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PII: DOI: Reference:	S0040-4039(17)30588-9 http://dx.doi.org/10.1016/j.tetlet.2017.05.017 TETL 48910
To appear in:	Tetrahedron Letters
Received Date:	16 February 2017
Revised Date:	20 April 2017
Accepted Date:	8 May 2017



Please cite this article as: Kim, S., Cho, H-J., Shin, D-S., Lee, S-M., Recyclable and eco-friendly Pd-complexed graphene oxide/*N*-heterocyclic carbene catalyst for various coupling reactions in aqueous phase, *Tetrahedron Letters* (2017), doi: http://dx.doi.org/10.1016/j.tetlet.2017.05.017

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# Recyclable and eco-friendly Pd-complexed graphene oxide/*N*-heterocyclic carbene catalyst for various coupling reactions in aqueous phase

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#### ARTICLE INFO

Article history: Received Received in revised form Accepted Available online

Keywords: Heterogeneous catalyst Graphene oxide N-heterocyclic carbene Palladium C-C cross coupling

#### ABSTRACT

In this study, we report recyclable Pd-complexed graphene oxide (GO) catalysts with a bulky Nheterocyclic carbene (NHC) ligand (GO/NHC-Pd) for various cross-coupling reactions in the aqueous phase. To prepare GO/NHC-Pd, the NHC precursor and a trimethoxy-silane linker were combined on the GO surface *via* condensation, followed by the Pd chelation over GO/NHC. The GO-based catalysts were applied to three types of C–C cross-coupling reactions including Suzuki, Heck and Sonogashira reactions in the aqueous phase, to evaluate their catalytic performance. The reusability of the catalysts was tested by performing five consequent crosscoupling reactions.

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Graphene oxide (GO) is composed of complete honeycomb lattices with sp<sup>3</sup> and sp<sup>2</sup> hybridized bonds. Apart from its large surface area, GO has hydrophilic properties owing to the presence of functional groups such as epoxy, hydroxyl, and carboxyl groups derived from oxidative preparation methods.<sup>1</sup> Controlling the degree of oxidation of GO or its coordination with metals can result in GO composites with a wide range of applications, e.g., in electrodes, fuel cell catalysts, and catalysts for chemical syntheses and so on.<sup>2</sup>

*N*-heterocyclic carbene (NHC) ligand has been widely studied because of its prominent nucleophilicity compared with some phosphines as well as thermal and chemical stabilities originating from the nature of the carbine–metal bond.<sup>3</sup> Over the last decades, NHC-chelated transition metals have been used in several types of homogeneous catalytic reactions, e.g., olefin metathesis and polymerization, hydrosilylation and carbon–carbon coupling reactions over NHC-Ru, NHC-Rh or NHC-Pt and NHC-Pd catalysts.<sup>4</sup> Electron bulkiness and sterically stability have been known to improve binding strength between NHC and transition metals, thereby leading to a significant increase in the catalytic efficiencies.<sup>5</sup> Moreover, the development of novel NHC ligands for homogeneous reactions and suitable solid supports for heterogeneous processes has enabled aqueous reactions by virtue of the noticeable performance of the active species.<sup>6</sup>

As mentioned above, NHC-Pd complexes have been applied as either homogeneous or heterogeneous catalysts in several C–C cross-coupling reactions such as Suzuki, Heck, Sonogashira, and Stille reactions. Owing to the disadvantages of using homogeneous catalysts, solid or polymer-based NHC-Pd catalysts with a number of advantages, e.g., easy separation, recycling, efficient production cost, and utilization of ecofriendly media, have been demonstrated by numerous research groups.<sup>7</sup> GO-supported NHC-Pd catalysts were reported for Suzuki coupling reactions using aqueous-organic mixed solvent system such as ethanol/water (1:1)<sup>8</sup> and DMF/water (1:1)<sup>9</sup>.

Mesoporous polystyrene beads are one of the most famous solid supports combined with NHC. This support is typically used with NHC-Pd *via* stable immobilization of ionic liquids, thereby affording excellent catalytic stability and large surface area.<sup>10</sup> In 2009, Fihri and coworkers developed a silica-based NHC-Pd catalyst with high catalytic activity and good stability.<sup>11</sup> Additionally, graphite or GO-supported Pd complexes have been shown to exhibit the excellent catalytic activity and stability during cross-coupling reactions.<sup>12</sup> Moreover, NHCs derived from bulky ionic liquids have been shown to exhibit good recyclability in heterogeneous catalytic systems.<sup>9</sup> GO has been covalently bonded with NHC-Pd *via* silylation and used as a catalyst in several cross-coupling reactions.<sup>13</sup>

