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### Highlights

- 1. We propose a strategy for applications ranging from the fabrication to the use.
- 2. DMF could play the multiple role during the solvothermal process.
- 3. Palladium particles could be tuned by the solvothermal temperture.
- 4. A new protocol for a ligand- and CO-free aminocarbonylation was demonstrated.
- 5. SRGO-Pd catalysts demonstrated excellent catalytic activity and recyclability.

# *N*, *N*-dimethylformamide solvothermal strategy: from fabrication of palladium nanoparticles supported on reduced graphene oxide nanosheets to their application in catalytic aminocarbonylation reactions

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# *N*, *N*-dimethylformamide solvothermal strategy: from fabrication of palladium nanoparticles supported on reduced graphene oxide nanosheets to their application in catalytic aminocarbonylation reactions

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ABSTRACT: A facile *N*, *N*-dimethylformamide (DMF) solvothermal strategy has been developed to fabricate palladium nanoparticles supported on reduced graphene oxide nanosheets (SRGO-Pd), which efficiently catalyze the aminocarbonylation of aryl halides. The palladium nanoparticles were uniformly anchored on the reduced graphene oxide nanosheets by a one-step DMF solvothermal approach. During the process, the palladium particles on the reduced graphene oxide nanosheets were tuned by the solvothermal temperture. DMF did not only play the role of the reductant for graphite oxide and Pd<sup>2+</sup>, but also restrained the aggregation of the graphene sheets and stablized the palladium nanoparticles. Under DMF solvothermal conditions, SRGO-Pd catalysts demonstrated an excellent catalytic activity and good recyclability for the aminocarbonylation reaction of aryl halides without using carbon monoxide and any other additive. The SRGO-Pd catalyst could be recycled at least 8 times with sustained activity. Such a strategy represents a promising route for applications ranging from the fabrication of graphene-supported materials to the use as catalysts.

*Keywords:* Pd nanoparticles; Graphene; Aminocarbonylation reactons; Catalysis; Solvothermal method.

#### **1. Introduction**

Various fabrication strategies have been developed for preparing palladium nanoparticles as heterogeneous or semi-heterogeneous catalysts for numerous catalytic reactions. [1-6] The high dispersion and precise size controlling are required to improve the catalytic activity and reduce the consumption of the catalysts. A high dispersion and precise size control are required to improve the catalytic activity and reduce the consumption of the catalysts. The aggregation of bare palladium nanoparticles, unfortunately, prohibits a fine tailoring of the morphology and catalytic activity of the corresponding particles. For this reason, many attempts have been made to immobilize or stabilize Pd nanoparticles on a wide variety of supports. [7-11]

Graphene is an attractive supporting material for catalyst loading owing to its fast 2D electron-transfer kinetics, large surface area, and high mechanical, thermal and chemical stability. Several graphene-based palladium nanoparticles have been used as catalysts with high activity and selectivity for carbon-carbon bond forming reactions. [12-14] However, there are still a number of limitations to the practical application of most graphene-supported metal nanocatalysts. First, the strong  $\pi$ – $\pi$  stacking interactions between graphene nanosheets can lead to serious aggregation and restacking, which inevitably blocks active catalytic sites, and thus significantly hampers the catalytic activity. [15, 16] Second, owing to their high surface energy, metal nanoparticles are typically unstable and tend to sinter into larger species, especially under harsh reaction conditions such as at the high temperatures required for many catalytic reactions and subsequent detoxification processes. This sintering results in a dramatic decrease in catalytic activity. To overcome these limitations, the dispersibility and stability of graphene-supported metal nanocatalysts must be improved by developing novel

methods in order to securely anchor palladium nanoparticles onto graphene supports. More recently, efforts have been made to retain the structure of the graphene network, such as keeping the graphene solvated by the vacuum filtration method [17], thus developing a range of 3D graphene-based composites by spray methods [18] and preparing graphene-nanosheet-supported metal nanoparticles covered by mesoporous silica layers. [19]

