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Heterogeneous Suzuki–Miyaura coupling of heteroaryl ester *via* chemoselective C(acyl)–O bond activation†

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A site-selective supported palladium nanoparticle catalyzed Suzuki–Miyaura cross-coupling reaction with heteroaryl esters and arylboronic acids as coupling partners was developed. This methodology provides a heterogeneous catalytic route for aryl ketone formation *via* C(acyl)–O bond activation of esters by successful suppression of the undesired decarbonylation phenomenon. The catalyst can be reused and shows high activity after eight cycles. The XPS analysis of the catalyst before and after the reaction suggested that the reaction might be performed *via* a Pd⁰/Pd^{II} catalytic cycle that began with Pd⁰.

Introduction

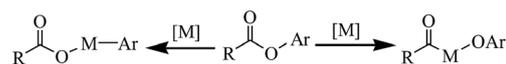
Transition metal-catalyzed Suzuki–Miyaura reactions have emerged as a powerful and indispensable tool to forge linkages between carbon atoms because of the inherent advantages of organoboron reagents.¹ Conventionally, halocarbon electrophiles are the most applied coupling partners in Suzuki–Miyaura reactions.² However, the corrosive halide-containing waste production does not meet the modern synthetic chemistry expectations with the growing interest in environmentally friendly protocol development nowadays. Hence, expanding the types of electrophiles that react *via* this pathway is thus an ongoing goal in organic synthesis.

Recently, (hetero)aryl esters, due to their ubiquitous nature, have gained significant interest as new aryl-coupling partners *via* nickel catalyzed C(aryl)–O cleavage (see Scheme 1a).³ Actually, the bond dissociation energy (BDE) of the C(acyl)–O bond is lower than the C(aryl)–O bond in (hetero)aryl esters.^{3h} But, catalyzed by transition-metal, there are challenges associated with C(acyl)–O bond cleavage because of the decarbonylation phenomenon.⁴ In 2001, Yamamoto reported the first example of palladium catalyzed coupling reaction of aryl esters with organoboron compounds *via* C(acyl)–O cleavage with carbonyl retention (see Scheme 1b). However, the reaction was limited to electronically activated esters, such as perfluoroaliphatic carboxylic esters.⁵ Chatani reported the palladium catalyzed coupling reaction of 2-pyridyl esters with organoboron compounds (see Scheme 1c).⁶ More recently,

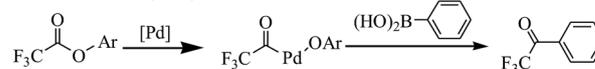
Newman developed an NHC-based Pd catalyst which can catalyze Suzuki–Miyaura coupling of phenyl esters (see Scheme 1d).⁷

Although these homogeneous palladium catalysts offer high selectivity and yields under relatively mild operating conditions, but their industrial applicability is limited by the inherent problem of catalyst separation from the product and its recycle.⁸ Moreover, the palladium residues in the product stream could be a serious issue in the pharmaceutical industry.⁹ With these considerations in mind, a wide variety of alternative methods for heterogeneous Pd-catalyzed Suzuki–Miyaura reactions have been introduced.¹⁰ But, to the best of our knowledge, there is no report for heterogeneous Pd-catalyzed Suzuki–Miyaura reactions using ester as coupling partners.

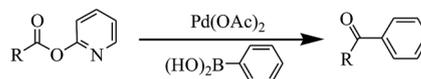
a) The selectivity of C–O activation of Aryl ester



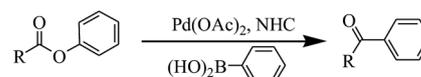
b) Yamamoto's work (2001)



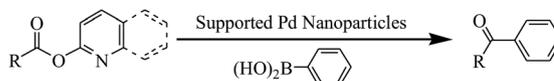
c) Chatani's work (2004)



d) Newman's work (2017)



this work



Scheme 1 C–O activation of (hetero)aryl ester.

