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## Pd(0) nanoparticles immobilized on multi-nitrogen functionalized Halloysite for promoting Sonogashira reaction: Studying the role of the number of surface nitrogens in catalytic performance

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Halloysite nanoclay, Hal, was amine-functionalized and subsequently reacted with 2,4,6trichloro-1,3,5-triazine, TCT, and ethylenediamine, EDA, to provide multi-nitrogen containing functionality on the surface of Hal. The resulting surface-modified Hal, Hal-2N-TCT-EDA, was then used for immobilization of Pd nanoparticles and affording a heterogeneous catalyst, Pd@Hal-2N-TCT-EDA, with utility for copper and ligand-free Sonogashira coupling of alkynes and aryl halides. The results established the efficiency of this protocol in terms of product yield, eco-friendly nature and reaction time. Study of the reusability of the catalyst confirmed that the catalyst could be recovered and recycled up to seven times with slight loss of catalytic activity and Pd leaching, indicating the efficiency of Hal-2N-TCT-EDA for embedding Pd nanoparticles. To elucidate the role of the number of surface nitrogens on the catalytic performance, the catalytic activity and recyclability of the catalyst was compared with those of Hal-2N and Hal-2N-TCT. It was found that more surface nitrogen atoms gave higher loading of Pd and lower Pd leaching. This result confirms the contribution of surface nitrogens to anchor the Pd species and suppress leaching.

*Keywords:* Halloysite clay; Functionality; Pd Nanoparticles; Copper and ligand-free; Sonogashira coupling reaction

#### **1. Introduction**

Sonogashira cross-coupling between aryl halides and aryl alkynes is an important synthetic route to construct C (sp<sup>2</sup>)-C (sp) bonds, which are very important in organic synthesis [1-3]. The products of these reactions have been widely used for synthesis of substituted alkynes [4],

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natural products [5], pharmaceutical compounds [6], polymers [7] and optical materials [8]. Palladium phosphine complexes with copper salt as co-catalyst for promoting Sonogashira coupling reaction have been extensively investigated, mostly in homogeneous conditions, and various ligands or additives were employed to achieve higher yields of the desired coupling products [9]. Pd salts are expensive and homogeneous palladium catalysts suffer from several drawbacks such as high price, low chemical and thermal stability, and tedious isolation and recovery from the reaction mixture [10]. These problems restrict the large scale applications of these catalysts. Attempts have been made to address the challenges by using supported Pd as heterogeneous catalysts. In this respect, several heterogeneous palladium catalysts have been developed for Sonogashira C-C coupling reactions [11]. Numerous solid supports, such as clay [12], carbon materials [13], metal oxides [14] and molecular sieves [15], have been exploited for developing Pd-based heterogeneous catalysts, in which Pd complexes or nanoparticles are involved as the active species in coupling reactions [16]. Supporting of Pd species on magnetic nanoparticles [17, 18] and functionalized SBA-15 [19] led to the development of efficient, green and mild protocols for promoting not only C-C coupling reactions, but also for diverse coupling reactions. Notably, in the case of magnetic supports, the facile separation of the catalyst is achievable.

Halloysite, Hal. is an alumino silicate with the chemical composition Al<sub>2</sub>(OH)<sub>4</sub>Si<sub>2</sub>O<sub>5</sub>(2-H<sub>2</sub>O) [20]. The water molecules in the structure of Hal are located between the interlayer spaces [21]. As a kaolonite mineral, Hal is mined from natural deposits and formed from amorphous allophone by long time weathering [20, 22]. The porous morphology of Hal as well as some other features of this clay such as inertness, availability, bio-compatibility and high mechanical and chemical stability and surface area make this clay a candidate for various applications such as drug delivery purposes [23], separation [24], catalysis [23] and water treatment [25]. The most interesting feature of Hal is its capability to be functionalized on its inner and outer surfaces and the incorporation of various active species such as nanoparticles [26].