Thanks to the unique features such as a very high self-generated pressure inside the sealed reaction vessel and containment of volatile products, the solvothermal approach [20] has in recent decades become a well-known and powerful technique for fabricating inorganic solid materials in which the solvent plays a crucial role. DMF is commonly used as a polar aprotic solvent with a high boiling point in the preparation of metastable catalysts via the solvothermal approach, either separately or cooperatively, taking advantages of the easy operation and the fact that it is environmentally benign and low-cost. [21]

The important role played by DMF as a solvent and reaction medium has motivated studies related to its redox activity and stability. [21-24] Recently, some researchers found that GO dispersion could be directly reduced to graphene sheet dispersion in DMF. [22, 25, 26] There are, however, only few reports on the direct preparation of graphene-based metal nanoparticles by the simple solvothermal reduction method. As a consequence, the DMF solvothermal approach is highly desirable for catalyst loading to fabricate graphene-supported Pd nanoparticle catalysts.

This work presents how the DMF solvothermal approach can be successfully used for fabricating Pd nanoparticles supported on reduced graphene oxide nanosheets (SRGO-Pd). Thanks to it, one can effectively avoid the close restacking of graphene nanosheets. The obtained catalyst maintains an excellent dispersing stability in DMF. The solvothermal

method offers significant advantages for the preparation since no reducing agents or stabilizing agents are required. More importantly, based on this DMF solvothermal situation , SRGO-Pd efficiently catalyzes the aminocarbonylation of aryl halides without the need for any ligand or base and can be reused whilst maintaining the inherent catalytic activity. The critical advance is the use of DMF as a resource of carbon monoxide and as an amide source. It acts both as a solvent and as a catalyst stabilizer, thereby facilitating an otherwise challenging transformation. To the best of our knowledge, this is the first report on applications of Pd nanoparticles supported on graphene to catalyze aminocarbonylation reactions.

### The preferred position for Scheme 1.

#### 2. Experimental

## 2.1. Fabrication of SRGO-Pd catalyst under DMF solvothermal conditions

In the experiments, GO was prepared by the oxidation of high-purity graphite powder (99.9999%, 200 mesh) with H<sub>2</sub>SO<sub>4</sub>/KMnO<sub>4</sub> according to the method of Hummers and Offeman [27]. After repeated washing of the resulting yellowish-brown cake with hot water, the powder was dried at room temperature under vacuum overnight. For the preparation of SRGO-Pd: 40 mg of the dried GO was sonicated in DMF until a homogeneous yellow dispersion was obtained. The solution was transferred to an autoclave after adding an appropriate amount of palladium acetate and heated at a certain temperature for 6 h. The SRGO-Pd were separated by using an Eppendorf 5804 centrifuge operated at 8000 rpm for 15 min and dried overnight under vacuum. The same method was also used for the preparation of SRGO.

# 2.2. General procedure for the aminocarbonylation of aryl halides under DMF solvothermal conditions

SRGO-Pd200 was sonicated in DMF until a homogeneous yellow dispersion was obtained. Aryl halides (2 mmol) was added to the reaction mixture with stirring over a period of 15 min. The reaction mixture was transferred to an autoclave and heated at 200°C for 6 h. After completion, the reaction mixture was cooled to room temperature and filtered. The filtrate was poured into a saturated solution of NaHCO<sub>3</sub>. The aqueous layer was then extracted with ethyl acetate. The combined organic layers were dried over MgSO<sub>4</sub> and the solvents were removed in vacuo to afford the crude product which was purified by column chromatography using petroleum ether/ethyl acetate as eluent. The same procedure was applied to the aryl halides.

#### 2.3. Procedure for recycling the catalysts

The catalyst obtained after filtration was washed with DMF to remove any organic impurities. The resulting catalyst was dried in oven at 50°C for 6 h and used for the next cycle. The catalyst was dissolved in DMF and sonicated until a homogeneous yellow dispersion was obtained. Iodobenzene was then added; The reaction was transferred to an autoclave and heated at 200°C for 6 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and filtered. The Pd nanoparticle catalyst was then directly transferred to another Teflon-lined stainless-steel autoclave along with fresh reagents for the next run. This procedure was repeated for every run, and the percent conversion of product was determined by the means of GC-MS spectroscopy.

