



Spatially isolated palladium in porous organic polymers by direct knitting for versatile organic transformations



Xinbo Wang^a, Shixiong Min^{a,c}, Swapan K. Das^a, Wei Fan^b, Kuo-Wei Huang^a, Zhiping Lai^{a,*}

^a Division of Physical Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

^b Chemical Engineering Department, University of Massachusetts, Amherst, MA 01003, United States

^c School of Chemistry and Chemical Engineering, Beifang University of Nationalities, Ningxia 750021, China

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ABSTRACT

We report here a direct knitting Method for preparation of highly robust, effective while air- and moisture-tolerant, and readily recyclable three-dimensional (3D) porous polymer-Pd network (PPPd) from the widely used Pd(PPh₃)₄. Electro-beam induced Pd atom crystallization was observed for the first time in organic polymer and revealed the ultrafine dispersion of palladium atoms. Challenging types of Suzuki-Miyaura couplings, reductive coupling of aryl halides and oxidative coupling of arylboronic acid were successively catalyzed by PPPd in aqueous media. Also catalytically selective C–H functionalization reactions were achieved with orders of magnitude more efficient than conventional Pd homogeneous catalysts. The strategy developed here provides a practical method for easy-to-make yet highly efficient heterogeneous catalysis.

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1. Introduction

Development of heterogeneous catalysts that can integrate the advantages of homogeneous catalysts has been the important target of chemists for decades yet still remains a major challenge [1,2]. Besides high selectivity, activity and reusability, the scalability and cost in preparation are also factors that must be considered for practical usage. Although progresses in surface organometallic chemistry [3,4], zeolitic supports of so-called “ship-in-bottle” catalyst [5], high surface area material such as metal-organic frameworks (MOFs) supported catalyst [6–8], single-atom catalyst (SAC) based on atomically dispersed metal atoms on the surfaces of metal crystal or graphene [9–11], have been well documented and made an essential contribution to the progress of research in heterogeneous catalysis [12–14], these methods are costly and not readily scalable, thus do not meet industrial demands. Single atom of palladium anchoring to a relatively cheaper carbon nitride (C₃N₄) has been achieved recently by stepwise loading metal-salt and a subsequent reduction [15], but introducing other coordination ligands, which may fully determine the properties of the catalyst, is still challenging.

Whereas supported noble metal heterogeneous catalysis has led to a plethora of effective catalysts used in practical applications,

porous organic polymers (POPs) are arguably one of the most ideal supports with unique features including excellent chemical tunability, insolubility but with adjustable wettability, recyclability, and so on [16–18]. Many organometallic and transition metal coordination catalysts contain electron-rich arene substituent groups, which from the structural view point are able crosslinked to form POP frameworks. While at the same time, their soluble nature allows easy purification from aggregated clusters and other by-products, which is unachievable when reduction occurs inside the insoluble network. A series of heterogeneous catalysts supported on POPs have been reported and excellent selectivity and higher activity than the corresponding homogeneous counterparts were observed [19,20]. By crosslinking benzene and triphenylphosphine followed by dispersing PdCl₂ into the framework, a highly active and stable Pd (II) organometallic heterogeneous catalyst was obtained by Tan et al. [21,22]. However, these catalysts are prepared by the conventional step-by-step method as shown in the top part of Fig. 1, where metal salts are loaded into the POP structure. In Tan's method, to obtain Pd in zero valence, a further reduction step is required. All of these post treatments will inevitably cause metal aggregation and result in decrease of reactivity and selectivity.

In this study, we utilized tetrakis(triphenyl phosphine) palladium (Pd(PPh₃)₄) as precursor, and for the first time in one step successfully obtained a POP structure with nearly single-atom dispersed Pd, through crosslinking the four triphenylphosphine

* Corresponding author.

E-mail address: zhiping.lai@kaust.edu.sa (Z. Lai).