Taking advantage of both experimental and theoretical studies, we have tried to understand the chemistry of functionalized Hal as a catalyst support [11, 27]. In this context, we have investigated the role of the number of heteroatoms on the surface by comparing Hal, functionalized with 3-aminopropyl-triethoxysilane (APTES) and *N*-[3-(trimethoxysilyl)propyl]

ethylenediamine (AEAPTMS) [28]. The results established that nitrogen is a potent heteroatom with high affinity to interact catalytic species. Nitrogen can effectively anchor the catalytic species and reduce its leaching. Additionally, the studies revealed that Hal functionalized with AEAPTMS with two nitrogens showed lower leaching of the catalytic species compared to Hal functionalized with APTES that possessed one nitrogen.

Thorough consideration of all these factors and in continuation of our previous studies on the catalytic utility of functionalized Hal and further confirming the role of the number of nitrogens on the anchoring of immobilized catalytic species [29-32], herein the preparation of a multi-nitrogen containing Hal-based heterogeneous catalyst, Pd@Hal-2N-TCT-EDA, through multi-step functionalization of Hal and incorporation of Pd nanoparticles (figure 1) is described and utilized for Sonogashira cross coupling. Additionally, the recyclability of Pd@Hal-2N-TCT-EDA as well as the role of the number of surface nitrogens in suppressing Pd leaching are reported.

#### 2. Experimental

#### 2.1. Materials and measurements

The chemicals used for preparation of Pd@Hal-2N-TCT-EDA and studying its catalytic activity included Hal, *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS), 2,4,6-trichloro-1,3,5-triazine (TCT), ethylenediamine (EDA), triethylamine, toluene, tetrahydrofuran (THF), Pd(OAc)<sub>2</sub>, NaBH<sub>4</sub>, halobenzenes, phenylacetylene, propargyl alcohol, K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, KOH, NaOH, distilled water and EtOH, all provided from Sigma-Aldrich and used as received. The formation of Pd@Hal-2N-TCT-EDA was confirmed by using various characterization techniques including, transmission electron microscopy (TEM), Fourier transform infrared (FT-IR, Perkin Elmer Spectrum 65 instrument) spectroscopy, X-ray diffraction (XRD, Siemens D5000 with Cu K\alpha radiation from a sealed tube), thermogravimetric analysis (TGA, Mettler Toledo instrument with a heating rate of 10 °C min<sup>-1</sup>, under nitrogen) and BET (Belsorp Mini II instrument, with degassing for 3 h at 423 K). The amount of Pd species supported on Hal-2N-TCT-EDA was also measured by applying an ICP analyzer (Varian, Vista-pro).

#### 2.2. Functionalization of Hal with AEAPTMS: Synthesis of Hal-2N

To prepare the catalyst, Hal was first functionalized with AEAPTMS. To this purpose, 2.4 g of Hal was highly dispersed in 60 mL of dry toluene by using ultrasonic irradiation of 100 W power for 25 min. Then, 1 mL (5 mmol) of AEAPTMS was added to the Hal suspension and the resulting mixture was stirred at 140 °C for 24 h. After that, the solid was filtered, washed with dried toluene three times and dried at 100 °C overnight.

#### **2.3.** Introduction of TCT: Synthesis of Hal-2N-TCT

To introduce TCT on Hal-2N, TCT (3.24 g) was dissolved in 50 ml of THF. Then, Hal-2N (3.5 g) was added and the obtained mixture was stirred in ice. Subsequently, triethylamine (2 mL) was introduced dropwise. After that, the solution was stirred at 25 °C overnight. Upon completion of the reaction, the precipitate was filtered off and washed with THF repeatedly. Hal-2N-TCT was achieved after drying for 12 h at 70 °C.

## 2.4. Conjugation of EDA to Hal-2N-TCT: Synthesis of Hal-2N-TCT-EDA

To the mixture of Hal-2N-TCT (1.2 g), EDA (2 mL) was gradually added and then the resulting mixture was refluxed at 70 °C for 24 h. After completion of the reaction, the precipitate was filtered, washed with THF several times and dried in an oven for 4 h at 70 °C.

