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Highly efficient and reusable hydrogel-supported nano-palladium catalyst: Evaluation for Suzuki–Miyaura reaction in water

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ABSTRACT

Ligand-free, palladium-supported, poly(*N*-isopropylacrylamide-*co*-potassium methacrylate) [poly(NIPA-*co*-PMA)] hydrogel nanocomposite with different comonomer ratios were synthesized. The developed hydrogel–palladium composites were characterized by SEM, TEM, UV–vis DRS and XRD. The catalytic performance of these hydrogel–palladium nanocomposites was examined for Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids in an aqueous medium. The hydrogel with comonomer ratio of 8.8:1.6 mmol of NIPA:PMA exhibited optimum catalytic activity, which can be effectively reused 5–6 times without loss of catalytic activity.

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1. Introduction

During the last two decades, palladium catalyzed C–C bond forming reactions have gained wide acceptance by synthetic chemists [1–9]. Among them, the Suzuki–Miyaura (SM) [10–12] reaction has become the most popular for accessing biaryls. The organoboranes are used in the SM reactions that are air/moisture stable with relatively low toxicity and easy to be removed as boron-containing by-products [13]. This reaction is used in the synthesis of natural products and widely practiced in the sythesis of pharmaceuticals, herbicides, and natural products as biaryl motif [14]. Natural products possessing such a structural motif are known to display antitumor, antiviral and estrogenic activities, and also present angiotensin II antagonistic or tubulin binding properties [15–24].

Most of the catalysts used in SM reaction are based on palladium phosphine complexes [25–26] or homogeneous nickel [27], which are difficult to recover and therefore economically and environmentally undesirable. Moreover, phosphine ligands are toxic, expensive and suffer from the contamination of the ligand residue in the products. In recent years there has been an increasing interest in heterogeneous catalysts, which are easy to recover and reusable in the aqueous medium for several cycles [28]. Catalytic activity of palladium (Pd) nanoparticles is found as one of the significant frontiers of research that can avoid the formation of phosphines as byproducts in the reaction. In this context, functional resins are considered to be intelligent supports for the immobilization of palladium nanoparticles. Further, reasonable chemical and thermal stability as well as fine tunability of nanostructure and physico-chemical properties make them attractive and environmentally friendly catalysts. Macro-reticular (permanent porosity) and gel (nano-porous in swollen state) type of macromolecular resins are extensively explored for effective immobilization of palladium nanoparticles [29]. Uozumi et al. studied the Suzuki–Miyaura coupling of aryl halides and aryl boronic acids under heterogeneous aqueous conditions by use of a PS-PEG resin-supported palladium-phosphine complex. Selective monoarylation of dibromoarenes was also performed using this catalyst in water [30–32]. Cross-linked polystyrene resins and silica gels have been reported to be useful catalysts for Suzuki–Miyaura reactions but they suffered from low mass transfer and selectivity [33–34]. Template synthesis of homogeneously dispersed and size

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controlled metal nanoparticles is possible by using cross-linked hydrogels [35]. The matrices of these functional hydrogels with ion exchange ability are considered to have "nano-reactors" designable for a variety of purposes. The appropriate selection of suitable co-monomers shall influence the physico-chemical features of the nano-reactors that can be tailor-made suitably [36].

Most of the reported literature is based on Pd anchored polymer supports with ligands. Recently, a polymer-supported palladium(II) salen-type complexes has been reported [37] for the coupling of aryl bromides with phenylboronic acid in a mini-continuous flow reactor system. This system requires elevated temperatures and demonstrates small-scale reactions. Palladium-dodecanethiolate nanoparticles [38] and amphiphilic polymer-supported *N*-heterocyclic carbene palladium complex [39] were reported to catalyze SM reaction. However, they suffer from long reaction times and handling. These polymer-supported Pd ligand complexes enable the SM reaction with aryl chlorides (lower reactivity) as well as aryl bromides and iodides, but the ability of recycling was not found in the case of the aryl chlorides. The ligand-free palladium acetate $Pd(OAc)_2$ was used as catalyst for aryl chlorides at higher temperatures of >150 °C [40–44]. Using water, the green solvent, is an integral part of a chemical manufacturing process. Therefore, it is of great importance to develop a reusable and ligand-free catalytic system for SM reaction in the aqueous medium.

In the present work, we describe the synthesis and characterization of Pd@Poly(*N*-isopropyl acrylamide-*co*-potassium methacrylate) [Pd@Poly(NIPA-*co*-PMA)] hydrogel supports. The catalytic performance of these supports in the SM cross-coupling reaction of aryl halides with aryl boronic acids in aqueous medium and the recycling efficiency are reported.

2. Experimental

2.1. Materials

Methacrylic acid, palladium chloride, *N*-isopropylacrylamide (NIPA), ammonium persulfate (APS), *N*,*N*^{I}-methylenebisacrylamide (MBA), *N*,*N*,*N*′,*N*″-tetramethylethylenediamine (TEMED) and hydrazine hydrate were purchased from Aldrich chemicals (Milwaukee, WI, USA). Potassium hydroxide was purchased from S.D. Fine Chemicals (Mumbai, India).

