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Original Research Paper

Polymeric hybrid mesoporous silica hollow nanospheres as a support for palladium and application of the Pd_{NPs}@PANI/HNS nanocomposite for aerobic benzyl alcohol oxidationSadegh Rostamnia^{*}, Saba Kholdi*Organic and Nano Group (ONG), Department of Chemistry, Faculty of Science, University of Maragheh, P.O. Box. 55181-83111, Maragheh, Iran*

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ABSTRACT

The polyaniline composition by silica based mesoporous hollow nanosphere (silica-HNS) was synthesized and selected as a promising solid support for palladium nanoparticle stabilization. Then the nanocomposite was applied as a nanocatalyst for aerobic benzyl alcohol oxidation reactions. Catalyst recyclability showed six successful runs for the reaction. TEM and SEM-EDX/mapping images were used to study the structure and morphology of the Pd_{NPs}@PANI/HNS. FT-IR spectroscopy, Thermal gravimetric analysis (TGA), and BET were used to characterize and investigate the catalyst nature. In addition, the amounts of Pd loading were characterized by ICP-AES technique.

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1. Introduction

The selective oxidation of benzyl alcohols to corresponding aromatic aldehydes is the foundation of many vital industrial and fine-chemical processes [1–5]. In this field, many oxidants are known for the oxidation of benzyl alcohols, however many of these oxidants are toxic and produce large amounts of wastes and also some of them are not controllable in reaction process for aldehyde preparation and goes to corresponding carboxylic acids. Much attention is being directed to selective methods of oxidations of alcohols to aldehydes as valuable and industrial interest intermediate and also avoid the acids generation [6,7]. Catalytic oxidation with molecular oxygen (O₂) or air is particularly attractive from economical and green chemistry points of view [7,8].

Mesoporous material with hollow sphere structure has attracted great research interests because of their multimodal porous structure and their potential applications in catalysis, adsorption, gas separation and so on [9–12]. The application of hollow nanosphere (HNS) in organic synthesis was regarded as one of the breakthroughs in the field of heterogeneous catalysis [13–15]. Currently, polymeric silica composites such as polyaniline/silica (PANI/SiO₂) are developed and engaged for many

applications in the chemistry and material fields [16–18]. There are also some reports for PANI-based mesoporous silica nanocomposites [19]. However, these materials suffer from lower surface area, mechanical properties, and decreasing pore sizes. Embedding PANI inside the walls of silica can be more useful to solve these problems.

Transition metal-based nanostructure, such as nanoparticles, nanoclusters and nanocrystals of Pd, Ru, Au are extensively studying due to their inherent ability in nano-size catalyzed organic transformations which leads to many kinds of cross-coupling, alcohol oxidation and reduction processes [7,20–28]. However, the traditional non-stabilized/ligandless palladium nanoparticles (Pd_{NPs}) catalysis in this area has reinforced the problems of palladium isolation and recyclability, and aggregation of Pd(0) to Pd-black and therefore its deactivation which in practice, they totally lead to an inconvenient catalyst specifically in pharmaceutical industry and from point view of green chemistry. Various inorganic and organic supports such as porous silica [29], carbon [30] and organic polymers [31] based materials have been explored to design and identify the eco-friendly protocols for Pd-stabilization for organic reaction process such as alcohol oxidations. Among various supports, nanoporous materials have been utilized in numerous diverse designs and systems which can be attributed to sort of mesoporous which are distinguished by their structures, grafted ligands and metals [32]. However, efforts on providing efficient system for transition metal nanoparticle stabilization are still

^{*} Corresponding author.

E-mail addresses: rostamnia@maragheh.ac.ir, srostamnia@gmail.com (S. Rostamnia).

under consideration. Hence, we embedded polyaniline (PANI) within the walls of silica-hollowed nanospheres (HNS) with assembly method to obtain an efficient and hybrid polymer-inorganic HNS as a solid support aims. Our investigations disclosed PANI/HNS act as a support for Pd^{2+} ions, which produces uniform and available Pd nanoparticles supported onto the surface of PANI/HNS. Then, we applied the $\text{Pd}_{\text{NPs}}@\text{PANI}/\text{HNS}$ s for selective aerobic alcohol oxidation reaction (Fig. 1).

