

Directed Aromatic C–H Activation/Acetoxylation Catalyzed by Pd Nanoparticles Supported on Graphene Oxide

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Graphene oxide

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Supporting Information

ABSTRACT: The first solid-supported directed aromatic C– H activation/acetoxylation has been successfully developed by using palladium nanoparticles supported on graphene oxide (PdNPs/GO) as a catalyst. The practicability of this method is demonstrated by simple preparation of catalyst, high catalytic efficiency, wide functional group tolerance, and easy scale up of the reaction. A hot filtration test and Hg(0) poisoning test indicate the heterogeneous nature of the catalytic active species.

atalytic C–H activation has become a powerful tool for \checkmark modern organic synthesis.¹ The directed functionalization of a specific C–H bond is the most atom-economical strategy for the construction of C–C and C–heteroatom bonds.¹ One of the most important methods to achieve selectivity in the C-H activation is to use palladium catalysis combined with an intramolecular directing group, such as a pyridinyl or other basic functional group.² Considering the expensive price and high toxicity of palladium catalyst, solid-supported palladiumcatalyzed directed C-H activation has appeared as a valuable alternative to the homogeneous one. There are fewer studies on solid-supported palladium-catalyzed C-H activations than there are of homogeneous reactions.³ Most of the protocols focus on the activation of heterocycles with an "acidic" C-H bond or intramolecular functionalization.⁴ Solid-supported directed aromatic C-H activation is more challenging. Until now, only limited arylations,⁵ cyanation,⁶ alkylation/alkenylation,⁷ alkyny-lation,⁸ halogenation,⁹ borylation,¹⁰ and cyclization¹¹ reactions have been reported by several groups. Good to excellent efficiency yield frequently required a fairly tedious preparation procedure that included catalyst, large loading of catalyst, and low functional group tolerance.

The directed C–H activation/oxidation reaction to construct the C–O bond using solid-supported catalysts is rare. Recently, the Cohen group developed solid-supported C–H alkoxylation using a metal–organic framework supported palladium catalyst (Pd/MOF) (Scheme 1, a).^{9a} The Ellis group developed C–H alkoxylation and halogenation with a multiwalled carbon nanotube supported palladium nanoparticle catalyst (Pd/ MWCNT) (Scheme 1, b).^{9b} From the Ellis group's work, only one single example of C_{sp3} –H acetoxylation¹² was achieved, which came from benzylic C–H activation with 8-methylquinoline as substrate (Scheme 1, b-2).^{9b} However, the effort to achieve aromatic C–H acetoxylation by the same Pd/MWCNT catalyst failed with no formation of the desired product (Scheme



Scheme 1. Solid-Supported Directed C–H Activation for Construction of C–O Bonds



1, b-3).^{9b} To the best of our knowledge, there is no report on successful solid-supported directed aromatic C–H acetoxylation.¹³

Graphene oxide (GO) coupled with high chemical, mechanical stability, as well as excellent dispersibility is a highly desirable two-dimensional support for metal nanoparticles (MNPs).

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Various MNPs supported on GO were used as the catalysts in diverse organic transformations.¹⁴ However, no C–H activation was realized by GO-based solid-supported catalyst. Herein, we report the first solid-supported directed aromatic C–H acetoxylation with moderate to excellent yields by using palladium nanoparticles supported on graphene oxide (PdNPs/GO) as the catalyst (Scheme 1, c).

The preparation of PdNPs/GO is a process of cation exchange and absorption with GO support.¹⁵ PdNPs/GO maintained the original layer structure as shown in Figure 1a, which is favorable



Figure 1. Field emission scanning electron microscopy image of PdNPs/GO (a). TEM images (b, c) and HRTEM image (d) of the catalysts in various scales.

for the dispersion in the reaction system. To further investigate the morphology of Pd nanoparticles, the dispersion of Pd nanoparticle was observed via transmission scanning electron microscopy (TEM) (Figure 1b,c). Palladium nanoparticles are well embedded in GO support without aggregation. The palladium nanoparticles had a spherical shape with an average diameter of 4 nm, which was confirmed by microtome cuts of the embedded samples. Figure 1d showed the high-resolution transmission electron microscope (HRTEM) image of palladium particles, which exhibited an atomic lattice fringe spacing of 0.226 nm corresponding well to the (111) plane of the palladium. The Pd content was found to be 3.9%, which was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES). X-ray photoelectron spectroscopy (XPS) showed that palladium nanoparticles existed as Pd(II) and Pd(0) on the GO support.

