Organic polymer composites as robust, non covalent support of metal salts

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Supplementary data

Materials

Styrene (St, >99%, Fluka) and divinylbenzene (DVB, 80% Tech, Aldrich) were extracted three times with an equal volume of 1 M aqueous NaOH and subsequently washed once with an equal volume of deionized water. They were dried with anhydrous $MgSO_4$ and degassed by Argon before use. Benzoyl peroxide (BPO, moistened with 25% water, Merck), 1,1′-Azobis(cyclohexanecarbonitrile (ACCN, 98%, Aldrich), 2-hydroxylpropyl acrylate (2-HPA, tech grade, Aldrich), N,N-dimethylacrylamide (DMAA, 99%, Aldrich), n-decane (99%, Aldrich), toluene (99.5%, Fisher Scientific) and poly(vinyl alcohol) (PVA, Molecular weight = 85,000~146,000, 87~89% hydrolyzed, Aldrich) were used as received without further purification. Palladium (II) acetate ($(CH_3COO)_2Pd$, 99.9+%, Sigma-Aldrich), cyclohexene (99%, Fluka), acrylonitrile (99+%, Aldrich) and 2-cyclohexen-1-one (97%, Alfa Aesar) were used as received.

General Experimental Section

Fourier transform infrared (FT-IR) spectroscopy was carried out on a Bio-Rad Excalibur FTS-3000MX FT-IR spectrometer. The gel loading of the polymer composite was estimated using an elemental analyzer (Euro EA3000 test for CHNS-O) measured by thermal conductivity detector (TCD) in the sequence of N_2, CO_2, H_2O and SO_2. The surface constituents of supported Pd catalyst were characterized by X-ray photoelectron spectroscopy, performed with an Escalab 250 spectrometer using Al Kα (1486.6 eV) X-rays radiation operated at 15 kV and 200 W, maintained at a vacuum of less than 10^{-8} mbar during analysis. Chemical shift peaks are charge referenced to the C1s peak (C-C/C-H) peak at 284.8eV. ^{1}H NMR spectra were

recorded on a Bruker Advance 400 (Standard Bore) spectrometer, operated at 400 MHz. The morphology characterization was carried out on JEOL JSM-6700 Field Emission Scanning Electron Microscope (Fe-SEM). The catalyst loadings were estimated by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-OES). 20mg of Pd supported beads were immersed in 0.5mL HCl/HNO$_3$ mixture (3/1 v/v) for 24 hours. After removal of solid, the solution was diluted to 10mL in volumetric flask for measurement of dissolved Pd species.

Synthesis of Porous Poly(styrene-co-divinylbenzene) [P(St-DVB)] Beads

Porous copolymer microspheres of styrene (St) and divinylbenzene (DVB) (St:DVB = 4:1 mol/mol) were synthesized by suspension polymerization using benzoyl peroxide (BPO, 0.5 mol%) as the initiator and 0.5 wt % water solution of polyvinyl alcohol (PVA) as dispersant. A mixture of toluene and decane (1:3 vol/vol) was added as the porogen. The mixture was stirred at fixed agitation rate of 600 rpm, to give a suspension of oil droplets dispersed in aqueous phase, under argon gas purging. A three-ramp temperature profile (75°C/2h, 85°C/4h, 90°C/4h) was implemented to conduct the polymerization. After polymerization, the resultant P(St-DVB) beads were extracted with hot hexane in Soxhlet extractor for 12 hours, washed with warm water and vacuum dried at 60°C for 24 hours. The isolated yield was 93% by mass.

Synthesis of P(St-DVB)-P(HPA-GDMA) and P(St-DVB)-P(DMAA-GDMA) Composites

The incorporation of the gel phase into the matrix of hard beads was carried out in two sequential steps: monomer loading and *in-situ* polymerization. In a typical procedure, 0.5 g P(St-DVB) were dispersed and swollen in a solution of toluene, 2-hydroxypropyl acrylate (2-HPA), glycerol dimethacrylate (GDMA) (2-HPA:GDMA=20:1 mol/mol, toluene:monomers=3:1 vol/vol) and initiator (1,1'-azobis(cyclohexanecarbonitrile), ACHN, 0.5mol%). After 24-hour stirring, the swollen beads were separated by filtration and immediately re-dispersed in saturated sodium chloride solution. The suspension was heated to 80°C for *in-situ* copolymerization of adsorbed 2-HPA and GDMA. After one day, the resultant composite powders were washed with copious amounts of water to remove NaCl, then rinsed repeatedly with acetone and hexane under sonication. Finally, the powders were vacuum dried at room temperature for 48 hours. For the synthesis of P(St-DVB)-

