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Research paper

Ternary hybrid system of halloysite nanotubes, polyacrylamides and cyclodextrin: an efficient support for immobilization of Pd nanoparticles for catalyzing coupling reaction

Samahe Sadjadi[a,*], Mohammad Atai[b]

[a] Gas Conversion Department, Faculty of Petrochemicals, Iran Polymer and Petrochemical Institute, PO Box 14975-112, Tehran, Iran
[b] Polymer Science Department, Iran Polymer and Petrochemicals Institute, PO Box 14975-112, Tehran, Iran

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ABSTRACT

Taking advantage of the properties of polyacrylamide (P), the capability of cyclodextrin (CD) to form inclusion complex and outstanding features of halloysite nanoclay as catalyst support, a ternary hybrid system, Hal-P-CD, was designed and synthesized through growing polyacrylamide on the surface of functionalized halloysite nanotubes followed by introduction of β-cyclodextrin. The hybrid system was successfully used for immobilization of Pd nanoparticles and formation of a heterogeneous catalyst, Pd@Hal-P-CD. The structure of Pd@ Hal-P-CD was confirmed by using SEM/EDS, TEM, XRD, BET, ICP-AES, TGA, FTIR and elemental mapping analysis and its catalytic activity was studied for promoting ligand and copper-free Sonogashira coupling reaction in aqueous media (1:1 mixture of water and ethanol). The results established that Pd@Hal-P-CD could catalyze the coupling reaction to afford the desired products in high yields and short reaction times. Notably, the catalytic activity of Pd@Hal-P-CD was superior to those of Pd@Hal-P and Pd@Hal. The study of the reusability of the catalyst up to 7 reaction runs as well as Pd leaching confirmed the heterogeneous nature of the catalysis and the efficiency of Hal-P-CD for suppressing the Pd leaching. Additionally, this catalyst could also be successfully used for promoting Heck coupling reaction.

1. Introduction

Use of clays as heterogeneous support for immobilizing catalysts is a well-established methodology for developing heterogeneous catalysts with simple recovery and improved reusability (Bokade and Yadav, 2011; Dar et al., 2013; Yadav and Yadav, 2013; Yadav and Tekale, 2014).

Halloysite nanotubes, mostly referred as Hal, are a class of natural clay minerals with the general formula of $(Al_2(OH)_4Si_2O_5{\cdot}2H_2O)$ and Al: Si ratio of 1:1 (Szczepanik and Słomkiewicz, 2016b; Yuan et al., 2016). The layers of Hal rolled in the way that tetrahedral siloxane units place on the external surface and aluminol units form the inner surface (Pasbakhsh and Churchman, 2015). Moreover, a monolayer of water separates the multiple rolled layers. Hal benefits from some unique physiochemical properties such as high surface area, bio and eco-compatibility, large diameter (the outer diameters vary between 50 and 70 nm while the lumen diameters range between 15 and 20 nm), inert nature, mechanical and chemical stability and high adsorption capacity (Tully et al., 2016). As, Hal can be found abundantly in some geographical areas such as China, Turkey, New Zealand, USA, France, and Belgium, their large scale applications are economically attractive (Zhang et al., 2016). To date, the utility of Hal for catalysis, energy storage, separation, electrical and optical applications, waste water treatment (Szczepanik and Słomkiewicz, 2016a; Szczepanik et al., 2017), and drug delivery (Zhai et al., 2010; Tan et al., 2014; Kumar-Krishnan et al., 2016; Sabbagh et al., 2017) has been confirmed. Recently, Yuan et al. reviewed the application of Hal (Yuan et al., 2015). A potent tool for improving the surface properties of Hal is surface functionalization (Massaro et al., 2017c). This can be achieved by use of various compounds such as organosilanes such as γ-aminopropyl-triethoxysilane (Yuan et al., 2008) and *N*-b-aminoethyl-γ-aminopropyl trimethoxysilane or more complicated functionalities such as cyclodextrin nanosponges (Massaro et al., 2017a). The functionalized Hal can be potentially used for immobilization of various catalytic species such as nanopartilces, complexes, heteropolyacids etc. (Zhang et al., 2013, 2014; Yang et al., 2015; Massaro et al., 2016; Yuan et al., 2016; Battistoni et al., 2017; Sadjadi et al., 2017c,d; Vinokurov et al., 2017).