2. Experimental

Triblock copolymer surfactant of F127, tetramethyl orthosilicate (TMOS) and polyaniline (emeraldine base) average $M_w \sim 5000$ were purchased from Sigma-Aldrich Company Ltd. Other reagents were obtained from Merck (Germany) and Fluka (Switzerland). GC analyses was recorded on GC Chrom (Teif Gostar Faraz Co., Iran). Scanning electron microscopy (SEM) images was recorded on Zeiss-DSM 960A microscope and EDX/mapping was recorded by same SEM machine. The N_2 adsorption-desorption isotherms were measured on Tristar 3000 (Micrometrics) after the samples were outgassed at 120°C for 3 h. Transmission electron microscopy (TEM) images were recorded on Zeiss EM 900 electron microscope. IR spectra were recorded on Shimadzu IR-460 spectrometer.

2.1. Synthesis of polyaniline embedded mesoporous silica (PANI/HNS)

Polyaniline embedded hollow sphere mesoporous silica of PANI/HNS was synthesized by dissolving F127 (1 g) and K_2SO_4 (3.49 g), in 60 mL H_2O and 1 g 1,3,5-trimethylbenzene (TMB) which were vigorously mixed together for 3 h at 13.5°C . Then, in another beaker, 0.106 g of PANI was added to 4 mL of DMF and allowed to stir for 30 min and then, 3 g TMOS was added to stir for next 30 min under the same conditions. Finally, the latter was to former glass and allowed to stir for subsequent 24 h at 13.5°C . The obtained solid was sealed in autoclave and allowed to age for 24 h at 100°C . Afterwards, reaction mixture was filtered and washed with methanol and water. The solid was stirred in 50 mL hot DMF (plus 5 mL NMP) for two days. Then, the template was extracted by ethanol for one week in Soxhlet.

2.2. Preparation of $\text{Pd}^{2+}@\text{PANI}/\text{HNS}$ and $\text{Pd}_{\text{NPs}}@\text{PANI}/\text{HNS}$

Firstly, 1 g of PANI/HNS was dispersed in 90 mL CH_3CN and 0.02 g of $\text{Pd}(\text{OAc})_2$ in 10 mL CH_3CN at room temperature added to PANI/silica-HNS and allowed to stir for 2 h. The reaction mixture was filtered the obtained solid was washed with methanol for

three time to gain pure $\text{Pd}(\text{OAc})_2@\text{PANI}/\text{HNS}$. Then, 5 mL of 0.2 mol/L of freshly prepared methanolic NaBH_4 added to mixture of prepared $\text{Pd}(\text{OAc})_2@\text{PANI}/\text{HNS}$ in 50 mL methanol during 15 min. Finally, $\text{Pd}_{\text{NPs}}@\text{PANI}/\text{HNS}$ collected by simple filtration. The amounts of Pd loading was 4.7 wt% characterized by ICP-AES technique (here $\text{Pd}(4.7)_{\text{NPs}}@\text{PANI}/\text{HNS}$). For 2.1 mol% Pd loaded catalyst, we used 0.01 g of $\text{Pd}(\text{OAc})_2$ in same condition and 3 mL of 0.2 mol/L of NaBH_4 (here $\text{Pd}(2.1)_{\text{NPs}}@\text{PANI}/\text{HNS}$).

