Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–12

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Pd(0) nanoparticle immobilized on cyclodextrin-nanosponge-decorated Fe_2O_3@SiO_2 core-shell hollow sphere: An efficient catalyst for C–C coupling reactions

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ARTICLE INFO

Article history:
Received 17 January 2018
Revised 23 February 2018
Accepted 27 February 2018
Available online xxx

Keywords:
Cyclodextrin nanosponge
Magnetic hollow sphere
Pd nanoparticles
Coupling reactions

ABSTRACT

Amine-functionalized core-shell Fe_2O_3 hollow spheres (h-Fe_2O_3@SiO_2–N) were decorated with Cl-functionalized cyclodextrin nanosponge, CDNS-Cl, covalently. The resulting hybrid system, h-Fe_2O_3@SiO_2–CDNS, was then used as a magnetically separable support for immobilization of Pd(0) nanoparticles, derived from a bio-based approach. The obtained catalyst, Pd@h-Fe_2O_3@SiO_2–CDNS, was characterized by using SEM/EDS, TEM, XRD, BET, ICP-AES, FTIR, TGA and VSM. Moreover, the catalytic activity of Pd@h-Fe_2O_3@SiO_2–CDNS was confirmed for ligand and copper-free Heck and Sonogashira coupling reactions in aqueous media. Comparison of the catalytic activity of the Pd@h-Fe_2O_3@SiO_2–CDNS and Pd@h-Fe_2O_3@SiO_2, established superior catalytic activity of former indicating the role of CDNS in catalysis. Furthermore, the catalytic activity and recyclability of Pd@h-Fe_2O_3@SiO_2–CDNS was higher than that of Pd@CDNS. The catalyst could be successfully recycled for several consecutive reaction times with slight loss of the catalytic activity. The ICP-AES analysis confirmed that the leaching of Pd nanoparticles was negligible upon each reaction cycle.

1. Introduction

The outstanding features of core-shell magnetic nanoparticles, such as significant magnetic susceptibility and coercivity and high surface area [1] resulted in their growing applications in many research areas, including delivery systems, magnetic separation, catalysis, sensors, drug-delivery and diagnosis. [2–6] In the case of catalysis, magnetic compounds can result in formation of magnetically separable catalysts, which can be easily recovered by using an external magnet [7–9]. This can lead to the cleaner and economical protocols for the synthesis of chemicals. Among various magnetic nanoparticles, hollow magnetic nanoparticles benefit from excellent features such as high surface area and low densities. However, they tend to form aggregates. To circumvent this problem, surface functionalization has been suggested [9].

The utility of cyclodextrin, CD, for the synthesis of nanoparticles as well as its role as phase transfer agent in the catalysis has been well-established [10–18]. Recently, cyclodextrin nanosponge (CDNS) [19–21], which are 3-D polymeric networks composed of CDs monomer, has also been used for the catalysis [22–24]. The features of CDNS can be easily tuned by adjusting the reaction variables such as type of CDs and cross-linking agent, preparation method [25,26]. As CDNS is biocompatible, thermally stable, non-toxic, insoluble in most solvents and capable to host various guest molecules [27,28], it can be considered as a promising catalyst support [22,29]. Besides catalysis, CDNS can be potentially used for drug delivery [30] and waste water treatment [25,31–41].

One of the most important organic transformations that can be catalysed by Pd-based catalysts is C–C coupling reaction. Various types of C–C coupling reactions such as Heck and Sonogashira reactions have been introduced. These reactions potentially can be applied for the synthesis of a wide range of synthetic compounds. Moreover, coupling reactions have been widely used for the synthesis of natural products [42]. Classic methodologies for coupling reactions contained use of homogeneous Pd catalysts along with co-catalysts and ligands [43]. Furthermore, disclosing novel catalysts, which didn't require use of co-catalyst and ligand and could promote the reactions in non-toxic solvents, has attracted intensive attention [44].

Recently, we have disclosed the utility of nano-magnetic Fe_2O_3 hollow spheres for development of heterogeneous catalyst [4,9]. Moreover, we confirmed the efficiency of CDNS as a support for immobilization of various catalytically active species [22–24]. In

Abbreviations: CDNS, Cyclodextrin nanosponge.