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#### Tetrahedron

In this study, we presented the water-compatible and recyclable Pd-complexed GO catalysts with bulky NHC ligand (GO/NHC-Pd) for several kinds of cross-coupling reaction in water. Unlike the previous reports, our purpose is to perform Suzuki coupling reaction as well as Heck and Sonogashira coupling reactions in water as a sole solvent. To prepare GO/NHC-Pd, NHC precursor with trimethoxy-silane linker was combined on the GO surface by condensation reaction, and followed by the Pd chelation with GO/NHC. The GO/NHC-Pd catalysts were applied to Suzuki, Heck and Sonogashira carboncarbon cross-coupling reactions in water to evaluate the catalytic performance. Finally, GO/NHC-Pd catalysts were applied in the recycling test to evaluate their reusability efficiency.

GO was prepared from graphite by a modified Hummers method and characterized by Raman spectroscopy. As shown in Figure 1, a sharp and strong G band of graphite was clearly observed at 1581 cm<sup>-1</sup>. However, the D band at 1350 cm<sup>-1</sup> associated with the edge distortion and destruction of the structural symmetry was hardly detected in the graphite sample. The D/G band intensity ratio ( $I_D/I_G$ ) of graphite was 0.23, while GO showed a broad and strong D band with a higher ratio (0.89).<sup>14</sup> Further modification of GO to GO/NHC and GO/NHC-Pd displayed  $I_D/I_G$  intensity ratios of 0.94 and 0.95, respectively. These results indicate that the chelation of Pd ions did not change the band intensity ratio as much as the silanization step.



Figure 1. Raman spectra of graphite, GO, GO/NHC and GO/NHC-Pd.

Scheme 1 describes the synthetic procedure to prepare the GO/NHC-Pd catalysts. First, GO was coupled with the 1-(2,6diidopropylphenyl)-3-(propyltrimethoxysilyl)imidazol-2-ylidene precursor in a THF solution by refluxing under a N<sub>2</sub> atmosphere. precursor. Thereafter.  $Pd(OAc)_2$ , the Pd-ion was stoichiometrically chelated with NHC-silane imidazolium in the deprotonated structure of carbene. Each step of the GO/NHC-Pd synthesis was confirmed by Fourier transform infrared spectroscopy (FT-IR) analyses (Figure 2). Initially, GO showed strong absorbance bands originating from the oxidation of graphite including C=O, C-O, and O-H stretching vibrations at 1692, 1082, and 3432 cm<sup>-1</sup>, respectively. Upon coupling the NHS-silane with GO, the absorbance bands corresponding to the imidazolium ring vibration (C-H bending) appeared at 779 and 1250 cm<sup>-1</sup>, thereby indicating that NHS-silane was successfully combined with the GO template.<sup>15</sup> The chelation of Pd(II) ion with GO/NHC was also characterized by FT-IR, as previously reported.<sup>13</sup> An absorbance band from C=C stretching in the Pd(II)-coordinated imidazole group was clearly observed at 1562 cm<sup>-1.16</sup> Moreover, absorption bands from C2–H and (–C=)C–H bendings in the Pd(II)-coordinated imidazole rings appeared at 1687 and 1123 cm<sup>-1</sup>, respectively. Inductively coupled plasma atomic emission spectroscopy (ICP-OES) analysis revealed that the palladium content of GO/NHC-Pd was calculated to be 0.55 mmol Pd /g catalyst.







Figure 2. FT–IR spectra of GO (red), GO/NHC (black line), and the GO/NHC-Pd catalyst (blue line).

One may concern the coordination efficiency of Pd(II) ions with imidazolium rings. If Pd(II) ions were reduced prior to a stable chelation with NHC ligands, their nanoparticles can be deposited on the GO/NHC surface. Thus, the generation of Pd nanoparticles was critically evaluated by scanning electron microscopy (SEM) analyses. For this purpose, the Pd precursors were applied to GO without NHC ligands under the same synthetic conditions as those used for GO/NHC-Pd. As seen from the SEM images, a large number of Pd nanoparticles were observed on the GO-Pd surface unlike GO/NHC-Pd (Figure S1 (a),(b), respectively). These findings indicate that Pd(II) ions were thoroughly chelated over the NHC ligands on the GO surface, thereby avoiding the formation of Pd nanoparticles.<sup>13, 17</sup> From the energy-dispersive X-ray spectroscopy (EDS) mapping results, we could observe the reacting materials incorporated into the GO complexes after each reaction step (Figure S2).