#### 3. Results and discussion

#### 3.1. Fabrication of homogeneous SRGO-Pd dispersion via the DMF solvothermal approach

The fabrication strategy for preparing SRGO-Pd is shown in **Scheme 1** (for the detailed experimental steps, please see the Experimental Section). A simple solvothermal process was employed for preparing SRGO-Pd through a heated DMF reduction of GO and palladium acetate in a sealed Teflon-lined stainless-steel autoclave at a certain temperature. A homogenous SRGO-Pd dispersion in DMF was obtained after several hours. Different temperatures, i.e., 160, 180, and 200°C, were used to prepare SRGO-Pd dispersions, and these homogeneous dispersions were denoted SRGO-Pd160, SRGO-Pd180, and SRGO-Pd200, respectively.

As shown in **Fig. S1**, the color of the dispersion changed from a yellowish brown (**Fig. S1(A)**) into deep black after the solvothermal reduction (**Fig. S1(B)**, (**C**), (**D**)). Furthermore, an intense odor resembling that of an amine could was given off from the SRGO-Pd dispersions. To our surprise , the as-prepared SRGO-Pd dispersion in DMF was very stable and did not aggregate, even after more than 1 month.

Meanwhile, solvothermal reduction of GO and palladium acetate was also carried out in other solvents, such as methanol, ethanol, THF, DMSO, and ethylene glycol. However, in these cases, no stable homogeneous dispersions could be obtained. Therefore, the DMF solvent played an important role in the preparation of homogeneous dispersions of SRGO-Pd in the solvothermal reduction process.

#### The preferred position for Fig. 1.

**Fig. 1** (**A-C**) represents the TEM micrographs of the SRGO-Pd catalyst prepared at three solvothermal temperatures. Wrinkles of SRGO-Pd, a characteristic feature of the graphene sheets, can be observed. As shown in **Fig. 1** (**A-C**), the individual Pd nanoparticles were well separated from each other and nicely spread out on the surface of the graphene sheets. In

contrast, Pd particles prepared in the control experiments without addition of GO at 180 °C tended to aggregate (**Fig. 1(D**)). The results thus prove that graphene has a potential for regulating growth processes of Pd nanoparticles. The good distribution of Pd nanoparticles on the graphene sheets guaranteed efficient catalytic properties of SRGO-Pd. The size of the Pd nanoparticles increased with the temperature, indicating that the solvothermal temperature could be very useful for tuning the size and dispersion of the Pd nanoparticles on graphene. Morphology of the catalysts was also examined by SEM. From **Fig. S2(a)**, an SEM image of the graphene oxide shows GO nanosheets are soft and can easily be imbedded small nanoparticles. In contrast to **Fig. S2a** in which any smaller particulate is not detected, many round-shaped Pd nanoparticles, which are decorated on some graphene sheets, can be clearly observed in the SEM image of SRGO-Pd (**Fig. S2(b-d**)). The palladium content of the obtained SRGO-Pd amounted to 354 ug mg<sup>-1</sup> as verified by ICP-MS. The obtained catalysts are listed in **Table S3**.

#### The preferred position for Fig. 2.

**Fig. 2** displays the XRD patterns of the initial graphite powder, the prepared GO, the SRGO and SRGO-Pd samples obtained by the DMF solvothermal method. The initial graphite powder showed the typical sharp diffraction peak at  $2\theta$ =26.6° with the corresponding d-spacing of 3.34 Å. The GO sample presented no diffraction peaks from the parental graphite material and only a new broad peak at  $2\theta$ =11.7° with a d-spacing of 7.56 Å could be observed. This suggested that the distance between the carbon sheets had increased due to the insertion of interplanar oxygen functional groups. [28-30] After performing the solvothermal process on the GO, the XRD patterns of the resultant graphene displayed the disappearance of the 11.7° peak confirming the reduction of the GO sheets. A similar XRD spectrum was observed

for the SRGO-Pd sample prepared by the simultaneous reduction of GO and palladium acetate using the solvothermal method. In the X-ray diffraction pattern of SRGO-Pd, there were three main peaks at scattering angles of 39.9, 46.5 and 68.0, corresponding to the crystalline planes of the face-centered cubic (fcc) structured palladium (JCPDS No. 46-1043), thus indicating that  $Pd^{2+}$  had been reduced to  $Pd^{0}$ .