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† Electronic supplementary information (ESI) available: GC-MS analysis of model reaction, characterization data for the products, ¹H NMR and ¹³C NMR spectra of the products. See DOI: 10.1039/c9ra02394a



Our previous work has confirmed that (hetero)aryl esters can generate an activated acyl intermediate and perform amidation reactions with tertiary amines or formamides to form amides under supported palladium nanoparticles catalyzed conditions.¹¹ These results prompt us to explore the heterogeneous palladium catalyzed Suzuki–Miyaura reaction of (hetero)aryl esters. But one obstacle to establish this heterogeneous catalysis is that the undesired Pd-catalyzed homocoupling of phenylboronic acid could be easily facilitated under these reaction conditions.¹² Another is that in most of the cases, Suzuki–Miyaura reaction need base condition which will give rise to side reactions for ester. Therefore, the choose of catalyst with moderate activity and (hetero)aryl ester with high selectivity is vital.

Herein, we describe a nano-palladium catalyzed Suzuki–Miyaura cross-coupling variant with heteroaryl ester and arylboronic acid components as coupling partners. This newly developed methodology provides a heterogeneous catalysis route for C–C bond formation in a straightforward fashion, which successfully suppresses the undesired decarbonylation phenomenon attendant upon C(acyl)–O bond activation of ester. In a series of supported PdNPs, Pd/ γ -Al₂O₃ catalyst with a PdNPs mean diameter of 3.34 nm exhibited the best catalytic activity and it maintained a relatively high activity after several recover cycles. The XPS analysis of the catalyst before and after reaction suggested that the reaction might be performed *via* a Pd⁰/Pd^{II} catalytic cycle that began with Pd⁰.

Experimental

Catalyst preparation

The PdNPs on the γ -Al₂O₃ and other supports were prepared by a low density lysine solution protected impregnation–reduction method. For example, 3 wt% Pd/ γ -Al₂O₃ was prepared by the following procedure: 0.97 g of γ -Al₂O₃ powder was dispersed into 50 mL of deionized water, followed by adding 28.2 mL of 0.01 M PdCl₂ aqueous solution while magnetically stirring. One milliliter of 0.03 M L-lysine was added with vigorous stirring. Then 0.1 M NaOH aqueous solution was added into the mixture to adjust the pH to 7. To this suspension, 4.5 mL of 0.35 M NaBH₄ solution was added dropwise in 10 min. The mixture was aged for 24 h, and then the solid was separated, washed with water (4 times) and ethanol (once), and dried at 80 °C. The dried solid was used directly as the catalyst.

Preparation of various esters (1a–s, 4a–h)

A mixture of carboxylic acid (10 mmol), pyridinol or phenol (10 mmol), DMAP (4-(dimethylamino)pyridine, 1 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl, 10 mmol) in THF (50 mL) was stirred overnight at 25 °C. The resulting mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl ether/petroleum ether = 1 : 3 to 1 : 10 as eluent), affording a corresponding esters **1a–s** and **4a–h**.

Activity test

The reaction in 25 mL over-dried reaction tube. The Suzuki–Miyaura cross coupling reaction between 2-pyridyl 4-methylbenzoate **1a** and phenylboronic acid **2a** was used as the model reaction. In a typical reaction catalyst (25 mg), 2-pyridyl 4-methylbenzoate (21.3 mg, 0.10 mmol), phenylboronic acid (24.4 mg, 0.20 mmol), K₃PO₄ (31.8 mg, 0.15 mmol), H₂O (4.5 μ L, 0.25 mmol), toluene (2 mL) were added into the reaction tube. The resulting solution was stirred at 120 °C for 48 h in an oil bath. After cooling to room temperature, the mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1 : 10 to 1 : 15 as an eluent) to afford the desired ketone **3**. All products were confirmed by comparison with the previously reported ¹H NMR and ¹³C NMR data.

Catalyst recycle experiment

After each reaction cycle, the solvent, substrate, and the products were removed by centrifugation; the separated catalyst was washed thoroughly with 0.1 M NaOH ethanol solution (twice), distilled water (4 times), and then washed twice with ethanol followed by centrifugal separation and drying at 80 °C for 12 h. The recovered catalyst was used for the next cycle.

