



Novel macroporous palladium cation crosslinked chitosan membranes for heterogeneous catalysis application



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ABSTRACT

A novel palladium supported on chitosan porous membrane heterogeneous catalyst has been prepared by freeze-drying of Pd²⁺-crosslinked chitosan gel solution. The prepared membrane catalyst has three-dimensional porous structure (porosity: >70%). The crosslinking effects of Pd²⁺ to chitosan were good for the improvement of the mechanical properties and thermal stabilities. Pd²⁺ cations have been shown not only as the crosslinker, but also as the catalytic active sites. The reductive palladium species of the recycled membrane catalysts was found in the nanometer scale (20–40 nm). Excellent cross-coupling yields were achieved using as low as 0.12 mol% palladium catalyst loading for the Heck-type reaction of aromatic halides with acrylates. The catalyst could be recycled six times without obvious decreased conversion.

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1. Introduction

Chitosan is an optically active biopolymer that is characterized by a strong affinity for transition metals. It can be used as a support for the preparation of heterogeneous transition metals catalysts in many forms [1–4]. Based on the reported literatures [5–12], during the catalysts preparation, adsorption method was often used in the process for metal immobilization on the supports. For the adsorption process, the resulting solid supports were immersed into a solution of transition metal ions by specific chelating or ion-exchange to realize metal immobilization. However, the bond strength between the solid supports and transition metals were often not power enough. For example, according to the preparation method of chitosan nanofibre mats supported palladium catalysts that reported recently by Iyer group [9], the nanofibre mat even need washing thoroughly with MilliQ to remove any weakly bound Pd species to improve the recycling stability when used in Heck reactions. The other process for metal immobilization on the supports is coordination method. In the coordination process, the chitosan solution is mixed with the metal ion solution and then the coordinate-covalent bonds can occur between chitosan and transition metal ions. Chitosan chains in solution state should be more

favorable to the formation fully coordinate with metal ions than in solid state because the functional groups of the polymer chains are exposed thoroughly to metal ions in the solution. It was found [13–15] that addition of a small amount of the Pd²⁺ cation could significantly increase the viscosity of chitosan acidic aqueous solution, and even turn it into a fixed gel, making it difficult to prepare as the suitable heterogeneous catalysts.

It is required for an ideal support to have well-defined porous microstructure, specific surface area, mechanical and handling properties. A lot of methods have been developed to fabricate polymeric porous structures: porogen leaching [16], microbead patterning [17], thermally induced phase separation [18,19], drying of polymer blend solution [20], gas foaming [21], supercritical CO₂ technique [22], 3D printing [23] and freeze drying [24–28]. Especially for polysaccharide gels, freeze drying was the mostly used technique to prepare sponge like materials suited for biomedical use [29,30]. Moreover, freeze drying method can tolerate the drawback of the poor processability due to the high viscosity of the gel solution. A simply efficient process consists of freezing a solution of chitosan and followed by sublimation of the solvent under reduced pressure. In the present study, novel palladium supported on chitosan porous membrane heterogeneous catalysts have been prepared by freeze-drying of Pd²⁺-crosslinked chitosan gel solution. Pd²⁺ acts as not only the crosslinker for chitosan but also the active catalytic sites when applied in coupling reactions. Heck reactions have been employed to evaluate the catalytic activities and

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stabilities of the palladium crosslinked porous chitosan membrane catalysts in dimethyl sulfoxide (DMSO) solution.

2. Experimental

2.1. Materials

Chitosan (pharmaceutical grade, 95% deacetylated, molecular weight: 1.2×10^5) was purchased from Aoxing Biotechnology Co., Ltd. (Zhejiang, China). Palladium chloride (PdCl_2) was purchased from Zhejiang Metallurgical Research Institute (Hangzhou, China). All solvents and chemical reagents were analytical grade or the best grade commercially available and used without further purification.

2.2. Preparation of the palladium crosslinked porous chitosan membranes (Pd@PCSM)

Chitosan was dissolved in a 0.35 M acetic acid to prepare the stock solutions containing about 0.67% weight of the substrates at room temperature. Then, Na_2PdCl_4 solution (0, 0.8, 1.6, 2.4, and 3.2 ml, respectively) was dropped into 60 ml of the resultant chitosan solution under magnetic stirring. The Na_2PdCl_4 solution was prepared as follows: 0.15 g PdCl_2 was dissolved in 50 ml 2% NaCl solution. As the Na_2PdCl_4 solution dropped in, the viscosity of the mixing solution increased. It was found that 3.2 ml (critical gel adding amount) of this Na_2PdCl_4 solution was dropped in, the mixture solution turned to fixed gel. Afterwards, the mixture was cast on a Petri dish. The Petri dish with cast solution was cooled at a controlled temperature (about -20°C) in a refrigerator to solidify the cast solution for 24 h. Then, it was freeze-dried with a FD-1A-50 vacuum freeze dryer (Boyikang Experimental Instruments Co. Ltd., Beijing, China) for 24 h. The drying condition was -50°C (condensing temperature) and $<10\text{ Pa}$ (vacuum degree). Then it was neutralized by 2% NaOH solution and washed by deionized water until pH 7. After drying, the porous membrane was obtained.

