



Silica-supported palladium complex: An efficient, highly selective and reusable organic–inorganic hybrid catalyst for the synthesis of E-stilbenes

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ABSTRACT

A novel, highly efficient and reusable palladium based catalyst has been synthesized by covalent grafting of diphenyldiketone–monothiosemicarbazone on silica gel followed by metallation with palladium chloride, and the resulting organic–inorganic hybrid material was found to be highly effective catalyst for Suzuki–Miyaura cross-coupling reaction of various aryl halides with alkenyl boronic acid to give stilbenes. The catalyst was characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, energy dispersive X-ray fluorescence (ED-XRF), BET surface area analysis, solid-state ^{13}C CP/MAS NMR spectroscopy, atomic absorption spectroscopy (AAS), scanning electron microscopy (SEM) and elemental analysis. High turnover frequency, mild reaction conditions, high selectivity for E-stilbenes, and easy recovery and reusability of the catalyst renders the present protocol highly indispensable to address the industrial prerequisites and environmental concerns.

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1. Introduction

Palladium catalyzed Suzuki–Miyaura coupling reaction is among the most widespread and highly selective transformations for the synthesis of stilbenes, as these are the precursors for various biologically active compounds, pharmaceuticals, liquid crystalline materials, herbicides and conducting polymers. Over the past few decades, wide range of palladium based homogeneous catalysts have been used in this coupling reaction due to their high selectivity [1–9]. In addition, several homogeneous catalysts have been exploited for directing the stereochemistry of the reaction products. However, despite these benefits and advancement, homogeneous catalysis contributes only 20% in industrial processes due to various drawbacks such as use of large amount of catalyst, difficulty in purification of products and separation of soluble catalyst from the reaction mixture. Moreover, these homogeneous catalysts endow with the metal contamination of products which may be harmful for human health as well as for environment. Consequently, there is a huge demand for the innovation and development of novel catalysts with superior catalytic activities, lower costs, good recyclability and also less pollutive to the environment. In this regard, the development of

heterogenized alternatives such as nanoparticle-supported, soluble polymer-supported and various organic/inorganic polymer supported catalysts has engrossed immense attention because they combine the advantages of both homogeneous and heterogeneous catalytic systems [10–16]. Among various inorganic supports for immobilizing palladium catalysts, silica is very promising because of its high surface area, good thermal stability, ready availability and economic viability, and relatively easy covalent modification with organic or organometallic moieties.

Similar to recoverable catalysts, microwave-promoted synthesis is also an area of escalating interest in both academic and industrial laboratories since microwaves are efficient and non-polluting mode of heating the reaction mixture [17–24]. So, the combination of microwave technology and heterogeneous catalysis is likely to have a great impact on sustainable chemistry, and proved to be a better catalytic system from both economic and environmental view point. Recently, we have reported an optimized procedure for preconcentration, determination and on-line recovery of palladium using highly selective diphenyldiketone–monothiosemicarbazone modified silica gel [25]. Following these results, and in continuation of our work on synthesis of inorganic–organic hybrid materials, and their applications as metal scavengers, sensors, and catalysts for various organic transformations [26–32], in the present paper we investigated the catalytic activity of silica supported Pd(II)diphenyldiketone–monothiosemicarbazone (Pd–DKTS–APSG) for the synthesis of stilbenes in microwave reaction system.

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