P(DMAA-GDMA) composite [PSt-PDMAA], *N,N*-dimethylacrylamide, GDMA and ACHN were used. Gel loading in the PSt-PHPA and the PSt-PDMAA is approximately 20% as determined by both gravimetric and elemental analyses.

Synthesis of Supported-Pd Catalyst Using Microspherical Composite

For the synthesis supported Pd-catalyst, a dark orange solution of 5mg palladium acetate [$Pd(OAc)_2$] in 2mL of Ar-purged acetone was added to 100mg of the PSt-PHPA or PSt-PDMAA composite beads. After stirring for 24 hours, the supernatant was removed and the solid was washed with acetone several times and dried under vacuum. The resultant PSt-PHPA-Pd(II) and PSt-PDMAA-Pd(II) catalysts were light yellow in colour. Reduction of Pd(II) to Pd(0) was achieved by treatment of Pd(II)-loaded beads under an atmosphere of H_2. After the first 20 hours, the beads were dried under vacuum in order to remove the acetic acid formed during the reduction of $Pd(OAc)_2$. The reduction was then continued for another 20 hours, and the beads were subsequently dried under vacuum for one day. The resultant PSt-PHA-Pd(0) and PSt-PDMAA-Pd(0) were grey in colour, with Pd loading of 65 and 75 µmol/g respectively.

Table 1. The characterization of gel-embedded polymer composites and the derived supported Pd catalysts

Supported-Pd catalyst	Elemental analysis	Gel loading (wt%)		Pd loading (µmol/g)
		EA method	Gravimetric method	
PSt-PHPA-Pd(II)	C:H:O = 81.72:7.49:10.79	19.01	20.30	65
PSt-PDMAA-Pd(II)	C:H:N = 81.19:8.13:2.88	22.19	19.74	75

Hydrogenation Studies

The PSt-PHPA-Pd(0) and PSt-PDMAA-Pd(0) catalysts prepared from pre-reduction of the Pd(II) composites, were tested for catalytic activity in the hydrogenation of

double bonds, typified by the reduction of acrylonitrile and cyclohexene. The reactions were performed with 1mL of substrate in the presence of 50mg of composite resin under an atmosphere of H_2. The latter translates to ca. 0.02 mol% of Pd relative to the acrylonitrile and 0.03 mol% of Pd relative to cyclohexene. The reaction mixture was sampled with a syringe at certain time interval, and diluted in $CDCl_3$ for proton NMR spectroscopy to estimate conversion. The reduction of 2-cyclohexen-1-one (0.75mmol in 1mL toluene) was also demonstrated with 1 mol% of PSt-PHPA-Pd(0). The reaction mixture was sampled and analyzed after 15 hours. To recycle the catalyst, the product was removed using an Ar-purged needle. The catalyst was washed with toluene several times under argon and then dried under high vacuum for 5 hours. The recycling reaction was carried out for 5 rounds.

Phosphine-free Suzuki-Miyaura Cross-Coupling Reaction

The reactions were carried out in low substrate concentration (~25mM) and low catalyst amount (0.06mol% with respect to the substrate). For a typical reaction, a round bottom flask was charged with of aryl bromide (0.25mmol), arylboronic acid (0.275mmol) and Na_2CO_3 (0.95mmol), water (5mL) and ethanol (5mL) was bubbled with Argon for 20 minutes. The reaction mixture was stirred at room temperature and PSt-PHPA-Pd(II) catalyst was added after clear solution was formed. The reaction was then carried out under argon atmosphere. At fixed time interval, ca. 0.02mL reaction mixture was sampled using an Ar-purged needle. The sample was diluted immediately by 0.8mL of acetone-d6 and characterized by proton NMR spectroscopy.