The representative ATR-FTIR peaks (**Fig. S4**) of the oxygen-containing functional groups of GO, which include the bands at 1055 cm<sup>-1</sup> (C-O stretching vibrations), 1393 cm<sup>-1</sup> (tertiary C-OH groups stretching), and 1726 cm<sup>-1</sup> (C=O stretching of COOH groups situated at the edges of the GO sheets), were absent in the ATR-FTIR spectrum of SRGO-Pd synthesized from GO, which indicates the reduction of these functional groups. A new absorption band at 1570 cm<sup>-1</sup> attributed to the skeletal vibration of the graphene sheets appeared in the ATR-FTIR spectrum of SRGO-Pd.[20]

#### The preferred position for Fig. 3.

In the survey spectrum (**Fig. 3A**), we can observe that the intensity of O1s decreased significantly from GO to SRGO-Pd200, indicating a considerable deoxygenation by the solvothermal process. **Table S5** lists the atomic composition of GO and SRGO-Pd200 obtained by XPS. From the data in **Table S5**, it can be found that the C/O atomic ratio increased from 2.36 for GO to 6.20 for SRGO-Pd200, which is comparable to the C/O ratio of chemically reduced GO. [29, 31, 32] The XPS spectrum of GO in the C1s region (**Fig. 3B**) clearly indicates a considerable degree of oxidation of the carbon atoms of the different functional groups: the carbon atoms in C=C (284.8 eV), the carbon atoms in C–O (285.7 eV), the epoxy carbon atoms (286.9 eV), the carbonyl carbon atoms (287.7 eV), and the carboxyl carbon atoms (288.8 eV). [30, 33] After the solvothermal treatment, SRGO-Pd200 showed

only one predominant peak at 284.8 eV (**Fig. 3C**), which could be attributed to graphitic carbon systems. Moreover, the tail of this signal at a high binding energy indicated that a small amount of carbon atoms was still covalently bound with the oxygen remaining in the SRGO-Pd200 after the solvothermal treatment.

**Fig. 3D** displays the XPS spectra of the Pd-3d electron in the SRGO-Pd catalysts. The data show that Pd nanoparticles were present as Pd (0), which is consistent with the observed binding energies of 335.1 eV (Pd (0) 3d5/2) and 340.5 eV (Pd(0) 3d3/2). [33, 34]

Above all, SRGO-Pd was successfully and directly synthesized by a facile one-step DMF solvothermal reaction, where the nanomaterial fabrication and reduction of GO sheets to graphene sheets could occur simultaneously. This DMF solvothermal process opens up new avenues to one-pot fabrication of graphene-supported metal composites.

# 3.2. The key role of the N, N-dimethylformamide solvothermal in fabricating SRGO-Pd catalyst

In this work, the DMF solvothermal played an important role in the fabrication of SRGO-Pd catalysts. A solvothermal mechanism was proposed according to **Fig. 4**. Firstly , the reduction mechanism of GO and Pd<sup>2+</sup> in the above process may be the result of: 1) thermal reduction, which has been reported for the reduction of GO in other solvents at high temperature, and 2) the production of the reductant CO from DMF during the solvothermal process. It is well known that carbon monoxide is a strong reducing agent, which can efficiently remove oxygen from many compounds. [25, 35] Therefore, the reduction process consists of simultaneous thermal and chemical reduction.

