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Palladium (II) anchored on polydopamine coated-magnetic nanoparticles ($\text{Fe}_3\text{O}_4@\text{PDA}@\text{Pd}(\text{II})$): A heterogeneous and core-shell nanocatalyst in Buchwald–Hartwig C–N cross coupling reactions

Hojat Veisi, Pegah Sarachegol, Saba Hemmati

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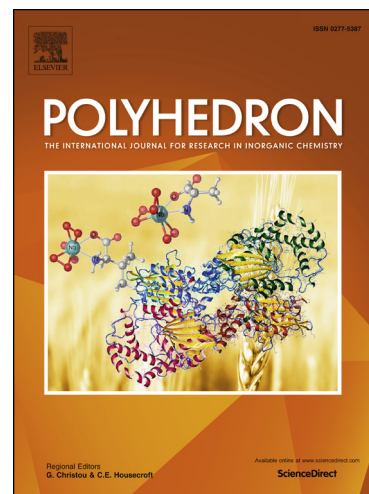
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Palladium (II) anchored on polydopamine coated-magnetic nanoparticles ($\text{Fe}_3\text{O}_4@\text{PDA}@\text{Pd}(\text{II})$): A heterogeneous and core-shell nanocatalyst in Buchwald–Hartwig C–N cross coupling reactions

Hojat Veisi,* Pegah Sarachegol, Saba Hemmati

*Department of Chemistry, Payame Noor University, Tehran, Iran
Email: hojatveisi@yahoo.com*

Abstract. An efficient method was proposed to synthesize polydopamine (PDA)-coated Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4@\text{PDA}$). For the first time, effective deposition of Pd complex is explained by using $\text{Fe}_3\text{O}_4@\text{PDA}$ as a core-shell magnetic coordinator and stabilizer agent. In this method, palladium ions were adsorbed on $\text{Fe}_3\text{O}_4@\text{PDA}$ surfaces through immersion of the $\text{Fe}_3\text{O}_4@\text{PDA}$ into a palladium plating bath. The structure, morphology and physicochemical features of the prepared particles were studied using various analytical methods including high resolution transmission electron microscopy (HR-TEM), field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDS), vibrating sample magnetometer (VSM), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma (ICP), thermogravimetric analysis (TGA) and FT-IR spectroscopy. Core-shell $\text{Fe}_3\text{O}_4@\text{PDA}/\text{Pd}(\text{II})$ nanoparticles showed excellent catalytic performance as a reusable nanocatalyst in Pd-catalyzed Buchwald–Hartwig C–N cross coupling reaction. A variety of aryl amines were prepared through reaction of aryl halides (chloride, bromide and iodide) and amines in high yields. The catalyst can be recycled and reapplied up to six cycles with no considerable change in its catalytic activity.

Keywords: Buchwald-Hartwig reaction, Polydopamine, Magnetic, Palladium, Amination

1. Introduction

Aryl- and heteroaryl amines derivatives have a key role as intermediates for agrochemicals, medicines, natural products [1], dendrimers [2], polymers [3], dyes, pigments [4] as well as materials with electronic and nonlinear optical features [5]. Buchwald and Hartwig individually proposed the procedures for the palladium-mediated amination of aryl halides [6]. Numerous conditions have been improved since then for the Buchwald–Hartwig amination reaction and this reaction has now arisen as an extremely useful and synthetically vital technique for synthesizing aryl- and heteroaryl amines. Comparing with the other approaches of carbon–nitrogen bond generation [7] like nucleophilic aromatic substitution, ullmann coupling and nitration followed by reduction, the Buchwald–Hartwig reaction provides a lower reaction temperature, usually in the range of 80-100 °C, a variety of substrate scope, a greater selectivity regarding the amines, better functional group compatibility [8] and the reaction does not contain extremely reactive reactants [9], which may lead to safety problems.

Many attempts have been done for finding suitable catalyst systems for accomplishing Pd-catalyzed *N*-arylation reactions under heterogeneous conditions due to the importance of recovery of the expensive Pd metal and the interest of industries to produce product without Pd species contamination. In this case, diverse kinds of heterogeneous Pd catalyst systems have been proposed for Buchwald–Hartwig C–N cross coupling reaction [10-16]. A number of the proposed palladium–catalyst systems for *N*-arylation reaction suffer from key drawbacks including tedious

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