Hot filtration test

In a testing reaction 3 wt% Pd/ γ -Al₂O₃ (25 mg), 2-pyridyl 4-methylbenzoate **1a** (21.3 mg, 0.10 mmol), phenylboronic acid **2a** (24.4 mg, 0.20 mmol), K₃PO₄ (31.8 mg, 0.15 mmol), H₂O (4.5 μ L, 0.25 mmol), toluene (2 mL) were added into the reaction tube. The hot filtration test is applied by filtering the reaction mixture through a pre-heated Celite pad after the reaction for 2 h. The filtrate was detected by GC to obtain the conversion of **1a**. Then the filtered reaction solution continued to react for 2 h under normal conditions, and was detected by GC again.

Gram-scale synthesis

In a gram-scale reaction, catalyst (1.17 g), 2-pyridyl 4-methylbenzoate **1a** (1.00 g, 4.69 mmol), phenylboronic acid **2a** (1.15 g, 9.39 mmol), K₃PO₄ (1.49 g, 7.04 mmol), H₂O (211 μ L, 11.73 mmol) and toluene (60 mL) were charged in a 100 mL oven-dried round flask. The resulting solution was stirred at 120 °C for 48 h in an oil bath. After cooling to room temperature, the mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1 : 10 as an eluent) to afford the desired product **3aa** (0.92 g, 84% yield).

Results and discussion

Our initial attempt was executed toward the supported palladium nanoparticles catalyzed Suzuki–Miyaura cross-coupling reaction using 2-pyridyl 4-methylbenzoate **1a** and phenylboronic acid **2a** as the coupling partners. Using 3 wt% Pd/ γ -Al₂O₃ as the catalyst, Cs₂CO₃ as base, and toluene as solvent, after 24 h of refluxing the desired ketone **3aa** was obtained in



54% yield (Table 1, entry 1). Meantime, along with the desired product only 9% yield of homocoupling byproduct of phenylboronic acid was isolated. This indicated that the heterogeneous palladium catalyst is showed higher selectivity. Then, various reaction parameters including catalyst, base, solvent, additive and temperature were screened. The PdNPs supported on other oxide powders, including α -Al₂O₃, CeO₂, TiO₂ and Fe₃O₄ were prepared by the impregnation–reduction method and applied to the model reaction (entries 2–5). Among them, the catalyst with 3 wt% Pd/ γ -Al₂O₃ exhibited the best performance. The effect of solvent on the coupling reaction was rather important, toluene proved to be the best choice of solvent, whereas other solvents such as cumene and dioxane gave rise to slightly lower yields (entries 6–8). Base was also found to show significant influence on the coupling reaction, and anhydrous K₃PO₄ showed the best efficiency for this transformation (entries 9–12). In sharp contrast, no reaction was occurred in the absence of the base. It is noteworthy that with the additive of water, higher conversion was achieved and the desired product was obtained in 68% yield (entry 13). A small amount of water might help dissolve the base into the reaction system. But only used water as solvent is inadvisable because water-insoluble property of ester. We also screened the effect of different temperature on the reaction (entries 14–16). We are pleased to find that increasing the temperature to 120 °C led to generate the highest yield of product, and further increasing the temperature of the reaction did not have any improvement on the yield. No product was observed under otherwise identical conditions in the absence of Pd (entry 17).

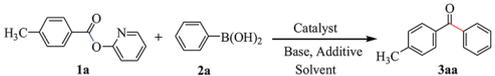
The Suzuki–Miyaura cross-coupling of phenylboronic acid **2a** with a set of 2-pyridyl esters was performed under the optimized

reaction conditions, and the results are presented in Table 2. Incorporation of electron-donating **3ca–3ga**, electron-withdrawing **3ha–3na** or naphthyl **3oa**, groups on the esters were tolerated. Compared with their *para*-isomers, 2-pyridyl 2-methylbenzoate **1c**, 2-pyridyl 3-methylbenzoate **1d** and 2-pyridyl 3-nitrobenzoate **1m** delivered a lower yield, which resulted from the steric hindrance effect. Encouragingly, various heterocyclic species could also be utilized **3pa–3ra** and (1*H*-indol-2-yl)(phenyl)methanone **3pa** was obtained quantitatively. The ability to obtain high yields of indolyl aromatic ketones is a significant advantage of this methodology. But when pyridin-2-yl propionate **1s** react with phenylboronic acid **2a**, no product was detected. The result indicated that the acyl C–O bond cleavage with the aid of palladium cannot tolerate aliphatic substituents. The ease of activating this type of bond can be attributed to the stabilizing interaction of the arene π system with palladium.¹⁴