#### 2.5. Immobilization of Pd nanoparticles on Hal-2N-TCT-EDA: Pd@Hal-2N-TCT-EDA

To incorporate Pd nanoparticles on Hal-2N-TCT-EDA, Hal-2N-TCT-EDA (1.2 g) was suspended in dry toluene (15 mL) containing  $Pd(OAc)_2$  (0.02 g) and then stirred at ambient temperature for 10 h. Reduction of Pd(II) to Pd(0) was achieved by using NaBH<sub>4</sub>. More precisely, a solution of NaBH<sub>4</sub> in methanol (10 mL, 0.2 N) was prepared and added to the above mentioned Pd(II)@Hal-2N-TCT-EDA dropwise. To assure complete reduction, the resulting mixture was vigorously stirred for 5 h. Pd@Hal-2N-TCT-EDA was obtained after filtration, washing with MeOH and drying in oven at 80 °C overnight. The schematic process of synthesis of the catalyst is illustrated in figure 1.

To prepare Pd@Hal-2N and Pd@Hal-2N-TCT, the same procedure was used, except Hal-2N and Hal-2N-TCT were applied as Pd support.

#### 2.6. Sonogashira coupling reaction

The catalytic activity of the synthesized Pd@Hal-2N-TCT-EDA was investigated for promoting the Sonogashira reaction. Pd@Hal-2N-TCT-EDA (10 mol%) and K<sub>2</sub>CO<sub>3</sub> (3.0 mmol) were added to the mixture of halobenzene (1.0 mmol) and acetylene (1.2 mmol) in EtOH. The reaction mixture was then refluxed at 90 °C for appropriate reaction time (scheme 1). The reaction was monitored by thin layer chromatography (TLC, n-hexane/ethyl acetate; 4:1). When the reaction was completed, Pd@Hal-2N-TCT-EDA was filtered. After that, the organic layer was extracted with diethyl ether and purified by column chromatography over silica gel by using hexane/ethyl acetate (4:1) as eluent to furnish the corresponding product. To recycle the catalyst, the recovered catalyst was washed with EtOH two times and dried in an oven at 90 °C overnight. The coupling products were characterized by comparing their melting points and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra with authentic samples (see Supporting Information).

#### 3. Results and discussion

#### 3.1. Catalyst characterization

TEM images of Pd@Hal-2N-TCT-EDA, depicted in figure 2, were recorded to investigate the morphology of the catalyst. The TEM images revealed that upon functionalization of the Hal nanotubes with TCT and EDA and immobilization of Pd nanoparticles, Hal preserved its tubular morphology. However, comparison of the TEM images of the pristine Hal (figure S1 in Supporting Information) and Pd@Hal-2N-TCT-EDA established that the latter possessed more compact morphology and the tubes of Hal closed together to form aggregates. This can be attributed to the intertwining of the surface functionalities of Hal and the presence of electrostatic interactions between surface heteroatoms and Pd nanoparticles. The observed dark spots on the Hal tubes can be assigned to the Pd nanoparticles. In some parts, Pd nanoparticles form small aggregations. Using TEM images, the average Pd particle size is estimated to be 15 nm.

FTIR spectroscopy was employed to establish the structure of Pd@Hal-2N-TCT-EDA (figure 3); the FTIR spectra of Hal, Hal-2N and Hal-2N-TCT-EDA were also recorded and compared with that of Pd@Hal-2N-TCT-EDA. In the FTIR spectrum of Hal, the bands at 538 and  $1034 \text{ cm}^{-1}$  are indicative of Al-O-Si vibration and Si-O stretching. The bands at 3698 and  $3624 \text{ cm}^{-1}$  demonstrate vibration of hydroxyl groups in the inner surface of Hal. The FTIR

spectrum of Hal-2N is very similar to that of Hal, except the band at 2937 cm<sup>-1</sup> is more pronounced, due to the incorporation of organosilane and presence of (-CH<sub>2</sub>) functional group.