Secondly, the stabilization mechanism might be the resultant derivative from DMF during the solvothermal process. In the solvothermal process, DMF can be hydrolyzed into

NH(CH<sub>3</sub>)<sub>2</sub> and CO (reaction formula in Fig. 4). Carbon monoxide can be confirmed by the in situ mass spectrometer. (Fig. S6) On the other hand, NH(CH<sub>3</sub>)<sub>2</sub> can be confirmed by the intense odor of amine given off by the dispersion after the reaction. As a result of protonation,  $NH(CH_3)_2$  becomes positively charged in the form of  $[NH_2(CH_3)_2]^+$  (reaction formula in Fig. 4). The XPS results show that there remained a small amount of carboxyl groups on the SRGO-Pd (Fig. 3C), and that  $[NH_2(CH_3)_2]^+$  could interact with the negatively charged –COO<sup>-</sup> on the edge of GO sheet driven by electrostatic interaction. With the alkyl groups modified on the edges of the SRGO-Pd sheets, the latter were stabilized, and their dispersibility enhanced. The existence of a nitrogen species was verified by XPS analysis for the N1s peak at 400 eV (Fig. 3a), and the increase at 285.7 eV was partially due to the C–N in the  $[NH_2(CH_3)_2]^+$  (Fig. **3c**). The *in-situ* produced  $[NH_2(CH_3)_2]^+$  acted as a stabilizer for the SRGO-Pd, wherefore, without any formed stabilizer in the dispersion of methanol, ethanol, THF, DMSO, and ethylene glycol, the carbon sheets aggregated together due to the  $\pi$ - $\pi$  interaction between the sheets. On the other hand, DMF molecules were efficient stabilizers of the metal nanoparticles. [21, 36]

Consequently, DMF could serve as a solvent, an endogenous reducing agent and a self-generated stabilizer during the solvothermal process.

#### The preferred position for Fig. 4.

# 3.3. Catalytic activity of SRGO-Pd toward aminocarbonylation during the N, N-dimethylformamide solvothermal approach

As mentioned, DMF is a much better solvent that others used and can be employed as a source of carbon monoxide and dimethylamine originating from its decomposition at boiling point. This observation has led to the use of DMF as a carbonylating agent.

In our experiment we investigated the catalytic activity of SRGO–Pd for the aminocarbonylation in DMF as the solvent under solvothermal conditions without any additive. In a model reaction, we employed iodobenzenes as the reactants with DMF as the solvent but were surprised to find that dimethylamide, rather than biphenyl, was the predominant product, formed in good yield after solvothermal treatment at 200 °C for 6 h (Scheme 1).

Control experiments under the open condition (the aminocarbonylation reaction of iodobenzene using DMF as the solvent) were performed with conventional thermal heating using 0.5 mol % of the catalyst. Here, only a small yield of 2% was observed after 6 h of refluxing in flasks at 160 °C. This result clearly demonstrated the effect of the solvothermal condition on increasing reaction rates by providing a direct and rapid heating source for aminocarbonylation. This observation is consistent with recent reports on the selective heating of the surfaces of heterogeneous catalysts and the formation of hot-spots by microwave irradiation which can lead to nonequilibrium local heating at the surface of the metal nanoparticle catalysts.[33, 37] Compared with the example reported by Kazushi Hosoi et al.[38] and Nasser Iranpoor et al.[39], a palladium-catalyzed coupling reaction of DMF with aryl halides could be successfully carried out in the absence of phosphoryl chloride to afford the corresponding tertiary amides in good yields.

#### The preferred position for Fig. 5.

To better understand the solvothermal approach, we performed experiments at four different temperatures, from 140 °C to 200 °C, bearing in mind that the boiling point of DMF is 153 °C. Moreover, we prolonged the reaction time to 6 h. As shown in **Fig. 5**, the yield increased with an increasing temperature. At 140 °C, very little product was formed, which

was due to the slow reaction rate at this low temperature. However, when the temperature was increased to 160 °C, the yield was 62%. According to the GC-MS analysis result, a small amount of biphenyl appeared, indicating that the side reaction could occur at 160 °C. Upon increasing the temperature to 180 °C, a yield of 82% was observed, and when further raising the temperature to 200 °C, the yield was nearly 100%. This demonstrates that the solvothermal approach can restrain side reactions at suitably high temperatures. We thus infer that the C–I bond of the substrate was activated, thus decreasing the reaction energy of the self-coupling reaction, which has the advantage of increasing the reaction rate of the desired reaction over that of the side reaction.