β-Cyclodextrin, β-CD, is a cyclic oligosaccharide, composed of seven glucopyranoside units and containes hydrophobic inner cavity and hydrophilic outer space (Manivannan and Ramaraj, 2012). CD can be

* Corresponding author.
E-mail addresses: s.sadjadi@ippi.ac.ir, samahesadjadi@yahoo.com (S. Sadjadi), m.atai@ippi.ac.ir (M. Atai).

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considered as a host for accommodating various guest molecules with proper polarity, shape, and size. The formation of host-and guest complex between guest and CD, mostly referred as inclusion complexes, has diverse applications such as drug delivery, transfer shuttle for catalysis, controlling the growth and morphology of nanoparticles etc. (Bai et al., 2013; Noël et al., 2014; Menuel et al., 2016; Gogoi and Sarma, 2017).

Among various organic transformations, C—C coupling reactions such as Heck and Sonogashira reactions, are of increasing importance due to their use in drug industry (Lin et al., 2010). Despite the promising features of C—C coupling reactions, their industrial uses are hampered due to the necessity of use of precious Pd-based catalysts as well as phosphine ligands and co-catalysts (Hajipour et al., 2014). To furnish a solution to this problem, development of heterogeneous Pd catalysts, which can promote the reactions in the absence of ligands and co-catalysts is suggested (Gholap et al., 2005; Thorwirth et al., 2010; Hajipour et al., 2014; Nasrollahzadeh et al., 2014b). To date, various eco-friendly protocols with use of aqueous media have been developed for promoting C—C coupling reactions (Bakherad, 2013; Nasrollahzadeh et al., 2014a; Roya et al., 2014; Zhou et al., 2014; Nasrollahzadeh et al., 2015; Shunmughanathan et al., 2015; Esmaeilpour et al., 2016; Bakherad et al., 2017; Rathod and Jadhav, 2017).

The utility of functionalized polymers as catalyst support has been well-established (Mahdavi et al., 2007; Tamami and Ghasemi, 2011). Polymeric support can facilitate the recovery of the catalyst and improve its reusability. In this line polyacrylamides have been wildly used (Tamami and Fadavi, 2005).

Following our research for developing novel heterogeneous catalysts through immobilization of catalytic species on the functionalized supports (Sadjadi et al., 2017a,b,e,f), recently, we focused on the functionalization of Hal and their use for embedding various catalytically active species (Sadjadi et al., 2017c,e; Sadjadi and Bahri-Laleh, 2017). Our results as well as other reports in the literature (Massaro et al., 2017b) confirmed the efficiency of Hal for heterogenizing the catalysts. Considering the potential of CD as phase transfer agent and its utility as template or capping agent for nanoparticles (Menuel et al., 2016; Gogoi and Sarma, 2017) as well as the utility of polyacrylamides for supporting the catalytic species, herein, we disclose a novel ternary hybrid system consists of Hal, CD and polyacrylamide for immobilizing Pd nanoparticles. The utility of Pd@Hal-P-CD for promoting Sonogashira C—C coupling reaction (Scheme 1) as well as a model Heck reaction (Scheme 2) was also studied. Moreover, the reusability of Pd@Hal-P-CD and Pd leaching was studied. Finally, the effect of reusing on the morphology and stability of the catalyst was investigated.

2. Experimental

2.1. Materials and instruments

The chemicals used for the preparation of Pd@Hal-P-CD and studying its catalytic activity included halloysite nanoclay, 3-(trimethoxysilyl) propyl methacrylate, β-cyclodextrin, potassium peroxydisulfate (KPS), *p*-toluenesulfonyl chloride, triethylamine, toluene, Pd $(OAc)_2$, $NaBH_4$, acrylamide, acetylenes, styrene, halobenzenes, K_2CO_3, distilled water and EtOH, all provided from Sigma-Aldrich and used as received with no further purification.

