



Heterogeneous palladium catalyst constructed with cross-linked hyperbranched poly(phenylacetylene) as polymer support: A reusable highly active ppm-level catalyst for multiple cross-coupling reactions

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ABSTRACT

We demonstrate in this work a unique strategy for the synthesis of heterogeneous Pd catalysts with the use of a hyperbranched poly(phenylacetylene) containing pendant alkyne groups as the cross-linkable polymer substrate. It utilizes the dual functions of Pd-based catalysts in catalyzing both alkyne polymerization/oligomerization and coupling reactions. In the synthesis, a homogeneous Pd(II) catalyst catalyzes the cross-linking of the hyperbranched polymer and simultaneously encapsulates itself into the cross-linked polymer matrix, rendering the heterogeneous catalyst at high yield and high percentage of Pd encapsulation. Three homogeneous catalysts having different ligands (triphenylphosphine, a diphosphine ligand, and a diimine ligand) have been examined for the cross-linking encapsulation and the resulting heterogeneous catalysts have been evaluated for their catalytic performance in coupling reactions. Among the various heterogeneous catalysts obtained, a triphenylphosphine-ligated catalyst, HBPPA-Pd-2, appears to be the optimum one. It shows high activity in catalyzing the Suzuki–Miyaura reactions, the Mizoroki–Heck reactions, and the allylic arylation reactions under air with the Pd loading at as low as mol ppm or even mol ppb levels relative to the reactants. Meanwhile, it facilitates the Suzuki–Miyaura reactions of challenging less reactive aryl chlorides/heteroaryl bromides and the Mizoroki–Heck reactions of aryl bromides as reactants. In addition, it behaves truly as a heterogeneous catalyst with high reusability and low catalyst leaching during the reactions.

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1. Introduction

Palladium-catalyzed carbon–carbon cross-coupling reactions [1–3], including the notable Suzuki–Miyaura [4–7] and Mizoroki–Heck reactions [8–13], have played an important role in modern organic synthesis by enabling many valuable organic transformations. Due to the high cost of Pd as well as environmental and health issues, reusable heterogeneous Pd catalysts have drawn increasing attention for the industrial applications of these coupling reactions since homogeneous Pd catalysts are difficult to recover and reuse. Numerous heterogeneous catalysts have been developed with the use of various organic polymeric and inorganic supports through different catalyst immobilization/encapsulation strategies [14–22]. But the search is continuing for high-performance heterogeneous catalysts of high activity with Pd loading needed at as low as ppm levels, high reusability with

minimum/negligible catalyst leaching during reactions, and high versatility with broad applicability to multiple types of coupling reactions and to difficult precursors such as aryl chlorides [23]. Such heterogeneous catalysts of combined performance properties are still limited despite the enormous investigations in the area.

Relative to the inorganic supports, organic polymer supports show the advantage in their convenient synthesis and the versatility in tuning their composition/functionality for controllable catalyst immobilization/encapsulation. A great variety of polymers, including both soluble polymers [24–28] with controllable linear [16,19,24–28] or dendritic/hyperbranched architectures [29–33] and insoluble polymers [14–22], have been used as the substrate for the immobilization/encapsulation of various Pd complexes or Pd nanoparticles. With soluble polymer substrates, high catalyst activity can be achieved due to their soluble nature, but at the compromise of relatively higher catalyst leaching and the requirement of special catalyst recovery methods such as biphasic solvent systems and polymer precipitation with proper solvents [24–28]. On the contrary, heterogeneous catalysts on insoluble polymers offer much more convenient catalyst recovery and reuse

