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Highly efficient recyclable polymer anchored palladium catalyst for C—C and C—N coupling reactions

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ABSTRACT

An inexpensive, air-moisture stable and reusable PS–Pd(II)-furfural complex was synthesized by reacting polymeric amine with furfural to get polymer anchored ligand which was then reacted with $Pd(OAc)_2$ to get polymer anchored complex. This complex was characterized by different spectroscopic and elemental analyses. The activities of the Pd-complex were tested for the C—C and C—N cross-coupling reactions under various reaction conditions. The catalyst exhibits high catalytic activities for the coupling of various aryl halides with organoboronic acid, alkene, alkyne and amine providing excellent yields of desired product. Further, the catalyst can be easily recovered by simple filtration and reused up to five times without significant loss of its catalytic activity.

1. Introduction

Palladium-catalyzed reactions have become part of the standard repertoire of the synthetic organic chemist [1,2]. Palladium metal is a very well-known catalyst for a variety of organic reactions, especially hydrogenation [3–6], coupling [7–10], cyanation [11–13], carbonylation reactions [14–18] and amination. Palladium-catalyzed cross-coupling reaction for the formation of carbon–carbon bonds has recently emerged as a powerful method in an organic synthesis [19]. The palladium-catalyzed coupling of an aryl halide with aryl boronic acid (Suzuki coupling) [20] or terminal alkyne (Sonogashira coupling) [21] is recognized as the most successful method for forming a $C(sp^2)$—$C(sp^2)$ and $C(sp)$—$C(sp^2)$ bond, respectively. These reactions have been widely employed in the synthesis of natural products, biologically active molecules and materials science [22]. Despite the remarkable utility of Pd catalysts in organic synthesis, they suffer from one significant drawback in that they often remain as contaminants in the organic products at the end of the reaction. Another problem with homogeneous palladium catalysts is related to catalyst recovery and/or reuse, affecting the overall economics of the process [23,24]. In the past few decades, heterogenization of metal complexes on solid supports has attracted great interest as a suitable method for solving many practical problems including catalyst recovery and recycling. Solid-phase organopalladium complexes having high activity and selectivity offer several significant practical advantages in synthetic and industrial chemistry; among those, the ease of separation of the catalyst from the desired reaction products and the ease of recovery and reuse of the catalysts are most important. The C—C coupling reaction generally proceeds in the presence of homogeneous palladium catalysts which possess high efficiency and are suitable for the study of the reaction mechanism but their susceptibility to drastic reaction conditions and the difficulties associated with their isolation from the product mixture restrict their reusability. This is a great disadvantage in C—C couplings using homogeneous catalysts. Recycling of catalysts is a task of great economic and environmental importance in the chemical and pharmaceutical industry, especially when expensive or toxic heavy metal complexes are employed [25]. A way to overcome these difficulties would be the use of heterogeneous palladium catalysts. Nowadays, efficient and recyclable heterogeneous catalysts have gained much attention [26–29]. The most readily available form of supported catalyst is palladium on charcoal, which is widely used for heterogeneous hydrogenation and also has a growing importance in carbon–carbon bond-forming reactions [30–32]. There are many examples of heterogeneous catalysts for C—C coupling reactions, and they are prepared by different approaches like encapsulation or immobilization of a catalytically active metal complex on solid supports such as zeolites [33–35], covalent grafting of such active complexes onto reactive polymer surfaces [36–38] or inorganic porous matrices [39,40], and ordered mesoporous silica such as MCM-41 [41–43].

In this present work, we report the synthesis and characterization of a new furfural functionalized polymer grafted with Pd(II)

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catalyst and used it in the Suzuki, Heck, Sonogashira, and amination of aryl halides in the presence of inorganic or organic bases. The effects of the various reaction parameters on the catalytic activity were studied. The catalyst shows a high catalytic activity in the coupling reactions of various aryl halides. This polymer anchored catalyst remains in a separate solid phase in the reaction mixture, as a result of which further easy catalyst recovery and excellent recycling efficiency of the catalyst make it an ideal system for coupling reactions without any precaution of inert atmospheric conditions.

2. Experimental

2.1. Materials and instruments

All the reagents were analytical grade and used as such without further purification. Solvents were purified and dried according to standard procedures. Polystyrene was purchased from Aldrich and $Pd(OAc)_2$ was procured from Arora Matthey. Other reagents were purchased from Merck.

