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# Biocompatible starch-halloysite hybrid: An efficient support for immobilizing Pd species and developing a heterogeneous catalyst for ligand and copper free coupling reactions

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ABSTRACT

Combining the exceptional features of halloysite and starch, a unique hybrid was synthesized based on conjugation of amine-functionalized starch with Cl-halloysite nanoclay followed by coordination of Pd (II) acetate. The resultant hybrid catalyst, Pd@Hal-SA, was used as a heterogeneous catalyst for promoting copper and ligand-free coupling reactions under mild reaction condition. The catalyst exhibited high catalytic activity and recyclability (up to 10 reaction runs) with slight loss of the catalytic activity that stemmed from slight Pd leaching. The comparison of the catalytic activity of Pd-Hal, Pd-SA and Pd@Hal-SA confirmed the superior performance of the latter, indicating the contribution of two components, SA and Hal to the catalysis. Moreover, the catalytic activity of Pd@Hal-SA was higher than that of Pd@Hal + SA, implying that the use of hybrid system was more efficient that use of individual components in a separated form, due to the synergism between SA and Hal.


## 1. Introduction

In recent year, development of heterogeneous palladium catalytic systems for use in some chemical transformations such as hydrogenation of alkenes and alkynes [1], C-C cross-coupling reactions are of great importance and received significant attentions [2–4]. Among C-C coupling reactions, Sonogashira and Heck reactions, which can be used for the synthesis of many biologically-active chemicals, have been widely investigated [5]. In this context, different types of Pd-catalytic systems have been developed. Many of the previously reported protocols suffer from main problems such as tedious and time-consuming workup processes, use of different additives and difficulty in the catalyst preparation [6]. In the case of homogeneous Pd catalysts, an important challenge is the recovery and recyclability of the catalyst [7]. To solve this problem, immobilization of Pd on the solid supports has been suggested [8,9].

Halloysite (Hal) is of a biocompatible natural occurring clays with the general formula of ($Al_2(OH)_4Si_2O_5 \cdot 2H_2O$) [10], composed of tetrahedral siloxane on external surface and aluminol groups on internal surface. From the morphological point of view, Hal possesses tubular morphology [11]. The nanotubes are 0.2–2 μm in length with internal and outer diameters ranging between 10 and 100 and 30–190 nm respectively. High surface area, physical and chemical stability, porosity and opposite charges on the external and internal surfaces of Hal nanotube render it an exceptional candidate for use in different applications [12–14]. Recently, there has been a growing interest in developing new functional materials based on Hal nanotubes for the applications ranging from catalysis, polymerization, drug delivery, to fabrication of polymer nanocomposites [15,16]. In addition, similar to mesoporous silicate base [17,18], Hal can be modified through surface functionalization [17,19–25]. Recently, diverse range of functionalized Hal and their utilities in the catalysis has been reviewed [26]. The studies confirmed that introduction of functional groups, especially; the functionalities with multi-heteroatoms can remarkably improve the recyclability through decrease of leaching of the catalytic species.

Naturally occurring substrates including cellulose, cyclodextrins, starch etc. are good candidates to be used as biocompatible supports for development of metal catalysts [27–32]. Starch, a glucose polymer, is one of the most abundant natural polysaccharides synthesized by plants. The use of starch in the field of catalysis has received considerable attentions due to its high reactivity and selectivity, low price, environmental friendly nature and structure diversity.

In continuation of our research for development of active and novel heterogeneous catalysts through immobilization of catalytic species on the functionalized supports, [24,25,32–36] in the present study, herein, we report a new approach for the synthesis of

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biocompatible heterogeneous catalyst based on immobilization of palladium (II) acetate on the starch-Hal hybrid system, obtained from covalent conjugation of amine-functionalized starch and Cl-functionalized Hal. The resulting system, Pd@Hal-SA, was used as an efficient and heterogeneous catalyst for promoting ligand and copper-free coupling reactions under mild reaction condition, (Schemes 1 and 2 in SI). The recyclability of Pd@Hal-SA up to ten reaction runs was also examined. Moreover, to elucidate the role of Hal and SA in catalysis two control catalysts, Pd@Hal and Pd@SA were synthesized and their catalytic activities were compared with that of Pd@Hal-SA. Furthermore, to investigate the possibility of synergism between the hybrid components, the catalytic activity of the catalyst was compared with that of Pd@Hal + SA.

## 2. Experimental

### 2.1. Materials and instruments

The reagents and chemicals employed for the synthesis of Pd@Hal-SA and studying its catalytic activity including, halloysite nanoclay, 3-bromopropan-1-amine hydrobromide, (3-chloropropyl)trimethoxysilane, starch, toluene, $Pd(OAc)_2$, acetylenes, halobenzenes, acrylates, $K_2CO_3$, distilled water, MeOH and EtOH, were analytical grade reagents, purchased from Sigma-Aldrich, and used with no further purification. The structure of Pd@Hal-SA was confirmed by using SEM/EDS, TEM, XRD, FTIR, TGA, BET and ICP-AES analysis. The SEM/EDS images were attained by using a Tescan instrument, applying Au-coated samples and acceleration voltage of 20 kV. The transmission electron microscope (TEM) images were obtained using Philips CM30300Kv field emission transmission electron microscope. The applied ultrasonic instrument for the synthesis Pd@Hal-SA was Bandelin HD 3200 with output power of 150 W and tip TT13. FT-IR spectra were recorded with potassium bromide pellets in the range of 400–4000 $cm^{-1}$ PERKIN-ELMER-Spectrum 65 instrument. The record of $N_2$-adsorption-desorption isotherm and study the textural properties of the catalyst were performed by BELSORP Mini II apparatus. Degassing of the samples was achieved by pre-heating at 423 K for 3 h. X-ray diffractions (XRD) were detected by using a Siemens, D5000. Cu Kα radiation from a sealed tube. Thermo gravimetric analyses (TGA) were carried out with a METTLER TOLEDO thermo gravimetric apparatus by a heating rate of 10 °C $min^{-1}$ from 50 to 600 °C under $N_2$ atmosphere. The progress of C-C coupling reactions was monitored 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 by an Electrothermal 9100 without further corrections, and FTIR spectra with authentic samples. For more confirmation, several 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. Synthesis of Hal-Cl