The FTIR spectrum of Hal-2N-TCT-EDA (figure 3) also possesses the characteristic bands of Hal, implying that the structure of Hal would be preserved upon functionalization with TCT and EDA. Moreover, some additional bands at 1508-1612 cm<sup>-1</sup> can be observed. These bands can be attributed to -C=N functionality and confirm the conjugation of TCT. Notably, the representative band of  $-NH_2$  stretch, due to the attachment of EDA, overlapped with bands of Hal. Comparison of the FTIR spectra of Hal-2N-TCT-EDA and Pd@Hal-2N-TCT-EDA established that they are similar with no dramatic shift. This observation can be attributed to the low amount of Pd loading on the catalyst.

TGA was also exploited for analysis of Pd@Hal-2N-EDA and disclosing the content of 2-N, TCT and EDA. Initially, the thermogram of pristine Hal and Hal-2N were recorded and compared (figure 4). Apart from the weight losses, which were observed for Hal and can be attributed to the loss of water and the dehydroxylation of Hal, the weight loss at 300 °C can be assigned to the loss of silanic functionality. Using these two thermograms, the content of 2N was calculated to be about 3 w/w%. Next, the thermogram of Hal-2N-TCT was obtained to estimate the content of TCT (figure 4). Considering the weight losses of this thermogram, which was due to the loss of water, loss of organosilane, TCT and dehydroxylation of Hal, the content of TCT was measured as 18 w/w%, indicating that most of the surface 2N were reacted with TCT. Finally, to estimate the content of EDA, the thermogram of the catalyst was obtained and compared with that of Hal-2N-TCT (figure 4). The results revealed that the content of EDA was about 7 w/w%.

According to the thermogram of pristine Hal, ~82 wt.% of the pristine Hal remained at 800 °C and the ash in the thermogram of Pd@Hal-2N-TCT-EDA is about 50 wt%.

XRD analysis, as a method for studying the structure of the catalyst, was also employed to characterize the Pd@Hal-2N-TCT-EDA. To elucidate whether the functionalization of Hal and immobilization of Pd can occur on the surface of Hal and whether this can destroy the structure of the pristine Hal, the XRD pattern of Pd@Hal-2N-TCT-EDA was compared with that of pristine Hal (figure 5). As shown in figure 5, functionalization and Pd immobilization did not lead to any significant displacement of the characteristic reflection bands of Hal (*i.e.* the bands at  $2 \theta = 12.2^{\circ}$ ,  $19.9^{\circ}$ ,  $24.7^{\circ}$ ,  $37.5^{\circ}$ ,  $55.5^{\circ}$ ,  $62^{\circ}$  (JCPDS No. 29-1487)) [33]. Observing no change in

the interlayer space can confirm that the functionalization took place on the surface of Hal. This fact is in accord with previous reports [33, 34]. Apart from the characteristic bands of Hal, no distinguished bands were observed for Pd nanoparticles. According to the literature, this can be attributed to the low loading of Pd (as confirmed via ICP analysis) and its high distribution [35].

As N<sub>2</sub> adsorption-desorption of the catalyst can reveal some features of the catalyst, Pd@Hal-2N-TCT-EDA was subjected to BET analysis (figure 6). Considering the types of isotherms, the Pd@Hal-2N-TCT-EDA isotherm can be attributed to type II isotherms with H3 hysteresis loops [33]. As Hal has a porous nature, this result was expected. BET results also disclosed that the specific surface area of Pd@Hal-2N-TCT-EDA ( $24 \text{ m}^2\text{g}^{-1}$ ) was lower than that of pristine Hal ( $51 \text{ m}^2\text{g}^{-1}$ ), confirming that 2N-TCT-EDA and Pd were located on the outer surface of Hal, not within the inner space. This result is in good agreement with the literature [11].

In the next step, the loading of Pd in Pd@Hal-2N-TCT-EDA was studied by using ICP analysis. Upon digesting the organic functionalities in concentrated acidic solution of nitric and hydrochloric acid, the extract was analyzed by ICP analysis and the calculations demonstrated that the content of Pd was very low, about 0.15 w/w%.

