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A palladium-loaded mesoporous polymer monolith as reusable heterogeneous catalyst for cross-coupling reactions

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ABSTRACT

A new palladium catalyst based on a mesoporous polymer monolith has been introduced. A polyacrylonitrile (PAN) monolith prepared by a phase separation technique was used as precursor material for chemical modification; the nitrile groups on the monolith surface were transformed into amidine groups and then bound to palladium dichloride via coordination. A series of Suzuki–Miyaura cross-coupling reactions were successfully demonstrated by using the monolith as catalyst. Moreover, the monolith was found to exhibit excellent stability for repeated use.

1. Introduction

Recycling of catalysts is one of the main objectives of green sustainable chemistry [1]. A promising approach for achieving this goal is the development of heterogeneous catalysts that are easy to recover and stable for their repeated use. In this context, a variety of carriers on which catalytic species are immobilized have been studied over decades. Examples of such carriers include polymers [2–8], dendrimers [9–12], inorganic solids [13–17], perfluorinated tags [18], and nanoparticles [19–21]. In addition, monolithic materials attract growing interest in application as solid supports. A monolith is a bulk material having a three-dimensionally interconnected, continuous pore structure. Such a porous structure is featured by high surface area and high permeability that are advantageous in terms of catalyst loading, substrate/product transport and access to catalytic centers, etc.

We recently developed a convenient method for preparation of monoliths made of polymers [22]. This method is based on a phase separation technique and widely applicable to a range of polymers [23,24]. The polymer monoliths are easy to be functionalized and crosslinked by chemical reactions, which allows for introduction of various functional groups on the surface and resistance to solvents, respectively. By utilizing such advantages, we have designed here a new heterogeneous catalyst based on a polymer monolith. The procedure is outlined as follows (Scheme 1). Firstly, a polyacrylonitrile (PAN) monolith was prepared by the phase separation method. This monolith was then treated with ethylenediamine (EDA) whereby amidine groups were introduced on the surface. The monolith was also internally crosslinked concomitantly. Finally, palladium dichloride was loaded on the monolith surface via coordination to the anchoring sites.

Palladium catalysts are known to play a key role in cross-coupling reactions [25]. Suzuki–Miyaura reaction is representative of such reactions and has been widely used for the synthesis of agrochemicals, semiconductive polymers and pharmaceutical compounds, etc. [26]. This reaction is of particular interest in terms of green chemistry because it proceeds in environmentally benign solvents such as water and ethanol producing non-toxic side products. Hence, Suzuki–Miyaura reaction was chosen to demonstrate its feasibility with the monolithic catalyst prepared in this study. Note that phosphine compounds are often employed as ligands for palladium catalysts [27–29]. However, they are not merely air-sensitive, expensive and toxic but also often cause ligand scrambling that is known as a detrimental side reaction [30]. Therefore, the present study can also form a part of the attempt to develop phosphine-free N-based ligands as represented by N-heterocyclic carbenes [31,32,5], N,O- or N,N-bidentate ligands [33–35], 4-aryloximes [36], arylimines [37,38], N-acylamidines [39], and simple amines [40–42].

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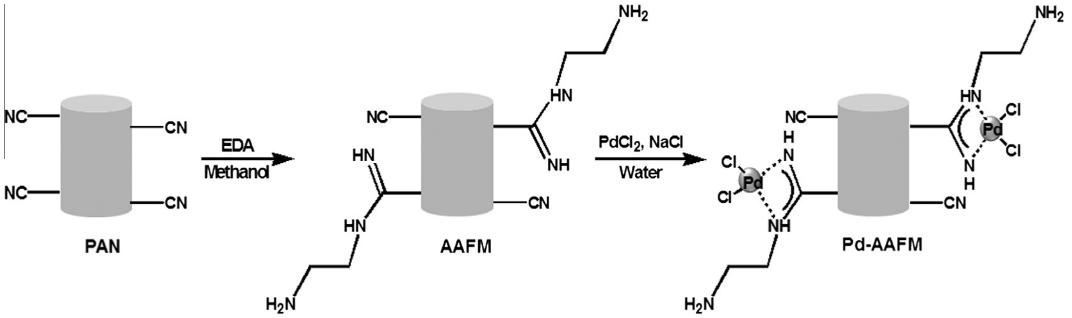


Scheme 1. Simplified cartoon depiction of the procedure for preparation of the palladium-loaded monolith.