Heck-Coupling Reaction

In the Heck-coupling reaction, a two-neck round flask was charged with 100mg catalyst and then evacuated-refilled with argon for three cycles. Subsequently, N-methylpyrrolidone (1.5mL), iodobenzene (1mmol, 204mg) and triethylamine (1.25mmol, 126.5mg) were added to the flask via argon-purged syringes. The mixture was stirred and heated up to 75°C. n-Butyl acrylate (1.5mmol, 151.7mg) was introduced using an Argon-purged syringe and the reaction mixture was further heated to 90°C. After 2 hours, the reaction mixture was filtered and the solid catalyst was washed with NMP (2×1.5mL) under argon atmosphere which was reused for the successive reaction. The conversion of aryl iodides was determined by proton NMR spectroscopy.

Fourier Transform Infra-Red Spectroscopy

The spectrum of P(St-DVB) displayed the common benzene ring character: aromatic C-H stretching vibration (3100-3000 cm^{-1}), ring carbon skeletal vibration (1600-1580 cm^{-1}), overtones and recombination bands (2000-1650 cm^{-1}), C-H out-of-plane bending vibrations between strongly coupled adjacent hydrogen (900-667 cm^{-1}) and a peak at 1447.3 cm^{-1} due to the bending (scissoring) motion of main chain saturated –CH$_2$– groups. The FTIR spectrum of PSt-PHPA composite clearly exhibited the presence of poly(2-hydroxypropyl acrylate-co-glycerol dimethacrylate) gel in the matrix of P(St-DVB): characteristic peaks at 1750-1735 cm^{-1} (sharp) and 1300-1030 cm^{-1} (broad) correspond to the C=O and C-O stretching vibrations of the ester functional group, respectively, broad –OH vibration band at 3550-3200 cm^{-1}. The FT-IR spectrum of PSt-PDMAA displayed the presence of poly(N,N-dimethylacrylamide-co-glycerol dimethacrylate) gel: distinct characteristic peaks at 1626.8 cm^{-1} (sharp) and 1403.7 cm^{-1} correspond to the C=O stretching vibration, and C-N stretching vibrations of the tertiary amide, respectively.
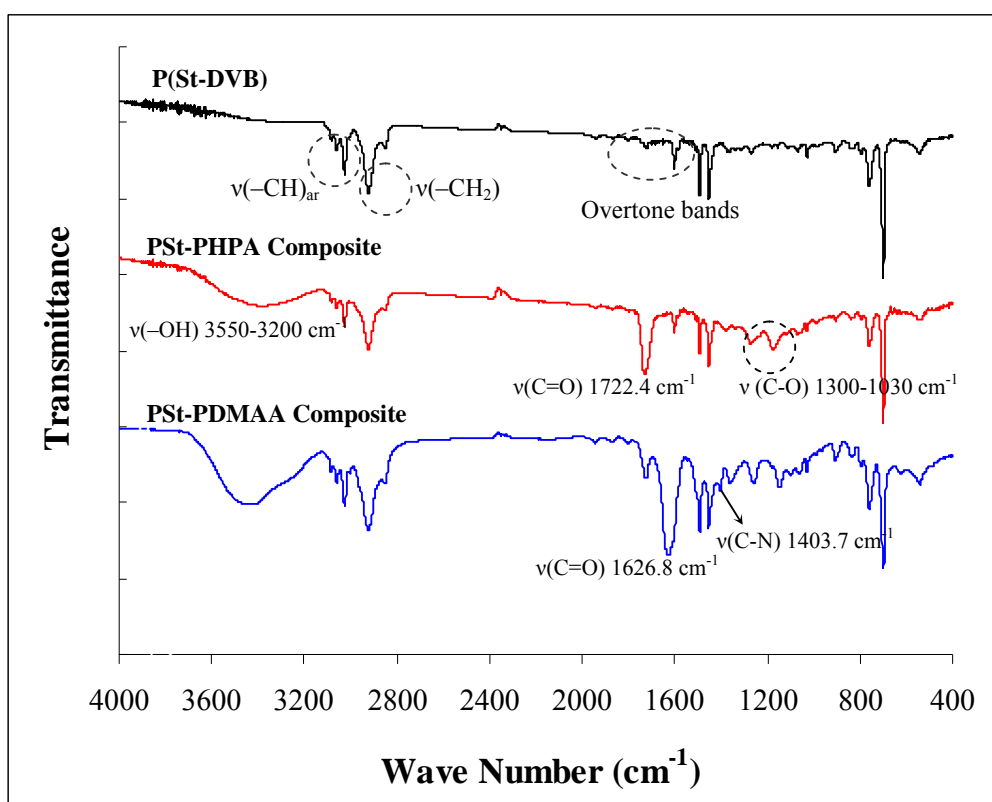