#### 3.2. Catalytic activity

The catalytic activity of the synthesized Pd@Hal-2N-TCT-EDA was investigated for Sonogashira C-C coupling in the absence of copper co-catalyst and ligand. Initially, the efficiency of the catalyst was studied for the model reaction of aryl iodide and phenyl acetylene in the presence of commercially available and cost-effective  $K_2CO_3$  as base in water. The results showed good catalytic activity of Pd@Hal-2N-TCT-EDA. Inspired by this initial finding, the reaction was thoroughly optimized in terms of the solvent, amount of catalyst, and bases (table 1). The efficiency of EtOH, H<sub>2</sub>O-EtOH (1:1), toluene, CH<sub>3</sub>CN, CHCl<sub>3</sub>, and water as solvents and  $K_2CO_3$ ,  $Cs_2CO_3$ , KOH and NaOH as base for promoting the synthesis of the product were screened. EtOH and  $K_2CO_3$  were the most suitable solvent and base, respectively. Among various tested amounts of the catalyst, the value of 10 mol% was selected as the optimum catalyst amount (table 1). Screening the effect of reaction temperature revealed that raising reaction temperature to 90 °C led to the highest yield of the model product. As Sonogashira coupling can be promoted by both Pd(0) and Pd(II)-based catalysts, initially the effect of Pd valence was investigated. To this purpose, Pd(II)@Hal-2N-TCT-EDA was also synthesized (the synthetic procedure was similar to that of Pd@Hal-2N-TCT-EDA, except the reduction step was omitted) and its catalytic activity was compared with that of Pd@Hal-2N-TCT-EDA. The catalytic activity of the latter was slightly higher than that of the former. Hence, Pd(0) was selected for further investigation. Moreover, the catalytic activity of homogeneous Pd(OAc)<sub>2</sub> and Pd(0)/Hal were also obtained for the model reaction under optimum reaction conditions. The results established that the catalytic activity of homogeneous Pd(OAc)<sub>2</sub> was the lowest. Notably, the recovery of the homogeneous catalyst was tedious. The catalytic activity of Pd(0)/Hal (60%) was higher than that of Pd(OAc)<sub>2</sub> but lower than Pd@Hal-2N-TCT-EDA.

In the following, the effect of the number of the surface nitrogens on the catalytic activity of the final catalyst was investigated. Two other catalysts, *i.e.* Pd@Hal-2N and Pd@Hal-2N-TCT were prepared and their catalytic performances were compared. The results showed that the order of the yield of the desired product in the presence of various catalysts varied in the following order: Pd@Hal-2N-TCT-EDA (95%) > Pd@Hal-2N-TCT (75) > Pd@Hal-2N (66%). The observed difference of the catalytic activity can be attributed to the different loading of Pd nanoparticles on the catalyst. To verify this assumption and estimate the loading of Pd, three prepared catalysts were subjected to ICP analysis. The loading of Pd in Pd@Hal-2N-TCT-EDA was the highest (0.15 w/w%) while Pd@Hal-2N showed the lowest Pd content (0.05 w/w%). Regarding Pd@Hal-2N-TCT, the loading of Pd was about 0.08 w/w%. This observation confirms the role of the number of surface nitrogens in anchoring Pd nanoparticles.

Having the optimized reaction conditions in hand, the generality of this methodology was confirmed by applying various alkynes and aryl halides with electron-withdrawing and electrondonating groups (table 2 [10, 30, 36-40]). As tabulated in table 2, not only aryl iodide could tolerate Sonogashira coupling reaction using Pd@Hal-2N-TCT-EDA, but also less active aryl halides, *i.e.* aryl bromides and aryl chlorides underwent the reaction to afford the corresponding biaryls. However, the yields of the reactions in these cases were lower than those of aryl iodides. According to the literature, this observation can be attributed to the lower activity of aryl bromides and aryl chlorides [40]. Comparing the yields of aryl halides with different functional groups, it can be concluded that the substrates with electron-withdrawing groups led to higher yields of products. Moreover, sterically demanding aryl halides (table 2, entry 10) resulted in lower yields of the products. The results also demonstrated that both aliphatic and aromatic alkynes could be applied in the protocol. However, the yield of the reactions by using aromatic alkynes were slightly higher than that of aliphatic ones.