2. Experimental section

2.1. Materials

PAN (incl. 7 wt% of vinyl acetate) was a gift from Mitsubishi Rayon Co. (Tokyo, Japan). A PAN monolith was prepared according to the procedure we previously reported [22]. All chemical reagents were purchased from NACALAI TESQUE (Kyoto, Japan), Wako Pure Chemical Industries (Osaka, Japan) or Tokyo Chemical Industry (Tokyo, Japan). They were of analytical grade and used as received without further purification.

2.2. Instrumentation

Fourier transform infrared (FT–IR) measurements by the attenuated total reflectance (ATR) method were performed by Thermo Scientific Nicolet iS5 with iD5 ATR accessory. Solid state ^{13}C MAS NMR studies were performed by using Chemagnetics 300 MHz CMX 300 Spectrometer. Scanning electron microscopic (SEM) images are recorded on a HITACHI S-3000N instrument at 15 kV. A thin gold film is sputtered on the samples before the images are collected. The energy dispersive X-ray spectrometric (EDX) measurement for elemental analysis of the monolith surface was conducted by a Hitachi Miniscope TM3000 with Swift3000 equipment. N_2 adsorption/desorption isotherms are measured with a NOVA 4200e Surface Area & Pore Size Analyzer (Quantachrome Instruments) at 77 K. Before the measurements, all samples are degassed at 100 °C under vacuum for at least 6 h. The Brunauer Emmett Teller (BET) method is utilized to determine the specific surface areas. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed with ICP-7510 Shimadzu sequential plasma spectrometer.

2.3. Preparation of AAFM

About 121 mg PAN monolith was mixed with EDA (0.5, 1.0 or 2.0 mol/L) and heated in methanol (6 mL) at 70 °C under reflux for 8 h. The monolith was then collected from the reaction mixture by filtration. It was washed repeatedly with methanol and dried under vacuum at room temperature to furnish AAFM. The conversion depended on the EDA concentration as shown in Table S1.

2.4. Preparation of Pd-AAFM

Sodium chloride (0.22 mmol) and palladium dichloride (0.1 mmol) were dissolved in 10 mL water and stirred at room temperature for 30 min. 80 mg AAFM was added to this solution and stirred for 12 h at room temperature. The monolith was then filtered out of the solution, washed repeatedly with water and dried under vacuum at room temperature to furnish Pd-AAFM.

2.5. Suzuki–Miyaura cross-coupling reaction with Pd-AAFM

A mixture of aryl halogenide (1.0 mmol), arylboronic acid (1.5 mmol), inorganic base (2.0 mmol) and Pd-AAFM (20 mg) in an ethanol/water mixed solvent (3.0 mL) was heated at 55 °C for 5–7 h. After cooling to room temperature, the mixture was filtered through a piece of filter paper. Products were extracted from the filtered solid with EtOAc (5 mL × 4) and the organic solution was washed with water (5 mL × 5). After separating the layers the aqueous layer was extracted with EtOAc (20 mL). The organic phases were combined, washed with brine (15 mL × 2) and dried over Na_2SO_4. The solvent was then evaporated under a reduced pressure, and the product was isolated by a short-column chromatography with aluminum oxide (Sigma–Aldrich, activated neutral form, pore size: 58 Å) using 95:5 (v/v) hexane/ethyl acetate as eluent. The isolated yield is shown in Tables 1 and 2. The structure of the product was confirmed by ^1H NMR (see Supporting Information).