The structure of Pd@Hal-P-CD was confirmed by using TEM, TGA, BET, XRD, SEM/EDS, FTIR, ICP-AES and elemental mapping analysis. The applied ultrasonic instrument for preparing Pd@Hal-P-CD was Bandelin HD 3200 with output power of 150 W and tip TT13. The SEM/EDS images were obtained by applying a Tescan instrument, using Au-coated samples and acceleration voltage of 20 kV. The applied transmission electron microscope, TEM, was Philips CM30300Kv field emission transmission electron microscope. PERKIN-ELMER- Spectrum 65 instrument was used for recording FTIR spectra. To record N_2-adsorption-desorption isotherm and study the textural properties of the catalyst, BELSORP Mini II apparatus was employed. Degassing of the samples was achieved by pre-heating at 423 K for 3 h. To perform thermo gravimetric analyses (TGA) a METTLER TOLEDO thermo gravimetric analysis apparatus with a heating rate of 10 °C min^{-1} from 50 to 600 °C under N_2 atmosphere was used. Room temperature powder X-ray diffraction patterns were obtained by using a Siemens, D5000. CuKα radiation from a sealed tube.

The progress of C—C coupling reactions was traced by using thin layer chromatography (TLC) on commercial aluminum-backed plates of silica gel 60 F254, visualized, using ultraviolet light. All organic products were known and identified by comparing their melting points, determined in open capillaries using an Electrothermal 9100 without further corrections, and FTIR spectra with authentic samples. To further confirmation, some selected products were also analyzed by ^{1}HNMR and ^{13}CNMR spectroscopies using Bruker DRX-400 spectrometer at 400 and 100 MHz, respectively.

2.2. Functionalization of Hal with 3-(trimethoxysilyl)propyl methacrylate: synthesis of Hal-A

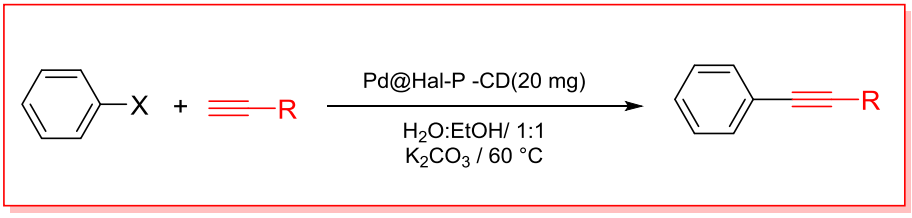
To prepare the catalyst, Hal was first functionalized with 3-(trimethoxysilyl) propyl methacrylate. Typically, to a suspension of Hal (2.4 g) in dry toluene (60 mL) 3-(trimethoxysilyl) propyl methacrylate (4 mL) was added drop wise. The obtained mixture was then subjected to the ultrasonic irradiation of power 100 W for half an hour to render the suspension highly dispersed. Subsequently, the resulting suspension was refluxed at 110 °C overnight. After that, the solid was filtered, washed with dried toluene for three times and dried at 100 °C overnight.

2.3. Decoration of Hal surface with polyacrylamide: synthesis of Hal-P

Hal-A (1.2 g) was suspended in distilled water and sonicated under ultrasonic irradiation of power 100 W for 15 min. To the resulting well-dispersed suspension, acrylamide monomer (1.2 g) and KPS (0.6 mg) as polymerization initiator were added. Then, the reaction temperature was increased to 60 °C and the mixture was stirred for 12 h to allow the polymerization proceed. Upon completion of the reaction, the precipitate was filtered and washed with distilled water repeatedly. Further purification was performed by soxhlet extraction with distilled water for 72 h. Hal-P was achieved after dying for 12 h at 70 °C.

2.4. Tosylation of β-CD: synthesis of CD-OTs

To tosylate β-CD, a previously reported procedure was exploited



Scheme 1. Sonogashira coupling reaction.