Next, the reaction versus time was studied and time-conversion profile for the model reaction was obtained (figure 7). The slope of the plot at the start of the reaction was relatively sharp and after 30 min, conversion reached 40%. Then, the slope of the plot decreased and conversion reached its highest value (95%) at 120 min. After that, no further increase in the conversion was observed.

Time-conversion profile was also studied for the less active chlorobenzene (figure 7). As depicted, the profile of chlorobenzene is similar to that of iodobenzene. However, the reaction of chlorobenzene is slower and at the first 30 min, the conversion reached 15%. Similar to iodobenzene, the slope of the time-conversion plot at the beginning of the reaction is sharper and the after reaching conversion of 55% (after 180 min), the slope of the plot decreased. In this case, the maximum conversion was observed after 390 min and the conversion did not increase by further reaction time.

Finally, to investigate the merit of this protocol, the catalytic activity of the catalyst for promoting the model reaction was compared with some previously reported catalysts (table 3). A number of protocols have been reported for Sonogashira coupling and the reported protocols for this reaction are not limited to the cases tabulated in table 3. As shown in table 3, both Pd-based and Pd-free catalysts have been reported for this reaction under different reaction conditions. The comparison of the catalytic activity of Pd@Hal-2N-TCT-EDA with those catalysts indicated the superior or comparative catalytic activity of Pd@Hal-2N-TCT-EDA. Moreover, this catalyst could promote the model reaction in the presence of cost-effective and non-toxic  $K_2CO_3$  as base and EtOH as solvent while some of the tabulated catalysts required expensive (table 3, entry 2) or toxic bases and/or solvents. Furthermore, the reaction time and temperature required for the reaction with Pd@Hal-2N-TCT-EDA catalysis were lower or comparative to the catalysts tabulated in table 3.

The aim of this research was design and preparation of a novel heterogeneous catalyst based on Hal and investigation of the effect of the number of surface nitrogens on the catalytic activity. In this line, Sonogashira coupling was selected as a model reaction to investigate the catalytic performance and the role of the number of surface nitrogens. Hence, it is not claimed that the developed protocol is the most efficient strategy for the Sonogashira reaction and there are other reports in which this reaction was promoted in comparative or even better yield [41, 42]. However, the comparison in table 3 [43-51] confirms that Pd@Hal-2N-TCT-EDA can be considered as an efficient catalyst for the Sonogashira coupling reaction.

#### 3.3. Recyclability of the catalyst

The recycling of the catalyst is one of the significant aspects of catalysts for practical applications. Therefore, the recyclability of Pd@Hal-2N-TCT-EDA was investigated in the model reaction of phenylacetylene with iodobenzene. The results showed that after seven consecutive reactions the yield of the model product decreased only 17% (figure 8).

To further confirm the role of the number of surface nitrogens in the immobilization of Pd nanoparticles, the recyclability of the catalyst was compared with those of Pd@Hal-2N and Pd@Hal-2N-TCT (figure 8). As shown, Pd@Hal-2N-TCT-EDA showed the highest catalytic recyclability among three catalysts. Moreover, the ICP analysis confirmed the lowest leaching of Pd in the case of Pd@Hal-2N-TCT-EDA, indicating that nitrogens on the surface of Hal can effectively suppress the leaching of Pd.

To elucidate whether recovery and recycling of Pd@Hal-2N-TCT-EDA can result in degradation of the catalyst structure, FTIR spectra of fresh and recycled Pd@Hal-2N-TCT-EDA were compared (figure 8). As shown in figure 9, FTIR spectra of both fresh and recycled Pd@Hal-2N-TCT-EDA exhibited the characteristic bands of the catalyst, implying that recycling did not lead to destruction of the structure of Pd@Hal-2N-TCT-EDA.

Finally, to study whether the catalysis is heterogeneous, hot filtration test was performed. The hot filtration test was accomplished according to the previously reported protocol [19]. The reaction under optimized condition was performed and then held after short reaction time. Then, the catalyst was filtered and the reaction in the filtrate was allowed to proceed. The results showed no further promotion of the reaction, indicating that the catalytic process was heterogeneous and did not proceed through leaching of Pd nanoparticles and their re-deposition on the support.