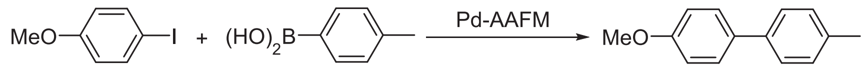
2.6. Reusability test

After the Suzuki–Miyaura reaction between 4-iodotoluene and 4-methylphenylboronic acid, Pd-AAFM was recovered by filtration, washed successively with ethyl acetate (5 mL × 4) and water (5 mL × 5), and dried under vacuum at room temperature. The recovered Pd-AAFM was transferred into a reaction vessel which contained a mixture of base (2.0 mmol), 4-methylphenylboronic acid (1.5 mmol) and 4-iodotoluene (1.0 mmol) in 1:1 ethanol/water (3.0 mL), and heated at 55 °C for 5 h. The product was isolated according to the above-mentioned. The catalyst was collected and reused for a next reaction/recovery cycle. The product yields are summarized in Table S2.

3. Results and discussion

A PAN monolith was prepared according to our reported procedure [22]. It was then treated with EDA in different concentrations (0.5–4.0 mol/L) under reflux in methanol for 8 h. Amino groups of EDA are able to undergo nucleophilic addition to the nitrile groups of PAN to generate amidines [43]. The conversion became higher as the concentration of EDA increased up to 2.0 mol/L (Table S1). 36% weight increase was achieved when 2.0 mol/L of EDA was used, which translates into ca. 36% conversion of nitrile to amidine [44–46]. This rather low conversion suggested that the reaction took place only near the surface. It was indeed confirmed that this chemical treatment maintained the porous monolithic structure (see below). In contrast, when the reaction was performed with even higher concentrations of EDA, the monolith was swollen (3.0 mol/L) or gradually dissolved (4.0 mol/L). Therefore, the monolith modified with 2.0 mol/L of EDA was selected for further study.

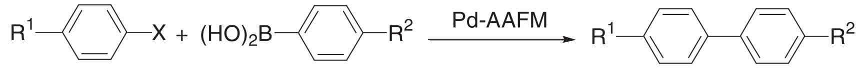
Table 1
Suzuki–Miyaura cross-coupling reaction between 4-iodoanisole and *p*-tolylboronic acid under various conditions using Pd-AAFM as catalyst[a].



Entry	Pd-AAFM (mg)	Water–ethanol ratio	Base	Yield (%)[b]
1	20	1:0	K_2CO_3	60
2	20	2:1	K_2CO_3	80
3	20	1:1	K_2CO_3	96
4	20	1:2	K_2CO_3	78
5	20	0:1	K_2CO_3	75
6	10	1:1	K_2CO_3	80
7	20	1:1	K_2CO_3	96
8	30	1:1	K_2CO_3	96
9	20	1:1	KOH	90
10	20	1:1	NaOH	80
11	20	1:1	$CsCO_3$	96
12	0	1:1	K_2CO_3	0

[a] Reaction conditions: 4-iodoanisole (1.0 mmol), *p*-tolylboronic acid (1.5 mmol), base (2.0 mmol), and 3 mL of water–ethanol mixed solvent at 55 °C for 6 h.
[b] Isolated yield.

Table 2
Suzuki–Miyaura cross-coupling reaction between various aryl halides and aryl boronic acids using Pd-AAFM as catalyst[a].