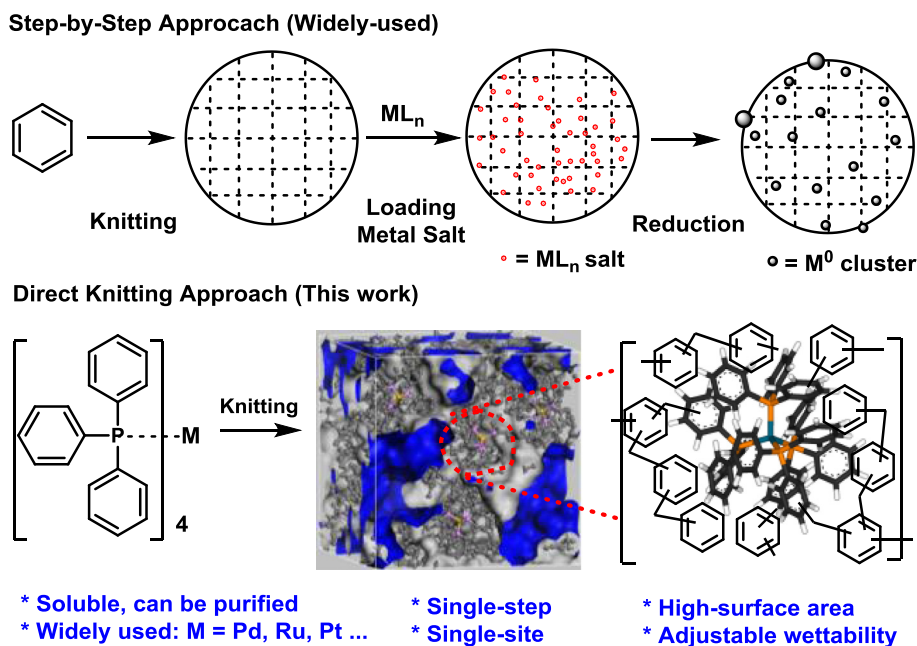


Fig. 1. Illustration of the difference between the conventional step-by-step approach and the direct knitting method.

ligands of Pd(PPh₃)₄, as illustrated in the bottom part of Fig. 1. Pd(PPh₃)₄ is one of the most widely used homogeneous coordination catalysts but suffering from air sensitivity and poor recyclability. While the crosslinked catalyst, which was named as PPPd, showed not only higher catalytic efficiency that surpassed its homogeneous form, but also much better stability and recyclability that allowed the catalytic reactions to be carried out in aqueous solutions under open conditions.

2. Experimental section

2.1. Catalyst PPPd synthesis

Benzene (Aldrich, 0.8 g, 10 mmol), dimethoxymethane (Aldrich, 2.3 g, 30 mmol) and Pd(PPh₃)₄ (Aldrich, 0.6 g, 0.5 mmol) were mixed together in 1,2-dichloroethane (Aldrich, 20 ml). Protected with nitrogen and cooled with ice, anhydrous FeCl₃ (Aldrich, 4.8 g, 30 mmol) was added portion by portion. The reaction mixture was then moved to oil bath and heated to 80 °C for 24 h. After cooling down to r.t., the resulted precipitate was immersed and washed with methanol until the filtrate was clear. Khaki solid powder PPPd was obtained after drying in vacuum oven at 70 °C for 48 h.

With similar procedure, 50 g PPPd was produced in a scale-up experiment.

2.2. General procedure for Suzuki-Miyaura cross coupling reaction [22]

Inside an argon atmosphere glove box, halide (0.5 mmol), boronic acid (0.75 mmol), K₃PO₄ (1.5 mmol), PPPd (4 mg, 1.4 wt% Pd, 0.0005 mmol), solvent (2 ml, H₂O/EtOH v/v = 2:3) were mixed in a 5 ml vessel and sealed. Then it was moved out of the glove box and heated in an oil bath to 80 °C for 2–6 h. After cooled down to r.t. for about half an hour, the mixture was filtered. Take a small amount of the liquid for GC analysis. The solid part was washed three times with ethanol. The combined liquid was dried and purified by column to give pure coupling product. For recycle experiments, the solid part after washing was degassed and used into

the next cycle. Combing the recycled catalyst from X reaction times was marked as Re-PPPd-X.

2.3. General procedure for Ullmann reductive homo-coupling reaction

Aryl halide (0.5 mmol), K₃PO₄ (1.5 mmol), PPPd (8 mg*1.4 wt% Pd, 0.001 mmol), solvent (2 ml, H₂O/EtOH v/v = 2:3) were mixed in a 5 ml vessel and sealed. Then it was heated in an oil bath at 80 °C for 20 h. After cooled down to r.t., the mixture was filtered. Take a small amount of the liquid for GC analysis. The solid part was washed three times with ethanol. The combined liquid was dried and purified by column to give pure coupling product.

2.4. General procedure for aryl boronic acid oxidative homo-coupling reaction

Aryl boronic acid (0.5 mmol), K₃PO₄ (1.5 mmol), PPPd (4 mg*1.4 wt% Pd, 0.0005 mmol), solvent (2 ml, H₂O/EtOH v/v = 2:3) were mixed in a 5 ml vessel and sealed. Then it was heated in an oil bath at 80 °C for 6 h. After cooled down to r.t. for about half an hour, the mixture was filtered. Take a small amount of the liquid for GC analysis. The solid part was washed three times with ethanol. The combined liquid was dried and purified by column to give pure coupling product.

2.5. General procedure for direct C-H bond selective alkoxylation and halogenation reactions [23]

Benzoquinoline (0.5 mmol), PhI(OAc)₂ (1.0 mmol), solvent (4 ml) and PPPd (15 mg*1.4 wt% Pd, 0.002 mmol) were mixed together in a 10 ml glass vessel under air. Then it was sealed and heated in an oil bath. The reaction was monitored by GC-MS.

2.6. Intermolecular regioselective C-H alkenylation of indole [24]

Indole (0.5 mmol), copper(ii) acetate (0.8 mmol), alkene (1.5 mmol) and PPPd (8 mg*1.4 wt% Pd, 0.001 mmol) were mixed together in a 10 ml glass vessel under air, then DMF/ DMSO (9:1 v/v, 4 ml), was added and the vessel was sealed to heat by

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