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Synthesis of hybrid interfacial silica-based nanospheres composite as a support for ultrasmall palladium nanoparticle and application of Pd<sub>NPs</sub>/HSN in Mizoroki-Heck reaction

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## Abstract:

The silica based hollow nanosphere (silica-HNS) containing polymer of polyaniline was synthesized and chosen as a promising support for  $Pd_{NPs}$ . Then it was applied as a green catalyst in the reaction of Heck coupling with high yield. TEM and SEM-EDX/mapping images were used to study the structure and morphology. FT-IR spectroscopy, Thermal gravimetry analysis (TGA), and BET were used to characterize and investigate the catalyst. Also, the amounts of Pd loading were characterized by ICP-AES technique. Catalyst recyclability showed 5 successful runs for the reaction.

Keyword: Mesoporous; Pd<sub>NPs</sub>/HSN; Mizoroki-Heck reaction; Green chemistry.

#### **1. Introduction**

Palladium-based catalysts are extensively studying due to their inherent ability in transition metal catalyzed transformations such as insertion, oxidative addition and reductive elimination which leads to many kinds of cross-coupling reactions such as Mizoroki-Heck reaction of organohalides and activated alkenes [1-3]. However, the traditional homogeneous catalysis in this area has reinforced the problems of product purification, palladium isolation and recyclability, and aggregation of Pd(0) 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. Over the past few decades, since the global concerns for environmental issues have been increased, demands and tendencies for the green or greener protocols and systems to develop recoverable and reusable catalysts and detoxified metals in the reaction medium have also been raised. Efficient palladium supported catalysts have had a major impact on this area. Various inorganic and organic supports such as porous silica [4], carbon [5] and organic polymers [6] based materials have been explored to design and identify the eco-friendly protocols for cross-coupling reactions. Specifically, low palladium loadings [7], phosphine-free [8] and recyclable catalyst systems have all been demonstrated as the suitable conditions reaction catalysis. Among various supports, nanoporous materials have been utilized in numerous diverse designs and systems which can be attributed to sort of mesopores which are distinguished by their structures, grafted ligands and metals [9]. However, concerns and efforts on providing a highly efficient and greener catalytic system for these reactions are still under consideration. Hence, we embedded polyaniline (PANI) within the walls of silica hollowed nanospheres (HNS) with assembly method to obtain a highly efficient and hybrid polymer-inorganic HNS. Our investigations disclosed PANI/HNS act as a support for Pd<sup>2+</sup> ions which produces uniform and available Pd nanoparticles supported onto the surface of PANI/silica-HNS. Currently, PANI-

silica gel composites are developed and engaged for analytical applications [10]. There are also some reports for PANI-based mesoporous nanocomposites [11] with advanced applications. 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. Therefore, we developed the synthesis of PANI/silica based HNS (PANI/silica-HNS) by a one-pot method. And its application and catalytic activity in the Mizoroki-Heck coupling reaction. In continues of our recent reports in mesoporous field [12], we report synthesis of Pd<sub>NPs</sub>@PANI/silica-HNSs and its catalytic application in Mizoroki-Heck reaction.

#### 2. Experimental

Materials were of analytical grade and used as received without any further purification. Triblock copolymer EO106PO70EO106 (F127), tetramethyl orthosilicate (TMOS) and polyaniline (emeraldine base) average Mw ~5,000 were purchased from Sigma-Aldrich Company Ltd. Other reagents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. All organic product yields were obtained as isolated method or by gas chromatography (GC). GC analyses was recorded on GC Chrom (Teif Gostar Faraz Co., Iran). Scanning electron microscopy (SEM/EDX/mapping) images was recorded on Zeiss-DSM 960A microscope microscope. Transmission electron microscopy (TEM) images were recorded on Zeiss EM 900 electron microscope. IR spectra were recorded on Shimadzu IR-460 spectrometer, and absorbents are reported in cm<sup>-1</sup>.

#### Synthesis of PANI/silica-HNS

PANI/silica-HNS was synthesized by dissolving F127 (1 g) and  $K_2SO_4$  (3.49 g), in 60 mL H<sub>2</sub>O and 1 g mesitylene which were vigorously mixed together for 3 h at 13.5 °C. Then, in another

glass, 0.106 g of PANI was added to 4 mL of DMF and allowed to stir for 30 min and the then, 3.04 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 template was extracted by ethanol for 24 h in soxhlet.