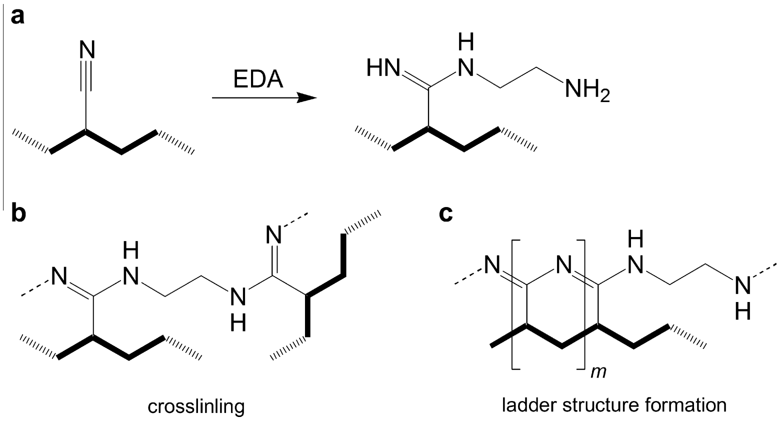


Entry	R^1	R^2	X	Time (h)	Yield (%)[b]
1	H	H	I	5	97
2	Me	Me	I	5	96
3	Me	Me	Br	5	95
4	OMe	Me	I	6	96
5	H	Me	I	5	97
6	H	Me	Br	5	95
7	Me	H	I	6	95
8	Me	H	Br	6	94
9	OH	H	Br	6	95
10	NO_2	Me	Br	7	96

[a] Reaction conditions: aryl halide (1.0 mmol), aryl boronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), Pd-AAFM (20 mg) and 3 mL of water–ethanol 1:1 at 55 °C.
[b] Isolated yield.

The modified monolith was found insoluble in solvents such as DMSO and DMF that could dissolve the original PAN monolith, proving that the monolith was internally crosslinked. Note that the nucleophilic addition at one end of EDA leaves the other amino group free. In addition, the resultant amidine group is also reactive. These groups could either remain as-is or undergo subsequent reactions with nitrile groups in proximity leading to bridges between polymer chains or ladder-type structures (Fig. 1).

Next, the amidine/amine functionalized monolith (AAFM) was subjected to the metal loading. Palladium dichloride is insoluble in pure water but could dissolve in the presence of sodium chloride due to the formation of sodium tetrachloropalladate [47]. AAFM was thus stirred in the aqueous solution of sodium tetrachloropalladate, followed by washing with water and drying under vacuum to



crosslinling

ladder structure formation

Fig. 1. Nucleophilic addition of EDA to a nitrile group of PAN (a). Thick lines show polymer main chains. Crosslinking (b) and ladder structure formation (c) can be caused by subsequent nucleophilic additions of the free amino/amidine groups to remaining nitrile groups in proximity.

furnish the palladium loaded monolith (Pd-AAFM). Successful metal loading on the monolith was suggested by brownish discoloration.

Infrared (IR) spectra of the original PAN monolith, AAFM and Pd-AAFM are compared in Fig. 2. In the spectrum of the PAN monolith, the peaks attributed to aliphatic hydrocarbons in the polymer chain are seen around 2900 cm^{-1} (C—H stretching). The peaks at 2250 cm^{-1} (C≡N stretching) and 1732 cm^{-1} (C=O stretching) are characteristic of nitrile and ester groups, respectively [48]. Note that the commercial PAN of the present use contained 7 wt% of vinyl acetate as comonomer. The reaction with EDA caused significant changes in the spectrum as expected. The intensity of the nitrile signal at 2250 cm^{-1} decreased, which was accompanied by the emergence of new peaks around 3300 and 1613 cm^{-1} due to the formation of amidine/amine groups [43]. The disappearance of the carbonyl signal at 1732 cm^{-1} was caused by deacetylation of the acetate [48]. The 1613 cm^{-1} peak shifted to 1593 cm^{-1} in the spectrum of Pd-AAFM, which is a sign of metal coordination to the amidine group [49]. The metal coordination was further supported by the NMR results shown below.

Fig. 3 shows solid-state ^{13}C magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectra of the three monoliths. The large peak around 30 ppm includes the signals of all aliphatic carbons in the PAN main chain. The peak at 121 ppm is assigned to the nitrile carbon. The small peaks at 67 and 171 ppm came from the comonomer. Several new signals appeared in the spectrum of AAFM, whereby the introduction of amidine/amine groups was confirmed here as well; the peaks at 45 and 52 ppm are characteristic of the ethylene group from EDA. The signals at 162 and 173 ppm are assigned to the carbons of amidine groups that are nonconjugated and conjugated, respectively (see Fig. 1) [43]. Noteworthy is the 162 ppm peak significantly shifted downfield and broadened in Pd-AAFM, while the position of the 173 ppm peak remained unchanged. These results point to a possibility that the bidentate metal coordination of the nonconjugated amidines was dominant in the present case over the other coordination modes [49–51].

