



Coupling reactions of aromatic halides with palladium catalyst immobilized on poly(vinyl alcohol) nanofiber mats

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ABSTRACT

Nanoporous poly(vinyl alcohol) (PVA) nanofiber mats prepared by means of electrospinning have been used for the immobilization of palladium catalyst. Thermal treatment of the palladium-loaded PVA nanofiber mats results in the cross-linking of the matrix PVA molecules as well as the reduction of the divalent palladium (Pd^{2+}) into zerovalent palladium (Pd^0) species. The palladium oxidation states were examined by X-ray photoelectron spectroscopic (XPS) analysis. The PVA nanofiber morphology was characterized by scanning electron microscopy (SEM). The catalytic activity and recyclability of the prepared heterogeneous palladium catalysts have been evaluated for the Ullmann, Heck–Mizoroki and Sonogashira coupling reactions of aromatic halides. The large structure of the Pd/PVA nanofiber mats can greatly facilitate its separation and recycling, and the high catalytic activity and stability of the prepared Pd/PVA nanofiber mats have been attributed to the chelation of palladium species with the abundant hydroxyl functional groups on the PVA matrix surface area.

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1. Introduction

The importance of palladium catalyst in synthetic organic chemistry can hardly be overestimated because palladium catalysis has become a routine tool for the preparation of fine chemicals and pharmaceutically active compounds in both academic studies and industrial productions [1]. However, the majority of the palladium catalysis is performed in the homogeneous system, in which the catalyst suffers from the difficult separation from the reaction media, nonreusability and deactivation due to aggregation of palladium particles [2]. Moreover for the homogeneous catalysis, the final products are frequently contaminated by residual transition metal at an unacceptable level, which could be difficult to remove, especially for large scale productions of pharmaceuticals where metal contamination is closely monitored [3]. Thus, it is not surprising why relatively few homogeneous catalysis systems have been commercialized [4].

Catalyst reuse can greatly increase the overall productivity and cost effectiveness while minimizing both waste generation and contamination of the metal traces in the final products, resulting in a greener and more sustainable chemical transformation process [5]. But the heterogenization of a homogeneous catalysis will significantly reduce the accessible catalytic centers because the catalytic

reactions can take place only on the heterogeneous surface, rather than all catalytic centers are accessible in the homogeneous system. Therefore, the solid matrices are generally fabricated into small fine particles to maximize the surface area to enhance the catalytic activities. However, the separation and recycling of the particulate catalysts from the reaction media are usually a tedious and time-consuming process due to the high pressure drop by filtration.

On the other hand, the palladium leaching is a common problem for the heterogeneous palladium catalysts [6,7]. Surface derivatization of the solid matrices with special ligand functional groups including phosphine and *N*-heterocyclic carbene could improve the chelation with the transition metal species to minimize the leaching, but the ligand synthesis as well as the surface modification are usually very challenging [2,8,9]. Nevertheless, only few low-leaching and ligand-free heterogeneous palladium catalysts have been reported in the literature [10]. Recently, we have demonstrated that the ground powder of the natural pearl shells is an excellent solid support for the immobilization of the palladium catalyst [11]. The high stability of the heterogeneous palladium catalyst has been attributed to the chelation of palladium species with the abundant hydroxyl and amino functional groups of the shell powder surface area. These results promoted us to explore the inexpensive, non-toxic and biodegradable poly(vinyl alcohol) (PVA) as the supported matrix to immobilize palladium catalyst because PVA has plentiful surface hydroxyl functional groups. To the best of our knowledge, electrospun PVA nanofiber mats have not yet been used for the preparation of the heterogeneous palladium catalysts.

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