#### Synthesis of Pd(OAc)<sub>2</sub>@PANI/silica-HNS and Pd<sub>NPs</sub>@PANI/silica-HNS

1 g of PANI/silica-HNS was dispersed in CH<sub>3</sub>CN and 0.02 g of Pd(OAc)<sub>2</sub> in CH<sub>3</sub>CN at room temperature was added to PANI/silica-HNS and allowed to stir for 2 h time. Finally, the reaction mixture was filtered the obtained was washed with methanol for three time to gain pure Pd(OAc)<sub>2</sub>@PANI/silica-HNS. Then, 5 mL of 0.2 mol/L of freshly prepared NaBH<sub>4</sub> (in methanol) was added to mixture of prepared Pd(OAc)<sub>2</sub>@PANI/silica-HNS in 50 mL methanol during 15 min. Finally, Pd<sub>NPs</sub>@PANI/silica-HNS collected by simple filtration. The amounts of Pd loading was 4.7 w% characterized by ICP-AES technique.

#### General procedure for synthesis of trans-alkenes

In a typical method, 1 mmol of bromobenzene, 1 mmol of methyl acrylate, 0.04 g of  $Pd_{NPs}$ @PANI/silica-HNS, and 2 mmol of Et<sub>3</sub>N were added to 5 mL of DMF:H<sub>2</sub>O (1:1) and allowed to stirrer at 130 °C. The reaction completion was monitored by TLC (n-hexane and ethyl acetate mixture as solvent-5:1). After completion of the reaction, the reaction was cooled to room temperature, the catalyst was removed by filtration. The catalyst was then washed with Et<sub>2</sub>O (3 × 5 mL). The organic layer was separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure to give the corresponding aryl-olefins. To optimize the reaction conditions, GC was used to investigate the yields under each condition. The NMR

spectroscopic data of known compounds were found to be identical with those reported in the *literature* [12].

#### 3. Results and discussion

#### Synthesis of Pd<sub>NPs</sub>@PANI/silica-HNS

For the synthesis of PANI/silica-HNS, F127 was used as a soft template and TMOS as a silica source. Co-assembly of PANI with silicate in the presence of F127 under the ambient conditions were performed. PANI was entrapped into silica shell using dissolving and entrapping PANI during the hydrolysis of TMOS to synthesize hybrid PANI/silica based HNS (PANII/silica-HNS). Then the surfactant was extracted from synthesized HNS. Finally,  $Pd(OAc)_2$  was added to dispersion of PANI/silica-HNS in CH<sub>3</sub>CN to support the Pd nanoparticles (NP) in which the Pd<sup>2+</sup> ions were reduced to Pd<sub>NPs</sub> by methanolic NaBH<sub>4</sub>. A schematic pathway to synthesize PANI/silica-HNS is indicated in Scheme 1.



Scheme 1. General synthesis pathway of Pd<sub>Nps</sub>@PANI/silica-HNS.

#### Characterization of Pd<sub>NPs</sub>@PANI/silica-HNS

To demonstrate the final structure of PANI/silica-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/silica-HNS, the bands at 1580, 1460, 1300 and 1130 cm<sup>-1</sup> arise from the the C=C stretching of the quinoid and benzenoid ring, C-N stretching of the benzenoid and quinoid unit, respectively. A Si-OH stretching band can also be found in the region of 920-830 cm<sup>-1</sup> [12c]. A peak at 1080 cm<sup>-1</sup> can be attributed to stretching of Si-O-Si bonds. The spectrum of Pd<sub>NPs</sub>@PANI/silica-HNS hybrid exhibited almost the same vibrational bands as PANI/silica-HNS, but some peaks of PANI shifted to a higher wave number (1580, 1460 and 1300 cm<sup>-1</sup>) that this result indicated the interaction between component of Pd<sub>NPs</sub>@PANI/silica-HNS nanocomposite. In the all samples, a broad silanol band in the region of 3400-3600 cm<sup>-1</sup> is appeared.



Figure 2. FT-IR analysis of PANI/silica-HNS (black) and Pd<sub>NPs</sub>@PANI/silica-HNS (red).

Thermal gravimetric analysis (TGA) was also performed to study the thermal behavior and for measuring the amount of entrapped PANI inside the walls of  $Pd_{NPs}@PANI/silica-HNS$ . According to this study, three weight losses were observed in this analysis. The first one at temperature below 100  $\Box$ C is assigned to removal of physically adsorbed water and methanol or acetonitrile solvents. The weight loss between 100 to 250  $\Box$ C attributed to elimination of remained F127 surfactant template and non-entrapped PANI. According to this study, more than 9% weight loss between 350-800 °C can be attributed to organic species which proves the presence of entrapped PANI (Fig. 2).



Figure 2. Thermal gravimetric analysis (TGA) of Pd<sub>NPs</sub>@PANI/silica-HNS.