Cross-sectional analyses of the PAN monolith, AAFM and Pd-AAFM were performed by scanning electron microscopy (SEM) (Fig. 4). The three dimensionally interconnected porous structures were found for all materials, showing that the monolithic structure was largely maintained throughout the chemical modifications. In addition, cross-sections of Pd-AAFM were analyzed by energy dispersive X-ray spectrometry (EDX), proving that Pd-AAFM was mainly composed of carbon, nitrogen, palladium and chloride as expected (Fig. S1). Elemental mapping on the cross-sections indicated homogeneous distribution of palladium over the polymer matrix (Fig. S2). The palladium amount was estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to be 69.3 mg (0.651 mmol) per gram of AAFM.

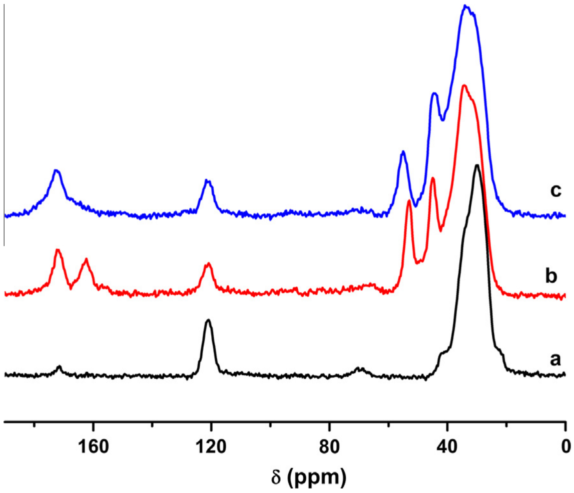


Fig. 3. Solid-state ^{13}C MAS NMR spectra of (a) the original PAN monolith (b) AAFM and (c) Pd-AAFM.

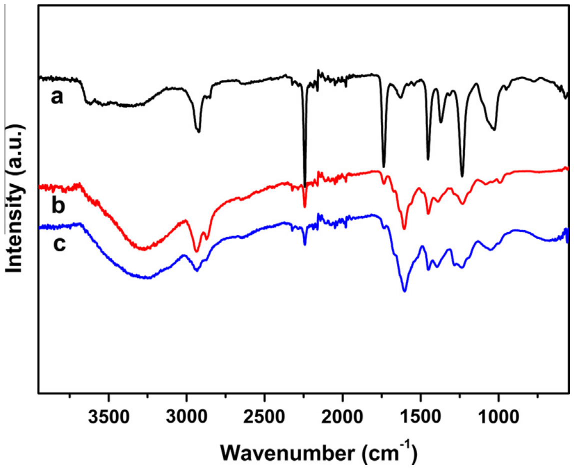


Fig. 2. IR spectra of (a) the original PAN monolith (b) AAFM and (c) Pd-AAFM.

In order to assess mesoscopic porosity of the monolith, nitrogen adsorption–desorption experiments were performed. The adsorption–desorption isotherms of the PAN monolith and Pd-AAFM are shown in Figs. S3 and 5, respectively. These isotherms followed a typical type IV isotherm with a H2 type hysteresis loop in the P/P_0 range from 0.4 to 0.9. The isotherm of Pd-AAFM showed a gradual increase of the adsorption amount at the relative pressure of $P/P_0 = 0.01–0.35$ but exhibited a sharp increase in the P/P_0 range of 0.4–0.9. After that the adsorption saturated, the specific surface area and the pore volume of Pd-AAFM were estimated by the Brunauer–Emmett–Teller (BET) method to be 124.3 $m^2 g^{-1}$ and 0.108 $cm^3 g^{-1}$, respectively. These values are slightly smaller than 139.2 $m^2 g^{-1}$ and 0.128 $cm^3 g^{-1}$ estimated for the PAN monolith, respectively. A remarkable difference between the two monoliths was found in the pore size distribution estimated by the non-local density functional theory (NLDFT) method [22]. The pore size of the original PAN monolith was distributed around 5.3 nm, whereas the distribution became bimodal with peaks around 3.8 and 1.5 nm for Pd-AAFM. These results suggest that the smaller pores were opened up by the chemical treatments.

