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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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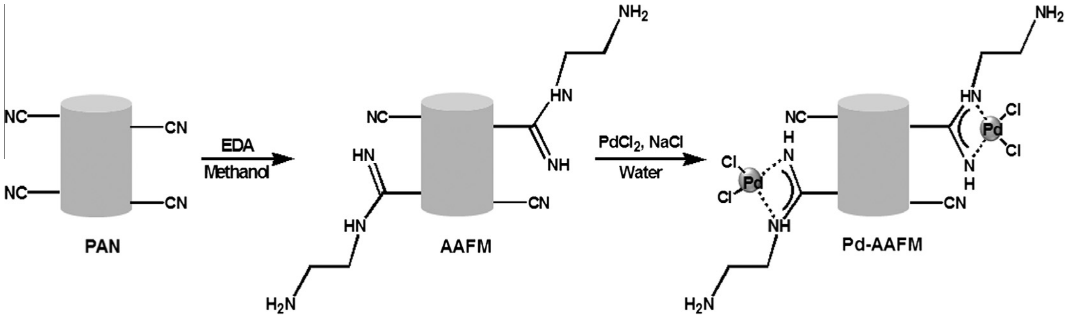

Scheme 1. Simplified cartoon depiction of the procedure for preparation of the palladium-loaded monolith.

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.