Figure 1. FT-IR fingerprints of pristine P(St-DVB), crosslinked PSt-PHPA and PSt-PDMAA composites

X-ray Photoelectron Spectroscopy Studies on Supported Pd Catalysts

Chemical shift peaks are charge referenced to the C1s peak (C-C/C-H) at 284.8eV. For the as-prepared PSt-PHPA-Pd(II), the Pd3d spectra exhibited the presence of Pd(II) and Pd(0) species. The binding energies of deconvoluted peaks were tabulated in Table 2. The XPS spectrum were characterized by two pairs of Pd3d peaks: the binding energies (BEs) of 337.8 and 343.1 eV were assigned to incarcerated Pd(II) species; the BEs of 336.4, 341.6 eV were assigned to Pd(0), for $3d_{5/2}$ and $3d_{3/2}$, respectively. Only one type of Pd(0) species was observed for PSt-PHPA-Pd(0) prepared via H_2 treatment. The XPS spectrum were characterized by peaks with BEs of 336.2 eV for $3d_{5/2}$ and 341.3 eV for $3d_{3/2}$, respectively. For the used catalyst after exposure to air for a few days, the XPS spectrum can be resolved into Pd3d peaks with binding energies (BEs) of 336.2, 345.2 eV for $3d_{5/2}$ and 341.3, 345.2 eV for $3d_{3/2}$, respectively. The lower BEs pair (335.2 and 341.3 eV) is attributed to the Pd(0) species, which was also present in the fresh catalyst. The higher BEs (+2 eV) pair was newly formed Pd species in higher oxidation states (Figure 2d).
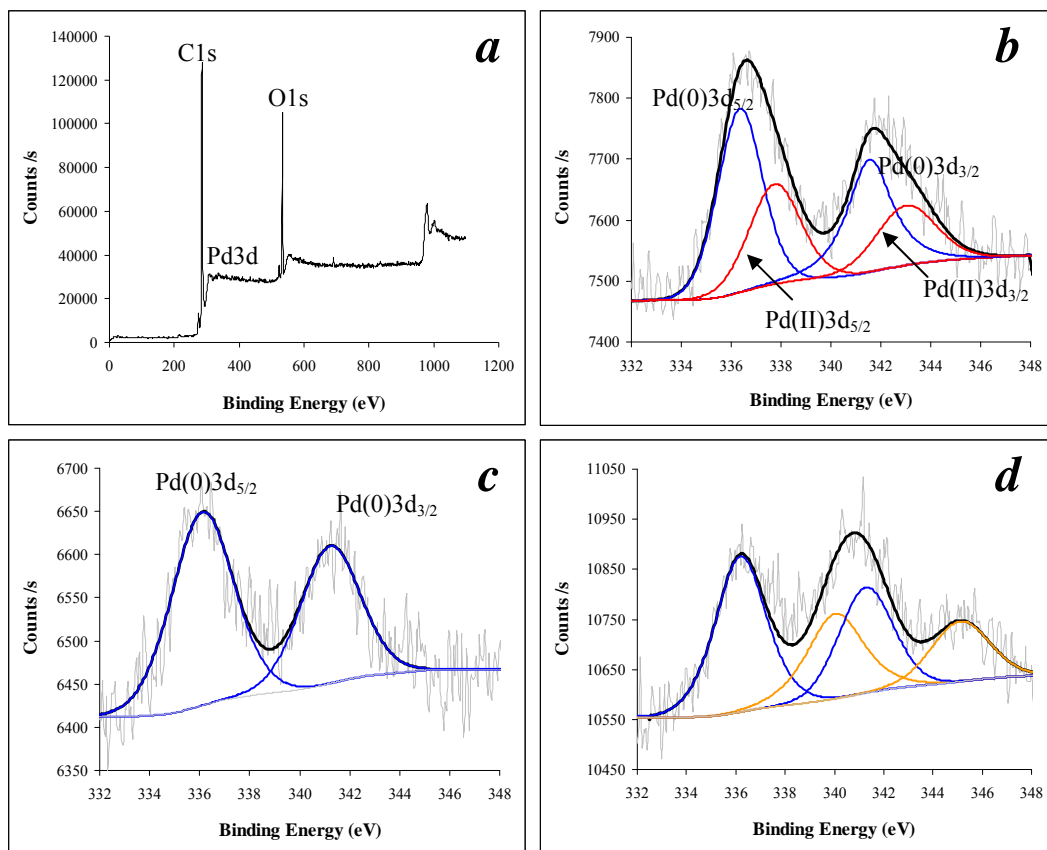