Suzuki–Miyaura cross-coupling reaction was demonstrated by using Pd-AAFM as catalyst. 4-Iodoanisole and 4-methylboronic acid were first chosen as substrates. The reaction was performed under various conditions using a water/ethanol mixed solvent with an inorganic base at 55 °C (Table 1) [52]. In the presence of Pd-AFFM the reaction proceeded to afford the product in the yield of 60–96%, while no reaction occurred in its absence. A decreased amount of Pd-AAFM lowered the yield. These results evidenced that Pd-AAFM catalyzed the reaction. The reaction in water gave the lowest yield (60%), which could be explained by poor solubility of the substrates. The yield was improved by increasing the ethanol content to be water/ethanol 1:1 (96%). However, further increases to 1:2 and 0:1 lowered the yields (78% and 75%, respectively), which may be caused by decreased solubility of the inorganic base. The use of weaker bases (K_2CO_3 and $CsCO_3$) resulted in higher yields than stronger bases (NaOH and KOH) that are prone to cause more side reactions such as protodeboronation [53,54].

The reaction was also tested by using other aryl halides and boronic acids as substrates (Table 2). Despite the difference in halogenide group (bromide or iodide) and para-substituent (electron donating or withdrawing group), the reaction gave the corresponding product in a high yield (94–97%). These results point to the versatility of the present protocol using Pd-AAFM as catalyst.