#### 4. Conclusion

Considering the role of surface nitrogen functionality of Hal, a heterogeneous Hal-based catalyst with high recyclability and low Pd leaching has been developed through conjugation of TCT on Cl-functionalized Hal followed by introduction of EDA and immobilizing Pd nanoparticles. Pd@Hal-2N-TCT-EDA catalyzed Sonogashira coupling in the absence of copper and ligand. The ICP results confirmed that the loading of Pd in Pd@Hal-2N-TCT-EDA was higher than for Pd@Hal-2N. This issue stemmed from the stronger electrostatic interaction of heteroatoms on the surface of Hal with Pd nanoparticles. Moreover, the recyclability tests revealed that the catalyst showed superior recyclability and lower Pd leaching compared to those of Pd@Hal-2N-TCT-EDA. This observation further confirmed the role of surface nitrogen in anchoring Pd species. This issue was confirmed by comparing the recyclability of Hal-2N, Hal-2N-TCT and Pd@Hal-2N-TCT-EDA. The results demonstrated superior recyclability and inferior leaching of Pd nanoparticle of the latter, indicating the role of the number of the surface nitrogens in anchoring Pd nanoparticles.

#### **Supplementary materials**

Reported TEM images of pristine HNTs as well as <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of coupling products are provided in the Supplementary Information.

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# Graphical abstract



Entry	Reaction condition	Time (h)	Catalyst amount mol%	Base	Yield (%) <sup>b</sup>
1	EtOH/rt	4	10	K <sub>2</sub> CO <sub>3</sub>	65
2	H <sub>2</sub> O/rt	4	10	K <sub>2</sub> CO <sub>3</sub>	51
3	H <sub>2</sub> O-EtOH (1:1)/70	4	10	K <sub>2</sub> CO <sub>3</sub>	60
4	H <sub>2</sub> O-EtOH (1:1)/100	4	10	K <sub>2</sub> CO <sub>3</sub>	75
5	EtOH/70	3	10	K <sub>2</sub> CO <sub>3</sub>	82
6	EtOH/90	2	10	K <sub>2</sub> CO <sub>3</sub>	95
7	CH <sub>3</sub> OH/60	3	10	K <sub>2</sub> CO <sub>3</sub>	80
8	Toluene/reflux	3.5	10	K <sub>2</sub> CO <sub>3</sub>	68
9	CH <sub>3</sub> CN/80	3.5	10	K <sub>2</sub> CO <sub>3</sub>	63
10	CHCl <sub>3</sub>	4	10	K <sub>2</sub> CO <sub>3</sub>	65
11	EtOH/90	3	15	K <sub>2</sub> CO <sub>3</sub>	75
12	EtOH/90	3	7	K <sub>2</sub> CO <sub>3</sub>	64
13	EtOH/90	2	10	Cs <sub>2</sub> CO <sub>3</sub>	85
14	EtOH/90	2.5	10	КОН	59
15	EtOH/90	2	10	NaOH	61

Table 1. Optimization of reaction conditions for Sonogashira coupling of iodobenzene with phenylacetylene<sup>a</sup>.

<sup>a</sup> Reactions were run in 5 ml of solvent with 1 mmol of iodobenzene, 1.2 mmol of phenylacetylene and 3 mmol of base. <sup>b</sup> Isolated yield.

Entry	Aryl halide	Terminal alkyne	Product	Time (h)	Yield <sup>b</sup> (%)	Ref.
1				2	95	[33]
2	O <sub>2</sub> N			2	97	[34]
3	MeO		MeO-	3.30	90	[35]
4	Me		Me-	2:30	91	[36]
5				5	80	[27]
6		OH	ОН	3:30	87	[27]
7	O <sub>2</sub> N	Он	0 <sub>2</sub> N	3	95	[27]
8	Me	ОН	-	4:30	83	[27]
9	MeO	ОН	МеО	4	85	[27]
10	I I	ОН	ОН	5	85	[27]

Table 2. Pd@Hal-2N-TCT-EDA catalyzed Sonogashira reaction of various halides with terminal alkynes<sup>a</sup>.



