



Direct aerobic oxidative homocoupling of benzene to biphenyl over functional porous organic polymer supported atomically dispersed palladium catalyst

Yangqing Liu^a, Yu Zhou^{a,b,*}, Jing Li^a, Qian Wang^a, Qin Qin^a, Wei Zhang^a, Hiroyuki Asakura^c, Ning Yan^{b,**}, Jun Wang^{a,*}

^a State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University (Formerly Nanjing University of Technology), Nanjing, 210009, China

^b Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585, Singapore

^c Department of Molecular Engineering, Graduate School of Engineering, Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Kyotodaigaku Katsura Nishikyo-ku, Kyoto 615-8510, 615-8245, Japan

ARTICLE INFO

Article history:

Received 5 December 2016

Received in revised form 26 February 2017

Accepted 9 March 2017

Available online 10 March 2017

Keywords:

C–C coupling
Palladium catalysis
Synthesis of biphenyl
Aerobic oxidation
Single-atom catalyst

ABSTRACT

Synthesis of biphenyl directly from the oxidative coupling of benzene with O₂ as the sole oxidant is an atom-efficiency and environmental-friendly route, which is however unattainable as yet due to the most inert nature of sp² C–H bond in benzene ring, especially for recyclable heterogeneous catalysis. In this work, single atomic dispersed palladium(II)-porous organic polymer (POP) catalyst with a high loading (>2 wt%) was constructed by anchoring Pd(II) species on the task-specifically designed POP support tethered with carboxyl acid and sulfonic acid groups. It exhibited efficient activity in the heterogeneous aerobic oxidative coupling of benzene with O₂, giving the highest biphenyl yield of 26.1% so far. The high electrophilicity of thus anchored single atomic Pd(II) species is demonstrated, endowing the unprecedentedly maximum turnover number (TON) of 487 and turnover frequency (TOF) of 352 h⁻¹ that respectively exceeds 15 and 88 times of previous heterogeneous catalyst. The catalyst can be facilely recycled and reused, and readily extendable to the conversion of other nonactivated arenes into corresponding biaryls. The designing strategy of POP materials developed in the study may provide a platform towards stable single atomic dispersed noble metal species with desirable electrophilicity as efficient catalysts for more sustainable C–C formation-involved organic transformations.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

As a fundamental transformation, C–C bond formation is widely academically studied and industrially applied in the production of numerous chemicals [1–4]. Transition metal-catalyzed oxidative coupling reaction by the direct C–H activation has attracted great attentions due to its high atom economy and low cost of reactants [5–9]. However, the majority of the catalytic systems rely on the application of high price and low natural abundant noble metals such as palladium (Pd). Fabricating efficient catalyst with high yield,

turnover number (TON), turnover frequency (TOF) and recovery is challengeable towards target reaction.

Heterogeneous catalyst is preferred, but the example for above reaction is scarce and the substrates are limited to electron-rich substrates like alkene and diphenylamine [10–14]. Such situations become serious particularly for the nonactivated arenes, among which benzene has the most inert sp² C–H bond with the dissociation energy of 110 kcal mol⁻¹ [15,16]. Biphenyl is an ubiquitous important building block with numerous applications in agrochemistry, pharmacy, electronics, conductors, polymers, and liquid crystals [17,18]. Pd(II) catalyzed direct oxidative coupling of benzene with O₂ is the most atom efficient, economical and environmental-favorable synthetic pathway [19–22]. Normally, homogeneous Pd(II) catalysts were applied in this reaction with the maximum TON value of 180 (yield: 25.2%) [22]. Up to now, only one heterogeneous Pd(II) catalyst was reported with the yield

* Corresponding authors at: State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University (formerly Nanjing University of Technology), Nanjing, 210009, China.

** Corresponding author.

E-mail addresses: njtzhouyu@njtech.edu.cn (Y. Zhou), ning.yan@nus.edu.sg (N. Yan), junwang@njtech.edu.cn (J. Wang).

of 18.3% and TON of 32 [21]. Unfortunately, this catalyst could not be reused due to the rapid deactivation in the second run.

Recently, atomically dispersed catalysts, including mononuclear metal complexes and single metal atoms anchored on supports, attract increasing attentions by taking the advantages of outstanding performances, such as extremely high atom efficiency, notable activity and well stability [23–33]. For example, single-site Pd(II) supported on 2,2'-bipyridine-grafted periodic mesoporous organosilica exhibited high activity (TON: 128) in the heterogeneous C–H olefination oxidative Heck reactions and could be reused with little loss in activity [25]. However, no such type catalyst is ready for aerobic oxidative coupling of nonactivated arenes to form aryl–aryl bond. The difficulty comes from the inert C–H bond in benzene, the activation of which requires highly electrophilic Pd(II) active sites. Ligands such as pyridine can provide strong affinity towards stable Pd(II) sites but will weaken their electrophilicity [34]. By contrast, weak affinity will result in low loading of Pd(II) species with unfavorable stability. How to make a trade-off between the electrophilicity and stability becomes a bottleneck to fabricate single atomic Pd(II) based heterogeneous catalyst for the activation of C–H bond in benzene.