2.2. Preparation of potassium methacrylate (PMA)

Potassium hydroxide (1 mol) solution was prepared in methanol and titrated against methacrylic acid (1 mol) taken in a 500-mL conical flask in methanol. The precipitated white solid (PMA) was filtered and dried in vacuum [45].

2.3. Preparation of hydrogels

Poly(NIPA-*co*-PMA) was synthesized by simultaneous free-radical cross-linking polymerization.

Polymerizations were carried out employing NIPA 8.8 mmol with varied PMA concentration from 0.4 to 2.0 mmol in the presence of 1 mL of MBA (1 wt.%). The above solution was purged with nitrogen gas for about 5 min to remove dissolved oxygen. Then, the polymerizations were initiated by adding 1 mL of APS (1 wt.%) and TEMED (1 wt.%). Subsequently solution turned into highly viscous liquid and finally formed solid gel within a few minutes at 25 °C. However, the reaction was left for 24 h to complete the reaction. The gels obtained were removed from a petri dish and cut into discs (3 mm high, 12 mm diameter). The hydrogel discs were thoroughly washed with distilled water for 3 days to leach out the un-reacted compounds.

2.4. Preparation of poly(NIPA-co-PMA)-Pd composites

To prepare these composite, 150 mg of dry gel was taken in 100 mL water and allowed to complete swelling for 24 h. After that, these swollen gel discs were utilized for complexation with palladium chloride (15 mg in 150 mL water) and the subsequent reduction reaction was performed with hydrazine hydrate.

2.5. Characterization

X-ray diffraction (XRD) of hydrogel and composites were done on a Rigaku Dmax-γA X-ray diffractometer (Rigaku, Tokyo, Japan) using Cu Kα radiation ($\lambda = 1.54178$ Å). Transmission electron microscope (TEM) images were obtained using a Technai-12 model instrument (FEI Company, Czech Republic) at an acceleration voltage of 100 kV. Scanning electron microscope (SEM) studies were performed on a Hitachi S 520 SEM (Hitachi, Tokyo, Japan) under high vacuum, 0.1 Torr, and high voltage of 1.2 kV, by mounting the gold-coated samples on aluminum stubs with double-sided adhesive tape. Diffuse reflectance UV–vis spectra for samples as KBr pellets were recorded on a GBC Cintra 10e UV–vis DRS spectrometer (Cintra, Australia) in the range of 200–800 nm with a scan speed of 200 nm/min.

2.6. Suzuki–Miyaura cross-coupling reaction

A mixture of aryl halide (1 mmol), aryl boronic acid (1.5 mmol), Pd catalyst (1% w/w Pd@GEL5 9.84 μmol Pd), Na_2CO_3 (3 equiv.), and H_2O (8 mL) was added to a 50 mL R.B. Flask fitted with a reflux condenser under nitrogen atmosphere. The reaction mixture was stirred at reflux temperature until the complete consumption of the starting material as judged by thin layer chromatography (TLC).

The reaction was carried out as above. After cooling to room temperature and addition of CH_2Cl_2 (10 mL), the reaction was vacuum filtered through a Buchner funnel. The organic layer was washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. The pure compound was obtained by column chromatography. The recovered catalyst was washed with CH_2Cl_2 twice, dried under vacuum at room temperature and reused for further reactions.

All reactions were monitored by thin layer chromatography (TLC) using silica-coated plates and visualizing under UV light. Light petroleum of the distillation range 60–80 °C was used. Yields refer to chromatographically and spectroscopically (^{1}H NMR, ^{13}C NMR) homogeneous material. Air sensitive reagents were transferred by syringe or with a double-ended needle. Evaporation of solvents was performed at reduced pressure, using a Buchi rotary evaporator. ^{1}H NMR spectra were recorded on Varian FT-200 MHz (Gemini) and Bruker UXNMR FT-300 MHz (Avance) spectrometers in $CDCl_3$. Chemical shift values were reported in parts per million (δ) relative to tetramethylsilane (δ 0.0) as an internal standard. Mass spectra were recorded under electron impact at 70 eV on LC-MSD (Agilent technologies). Column chromatography was performed on silica gel (60–120 mesh) supplied by Acme Chemical Co., India. Thin-layer chromatography was performed on Merck 60 F-254 silica gel plates.

2.6.1. Spectral data for selected compounds

Compound **3b** IR (KBr): ν 2924, 2848, 1693, 1599, 1213, 831, 760 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.85 (t, 2H, *J* = 8.5 Hz), 7.65–7.68 (m, 2H), 7.53–7.60 (m, 2H), 7.31–7.40 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 191.9, 147.2, 139.8, 135.1, 130.4, 129.0, 128.6, 127.5, 127.4. Mass: *m*/*z* 205 [M+Na]$^+$.

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