Next, the scope of this reaction between 2-pyridyl 4-methylbenzoate **1a** with a variety of boronic acids was investigated and the results are summarized in Table 3. Various functional groups including alkyl, ethoxy, fluoro, bromo, trifluoromethyl, thiomethyl and phenoxy were compatible and the desired products were achieved in moderate to good yields. But the *ortho*-ethoxy phenyl boronic acid did not perform the reaction. The result indicated that the steric hindrance effect of boronic acids is a determining factor of the coupling reaction (see **3ag**). Interestingly, the Suzuki–Miyaura could be used to synthesize benzodioxole ketone **3an** which is an important pharmaceutical intermediate albeit in lower yield.

In order to verify that the *ortho*-directed effect of nitrogen on C(acyl)–O bond cleavage of ester, pyridin-3-yl 2-methylbenzoate

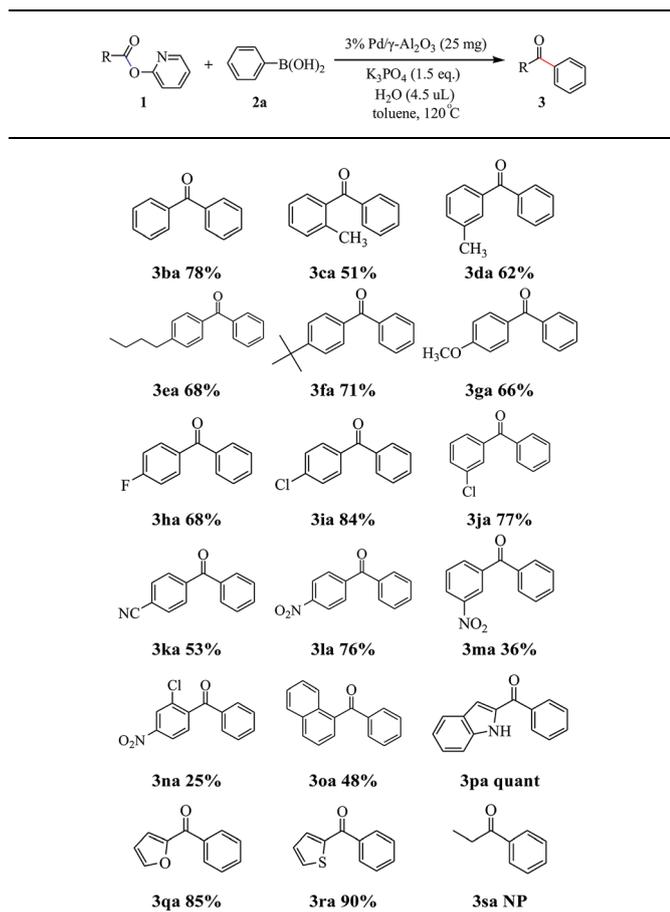
Table 1 Optimization for the reaction conditions^a