In order to address this challenge, we develop a new strategy to heterogenize the Pd(II) species in porous organic polymers (POPs) through an ion exchange process. The POPs have tunable chemical composition and porosity, and more importantly, their surface groups can be facilely adjusted by magnifying the monomers in molecular level to achieve required host–guest interaction [35–40]. In this work, we demonstrate how the surface groups of POPs affect the stability, electrophilicity and the catalytic performance of immobilized Pd(II) species. A new POP material tethered with adjacent double –COOH groups and –SO₃H groups is constructed (Scheme 1), and atomically dispersed Pd(II) with high electrophilicity are anchored via the interaction with these surface groups in an ion-exchange process, in which the adjacent double –COOH groups can stabilize the anchored Pd(II) species through the formation of unique seven-membered ring structure [41] while the –SO₃H groups will further enhance the electrophilicity. The obtained heterogeneous catalyst exhibits efficient activity, superior TON and TOF in the direct oxidative coupling of benzene to biphenyl by using O₂ as the sole oxidant. After reaction the catalyst can be facilely separated and reused, which was not possible with previous catalysts. The substrate scope is investigated on other nonactivated arenes to illustrate the versatility of this methodology. To the best of our knowledge, it is the first atomically dispersed Pd(II)-POP catalyst that effectively promotes the oxidative coupling of even the least activated arenes via direct C(sp²)–H activation.

2. Experimental

2.1. Materials

All reagents were of analytical grade and used as purchased without further purification.

2.2. Preparation of porous organic copolymer

The porous organic copolymer (POP) sample PDMS was prepared through the following steps (Scheme 1). Firstly, the copolymer precursor PDMS-I was prepared through free radical copolymerization by using potassium persulfate (KPS) as the initiator. In detail, maleic anhydride (MA, 0.152 g, 1.55 mmol), sodium p-styrene sulfonate (SS, 0.64 g, 3.1 mmol), divinylbenzene (DVB, 1.21 g, 9.3 mmol) and KPS (0.04 g, 0.15 mmol) were dissolved in a mixed solution of ethanol (20 mL) and water (40 mL). The obtained solution was stirred at 60 °C for 12 h under nitrogen atmosphere.

The white solid was collected by filtration, washed with ethanol and water successively, giving the product PDMS-I. In the second step, PDMS-I was treated by NaOH aqueous solution (0.25 mol/L) at 90 °C for 1 h to generate carboxylate groups from the potential ester groups that formed through the reaction of MA with ethanol during the copolymerization process. The solid PDMS-II was separated by filtration and washed with water. Finally, PDMS-II was treated with aqueous sulfuric acid solution (1 mol L⁻¹). After stirring at room temperature for 24 h, the solid was collected by filtration, washed with water until the filtrate was neutral, and then dried at 80 °C for 12 h. The white solid PDMS (1.2 g) was obtained in 60% yield.

Several other POPs materials were synthesized with a similar procedure by varying the monomers (Scheme S1). They were PDS (copolymer of DVB and SS), PDM (copolymer of DVB and MA), PDAS (copolymer of DVB, acrylic acid (AC) and SS) and PDVB (homopolymer of DVB). Details are seen in the Supporting Information.

2.3. Preparation of Pd^{II}@POPs

Pd(II) loaded sample Pd^{II}@PDMS was prepared through anchoring Pd(II) on the polymer PDMS by using DMSO (dimethyl sulfoxide) as the solvent and Pd(OAc)₂ as the precursor [25]. Typically, PDMS (0.1 g) was placed in a 25 mL Schlenk tube and dried under vacuum at 90 °C. After that, 5 mL DMSO solution containing Pd(OAc)₂ (0.01 g, 0.045 mmol) was added and the mixture was stirred at room temperature for 2 h under nitrogen atmosphere. The brown solid Pd^{II}@PDMS was collected by filtration, washed with acetone to remove the weak physically adsorbed Pd(OAc)₂, and finally dried under vacuum at room temperature for 24 h. The acetic acid amount in the filtrate was analyzed as follows. After the loading process, 1, 4-dioxane (2 μL) was added to the solution as the internal standard. The solid was removed by filtration and the filtrate was analyzed through gas chromatography (GC, Agilent 7890B) equipped with a FID (flame ionization detector) and a capillary column (HP-5, 30 m × 0.25 mm × 0.25 μm). Pd(II) loaded on other POPs were prepared similarly and the obtained products were denoted as Pd^{II}@POP (POP: PDS, PDM and PDAS).

2.4. Characterization methods

Pd K-edge X-ray absorption spectra of Pd^{II}@PDMS and reference materials, Pd foil and Pd(OAc)₂, were recorded at the BL01B1 beamline of the SPring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan) in transmission mode at ambient temperature. X-ray energy was calibrated at the inflection point (24350.0 eV) of the absorption edge of Pd metal foil. Data analysis was carried out with Athena and Artemis included in the Demeter package [42]. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on an Agilent Cary 660 instrument (KBr disks) ranging from 4000 to 400 cm⁻¹. Elemental analyses were performed on a CHN elemental analyzer Vario EL cube. The nitrogen sorption isotherms were measured at the temperature of liquid nitrogen (77 K) by using a BELSORP-MINI analyzer with the samples being degassed at 100 °C for 3 h before analysis. The surface area and pore-size distribution curves were calculated by the BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) method, respectively. Scanning electron microscopic (SEM) images were viewed on a Hitachi S-4800 field-emission scanning electron microscope. Transmission electron microscopy (TEM) analysis with energy-dispersive X-ray spectrometry (EDS) was conducted on a JEM-2100 (JEOL) electron microscope operating at 200 kV. The X-ray photoelectron spectra (XPS) was conducted on a PHI 5000 Versa Probe X-ray photoelectron spectrometer equipped with Al K α radiation (1486.6 eV). The XPS peaks were systematically analyzed by decomposing the results with the CasaXPS software, using a sum of Gaussian/Lorentzian (80/20) after subtraction of a Shirley-type

Download English Version:

<https://daneshyari.com/en/article/6454262>

Download Persian Version:

<https://daneshyari.com/article/6454262>

[Daneshyari.com](https://daneshyari.com)