Hal-Cl was prepared according to the previous method with slight modification [37]. Typically, Hal (1.2 g) in toluene (60 mL) was dispersed by ultrasonic irradiation of power 100 W for 0.5 h to furnish a well-dispersed suspension. Then, (3-chloropropyl) trimethoxysilane (2 mL) was added into the resulting suspension and the resulting mixture was sonicated for 0.5 h followed by refluxing for 24 h. Upon completion of the reaction, the reaction mixture was filtered off and the obtained precipitate was washed several times with pure toluene and dried at 80 °C.

### 2.3. Synthesis of 2-bromoethyl amine-functionalized starch (SA)

To activate starch, starch (2 g) and $CaH_2$ (3 g) were mixed in 50 mL water and stirred for 0.5 h. Then, the solid was filtered off and dried at 100 °C. Next, 2-bromoethyl amine (1 g) was dissolved in 20 mL ethanol and stirred for 0.5 h. In the next step, activated starch (1.5 g) was added drop wise. Subsequently, the reaction mixture was refluxed at 110 °C overnight. Upon completion of the reaction, the resulting solid was filtered off and dried at 80 °C.

### 2.4. Hybridization of Ha-Cl with SA (Hal-SA)

In this step, Hal-Cl (1 g) and SA (1 g) and pyridine (2 mL) as a suitable base were mixed in 40 mL toluene and refluxed at 140 °C. After 24 h, the obtained product was filtered off, washed with toluene and dried at 80 °C for 12 h.

### 2.5. Synthesis of Pd@Hal-SA catalyst

Initially, Hal-SA (1.2 g) was dispersed in toluene (30 mL). Then, a solution of 0.02 g $Pd(OAc)_2$ in MeOH (15 mL) was added and the mixture was stirred at room temperature for 8 h. Upon completion of the reaction, the achieved product was filtered off, washed with MeOH and dried at 80 °C for 12 h.

The schematic synthetic route of Pd@Hal-SA as a catalyst is demonstrated in Fig. 1.

### 2.6. Typical procedure for the Sonogashira reaction

To a mixture of acetylene (1.2 mmol) and halobenzene (1.0 mmol) and aqueous solution of $K_2CO_3$ (2 mmol in 1 mL of water) in 5.0 mL of EtOH, Pd@Hal-SA (0.78 mol%) as a catalyst was added. The resulting mixture was then heated at 90 °C for suitable reaction time. Upon completion of the reaction (traced by TLC), the reaction mixture was filtered, and the residue catalyst was separated, washed with ethanol and dried under air for use in the next run. Then, the filtrate was extracted with $Et_2O$ (15 mL) three times; the organic layer was separated, washed with water, dried and evaporated over anhydrous $Na_2SO_4$ and then the mixture was purified by recrystallization to afford pure product.

### 2.7. Typical procedure for the catalytic Mizoroki–Heck Reaction

Alkene (1.2 mmol) and iodobenzene (1.0 mmol) was mixed in 5.0 mL EtOH in the presence of Pd@Hal-SA (0.78 mol%) and aqueous solution of $K_2CO_3$ (2 mmol in 1 mL of water) and the resulting mixture was heated at 90 °C for appropriate time. Upon completion of the reaction (monitored by TLC), the mixture was filtered off, and the residue catalyst was washed with ethanol and dried under air for the next reaction run. Additionally, the filtrated was extracted with $Et_2O$ (3*15 mL) and the organic layer was washed with deionized water, dried over anhydrous $Na_2SO_4$ and purified by recrystallization to afford a high purity of product.

## 3. Results and discussion

### 3.1. Catalyst characterization

To study the structure of Pd@Hal-SA and confirm the successful progress of each steps of synthesis of the catalyst, raw materials, the product of each step of the synthesis of the catalyst, i.e., SA, Hal-SA were subjected to FTIR spectroscopy, Fig. 2. The FTIR spectra of Hal is in good accordance with the previous reports [38] and exhibited the characteristic bands at 1035 $cm^{-1}$, Si—O stretching, 536 $cm^{-1}$, Al—O—Si vibration, and 3624–3697 $cm^{-1}$, inner —OH groups [24]. As shown, the characteristic bands of starch can be observed at 1423 and 3355 $cm^{-1}$ (-OH groups). The FTIR of SA, Fig. 2, showed the characteristic bands of starch as well as an additional band at 3646 $cm^{-1}$, which is representative of —$NH_2$ group and confirms the successful formation of SA. In the FTIR spectrum of Hal-SA, both characteristic bands of Hal and starch can be detected, implying the conjugation of these two

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