Our study began with 2-(o-tolyl)pyridine as a model substrate by using PdNPs/GO (0.8 mol %) as catalyst, and a variety of solvents, amounts of oxidant, and reaction temperatures were investigated. Among several solvents screened, DMF was found to be superior to other solvents with 98% isolated yield (Table 1, entries 1-7). It might be that polar DMF was a more suitable solvent for dispersion of the catalyst.¹⁶ PdNPs/GO could be distributed uniformly in DMF with stirring for only 1 min at room temperature, but the catalyst could not be scattered in toluene even for 1 h at 100 °C. When the quantity of iodosobenzene diacetate was increased from 1.1 to 2 equiv, a nearly quantitative yield of acetoxylated product was achieved. Further decreasing the reaction temperature to 80 or 60 °C resulted in lower conversion or even trace product (Table 1, entries 9 and 10). In the absence of solid-supported Pd catalyst or with only addition of graphene oxide support, no desired product was observed. Interestingly, we discovered that the catalytic efficiency of PdNPs/GO was superior to that of free $Pd(OAc)_2$.



	$\frac{1}{N} + PhI(OAc)_2 \frac{0.8 \text{ m}}{2a}$	ol % PdNPs/GO
entry	deviation from standard cond	itions GC yield ^{b} (%)
1	none	99 (98 ^c , TOF^d : 24.8 h ⁻¹)
2	toluene instead of DMF	21
3	AcOH instead of DMF	73
4	DMSO instead of DMF	25
5	DCM instead of DMF	4
6	DCE instead of DMF	84
7	dioxane instead of DMF	71
8	1.5 equiv of $PhI(OAc)_2$	65
9	80 °C	72
10	60 °C	trace
11	0.8 mol % of $Pd(OAc)_2$	76 (TOF: 19.0 h ⁻¹)

^{*a*}Standard conditions: 1a (0.25 mmol), PdNPs/GO (0.8 mol %), PhI(OAc)₂ (2 equiv), DMF (1.1 mL), argon atmosphere, 100 °C, 5 h. ^{*b*}Determined by GC using biphenyl as an internal standard. ^{*c*}Isolated yield. ^{*d*}TOF: turnover frequency.

The TOF value of PdNPs/GO (24.8 h⁻¹) was higher than that of Pd(OAc)₂, as 0.8 mol % Pd(OAc)₂ instead of PdNPs/GO gave only 76% yield (TOF: 19.0 h⁻¹) (Table 1, entry 11), which indicated that GO is an ideal support for Pd nanoparticle catalyst.

With the optimized conditions in hand, we next examined the substrate scope. A wide range of different functional groups were tolerated under the oxidative conditions (Scheme 2). Organic halides such as aryl bromides (3e, 3i) and aryl chloride (3h) were tolerated in this catalytic system, so that they can be used as a

Scheme 2. Substrate Scope^a



^{*a*}General reaction conditions: 1 (0.25 mmol), PdNPs/GO (0.8 mol %), PhI(OAc)₂ (2 equiv), DMF (1.1 mL), argon atmosphere, 100 °C, 5 h; isolated yields are given; the yields in parentheses were obtained using free Pd(OAc)₂ (0.8 mol %) instead of PdNPs/GO as the catalyst. ^{*b*}Iodobenzene dipivalate as oxidant.

handle for further transformation. The trifluoromethoxy group (3f, 3g), alkyl group (3a, 3c, 3j), methoxyl group (3b, 3d), and mesyl group (31) were compatible. Substrates with an electrondonating group were particularly effective; however, decreased vields were obtained when electron-withdrawing groups were present on the aromatic ring. Interestingly for meta-substituted arenes, the transformation proceeded with excellent regioselectivity for functionalization of the less sterically hindered ortho-C-H bond. The electron deficient para-substituted substrates afforded monoacetoxylated products (31), while the electron rich one gave mixtures of mono- and diacetoxylated products even when $PhI(OAc)_2$ was increased to 5 equiv (3j). This could be explained by the sterically hindrance from the support graphene oxide. For bulky iodobenzene dipivalate, excellent yield was achieved (30). The scope of the directing groups was also explored. Substituted pyridines (3m, 3n) showed good reactivity for this functionalization. However, low yield (3p) was obtained for benzo [h] quinolone because of the steric hindrance.