#### The preferred position for Table 1.

This finding encouraged us to study in more detail the scope and limitations of DMF as a potential carbon monoxide precursor for carbonylation reactions. A series of aryl halides were screened, and the results are presented in **Table 1**. The *in-situ* carbon monoxide generation methodology worked efficiently with iodobenzene and more electron-rich aryl iodides, whereas aminocarbonylation of electron-deficient aromatic systems failed. Although only a limited number of examples are presented here, we believe that the method will attract attention due to its experimental simplicity and the fact that no external carbon monoxide gas and ligand need to be added. It should serve as a convenient alternative to other existing methodologies for aminocarbonylation of aromatics, in particular for large-scale reactions.

#### The preferred position for Table 2.

 Table 2 illustrates the catalytic activity of the catalysts at different catalyst loadings for the

 aminocarbonylation reaction of iodobenzene under solvothermal conditions in the absence of

additives. To our great delight, SRGO–Pd showed a superior activity at lower concentrations. With 0.5 mol% loading, the catalysts displayed a nearly complete conversion (98%) of iodobenzene into the product. Similarly, when 0.05 mol% loading was used, the catalysts still worked effectively, giving rise to a conversion of 89% for SRGO–Pd. However, further reducing the concentrations provided some insight into the relative reactivity. With the lowest loading of 0.005 mol%, the reaction was completed after 6 h with SRGO–Pd, affording a yield of 50% of the product. These results demonstrate the remarkable catalytic activity of SRGO–Pd.

Although the real mechanism remains unclear at this stage, in agreement with previous studies on the catalytic aminocarbonylation reactions and our current observations, [8, 9, 38-45] the catalytic mechanism shown in **Scheme 2** can be proposed. It is well established that DMF decarbonylates under solvothermal heating conditions to yield carbon monoxide and dimethylamine without base. However, the present methodology is, to the best of our knowledge, the first example where the carbon monoxide is both liberated from the solvent and thereafter utilized in an efficient organic carbonylation procedure in the absence of base.

### The preferred position for Scheme 2.

The DMF solvent has been shown to be an excellent source of carbon monoxide and dimethylamine, with both gases serving as building blocks in the SRGO-Pd-catalyzed aryl amide synthesis, in the absence of a strong base under solvothermal conditions. Based on this, it can be concluded that the current SRGO-Pd nanoparticles under solvothermal DMF provide an efficient strategy for the aminocarbonylation of aryl halides.

#### 3.4. Recycling the SRGO-Pd catalysts

A significant practical application of heterogeneous catalysis lies in the ability to easily remove the catalyst from the reaction mixture and reuse it for subsequent reactions until the catalyst is sufficiently deactivated. Thus, the ability to recycle the SRGO–Pd catalysts was studied for the aminocarbonylation reaction of iodobenzene utilizing 0.5 mol% of these catalysts at 200 °C for 6 h under solvothermal conditons. After each reaction, the catalyst was recovered by simple washing with DMF and re-used in a subsequent run.

### The preferred position for Fig. 6.

As shown in **Fig. 6**, the results indicated that SRGO–Pd can be reused 8 times without significant loss in the catalytic activity. In order to address priority of the SRGO-Pd over other catalysts, control experiments (the aminocarbonylation reaction of iodobenzene using commercialized 10 wt% Pd/C, activated carbon/Pd and SRGO-Pd as the catalysts) were performed under solvothermal conditons. (**Fig. S7**) Analysis of the reaction mixture by ICP-MS after the 8th run also displayed a very low palladium leaching of 107 ppm. The results demonstrated that the DMF solvothermal approach could efficiently prevent leaching of Pd. TEM images of SRGO-Pd200 after 0 (a), 4 (b) and 8 (c) runs are shown in **Fig. S8**. As can be seen from **Fig. S8**, the size of Pd nanoparticles on the surface of the graphene sheets slightly increased with an increasing recycling time. However, well distributed Pd nanoparticles on the graphene sheets can still observed after eight runs. (**Fig. S8 (c)**) The results indicate that DMF plays an important role in improving the dispersibility of Pd. This is the reason why the SRGO-Pd catalyst could be recycled at least 8 times with sustained activity.