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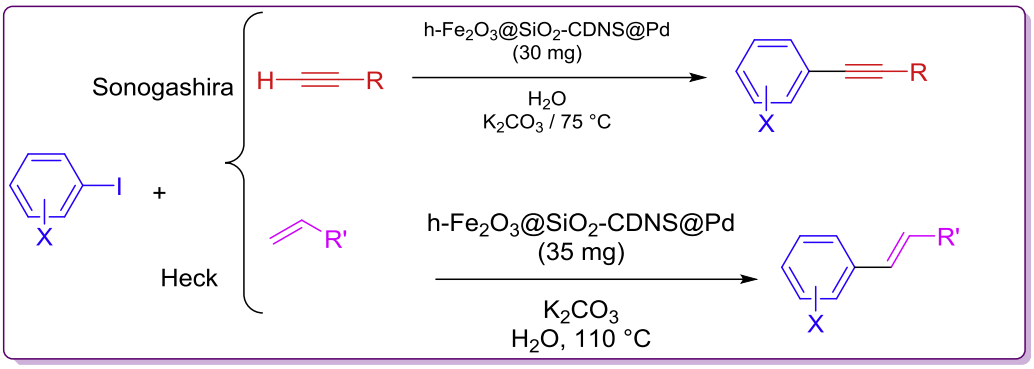
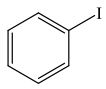
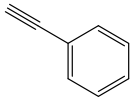
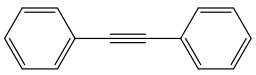
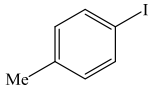
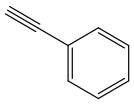
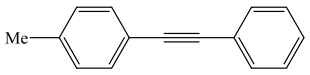
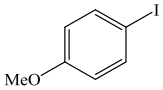
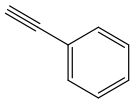
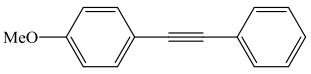
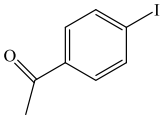
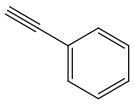
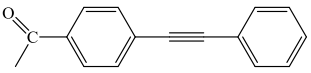
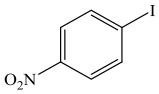
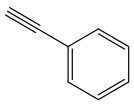
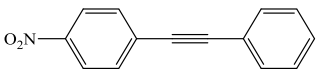
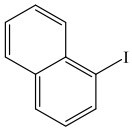
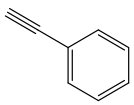
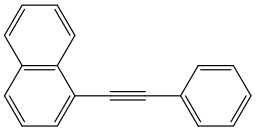
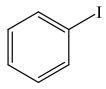
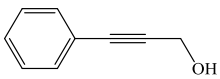
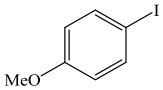
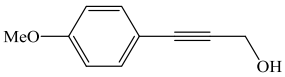
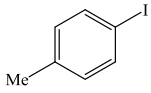
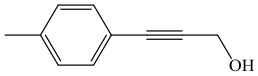
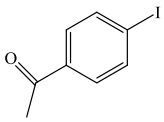
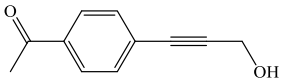
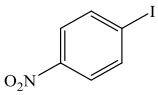
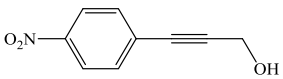
https://doi.org/10.1016/j.jtice.2018.02.033
1876-1070/

Table 1
h-Fe_2O_3@SiO_2–CDNS@Pd catalyzed Sonogashira and Heck reactions.



Entry	Aryl halide	Terminal alkyne or alkene	Product	Time (h)	Yield[b] (%)	[Ref]
			Sonogashira reaction			
1[a]				2	97	[8]
2[a]				2:30	90	[8]
3[a]				3	92	[8]
4[a]				4	90	[8]
5[a]				2:30	90	[8]
6[a]				4:30	80	[8]
7[a]				3	90	[9]
8[a]				3:40	91	[9]
9[a]				3:30	88	[9]
10[a]				3:30	91	[10]
11[a]				3	95	[9]

(*continued on next page*)

Please cite this article as: S. Sadjadi et al., Pd(0) nanoparticle immobilized on cyclodextrin-nanosponge-decorated Fe_2O_3@SiO_2 core-shell hollow sphere: An efficient catalyst for C-C coupling reactions, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.02.033