Entry	Catalyst	Base	Solvent	Additive	Temp (°C)	Yield (%)
1	3% Pd/ γ -Al ₂ O ₃	CS ₂ CO ₃	Toluene	—	100	54
2	3% Pd/ α -Al ₂ O ₃	CS ₂ CO ₃	Toluene	—	100	25
3	3% Pd/CeO ₂	CS ₂ CO ₃	Toluene	—	100	38
4	3% Pd/TiO ₂	CS ₂ CO ₃	Toluene	—	100	49
5	3% Pd/Fe ₃ O ₄	CS ₂ CO ₃	Toluene	—	100	37
6	3% Pd/ γ -Al ₂ O ₃	CS ₂ CO ₃	Cumene	—	100	35
7	3% Pd/ γ -Al ₂ O ₃	CS ₂ CO ₃	Dioxane	—	100	20
8	3% Pd/ γ -Al ₂ O ₃	CS ₂ CO ₃	THF	—	100	NP
9	3% Pd/ γ -Al ₂ O ₃	Na ₂ CO ₃	Toluene	—	100	30
10	3% Pd/ γ -Al ₂ O ₃	K ₂ CO ₃	Toluene	—	100	47
11	3% Pd/ γ -Al ₂ O ₃	—	Toluene	—	100	NP
12	3% Pd/ γ -Al ₂ O ₃	K ₃ PO ₄	Toluene	—	100	58
13	3% Pd/ γ -Al ₂ O ₃	K ₃ PO ₄	Toluene	H ₂ O	100	68
14	3% Pd/ γ -Al ₂ O ₃	K ₃ PO ₄	Toluene	H ₂ O	110	73
15	3% Pd/ γ -Al ₂ O ₃	K ₃ PO ₄	Toluene	H ₂ O	120	88
16	3% Pd/ γ -Al ₂ O ₃	K ₃ PO ₄	Toluene	H ₂ O	130	70
17	γ -Al ₂ O ₃	K ₃ PO ₄	Toluene	H ₂ O	120	NP

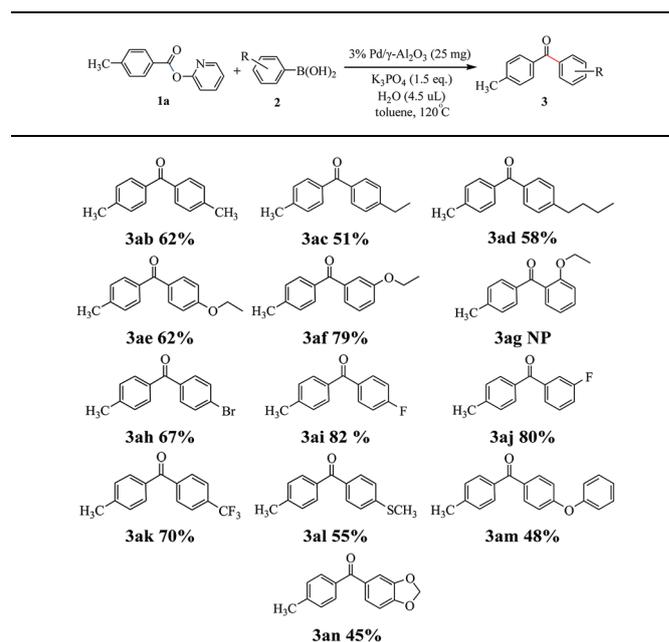
^a Reaction condition: **1a** (0.10 mmol), catalyst (25 mg), Pd (7 mol%), phenylboronic acid **2a** (2.0 equiv), base (1.5 equiv), H₂O (2.5 equiv), solvent (2 mL), 120 °C, 48 h.



Table 2 Scope of Suzuki–Miyaura coupling with 2-pyridyl esters^a

^a Reaction conditions: **1** (0.10 mmol), **2a** (2.0 equiv), 3 wt% Pd/γ-Al₂O₃ (25 mg), Pd (7 mol%), K₃PO₄ (1.5 equiv), H₂O (2.5 equiv), toluene (2 mL), 120 °C, 48 h. Isolated yield.

4a and pyridin-4-yl 2-methylbenzoate **4b** were used to react with phenylboronic acid **2a** (see Table 4, entries 1 and 2). After 24 h reaction, the desired ketone was not obtained, but instead phenyl 4-methyl benzoate **5aa** was obtained in 48% and 44% yield, respectively. These results confirmed the *ortho*-directed effect of nitrogen on C(acyl)–O bond cleavage of ester catalyzed by palladium. The reason for generating phenyl ester is that catalyzed by palladium, phenylboronic acid transferred to phenol¹¹ in the presence of H₂O which performed the transesterification reaction with pyridin-2-yl 2-methylbenzoate **1a** to generate new ester catalyzed by K₃PO₄.¹⁵ Interestingly, when quinolin-8-yl 4-methylbenzoate **4c** containing transannular directing group was used as substrate, no reaction was detected (entry 3). When other heteroaryl benzoate containing *ortho*-nitrogen, quinolin-2-yl 4-methylbenzoate **4d**, **4f** and pyrazin-2-yl 4-methylbenzoate **4e** were employed instead of **1a**, the Suzuki–Miyaura cross-coupling reaction also proceed to afford the same ketone **3aa** but with the lower selectivity (entries 4–6). Under the identical reaction conditions, the activated ester per-fluorophenyl benzoate **4g** only give the transesterification product rather than desired ketone (entry 7). Not only that, when *p*-tolyl picolinate **4h** was used as substrate, no reaction