We also compared the catalytic activity of PdNPs/GO with free $Pd(OAc)_2$ under the same reaction conditions. The experimental results showed that Pd(OAc)₂ was not very effective for electron-poor substrates, as very low yields (5-18%) were obtained in most cases (Scheme 2, entries 3e-i, 3l, and **3n**). Gratifyingly, we found out that PdNPs/GO is superior to Pd(OAc)₂ for electron-deficient substrates (with up to 9-fold yield compared to $Pd(OAc)_2$ (Scheme 2, entry 3n). The yields of electron-rich substrates are close for PdNPs/GO and Pd(OAc)₂, with PdNPs/GO still affording slightly higher yields. The above comparison results have demonstrated GO not only is an ideal support for Pd nanoparticle catalyst, but also can efficiently improve the activity of Pd catalyst. The higher catalytic activity could be attributed to the high dispersibility of PdNPs and oxygen functional groups on GO nanosheets, as proposed by Nishina et al.¹⁷

To obtain a better understanding of this transformation, we used a hot filtration test.¹⁸ After removing the catalyst by hot filtration after the first hour of the reaction, no further conversion to product was observed, which indicated the removal of active catalytic species during filtration and probably that the catalytic species were heterogeneous. Hg(0) poisoning test results corroborated this proposal (see the Supporting Information for details). However, the three-phase test failed, so the PdNPs/GO was named a solid-supported catalyst at the current stage. Then the recyclability of PdNPs/GO was investigated. With use of 0.8 mol % catalyst, the reaction could be recycled two times without a significant decrease in yields; however, a drastic decrease of yield was observed in the third run (only 8% yield) (see the SI for details). The unsatisfactory recyclability of the catalyst is similar to other reports on solid-supported C–H activation reac-tions.^{4f,h,7,11,19} We removed the catalyst by filtration over Celite from the reaction mixture and measured the palladium content in reaction solution by ICP-MS after the first circle. The palladium content of the reaction solution was found to be 85 ppm; about 40% of palladium on catalyst leached into reaction solution, so it should be the major reason for the loss of catalytic activity. Moreover, the aggregation of palladium nanoparticles after the reaction which was confirmed by TEM results (see SI) was another reason for the loss. It should also be pointed out that the yield for the second run is still high; this could be attributed to the oxidation of Pd(0) in initial PdNPs/GO catalyst to Pd(II), so as to guarantee the enough concentration of effective Pd(II) species, which could start the efficient Pd(II)/Pd(IV) or Pd(II)/ Pd(III) catalytic cycle of C-H acetoxylation.²⁰ The assumption

was supported by the XPS study result, which showed that after completion of the first reaction, Pd(0) was converted to Pd(II) under oxidative conditions (see the SI).

Besides the acetoxylation, we also tested halogenations using PdNPs/GO as the catalyst with high yield for bromination (81%), low yield for chlorination (15%), and no desired product for iodation (Scheme 3, a). To test the feasibility of scaling up the

Scheme 3. Halogenation and Gram-Scale Acetoxylation



current reaction, a gram-scale C–H acetoxylation was conducted (Scheme 3, b). 2-(o-Tolyl)pyridine was directly scaled up 23.6 times to give the corresponding product (1.2 g) with 89% isolated yield.

In conclusion, we have prepared a solid-supported nanopalladium catalyst with commercial graphene oxide as the support in a convenient procedure. The physicochemical properties of PdNPs/GO catalyst were characterized by SEM, TEM, ICP-OES, and XPS. The first solid-supported directed aromatic C–H acetoxylation has been developed successfully with PdNPs/GO as the catalyst. PdNPs/GO showed excellent catalytic efficiency (with much better catalytic activity than free Pd(OAc)₂) for acetoxylation and good catalytic activity for bromination. The low catalyst loading, wide substrate scope, and easy scale up of the reaction make this method more practical in organic synthesis. Mechanistic studies (including hot filtration test and Hg(0) poisoning test) suggest a heterogeneous mechanism.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02967.

Experimental procedures, characterization of products, and ¹H and ¹³C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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