

the unique advantages of HNT and PNIPAM were successfully utilized for the SM reactions in this work. Applications of similar approaches to other Pd-catalyzed reactions such as Heck, Stille, Sonogashira, Hiyama, Negishi and oxidation/reduction reactions can be readily envisaged.

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