2.3. O_2 -mediated oxidation alcohols by $\text{Pd}_{\text{NPs}}@\text{PANI}/\text{HNS}$

The catalytic performance was assessed by the oxidation of various benzyl alcohols in aerobic condition. In a typical run, a dry 25 mL, two-necked, round-bottomed flask was equipped with a reflux condenser connected with a balloon filled with oxygen was charged with freshly prepared $\text{Pd}(2.1)_{\text{NPs}}@\text{PANI}/\text{HNS}$ catalyst (20 mg, 0.4 mol%), alcohol (1 mmol), 1 mmol of K_2CO_3 and toluene (5 mL). The resulting mixture was stirred at 80°C . After completion of the reaction, by simple centrifuge, $\text{Pd}_{\text{NPs}}@\text{PANI}/\text{HNS}$ was separated and washed several times by water and CH_2Cl_2 before next reuse.

3. Results and discussion

For the synthesis of PANI/HNS, F127 and TMOS as a silica source were used and co-assembly of PANI with silicate in the presence of F127 were performed. PANI was entrapped into SiO_2 shell using dissolving and entrapping PANI during the hydrolysis of TMOS to synthesize hybrid PANI/silica based HNS. Then the surfactant was extracted from synthesized HNS. Finally, $\text{Pd}(\text{OAc})_2$ was added to dispersion of PANI/HNS in CH_3CN to support the Pd nanoparticles (NP) in which the Pd^{2+} ions were reduced to Pd_{NPs} by methanolic NaBH_4 . A schematic pathway to synthesize PANI/silica-HNS is indicated in Scheme 1. We prepared two kinds of supported Pd_{NPs} catalysts with PANI/HNS supports. The palladium contents in $\text{Pd}_{\text{NPs}}@\text{PANI}/\text{HNS}$ solids were 4.7 [$\text{Pd}(4.7)_{\text{NPs}}@\text{PANI}/\text{HNS}$] and 2.1 [$\text{Pd}(2.1)_{\text{NPs}}@\text{PANI}/\text{HNS}$] wt%, respectively.

3.1. Characterization of PANI/HNS and $\text{Pd}_{\text{NPs}}@\text{PANI}/\text{HNS}$

To demonstrate the final structure of PANI/HNS, FTIR, TGA, BET/BJH, EDAX, and transmission electron microscopy (TEM) were used. FT-IR spectra provided evidence of interaction between silica-HNS, PANI and Pd_{NPs} in the composite as shown in Fig. 2. In the FT-IR spectrum of PANI/HNS, the bands at 1740, 1630, 1470, 1400 and 1180 cm^{-1} arise from the C=C stretching of the quinoid and benzenoid ring, C–N stretching of the benzenoid

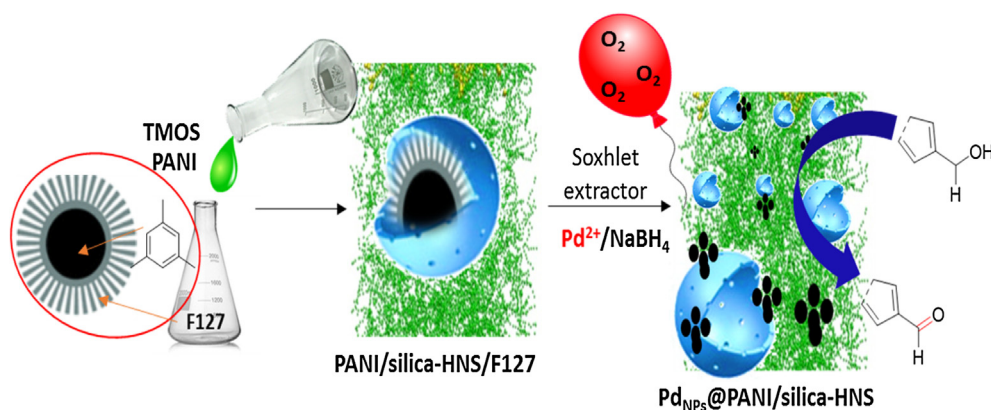


Fig. 1. $\text{Pd}_{\text{NPs}}@\text{PANI}/\text{silica-HNS}$ nanocatalysts for benzylic alcohol oxidations.

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