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through simple procedures like filtration. In particular, insoluble cross-linked polymers show the further added advantage of reduced catalyst leaching because the tightly cross-linked 3-dimensional networks minimize the aggregation and leaching of the encapsulated catalyst species. Due to these advantages, various insoluble cross-linked polymers have been developed and used to immobilize/encapsulate Pd nanoparticles and Pd complexes as heterogeneous catalysts [17,18,34]. They include broadly cross-linked amphiphilic copolymer micelles [17,18,35–37], cross-linked polymethacrylates [38,39], cross-linked polystyrene-poly(ethylene glycol) resins [40–42], cross-linked poly(amidoamine) dendrimers [43], polyurea [44,45], self-assembled poly(imidazole) via binding with Pd species [46,47], cross-linked hyperbranched polyethylenes with self-supported Pd nanoparticles [48], cross-linked microporous polymers [49–51], cross-linked reverse micelle [52], cross-linked polystyrenes with different covalently tethered functionalities [53–56], cross-linked ionic copolymers [57–59], hydrogels [60,61], cross-linked chitosan [62,63], cross-linked poly(1,3-diethynylbenzene) [64], etc.

The majority of heterogeneous Pd catalysts on cross-linked polymer supports have been synthesized via stepwise procedures comprised of the synthesis of the cross-linked polymers with desired functionalities followed with catalyst immobilization. With this synthetic strategy, the immobilized Pd catalysts are thus bound either covalently or noncovalently on the internal surface of the cross-linked polymer substrates instead of being incorporated within the polymer matrix. This increases the risk of catalyst leaching. Only in some cases [35–37,41,43–48,52,62–64] the Pd catalysts are embedded desirably within the cross-linked polymer matrix wherein Pd encapsulation occurs during or prior to polymer cross-linking in the synthesis. Meanwhile, the majority of the heterogeneous catalysts on cross-linked polymer supports show relatively low activity with a large Pd loading often required to facilitate the coupling reactions, and often have limited applicability to only one or two types of couple reactions.

In this article, we report a convenient alternative one-step synthetic strategy that leads to a reusable, high-activity, high-versatility heterogeneous catalyst with Pd species encapsulated within a cross-linked hyperbranched poly(phenylacetylene) (HBPPA) matrix. Different from all other previously reported syntheses, a triphenylphosphine-ligated cationic Pd catalyst is herein used as an alkyne polymerization catalyst to cross-link the hyperbranched poly(phenylacetylene) having pendant alkyne groups. During the cross-linking, the Pd catalytic species are simultaneously embedded within the formed polymer networks, turning themselves uniquely from a homogeneous polymerization catalyst into a heterogeneous cross-coupling catalyst. The heterogeneous catalyst synthesized herein has been found to efficiently catalyze the Suzuki–Miyaura, Mizoroki–Heck, and allylic arylation reactions at the Pd loadings of as low as ppm levels relative to reactants, as well as good reusability with low catalyst leaching during the reactions.

2. Experimental

2.1. Materials

All manipulations and reactions were performed under atmospheric conditions unless otherwise noted. In order to avoid the influence of any residual Pd species absorbed on the surface, all the glassware and magnetic stirrers used for cross-coupling reactions were pre-treated with aqua regia, then washed with distilled water before being dried. The acetonitrile Pd-diimine catalyst, $[(\text{ArN}=\text{C}(\text{Me})-(\text{Me})\text{C}=\text{NAr})\text{Pd}(\text{CH}_3)(\text{N}=\text{CMe})]^+\text{SbF}_6^-$ ($\text{Ar} = 2,6\text{-}(i\text{Pr})_2\text{C}_6\text{H}_3$), was synthesized according to a literature

