



Superb efficient and recycle polymer-anchored systems for palladium catalyzed Suzuki cross-coupling reactions in water

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ABSTRACT

A set of three new polymer-anchored palladium(II) Schiff base catalysts have been synthesized, characterized and their catalytic activity was investigated in the Suzuki cross-coupling reaction between aryl halides and arylboronic acid in the presence of Cs_2CO_3 as a base. They show excellent catalytic activity in coupling of aryl bromides or aryl iodide with phenylboronic acid under the optimized reaction conditions in water. Polymer-anchored Pd(II) complexes provided turnover frequency of 29,700 or 58,200 h^{-1} in Suzuki coupling reactions of phenylboronic acid with *p*-bromoacetophenone or *p*-iodobenzene, respectively, which are the highest values ever reported for the Suzuki coupling reactions in water as sole solvent. The catalyst **1** could be used for 15 reaction cycles in the Suzuki coupling of *p*-acetobromobenzene at 100 °C with no loss of catalytic activity.

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1. Introduction

The palladium-catalyzed Suzuki cross-coupling reaction of arylboronic acids with aryl halides is one of the most powerful and versatile methods for the selective construction of carbon–carbon bonds and has been widely used in the synthesis of pharmaceuticals, herbicides, natural products, and advanced materials [1–5]. Although nickel [6] and copper [7] catalysts have also been reported, the palladium appears to be the best catalyst for the C–C coupling reactions due to the higher reaction yield and shorter reaction time [8,9]. In recent years, there has been a considerable interest in the preparation of highly active palladium catalysts to facilitate such transformations [10–13]. Most of the palladium catalyzed Suzuki coupling reactions have been performed in organic solvents. However, the use of an environmentally benign reaction medium, minimization of steps, better yields, and faster reaction remained challenges in the context of green chemistry for the Suzuki coupling reaction [14]. In this regard, the use of water, the most abundant and non-toxic solvent for organic reactions, is reclaiming its importance due to the pressing environmental, economical, and safety concerns [15–17]. Thus far, various catalytic systems have been reported for the Suzuki coupling reaction

in water, even though this may be less efficient than that in a suitable organic solvent [18–21]. The palladium catalysts with phosphine ligands [22], carbene ligands [23], palladacycle [24] and other coordinates [25] have shown high activity in the Suzuki coupling reactions in water. However, problems such as expensive poisonous phosphine ligands and non-reusability of the homogeneous catalyst extremely limited the industrial applications. Thus, the development of an easily available or readily prepared, inexpensive palladium catalyst with a high activity toward Suzuki cross-coupling reactions in the sole solvent of water is a highly desirable goal.

There have been many successful demonstrations of homogeneous catalysis for coupling reactions [26–30]. However, these homogeneous catalyst systems have some basic problems in terms of the separation and recycling of the catalysts [31]. Additionally, they induce contamination of the ligand residue in the products. Polymer metal complexes continuously attract the interest of a growing part of the scientific community for the advantages they offer with respect to their soluble counterparts [32–37]. Functionalized polymers have also been used as carriers in various organic and inorganic synthetic transformations [38]. Such heterogeneous catalytic systems have several advantages, such as robustness, increased air and moisture stability, fast recovery and simple recycling of the catalysts by filtration, which in turn prevent the contamination of the ligand and decrease the environmental pollution caused by residual metals in the waste. Although

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