Table 3 Scope and limitations of Suzuki–Miyaura coupling with arylboronic acids^a

^a Reaction conditions: **1a** (0.10 mmol), **2** (2.0 equiv), 3 wt% Pd/γ-Al₂O₃ (25 mg), Pd (7 mol%), K₃PO₄ (1.5 equiv), H₂O (2.5 equiv), toluene (2 mL), 120 °C, 48 h. Isolated yield.

was performed (entry 8). These results clearly show that the pyridyl group serves as a directing group for cleavage of the acyl C–O bond of the ester and that coordination of the nitrogen atom to the catalyst is crucial for the catalyzed reaction. This result is different from Chatani's work.

To investigate the practical application of this newly developed Suzuki–Miyaura cross-coupling reaction in organic synthesis, we conducted a gram-scale reaction of **1a** (1 g) with **2a** in the presence of 3 wt% Pd/γ-Al₂O₃ catalyst, and isolated the desired product **3aa** in 84% yield. As we can see, even though the reaction scale was magnified up to 47 times, ideal synthetic yields could be still obtained.

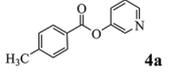
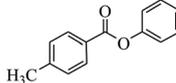
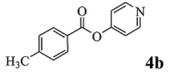
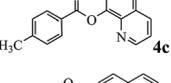
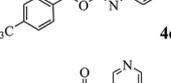
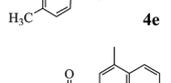
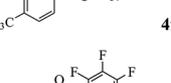
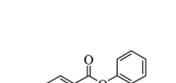
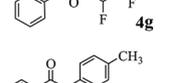
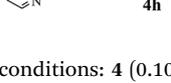
The recyclability of catalyst was examined in the reaction of 2-pyridyl 4-methylbenzoate **1a** and phenylboronic acid **2a** as provided in the experimental section. As shown in Fig. 1, the catalyst can be reused for eight cycles with only 13% decline of activity after the 8th recycle.

To have a good knowledge of the information for the catalyst, the fresh and used (recovered after 8th cycle) PdNPs on γ-Al₂O₃ catalysts were studied by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and so on. The transmission electron microscopic (TEM) analysis of the fresh and used catalysts are represented in Fig. 2. The PdNPs are distributed evenly on the γ-Al₂O₃ surface, and the mean diameters of the PdNPs are 3.34 nm of fresh catalyst and 3.48 nm of used catalyst, respectively. It does not cause obvious increase in the average size of PdNPs after eight runs.

In order to understand the state of PdNPs supported on γ-Al₂O₃, the catalysts before and after reaction were tested by XPS



Table 4 Scope and limitations of Suzuki–Miyaura coupling with other (hetero)aryl esters^a

Entry	Esters	Product	Yield (%)
1			48%
2			44%
3		—	NP
4			53%
5			39%
6			25%
7			36%
8		—	NP

^a Reaction conditions: **4** (0.10 mmol), **2a** (2.0 equiv), 3 wt% Pd/ γ -Al₂O₃ (25 mg), Pd (7 mol%), K₃PO₄ (1.5 equiv), H₂O (2.5 equiv), toluene (2 mL), 120 °C, 48 h. Isolated yield.