procedure [65]. HPLC-grade CH_2Cl_2 (99.5%, Fisher Scientific) was deoxygenated and dried by using a solvent purification system (Innovative Technology) before use. Methanol (ACS reagent, Fisher Scientific) was dried with $3\text{Å}/5\text{Å}$ molecular sieves before use. Deionized Water was obtained from a Barnstead/SynbronNanopure II water purification system. A palladium atomic absorption standard solution, containing 1011 ppm of Pd in 5.1 wt% HCl, was purchased from Aldrich. *N,N*-dimethylformamide (DMF, certified ACS grade), tetrahydrofuran (THF, certified grade), hydrochloric acid (35–38 wt.% in water), KF (granular powder, certified ACS grade) and K_2CO_3 (granular powder, certified ACS grade) were received from Fisher Scientific and used without further purification. Palladium (II) acetate ($\text{Pd}(\text{OAc})_2$, 98%) and α,α' -bis(*di-t*-butylphosphino)-*o*-xylene (97%) were obtained from Strem Chemicals and used as received. Mesoporous silica SBA-15 was purchased from Claytec Inc., and was vacuum dried at 160°C for 8 h before use. All other chemicals or solvents, including 1-methyl-2-pyrrolidinone (NMP, ReagentPlus), CsF (>99%), 1,3-diethynylbenzene (DEB, 96%), methanesulfonic acid (MSA, 99.5%), triphenyl phosphine (PPh_3 , 99%), iodobenzene (PhI, 98%), 4'-iodoacetophenone (98%), bromobenzene (PhBr, 99%), 1-bromo-4-nitrobenzene (99%), 4-bromobenzonitrile (99%), 4'-bromoacetophenone (98%), 4-bromoanisole (99%), 4-bromotoluene (98%), 2-bromotoluene (99%), 3-bromotoluene (98%), 2-bromomesitylene (98%), 1-bromonaphthalene (97%), 2-bromopyridine (99%), 3-bromothianaphthene (95%), chlorobenzene (PhCl, ReagentPlus), 4'-chloroacetophenone (97%), 4-chlorotoluene (98%), 4-chloroanisole (99%), 4-chlorobenzonitrile (99%), 4-methoxyphenylboronic acid ($\geq 95\%$), 4-acetylphenylboronic acid, *n*-butyl acrylate (BA, >99%), styrene (99%), triethyl amine (Et_3N , 99%), phenylboronic acid (PBA, >97%), cinnamyl acetate (99%), prenyl acetate ($\geq 98\%$), sodium tetraphenylborate (NaBPh_4 , ACS Reagent), nitric acid (HNO_3 , 70%), and hydrogen peroxide (H_2O_2 , 50 wt.% in water), were all purchased from Aldrich and used as received.

2.2. Measurements and characterizations

The characterization of HBPPA with gel permeation chromatography (GPC) was carried out on a Polymer Laboratories PL-GPC220 system equipped with a triple-detection array comprising of a differential refractive index (DRI) detector (from Polymer Laboratories), a three-angle (45° , 90° , and 135°) light scattering (LS) detector (from Wyatt Technology) at a laser wavelength of 687 nm, and a four-bridge capillary viscosity detector (from Polymer Laboratories). Details in the characterization have been reported in our earlier paper [66].

All measurements with proton nuclear magnetic resonance (^1H NMR) spectroscopy were carried out on a Bruker AV500 spectrometer (500 MHz) at ambient temperature with CDCl_3 as solvent. Atomic absorption (AA) spectroscopy was performed on a Perkin Elmer Precisely AAnalyst 400 spectrometer (Perkin Elmer) equipped with a Pd element lamp (max. 30 mA, Perkin Elmer). The data was collected with a WinLab32 software (Perkin Elmer). The blank solution for the preparation of the standard Pd solutions and sample dilution was composed of 11.1 vol% THF, 6.7 vol% HCl, and 3.4 vol% H_2O_2 in deionized water. For all the analyses, a calibration curve was first established with Pd standard solutions with [Pd] in the range of 0.25–10 mg/L. X-ray photoelectron spectroscopy (XPS) measurements of the heterogeneous Pd catalysts were carried out on a Thermo Scientific Theta Probe XPS spectrometer (ThermoFisher). A monochromatic Al $\text{K}\alpha$ X-ray source was used, with a spot area $400\ \mu\text{m}^2$. The samples were run in a standard mode, i.e., all angle collected (60° angular acceptance) for the survey spectra, and for the region spectra. Transition electron

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