As another characterization of GO/NHS-Pd catalysts, the thermogravimetric analysis (TGA) was performed using GO, GO-NHC, and GO/NHC-Pd (Figure S3). In the case of GO, 16% weight loss at ca. 110 °C was initially observed due to the loss of

physisorbed water. Subsequently, the thermal elimination of labile oxygen containing hydroxyl or epoxy groups led to 30% of weight loss at ca. 200-250°C.<sup>18</sup> The further weight loss at 500°C indicated a rapid decomposition of oxygen species.<sup>19</sup> On the other hand, a smaller elimination of water and oxygen containing group was observed after the trimethoxysilane linker was combined to GO by condensation reaction. The breakage of siloxane groups led a degradation step between 300-400°C of GO/NHC and GO/NHC-Pd.<sup>20</sup>

Before applying the GO/NHS-Pd catalysts to various Suzuki cross-coupling reactions, inorganic bases were examined as a cocatalyst by coupling 4-iodoanisole and phenylboronic acid. Inorganic bases are generally known to be more suitable for cross-coupling reactions in the aqueous phase than organic bases.<sup>21</sup> The coupling reactions were performed at 100 °C for 6 h. As shown in Table S1, most of the carbonates (Cs<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>) and KOH showed GC yields between 70% and 80%, whereas K<sub>3</sub>PO<sub>4</sub> showed the poorest coupling yield (62.3%). However, Na<sub>3</sub>PO<sub>4</sub> showed the best Suzuki cross-coupling yield with 4-methoxydiphenyl (83.3%). Thus, Na<sub>3</sub>PO<sub>4</sub> was chosen as a base for the following Suzuki cross-coupling reactions in the aqueous phase.

Based on the optimized base, various aryl iodides or 2iodothiophene were coupled with phenylboronic acid over the GO/NHC-Pd catalyst (Table 1). In the aqueous phase, phenyl iodide showed a high coupling yield of ca. 91.6% at 100 °C for 6 h (entry 4), while phenyl derivatives bearing an electron donating group, e.g., 4-iodoanisole, showed poorer yields than phenyl iodide under similar conditions (entries 1 and 2). However, acetophenyl iodide was perfectly cross-coupled with phenylboronic acid owing to the electronic deficiency effect in the phenyl ring caused by the electron-withdrawing group (99.9%, entry 3). The coupling compounds of 2-iodothiophene and 4-iodotoluene were obtained in moderate GC yields of 78.2% and 70.5%, respectively. As an example of bromobenzene, when 4-bromoanisole was coupled with phenylboronic acid in the sole water solvent at 100 °C for 12 h, the GC coupling yield was 21.2%. However, the yield increased to 88.0% when the ratio of the solvents was DMF/water (1:3).

Table 1. Suzuki cross-coupling reactions catalyzed by the GO/NHC-Pd catalyst.<sup>a</sup>





<sup>b</sup> GC yields.

In addition to Suzuki cross-coupling, Heck and Sonogashira cross-coupling reactions using Pd catalysts were tested with aryl halides and alkynes or alkenes to afford more diverse compounds.<sup>22</sup> To evaluate the feasibility of the GO/NHC-Pd catalyst for Heck cross-coupling reactions, a base screening was performed in the aqueous phase, as demonstrated Suzuki coupling in the previous section (120 °C, 12 h). As shown in Table S2, three types of representative inorganic bases containing different anions were used as an appropriate model reaction for the coupling between 4-iodoanisole and styrene; K<sub>2</sub>CO<sub>3</sub> (a carbonate) showed the highest yield (ca. 92%) in comparison to a phosphate (entry 1) and hydroxide (entry 2).<sup>23</sup> Thus, several Heck cross-coupling reactions between styrene and aryl iodide derivatives were demonstrated using the GO/NHC-Pd catalyst in the presence of  $K_2CO_3$  as an optimum base in the aqueous phase. In Table 2, 4-Iodoacetophenone bearing an electron donating group showed the maximum GC yield (>97%, entry 3). Moreover, 1-nitro-4-iodobenzene and 4-iodoanisole afforded high efficiencies (92.8% and 91.6%, entries 2 and 4, respectively), while iodobenzene showed a significantly lower yield (55.0%).

Table 2. Heck cross-coupling reactions catalyzed by the GO/NHC-Pd catalyst.<sup>a</sup>





4

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#### Tetrahedron

<sup>a</sup> Conditions: aryl iodide (0.114 mmol), styrene (0.137 mmol), the GO/NHC-Pd catalyst (1 mol%), and  $K_2CO_3$  (0.274 mmol) in water (2 mL) at 120 °C for 12 h.

<sup>b</sup> GC yields.

