Chinese Journal of Catalysis 36 (2015) 1560–1572

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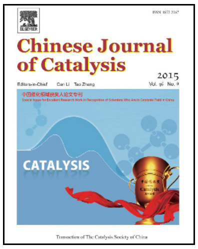

Article (Special Issue for Excellent Research Work in Recognition of Scientists Who Are in Catalysis Field in China)

A nanoparticulate polyacetylene-supported Pd(II) catalyst combining the advantages of homogeneous and heterogeneous catalysts

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ARTICLE INFO

Article history:
Received 26 April 2015
Accepted 5 June 2015
Published 20 September 2015

Keywords:
Suzuki coupling
Acetylene
Palladium complex
Aqueous reaction

ABSTRACT

A novel nanoparticulate polyacetylene-supported Pd(II) catalyst (NP-Pd(II)) for use in the aqueous Suzuki-Miyaura cross coupling reaction was successfully synthesized by simply treating an aqueous solution of $PdCl_4^{2-}$ with acetylene under ambient conditions. Electron microscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy and X-ray absorption spectroscopy were employed to characterize the NP-Pd(II) structure in detail. These analyses demonstrated that the Pd atoms in the NP-Pd(II) were present as Pd(II) and were coordinated with both the Cl atoms and the C=C bonds of the polyacetylene. Both the homogeneous distribution of the Pd(II) along the polyacetylene backbone and the aggregation of the NP-Pd(II) in solution work in conjunction to make this material an ideal catalyst, combining the advantages of both homogeneous and heterogeneous catalysts.

1. Introduction

The development of efficient, cost-effective and recyclable catalysts is a constant challenge for industries working with chemical transformations [1,2], and transition metal complexes with atomically-dispersed active centers have become one of the most intensively studied systems for this purpose. These homogeneous catalysts have well-defined structures, allowing for the fine-tuning of their electronic and steric properties [2–4]. However, a tedious ligand screening process is typically necessary to optimize the stability, activity and selectivity of a homogenous catalyst. Moreover, this class of catalysts has the disadvantage of not being easily separated from the reaction mixture, presenting more than a few engineering issues [5,6]. Heterogeneous catalysts are a promising means of addressing the separation issue [7]. Unfortunately, intrinsically heterogeneous catalysts, such as supported metal nanoparticles, are usually less active than their homogeneous analogues. Heterogenization of homogeneous catalysts through chemical bonding on various supports, such as polymers or oxides, is an alternative strategy to mitigate the separation problem while maintaining high catalytic activity. In such cases, however, multistep

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This work was supported by Ministry of Science and Technology of China (2011CB932403, 2015CB932303) and the National Natural Science Foundation of China (221420102001, 21131005, 21390390, 21333008).
DOI: 10.1016/S1872-2067(15)60930-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 9, September 2015

synthetic procedures are normally required, limiting their large-scale applications [8−12]. Thus, it would be highly desirable to develop a simple and efficient synthetic route for the preparation of materials combining the advantages of homogeneous and heterogeneous catalysts.

We report herein the effective one-step synthesis of a novel nanoparticulate polyacetylene-supported Pd(II) catalyst, denoted as NP-Pd(II), that functions as a highly efficient and recyclable catalyst for the Suzuki-Miyaura cross coupling reaction. This material was obtained by simply treating an aqueous solution of $PdCl_4^{2-}$ with acetylene under ambient conditions. Systematic characterization using electron microscopy, Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) analysis demonstrated that the resulting NP-Pd(II) contained micron-sized aggregates of fine nanoparticles composed of polyacetylene-supported Pd(II) complexes. The homogeneous distribution of Pd(II) along the polyacetylene backbone, combined with the tendency of the material to aggregate, makes NP-Pd(II) an ideal catalyst, with the advantages of both homogeneous and heterogeneous catalysts [13,14]. The prepared NP-Pd(II) was both air- and moisture-stable and exhibited high catalytic activity comparable to that of homogenous catalysts and better recyclability than carbon-supported Pd catalysts, especially in aqueous systems.