#### 4. Conclusions

In conclusion, we here propose a simple yet general DMF solvothermal strategy for applications ranging from the fabrication of palladium nanoparticle catalysts supported on reduced graphene nanosheets to the use as aminocarbonylation catalysts. Our experiments demonstrated that the prepared SRGO-Pd dispersions were stable for at least one month without any surfactant/polymer stabilization. In the process, the DMF played versatile roles: as a green reactive medium, a reductant and a stabilizer. DMF solvothermal hydrolysis reactions can take place under these conditions leading to the generation of aminocarbonylation products. A simple and highly efficient protocol for a ligand- and CO-free aminocarbonylation of aryl iodides or bromides catalyzed by SRGO-Pd catalyst in DMF under solvothermal conditions was thus demonstrated. The catalyst could be readily recovered and reused. We expect it to be widely used in applications of graphene-based catalyst preparation and coupling transformations.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at

http://dx.doi.org/.

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### Legends

- Scheme 1. Representation of SRGO-Pd catalyzed aminocarbonylation.
- Scheme 2. Proposed mechanism for SRGO-Pd catalyzed aminocarbonylation.
- Fig. 1. TEM images of SRGO-Pd160 (a), SRGO-Pd180 (b), SRGO-Pd200 (c), Pd200 without
- GO.
- Fig. 2. XRD patterns of graphite (A), GO (B), SRGO200 (C), and SRGO-Pd200 (D) samples.
- Fig. 3. (A) XPS survey spectrum of GO and SRGO-Pd, and XPS spectra of (B) C1s region of
- GO, (C) C1s region of SRGO-Pd and (D) Pd-3d electron of SRGO-Pd.
- Fig. 4. Mechanism of the formation of SRGO-Pd.
- Fig. 5. Effect of temperature on the reaction.
- Fig. 6. Recycling test for reactions.
- Table 1. SRGO-Pd-catalyzed aminocarbonylation of aryl halides<sup>a</sup>.
- Table 2. Effect of Pd loading on reaction



Scheme 1. Representation of SRGO-Pd catalyzed aminocarbonylation.



Scheme 2. Proposed mechanism for SRGO-Pd catalyzed aminocarbonylation.



Fig. 1. TEM images of SRGO-Pd160 (a), SRGO-Pd180 (b), SRGO-Pd200 (c), Pd200 without GO.



Fig. 2. XRD patterns of graphite (A), GO (B), SRGO200 (C), and SRGO-Pd200 (D) samples.



**Fig. 3.** (A) XPS survey spectrum of GO and SRGO-Pd, and XPS spectra of (B) C1s region of GO, (C) C1s region of SRGO-Pd and (D) Pd-3d electron of SRGO-Pd.



Fig. 4. Mechanism of the formation of SRGO-Pd.



Fig. 5. Effect of temperature on the reaction.







**Table 1.** SRGO-Pd-catalyzed aminocarbonylation of aryl halides<sup>a</sup>.

<sup>*a*</sup>Reaction conditions: aryl halides (2 mmol), SRGO–Pd (0.5 mol%, 3 mg), DMF (10 mL), solvothermal heating at 200 °C for 6 h. <sup>*b*</sup>Isolated yield (%)

Table	2.	Effect	of Pd	loading	on	reaction <sup>a</sup>
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	O ↓ + HC−N STG-Pd	O −C−N
Entry	Pd loading (mol %)	Yield <sup>b</sup> (%)
1	0.005	50
2	0.05	89
3	0.2	95
4	0.5	98

<sup>a</sup>Reaction conditions: Iodobenzene (2 mmol), DMF (10 mL), SRGO–Pd (0.5 mol%, 3 mg), solvothermal heating at 200 °C for 6 h. <sup>b</sup>Yields based on GC analysis.