The GO/NHC-Pd catalyst was used for performing the Sonogashira cross-coupling reactions in the aqueous phase. Piperidine, a well-known effective organic amine for Sonogashira coupling, was used without additional base screening, while CuI was used as a co-catalyst to react with terminal alkynes to form Cu(I) acetylide species, which then undergoes oxidative addition with aryl halide.<sup>24</sup> As shown in Table 3, various aryl or heterocyclic halides were cross-coupled with acetvlene in the aqueous phase. Unexpectedly, most of the substrates provided moderate GC yields (55.3%-69.9%) despite the functionalities of the aryl halides. Thus, the GO/NHC-Pd catalyst was less effective in Sonogashira coupling compared with the other two cross-coupling reactions. These results suggest that homocoupling reactions between aryl halides are rapid in water that the functional groups (related to the electron density of the aryl halide) hardly influence the efficiency of the GO/NHS-Pd catalyst.

Table 3. Sonogashira cross-coupling reactions catalyzed by GO/NHC-Pd.<sup>a</sup>



<sup>a</sup> Conditions: aryl iodine and heterocyclic halide (0.114 mmol), phenylacetylene (0.171 mmol), the GO/NHC-Pd catalyst (1 mol%),

piperidine (0.274 mmol) and CuI (0.001 mmol) in water (2 mL) at 80  $^{\circ}\mathrm{C}$  and 12 h.

#### <sup>b</sup> GC yields.

Heterogeneous Pd catalysts have been actively developed mainly because they exhibit outstanding recyclability without causing a significant loss in efficiency. Thus, the GO/NHC-Pd catalysts were reused four times for the Suzuki coupling between 4-iodoacetophenone and phenylboronic acid and Sonogashira coupling between 2-idodothiophene and phenyl acetylene after the first test. As shown in Figure 3, the initial Suzuki coupling vield was 99.9%, which was effectively maintained (>90%) after the fourth recycling test. However, this yield decreased to 79% after the fifth test, which might be associated with the deactivation or dissociation of NHC-Pd complex form the GO surface. Similarly, the efficiency of the Sonogashira reaction remained nearly constant at the initial yield value (69.9%) during the first four recycling tests, followed by a sharp drop to 50% for subsequent cycles. As seen from the transmission electron microscopy (TEM) images before and after 5 cycles of crosscoupling reaction, we could conclude that there was no significant geometric difference even though some salts were observed (Figure S4). From X-ray photoelectron spectroscopy (XPS) results, two single Pd peaks corresponding to NHC-Pd(II) were observed from the fresh GO/NHC-Pd (Figure S5). Also, we could observe Pd metal peaks after 3 cycles of coupling reaction.<sup>25</sup> Although the recyclability test of GO/NHC-Pd is proceeded until three times, the substantial area of Pd(II) peaks (Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub>) of NHC-Pd(II) was maintained. Our finding indicates that our heterogeneous GO/NHC-Pd catalyst is suitable for performing 4 or 5 cycles of cross-coupling reactions.



Figure 3. Recycling efficiencies of the GO/NHC-Pd catalysts for the Suzuki and Sonogashira cross-coupling reactions.

In summary, we prepared a recyclable GO/NHC-Pd catalyst suitable for the Suzuki, Heck, and Sonogashira cross-coupling reactions in the aqueous phase. Every synthetic step was confirmed by FT–IR and SEM analyses, including the identification of Pd(II)-ion chelation on GO/NHC without the formation of Pd nanoparticles. The optimized inorganic bases for the Suzuki and Heck cross-coupling reactions were  $Na_3PO_3$  and  $K_2CO_3$  at each specific reaction condition, respectively. Various aryl iodide substrates were cross-coupled in the aqueous phase, with phenylboronic acid for the Suzuki reactions and styrene for the Heck reactions resulting in GC yields of 86%~99.9% and 55%~97%, respectively. Moreover, the GO/NHC-Pd catalyst showed relatively moderate yields of 55.4%~69.9% for coupling reactions between several phenyl iodides and phenyl acetylene

with piperidine as a co-catalyst. Finally, the GO/NHC-Pd catalysts were recycled during the Suzuki and Heck reactions, and their performance was mostly maintained for four consecutive cycles. We believe that this GO/NHC-Pd catalyst can be used in further eco-friendly applications to produce noble pharmaceuticals.

#### Acknowledgments

This work was supported by the Ministry of Trade, Industry & Energy (MOTIE) and Korea Institute for Advancement of Technology (KIAT) through Encouragement Program for The Industries of Economic Cooperation Region (R0004027), the Ministry of Science, ICT & Future Planning and National Research Foundation of Korea through Basic Science Research Program (NRF-2014R1A1A1006711) and 2014 Research Grant from Kangwon National University (C1010942-01-01).

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#### **Supplementary Material**

Supplementary material is available.

Tetrahedron

### **Graphical Abstract**



### Highlight

- Recyclable Pd-complexed graphene oxide (GO) catalysts were prepared.
- Cross-coupling reactions were performed in the aqueous phase.

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