<sup>a</sup> Reaction conditions: aryl halide (1.0 mmol), terminal alkyne (1.2 mmol), Pd@Hal-2N-TCT-EDA (10 mol%) and K<sub>2</sub>CO<sub>3</sub> (3.0 mmol) in EtOH (5.0 mL) at 90 °C. <sup>b</sup> Isolated yield

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Entry	Catalyst/Catalyst precursor	Time (h)	Temp. (°C)	Yield (%)	Solvent	Base	Ref.
1	NiCl <sub>2</sub> ·6H <sub>2</sub> O	2	120	86	EG	NaOH	[40]
2	[Pd(dppe)(OTf) <sub>2</sub> ]	24	60	70	CH <sub>3</sub> OH	Cs <sub>2</sub> CO <sub>3</sub>	[41]
3	$[(P^{C})PdCl_2]^{b}$	6	130	81	DMF	K <sub>2</sub> CO <sub>3</sub>	[42]
4	$[(C^C)PdCl_2]^c$	4.5	130	87	DMF	K <sub>2</sub> CO <sub>3</sub>	[42]
5	$[(Pd\{k^2 - C, N) - (3 - (dimethylaminomethyl)indole)\}\mu - OAc)_2]$	3	120	85	DMF/H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	[43]
6	$PdCl_{2}{C(N(H)-NPh_{2})@N(H)Cy}(C,,NCy)$	2	80	95	EtOH	K <sub>2</sub> CO <sub>3</sub>	[44]
7	CuI/L <sup>d</sup>	6	145	90	DMF	K <sub>2</sub> CO <sub>3</sub>	[45]
8	[N-benzyl DABCO] <sup>+</sup> [Cu <sub>4</sub> Cl <sub>5</sub> ] <sup>-</sup>	3	135	55	DMF	K <sub>2</sub> CO <sub>3</sub>	[46]
9	Cu(OAc) <sub>2</sub>	24	140	65	Et <sub>3</sub> N	Et <sub>3</sub> N	[47]
10	Et <sub>2</sub> Zn/DMEDA	48	125	54	Dioxane	K <sub>3</sub> PO <sub>4</sub>	[48]
11	Pd@Hal-2N-TCT-EDA	2	75	95	EtOH	K <sub>2</sub> CO <sub>3</sub>	This work

Table 3. Comparison of the catalytic activity of Pd@Hal-2N-TCT-EDA with some other catalysts<sup>a</sup>.

<sup>a</sup> Reaction of iodobenzene with phenylacetylene. <sup>b</sup> Five-membered palladacycle. <sup>c</sup> Seven-membered analogs.  ${}^{d}N,N$  -dibenzyl BINAM.

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Scheme 1. Sonogashira coupling reaction.

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Figure 1. The schematic route for the preparation of Pd@Hal-2N-TCT-EDA catalyst.



Figure 2. TEM images of Pd@Hal-2N-TCT-EDA.



Figure 3. The FTIR spectra of Hal, Hal-2N, Hal-2N-TCT-EDA and Pd@Hal-2N-EDA.

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Figure 4. The TGA analysis of pristine Hal, Hal-2N, Hal-2N-TCT and Pd@Hal-2N-TCT-EDA.

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Figure 5. The XRD pattern of Pd@Hal-2N-TCT-EDA and pristine Hal.

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Figure 7. Time-conversion profile for Sonogashira coupling reaction of a) iodobenzene and phenylacetylene and b) chlorobenzene and phenylacetylene in the presence of Pd@Hal-2N-TCT-EDA under optimum reaction conditions.

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Figure 8. Reusability of the Pd@Hal-2N-TCT-EDA (a), Pd@Hal-2N-TCT (b) and Pd@Hal-2N. (c) catalysts for Sonogashira coupling.

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Figure 9. FTIR spectra of (a) fresh Pd@Hal-2N-TCT-EDA and (b) recycled catalyst.

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