Because the Suzuki reaction is one of the most efficient methods of constructing biaryl and substituted aromatic molecules, its impact on both academic and industrial research has been immense [8,15−21]. To date, many Pd complexes have been applied as homogenous catalysts in the Suzuki reaction and the continual search for effective ligands has been one of the most fascinating aspects of this field. As an example, significant success has been achieved in using phosphine ligands, especially in conjunction with low-reactivity substrates [22−24]. Investigations of other ligands, such as N-heterocyclic carbenes [25−27], amines [28,29] and cyclic compounds [30], have also been widely reported in the literature. The demonstration of polyacetylene as an effective ligand for Pd(II) in this work further expands the range of ligands applicable to efficient Suzuki coupling catalysts. More importantly, the facile, one-step, readily scaled-up synthesis of NP-Pd(II) makes this heterogeneous Pd catalyst highly desirable for practical applications.

2. Experimental

2.1. Synthesis of NP-Pd(II)

A H_2PdCl_4 aqueous solution(20 mmol/L) was prepared by reacting $PdCl_2$ with concentrated aqueous HCl in stoichiometric amounts at 70 °C for 1 h. A suitable quantity of this aqueous solution was subsequently transferred to a glass pressure vessel and acetylene was introduced with stirring at ambient temperature (25 °C) while the relative pressure was maintained at 0.3 atm for 15 min. On contact with the acetylene gas, the H_2PdCl_4 solution immediately became turbid. The resulting NP-Pd(II) was readily separated by centrifuging this colloidal suspension and the powder thus obtained was washed twice with H_2O and ethanol, followed by further centrifugation. Finally, the NP-Pd(II) was dried under vacuum at 40 °C overnight. Inductively coupled plasma (ICP) analysis of the resulting dry NP-Pd(II) confirmed almost complete conversion of the original $PdCl_4^{2-}$ to NP-Pd(II). This synthetic procedure was readily scaled up. As shown in Fig. S1, 1 g of NP-Pd(II) was successfully obtained from a larger scale reaction performed in a 250-mL flask. Synthesis using an acetylene pressure of 1 atm rather than 0.3 atm gave a material termed NP-Pd(II)-1atm that was found to have a similar composition and morphology (Fig. S2) to the NP-Pd(II), and to generate similar XPS (Fig. S3) and FT-IR (Fig. S4(a)) spectra as well as exhibiting the same catalytic performance (Fig. S4(b)).

2.2. A typical procedure for the NP-Pd(II)-catalyzed aqueous Suzuki coupling reaction

In a glass vessel, 15 mL H_2O, 212 mg Na_2CO_3, 183 mg phenylboronic acid and 112 μL iodobenzene were added. The vessel was then placed into a pre-heated water bath and the reaction was initiated by adding 0.24 mg NP-Pd(II). After the reaction was complete, diethyl ether (3×3 mL) was added to extract the products for gas chromatographic (GC) analysis. The prod-

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Zheng Nanfeng *(College of Chemistry and Chemical Engineering, Xiamen University)* ***received Chinese Chemical Society-Royal society of Chemistry Young Chemist Award*** *(2014), which was presented by the Chinese Chemical Society and the Royal Society of Chemistry. Prof. Zheng received his B.S. from the Department of Chemistry, Xiamen University in 1998. In 2005, he obtained his Ph.D. degree from the Department of Chemistry, University of California–Riverside supervised by Prof. Pingyun Feng. His thesis was on the synthesis and characterization of chalcogenide nanoclusters and their superstructures. During 2005–2007, he worked on gold catalysis with Prof. Galen D. Stucky as a research associate at University of California–Santa Barbara. In 2007, he moved to Xiamen University as a full professor. He is currently a Changjiang Chair professor at Xiamen University. His research interests mainly focus on the development of advanced functional materials for both fundamental research and practical applications, particularly in the fields of catalysis and biology. His ultimate goal is to gain understanding of the synthesis, properties and also applications of functional nanomaterials at the molecular level. Most of current research efforts of his group are directed to surface and interfacial chemistry of functional materials, and nanocluster chemistry.*