Highly active bio-waste cellulose supported poly(amidoxime) palladium(II) complex for Heck reactions

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A B S T R A C T

Corn-cob cellulose supported poly(amidoxime) Pd(II) complex was synthesized and characterized by field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), energy dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses. The cellulose supported heterogeneous Pd(II) complex showed high stability and catalytic activity towards Mizoroki-Heck reaction of aryl halides and arenediazonium tetrafluoroborate with a variety of olefins to give the corresponding cross-coupling products in up to 97% yield. The Pd(II) complex was separated from the reaction mixtures and repeatedly used up to seven times without any significant decrease of its catalytic performance.

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1. Introduction

Palladium catalyzed Mizoroki-Heck reaction (Heck and Nolley, 1972) which represents often a crucial synthetic reaction step has received considerable attention due to its functional group tolerance as well as its broad application ranging from synthetic organic chemistry to applied materials science (Nicolaou et al., 2005). Aryl halides are successfully employed as electrophiles in the Heck reaction due to their high reactivity but it suffers numerous drawbacks such as high temperature and long reaction time. Thus, a new kind of electrophile replacing with aryl halide is still in demand. Recently, Fu (Fu et al., 2002), Skrydstrup (Hansen et al., 2006), Wang (Gong et al., 2016) and their co-workers have reported Pd-catalyzed Heck reaction of tosylate with electron poor olefins. Jamison and his co-workers (Tasker et al., 2014) described Ni-catalyzed Heck reaction of arenediazonium tetrafluoroborate salts also can be used instead of aryl halides and tosylates in the Heck-Matsuda cross-coupling reaction (Jadhava et al., 2016). The practical benefits by using of arenediazonium salts over common electrophiles such as aromatic halides and triflates are economic, environment-friendly and synthetic accessibility since these salts can be easily prepared from cheap and commercially available amines (Bu et al., 2015).

Nevertheless, homogeneous palladium-based catalyzed Heck reaction (Gøgsig et al., 2012) has significant drawbacks including low stability of the metal catalysts, toxicity caused by residual metal species, and difficult to recover the catalysts, which have impeded large-scale production in industry. Moreover, the homogeneous palladium catalysts tend to lose their catalytic activity because of aggregation and precipitation as a palladium metal (Astruc, 2007). High cost of metal catalysts, toxicity of the reaction residues, complicated to isolate the final product and the catalyst precursors demanded to develop easily recoverable metal catalysts that can be reused without reduction of their catalytic activity (Rouhi, 2004). To overcome these serious issues a common strategy has been adopted to prepare heterogeneous metal catalysts by anchoring of the suitable metal salts onto the solid support which provides high catalytic activity and selectivity. In recent years, numerous heterogeneous supported palladium catalysts have been successfully employed to the Mizoroki-Heck reaction such as mesoporous materials MCM-41 (Sarkar et al., 2007), MCM-48 (Sarkar et al., 2015), polymers (Yamada et al., 2012), activated carbons (Xu et al., 2012), graphene (Benyounes et al., 2015) and cellulose (Jadhav et al., 2016). However, instead of these hybrid systems, the number of examples