The energy dispersive X-ray (EDAX) analysis showed the signals of silicon, oxygen, carbon, nitrogen and palladium for the Pd<sub>NPs</sub>@PANI/silica-HNS material. These analyses successfully confirm well incorporation of PANI, silica-HNS and palladium species into/onto material composite. Further, the EDX-mapping images is conducted with the Pd<sub>NPs</sub>@PANI/silica-HNS sample and the results are shown in Figure 3. Figure clearly showed that the Pd<sub>NPs</sub>@PANI/silica-HNS

HNS solid is possessed carbon, nitrogen (from PANI) indicated the sample is contained with silica, and also mapping image for Pd (L) indicates that Pd has been successfully supported to the PANI/HNS (Fig.3).



Figure 3. EDX of Pd<sub>NPs</sub>@PANI/silica-HNS solid (a) and its related mapping image(b).

TEM images of PANI/silica-HNS and Pd<sub>NPs</sub>@PANI/silica-HNS were shown in Fig. 4 (a and b). The results reveals that palladium nanoparticles were successfully incorporated and dispersed on the PANI/silica-HNS matrix. PANI/silica-HNS composite indicated hollow sphere-shaped (HNS) silica in nanoparticles format called as hollow nanospheres (HNS) with average particle size of nearly 21 nm (Fig. 4a). Moreover, Pd<sub>NPs</sub>@PANI/silica-HNS composite evidently showed particles of palladium with spherical shape onto the PANI/HNS matrix with the average particle

size of 3.5 to 6 nm (Fig. 4b, c). The particle size histogram of Pd nanoparticle) over the matrix shows that particle size ranged from 3.5 nm to 6 nm (Fig. 4c). The estimated average particle size of deposited Pd nanoparticles by TEM and its particle size histogram from the Binary-TEM is around 4.5 nm (Fig. 4c,d).



**Figure 4.** TEM images of PANI/silica-HNS (a) and Pd<sub>NPs</sub>@PANI/silica-HNS (b) and Binary-TEM (d) and particle size histogram of Pd<sub>NPs</sub>@PANI/silica-HNS (c).

Nitrogen adsorption/desorption isotherm (BET analysis) of each PANI/silica-HNS (a-red) and Pd<sub>NPs</sub>@PANI/silica-HNS (a-blue) are indicated in Fig 5. Accordingly, by increasing the amount

of loaded Pd, the surface area decreases from 277 to 238  $m^2.g^{-1}$  for PANI/silica-HNS and Pd<sub>NPs</sub>@PANI/silica-HNS, respectively. BJH pore size distribution analysis of PANI/silica-HNS shows a pore diameter 21 nm. Adsorption-desorption isotherm truly showed that the both structures of PANI/silica-HNS and Pd<sub>NPs</sub>@PANI/silica-HNS are mesoporous and the other BET analysis exhibited the surface area of 277 and 238  $m^2.g^{-1}$  which is maintained after Pd nanoparticle deposition.



**Figure 5.** N<sub>2</sub>-adsorption/desorption isotherm of PANI/silica-HNS (a-red) and Pd<sub>NPs</sub>@PANI/silica-HNS (a-blue). BJH pore size distribution of PANI/silica-HNS (c).

# Catalytic performance of Pd<sub>NPs</sub>@PANI/silica-HNS

Mizoroki-Heck cross-coupling reaction was selected in investigating the catalytic performance of  $Pd_{NPs}@PANI/silica-HNS$  based on this reaction importance in chemistry, industrial and pharmacy [13]. In the case of Heck reaction, many different parameters were studied by the model reaction of bromobenzene and methyl acrylate to observe the catalytic behavior. Based on this study, solvent has a major effect on catalytic activity. In this regard, polar solvents were more effective in the catalytic efficiency. Hence, the catalytic activity was excellent in the presence of



 $H_2O:DMF$  solvent [ $H_2O:DMF$  (5 mL, 1:1)] Therefore, we chose the mixture of water and DMF medium as a green, optimal, and alternative solvent (Fig.6).

**Figure 6.** The solvent effect on the progress of Heck coupling reaction (reaction conditions: bromobenzene (1 mmol), methyl acrylate (1 mmol), Et<sub>3</sub>N (2 mmol), and Catalyst (40 mg of Cat.) and 5 mL solvent in 3 h).