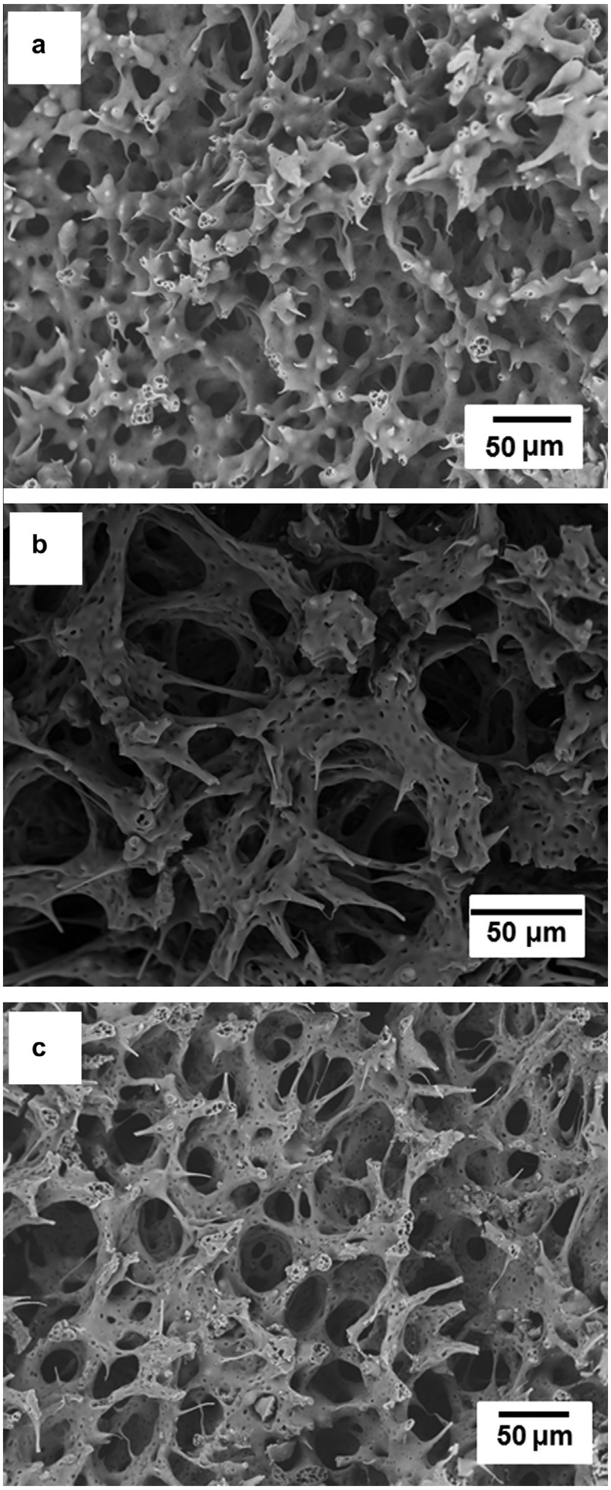


Fig. 4. SEM cross-sectional images of (a) the original PAN monolith, (b) AAFM and (c) Pd-AAFM.

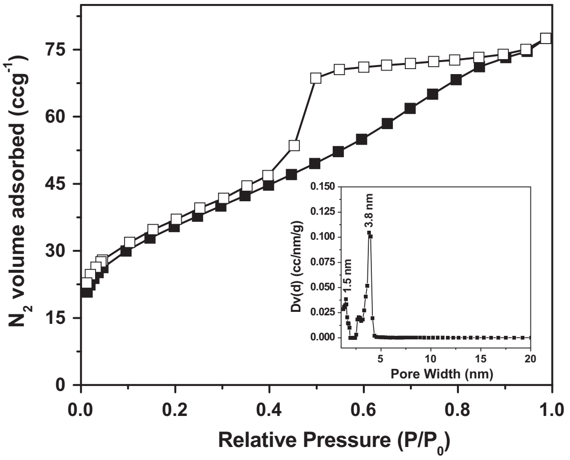


Fig. 5. N_2 adsorption (■)–desorption (□) isotherm of Pd-AAFM. The inset shows the pore size distribution on the basis of the NLDFT model.

Pd-AAFM was also found to be reusable. After the reaction between 4-iodotoluene and *p*-tolylboronic acid afforded the product in 96% yield, Pd-AAFM was filtered out from the reaction mixture, washed and dried. The recovered Pd-AAFM was then directly reused for a next reaction under the same conditions. This procedure was repeated five times but little decrease of the product yield was observed, proving the excellent reusability of Pd-AAFM as catalyst (Table S2). The stability of both chemical and porous structures of the monolith was confirmed by IR and SEM analyses of Pd-AAFM, respectively; IR spectra and SEM cross-sectional images of the monolith little changed before and after the five reaction/recovery cycles (Figs. S4 and S5). The overall shape of the monolith was largely retained as well. However, surface roughening as well as 10% weight loss of the monolith were observed after the five reaction/recovery cycles. This is attributed to partial fragmentation caused by the mechanical forces imposed to the monolith during the reaction and workup processes. The small fragments stripped from the monolith surface formed a fine powder and trapped by the filter paper. This accounts for the weight loss of the monolith.

4. Conclusion

A new palladium catalyst based on a mesoporous polymer monolith has been introduced. By taking advantage of a phase separation technique we previously developed, a mesoporous polyacrylonitrile (PAN) monolith was firstly prepared as precursor material. This monolith was then treated with ethylenediamine to introduce amidine groups on the surface and concomitantly fixate the porous structure by crosslinking. Finally, $PdCl_2$ was loaded on the monolith via coordination to the amidine groups as anchoring sites. The resultant monolith was characterized by using a range of analytical tools such as IR, ^{13}C MAS NMR, SEM, EDX, ICP-AES as well as the BET method. A series of Suzuki–Miyaura cross-coupling reactions were successfully demonstrated with the Pd-loaded monolith as catalyst. The catalyst was also confirmed stable over repeated use. These results qualify the present monolith as a promising heterogeneous catalyst that is easy to prepare and handle, efficient, versatile and reusable. Further studies on integration of the present monolith into flow reactors are underway in our laboratory.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym.2014.03.002.

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