The palladium content of the Pd@PCSM was determined by means of an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Leemann ICP-AES Prodigy XP (Leeman Labs, USA) after the Pd@PCSM were completely dissolved in a mixture of fuming HNO_3 and concentrated HCl (v/v, 1/3). The weight content of metal in such Pd@PCSM with critical gel adding amount of Pd^{2+} solution (3.2 ml) analyzed by ICP is 1 wt%. Correspondingly, the weight content of palladium in the other Pd@PCSM catalysts (addition of 0, 0.8, 1.6, 2.4 ml of Pd^{2+} solution) was 0, 0.25, 0.5, 0.75 wt%, respectively.

2.3. Characterization of the Pd@PCSM

The mechanical properties of the membrane in dry state were performed at 25°C using a universal materials testing instrument (SANS Testing Machine Co. Ltd., Shenzhen, China) with a crosshead speed of 200 mm/min. The results presented were the mean values of five independent measurements.

In order to measure the porosity of the sample, the dense palladium crosslinked chitosan membrane was prepared at first and its density (ρ_1) was determined through the measurement of membrane volume and weight. In the same way, the density of porous chitosan membrane (ρ_2) can be obtained. The porosity of the sample was estimated by Eq. (1):

$$\text{Porosity} = \left(1 - \frac{\rho_2}{\rho_1}\right) \times 100\% \quad (1)$$

Thermo gravimetric analysis was performed using a Seiko TG/DTA 6300 (Seiko Company, Japan) thermal analyzer. The

samples were heated from 50°C to 700°C at a heating rate of $20^\circ\text{C}/\text{min}$ under air atmosphere.

The FTIR spectra of the samples were measured with a FTIR-Nicolet 740 spectrometer (Nicolet Instrument Co., USA) in the wave number range of $500\text{--}4000\text{ cm}^{-1}$. Samples for FTIR spectroscopic characterization were prepared by grinding membranes with KBr and compressing the mixtures to form sheets.

The X-ray diffraction (XRD) analysis for the membranes was performed on an Empyrean X-ray Diffraction System (Panalytical Company, the Netherlands) at a scanning rate of $10^\circ/\text{min}$ in the 2θ range from 3 to 70° .

X-ray photoelectron spectroscopic (XPS) analysis was performed for the Pd@PCSM catalysts using a Thermo Scientific Escalab 250Xi X-ray Photoelectron Spectrometer (USA). The electron binding energies were calibrated using C_{1s} of 284.6 eV as the internal reference.

Specific surface area of the Pd@PCSM samples was determined by nitrogen adsorption/desorption at liquid nitrogen temperature using a Micromeritics Tristar II 3020 apparatus (USA). The samples were degassed under vacuum for 2 h at 200°C before the measurements. Specific total surface area was calculated using the Brunauer–Emmett–Teller (BET) equation.

The morphology and elements analysis of the Pd@PCSM catalysts were examined by means of a scanning electron microscope (SEM) JEM-6360 (Japan) equipped with energy dispersive X-ray spectroscopy (EDS, Oxford EDX System). High resolution transmission electron microscopy (HR-TEM) observation of the Pd@PCSM catalysts was performed with a JEM-2100F (Japan). The samples for HR-TEM observation were prepared as follows. The grounded Pd@PCSM catalyst particles were dispersed sonically in 5 ml ethanol. Then the solution was dropped on a copper net and dried.

2.4. Heck cross-coupling reactions as catalyzed by Pd@PCSM in DMSO

To a 20 ml round bottom flask were added aromatic halide (1.0 mmol), alkenes (2.0 mmol), palladium catalyst (1.2 μmol Pd@PCSM) and potassium acetate (3.0 mmol) in 3.0 ml DMSO and 0.2 ml ethylene glycol. The reaction progress was monitored by TLC and/or GC/MS analysis. After completion, the reaction mixture was cooled down to the room temperature, and then quenched with 10 ml of water and extracted three times with ethyl acetate ($3 \times 20\text{ ml}$). The combined organic layer was washed with water, saturated brine, and then dried over anhydrous sodium sulfate. Solvent was removed under a reduced pressure. The cross-coupling products were purified by silica gel chromatography with a mixture of petroleum ether and ethyl acetate. The cross-coupling products were confirmed by melting point and spectroscopic (^1H NMR and GC/MS) analysis.

2.5. Recycling and reuse of the Pd@PCSM

The Pd@PCSM catalysts were recycled from the reaction mixture by filtration, then rinsed with 2.0 ml ethanol, followed by activation at 110°C for about 20 min to remove the residue ethanol before next run reaction.

2.6. General procedures of the characterization of the coupling reactions

The quantitative analysis was performed on an Agilent GC/MS spectrometer with a programmable split/splitless injector. The initial oven-temperature was set at 140°C and then ramped to the injector-port temperature (270°C) at $10^\circ\text{C}/\text{min}$, and maintained for 2 min at each step. Proton NMR spectra were recorded in CDCl_3 solution on an AVANCE III 400 MHz spectrometer. The proton

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