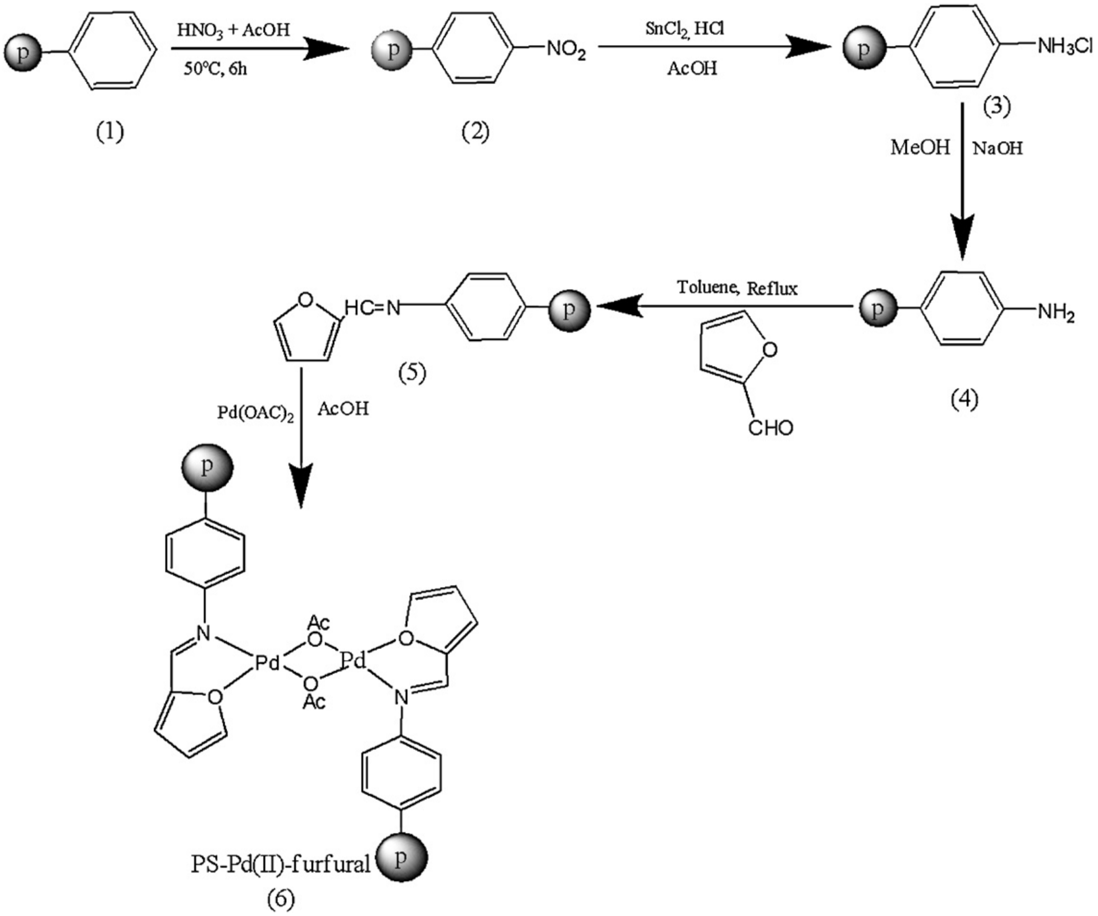
The palladium content was determined by Varian, USA, AA240 atomic absorption spectrophotometer (AAS). A Perkin Elmer, USA, 2400C elemental analyzer was used to collect microanalytical data (C, H and N). Surface morphology of functionalized polystyrene ligand and metal complex were analyzed using a scanning electron microscope (ZEISS EVO40, England) equipped with EDX facility. Fourier transform infrared (FT-IR) spectra for the catalyst and its precursors were recorded on a Perkin Elmer, USA, FT-IR 783 spectrophotometer using KBr pellets. UV–vis spectrum was taken using a Shimadzu, Japan, UV-2401PC double beam spectrophotometer having an integrating sphere attachment for solid samples. The thermal stability of the immobilized catalyst was determined using a Mettler Toledo, Switzerland, TGA/DTA 851e instrument. The reaction products were analyzed using a Varian, USA, 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a flame ionization detector. All reaction products were identified by using an Agilent, USA, GC–MS (QP-5050) equipped with a 30 m HP-5ms capillary column.

2.2. Synthesis of catalyst

The synthetic procedure of polymer anchored palladium complex is illustrated in Scheme 1. Catalyst was prepared in two steps. Firstly, p-amino-polystyrene was prepared earlier [44]. The suspension of macroporous amino polystyrene (2 g) in toluene (20 ml) was taken in a round bottom flask. Furfural (0.01 mol) was added drop wise to the stirring suspension of amino-polystyrene. The reaction mixture was refluxed for 24 h. After cooling to room temperature, the polymer anchored ligands were filtered, washed thoroughly with toluene followed by methanol and finally dried under vacuum. Finally, this polymer anchored furfural ligand (500 mg) subsequently reacted with $Pd(OAc)_2$ (25 mg) in acetic acid (10 ml) at 80° C for 10 h to generate the corresponding polymer anchored Pd(II) complex.

2.3. General experimental procedure for Suzuki coupling reaction

A mixture of aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), DMF–H_2O (3–3 ml), and n-dodecane (15–20 mg) as an internal GC standard and 0.5 mol% of catalyst was stirred at



Scheme 1. Synthesis of polymer anchored Pd(II) catalyst.