Figure 2 (a) Survey scan for PSt-PHPA-Pd(II). XPS Pd3d spectra of (b) PSt-PHPA-Pd(II), (c) PSt-PHPA-Pd(0) formed after reduction in hydrogen gas and (d) used catalyst.

Table 2. XPS peak parameters for PSt-PHPA-Pd(II) and PSt-PDMAA-Pd(II) at different stages

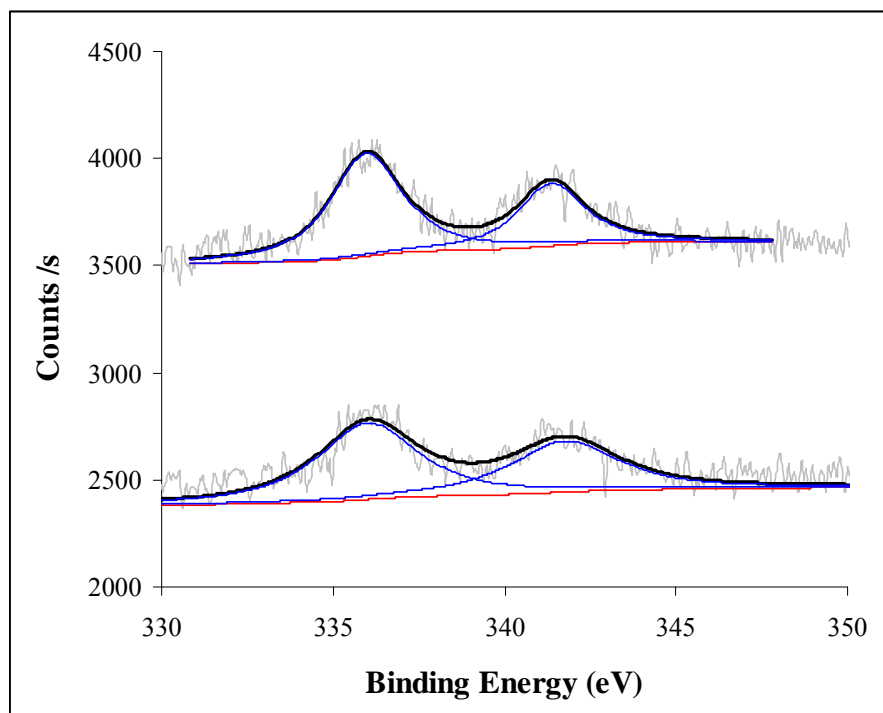| Composite	Species	Binding Energy (BE) /eV	
		Pd3d$_{5/2}$	Pd3d$_{3/2}$
PSt-PHPA Composite	PSt-PHPA-Pd(II)	336.37 337.82	341.57 343.12
	PSt-PHPA-Pd(0)	336.17	341.27
	Pd Catalytic Species After Reaction	336.21 340.11	341.31 345.16
PSt-PDMAA Composite	PSt-PDMAA-Pd(II)	336.10 337.75	341.25 342.85

Figure 3. XPS Pd 3d spectra for catalyst PSt-PHPA-Pd(II) after
(a) 1st Heck reaction and (b) 10th Heck reaction