On the other hand, various temperatures and base were monitored to observe the catalytic activity of  $Pd_{NPs}@PANI/silica-HNS$  over the model reaction. This study showed that the maximum catalytic activity is shown at 130 °C and higher than that, no significant change was observed in the reaction progress. To obtain better results, KOH, Et<sub>3</sub>N, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> (2 eq) were tested as the base in the model reaction of Heck using  $Pd_{NPs}@PANI/silica-HNS$ . This study showed that the maximum catalytic activity is shown for KOH and Et<sub>3</sub>N, but in case of KOH the reaction had the highest leaching and Pd-black was also observed in this catalyst. In finding an ideal duration for reaction completion, the reaction progress was monitored in each half an hour and the kinetic

of the reaction was also depicted in the Fig. 7b. According to this plot, the reaction, the reaction rate is initially slow and then the rate increases along the progress and finally, the reaction progress stops after 3 h. Therefore, no significant change was observable after 3 h (Fig. 7b).



Figure 7. The effect of base (a) and time effect (b) on the progress of Heck reaction.

Various amounts of Pd<sub>NPs</sub>@PANI/silica-HNS in terms of Pd mol% was examined in the model reaction to reach an optimal amount of catalyst. According to this study, the ideal amount of catalyst was 40 mg per each mmol of substrate which equals to 1.76 mol% Pd (Fig. 8).



After a careful and successful catalytic study on the Heck coupling of bromobenzene with methyl acrylate, and finding out that the catalyst can proceed the reaction. Under the optimized

conditions, the reaction was carried out under basic conditions (by  $Et_3N$ ) in the presence of 40 mg of the catalyst at 130 °C and 5 mL DMF/H<sub>2</sub>O (1:1) as solvent.in 3h, we turned to test its catalytic power on different haloaryls and active alkenes. In this part, we found our proposed catalyst active in every single derivatives of aryl bromides and aryl iodides. Because every derivative had high to excellent yield, there was no distinguishable difference among derivatives. However, aryl iodides had better results in yields under the similar conditions (Table 1).

	Pd <sub>NPs</sub> @PANI/HNS				
	Ar-Hal +	$E_{\rm B} = E_{\rm t_3N} (2  \rm eq) $ Ar			
			130 °C		ĸ
Entry	Ar-	R	-Hal	Time/Conv. (h/%)	Yield (%)
1	Ph-	CO <sub>2</sub> Me	-I	2.5/97	95
2	Ph-	CO <sub>2</sub> Et	-I	3/96	95
3	3-NO <sub>2</sub> -Ph-	CO <sub>2</sub> Et	-I	3/97	96
4	3-NO <sub>2</sub> -Ph-	CN	-I	3/98	96
5	4-Me-Ph-	CO <sub>2</sub> Me	-I	3/94	91
6	4-MeO-Ph-	CN	-I	3/93	85/7 (trans/cis)
7	Ph-	Ph	-I	3/90	88
8	Ph-	$CO_2Me$	-Br	2.5/92	90
9	Ph-	CO <sub>2</sub> Et	-Br	3/91	90
10	Ph-	Ph	-Br	4/88	73/11 (trans/cis)
11	4-MeCO-ph	CO <sub>2</sub> Me	-Br	3/94	91

Table 1. Synthesis of alkene derivatives under the optimized conditions.<sup>a</sup>

Reaction conditions: haloaryl 1 mmol, 1 mmol of alkene, 40 mg of Pd, and 2 mmol of  $Et_3N$  at 130 °C in 5 mL of H<sub>2</sub>O:DMF (1:1).

For Heck reactions, we recovered the catalyst and reused it in the same reaction with the same reaction conditions. In this study, all the reaction conditions were under the optimized parameters except the catalyst in which was recovering and reusing at the end after each reaction cycle. Accordingly, the kinetics of reaction in each cycle was similar to first run. However, small decrease on the product yields happened after five consecutive cycles which is natural due to small loss of catalyst in each recovery (Fig. 9). The stability of the catalyst was also investigated

by the BET study of the reused catalyst (after 5th reaction cycle) in comparison of initial mesoporous PANI/silica-HNS. These studies showed that the porosity of solid destroyed after 5<sup>th</sup> cycle (Fig. 9b).





## Conclusion

In conclusion, we herein synthesized a new polymer-inorganic hollow nanospheres (PANI-silica-HNS) for supporting and stabilizing of nanoparticles of Pd and developed it as a new efficient and promising green catalyst catalytic system in the synthesis of *trans*-alkene derivatives which were produced from Mizoroki-Heck cross-coupling reaction. In addition, low Pd leaching and therefore low toxicity, ease of separation and work-up, and high yields and conversions were the other scopes of this catalyst.

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# **Research highlights**

- ► Synthesis of hybrid interfacial silica-based nanospheres.
- ► Hollow nanospheres as advanced support for Pd.
- ▶ Pd<sub>NPs</sub>/HSN as green and interfacial nanocatalyst for Mizoroki-Heck reaction.