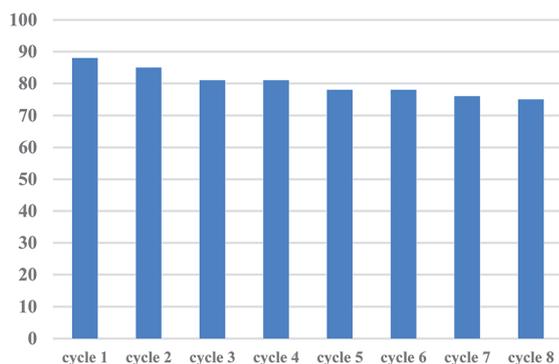


Fig. 1 Recyclability of the catalyst.

analysis. The XPS results of the catalysts confirm that palladium exists in the metallic state on γ -Al₂O₃ supports before and after reaction. As shown in Fig. 3, the binding energies of Pd 3d_{5/2} and Pd 3d_{3/2} electrons are 335.69 eV and 340.93 eV of fresh

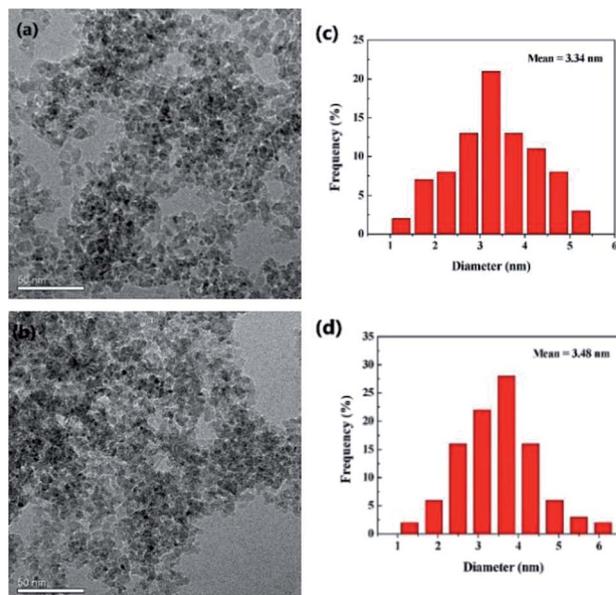


Fig. 2 (a and b) TEM images of fresh 3 wt% Pd/ γ -Al₂O₃ and used 3 wt% Pd/ γ -Al₂O₃, respectively; (c and d) PdNPs size distributions of fresh and used catalysts, respectively.

catalyst and 335.80 eV and 341.00 eV of used catalyst respectively. The binding energies of Pd⁰ in literature are 335.20 eV of Pd 3d_{5/2} and 340.50 eV of Pd 3d_{3/2}, respectively, whereas the values of Pd^{II} are 336.70 eV of Pd 3d_{5/2} and 342.00 eV of Pd 3d_{3/2}, respectively.¹³ It is clearly shown that Pd⁰ as the active center completes the catalytic cycle.

The Brunauer–Emmett–Teller (BET) specific surface areas of the catalysts were derived from N₂ physical sorption data of the samples using the BET model (Table 5). The γ -Al₂O₃ is a kind of support which has a large specific surface area, and it does not cause obvious change in the specific surface area of these catalysts after loading a small amount of the PdNPs. The amounts of Pd loading of the catalysts were derived from atomic absorption spectrophotometer (AAS), and the Pd content of fresh catalyst is approximately 3 wt%. We did note a slight

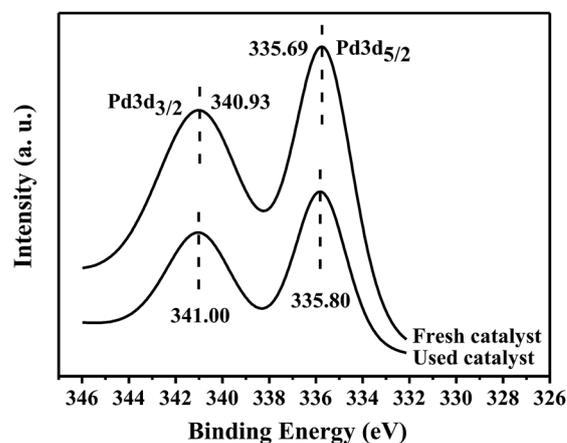


Fig. 3 XPS spectra of fresh and used 3 wt% Pd/ γ -Al₂O₃.

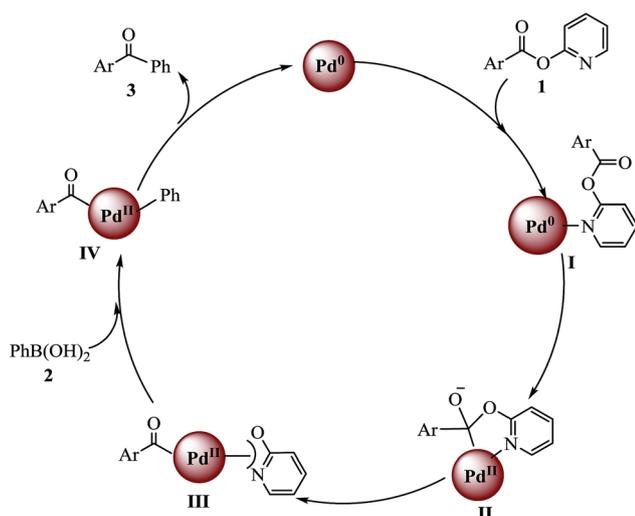


Table 5 Characterization results of BET, AAS of catalysts

Samples	SBET (m ² g ⁻¹)	Pd loading (wt%)
γ-Al ₂ O ₃	161	—
3 wt% Pd/γ-Al ₂ O ₃ (fresh)	166	3.02
3 wt% Pd/γ-Al ₂ O ₃ (used)	159	2.89

Table 6 The results of hot filtration test

Time (hour)	Conversion ^a (%)
0	0
2	42.41
4 (after hot filtration)	42.81

^a GC data.

Scheme 2 Proposed reaction mechanism.

decrease in Pd content after being cycled eight times (2.89%, Table 5), which can decrease the catalytic activity on the basis of available Pd on the support surface.

In order to prove whether the present reaction proceeded with a heterogeneous catalyst or homogeneous catalyst, the hot filtration test of the model reaction mixture was executed and GC data are given in Table 6. The conversion rate of **1a** indicated that after filtration the substrate turnover ceases. This is intended to preclude the possibility of homogeneous catalysis. This result was also proved by Hg(0) poisoning test (see ESI†).

To identify a byproduct, which is formed by the cleavage of the C(acyl)–O bond, the model reaction solution was detected with GCMS after the end of the reaction (see the ESI†). The GCMS data indicated that along with desired product **3aa** a small amount of biphenyl was obtained and that alkoxy group of ester eliminated to pyridin-2-ol. Based on the GC-MS analysis results and the commonly accepted mechanism from the literature, the proposed reaction pathway is shown in Scheme 2.

Initially, the nitrogen atom in **1a** coordinates with Pd⁰ to form intermediate **I**, and then Pd attacks the carbonyl carbon to give five-membered palladium ring intermediate **II**. C–O bond cleavage takes place with re-formation of the carbonyl group and acylpalladium **III** is generated. Transmetalation between **III** and organoboron compounds affords intermediate **IV**.^{6,16} Finally, reductive elimination from **IV** yields ketone with regeneration of active Pd⁰.

Conclusions

In summary, the results reported herein represent the first example of heterogeneous and site-selective nano-palladium catalyzed Suzuki–Miyaura cross-coupling reaction with heteroaryl ester and arylboronic acids as coupling partners. The utility of this newly developed protocol has been demonstrated by the broad functional group tolerance and the application in the synthesis of bioactive compounds. It is also shown that the coordination of the nitrogen of the pyridyl group to the catalyst is essential for the efficient reaction. This reaction involves the heterogeneous catalytic generation of acylpalladium intermediates from esters by successful suppression of the undesired decarbonylation phenomenon, and its application to aryl ketone synthesis is achieved. The catalyst can be readily recovered and reused for eight cycles with only 13% decline of activity after the 8th recycle. The XPS analysis of the catalyst before and after reaction suggested that the reaction might be performed *via* a Pd⁰/Pd^{II} catalytic cycle that began with Pd⁰. The practicality of this study may inspire further studies on heterogeneous catalyzed C–O activation reactions.

Conflicts of interest

There are no conflicts to declare.

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