

负载纳米钯颗粒在邻位导向磺化反应中的催化特性探究

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摘要 报道了一种负载钯纳米颗粒催化 2-苯基吡啶与芳磺酰氯的邻位导向磺化反应. 对反应前后的负载钯纳米颗粒催化剂进行 X 射线光电子能谱(XPS)分析, 发现反应后钯完全被氧化. 结果证明钯催化的邻位导向磺化反应是由 $\text{Pd}^{\text{II/IV}}$ 催化循环, 而不是 $\text{Pd}^{0/\text{II}}$ 催化循环. 热过滤实验及其催化剂的表征进一步证明了这个假设, 提供了在邻位导向磺化反应中确定钯价态变化的直接方法.

关键词 C—H 功能化; 钯纳米颗粒催化剂; 磺化; XPS 分析

Insight into Catalytic Properties of Supported Palladium Nanoparticles Catalyzed *ortho*-Directed Sulfonylation

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Abstract Catalyzed by supported palladium nanoparticles, an *ortho*-directed sulfonylation reaction between 2-phenylpyridine and arylsulfonyl chlorides has been developed. The full oxidation-state change of palladium was detected in the X-ray photoelectron spectroscopy (XPS) analysis of the supported palladium nanoparticles catalyst before and after reaction, which confirmed that Pd-catalyzed *ortho*-directed sulfonylation reaction was performed via a $\text{Pd}^{\text{II/IV}}$ catalytic cycle instead of $\text{Pd}^{0/\text{II}}$. The hot filtration test and other tests of catalysts further confirmed the hypothesis. This report afforded the most straightforward approach to confirm the variation of valence of palladium in *ortho*-directed sulfonylation reaction.

Keywords C—H functionalization; X-ray photoelectron spectroscopy (XPS) analysis; palladium nanoparticles catalyst; sulfonylation

1 Introduction

Compared with the traditional cross coupling methods, the C—H activation/functionalization approach avoids the use of prefunctionalized substrates, and thereby provides means for environmentally-benign and economically attractive organic syntheses.^[1] Palladium complexes are particularly attractive catalysts for such transformations because that C—H functionalization at Pd centres can be used to install many different types of bonds and palladium participates in cyclometalation with a wide variety of directing groups and readily promotes C—H activation at both sp^2 - and sp^3 -C—H sites.^[2] But one can question whether the C—H functionalization reaction mechanisms involving Pd are fully understood. To date the mechanistic picture is dominated by homogeneous catalytic cycles involving one or two

Pd atoms, involving Pd^0 , Pd^{II} , Pd^{III} and Pd^{IV} oxidation states.^[3] The directed palladium catalyzed oxidative functionalizations of C—H bonds are typically believed to proceed through $\text{Pd}^{\text{II}}/\text{Pd}^{\text{IV}}$ redox cycles.^[4] Ritter *et al.*^[5] proposed a challenging mechanism for C—Cl, C—B and C—O reductive eliminations from discrete bimetallic Pd^{III} complexes. By contrast, it was proposed that the majority of palladium catalyzed C—H activation reactions do in fact proceed through a $\text{Pd}^{0/\text{II}}$ manifold,^[6] because the propagation of Pd black, Pd mirror or PdNPs from common Pd precursors ($\text{Pd}(\text{OAc})_2$) was found in many reactions.^[7] But sometimes the mechanism understanding of the same palladium catalyzed C—H activation reactions is often different in proceeding $\text{Pd}^{0/\text{II}}$ or $\text{Pd}^{\text{II/IV}}$ process because of the difficulty of isolating the Pd intermediates in the homogeneous catalytic system.^[8] It is believed that this has become

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one of the most intriguing open problems in homogeneous catalysis.

In recent years, pre-supported palladium nanoparticle (PdNP) catalysts have attracted broad interest of chemists due to their high selectivity and efficiency as the heterogeneous catalyst for various reactions, such as hydrogenation of conjugated dienes, enantioselective allylic alkylation, carbon-carbon coupling, asymmetric allylic substitution, and electrocatalytic formic acid oxidation.^[9] Compared with homogeneous catalysts, the easy separation and reusability of heterogeneous catalysts would be desirable to develop novel and efficient approach for mechanism study. The most straightforward approach to confirm the valence states of palladium in reaction is the X-ray photoelectron spectroscopy (XPS) analysis of the catalyst.^[10] XPS is sensitive to small changes in the chemical environment and thus is the ideal tool to verify the effect of functionalization on the surface chemistry of Pd nanoclusters.^[11] In heterogeneous catalysis system, the beginning and ending of catalytic cycle could be confirmed by the XPS analysis of the catalyst before and after reaction (commonly after multiple cycles).^[12] In 2011, Qi and co-workers^[13] used the XPS studies to speculate that the Pd/SP catalyzed reductive homocoupling of aromatic halides in ethanol/dimethyl sulfoxide (DMSO) solution proceeds through a Pd⁰/Pd^{II} cycle catalytic mechanism. Xing and co-worker^[14] reported an effective redox cycle between Pd⁰ and Pd^{II} in the catalytic hydrochlorination of acetylene using the XPS studies. But, as far as we know, there is rare report on using the XPS studies to research the change of valence state of palladium in C—H activation reaction.

Sulfones have been extensively proven to be vital intermediates in organic synthesis, because of unique chemical properties and bioactivities, such as anticancer, anti-HIV and antibacterial.^[15] In 2009, Dong and co-workers^[8b] reported that Pd(CH₃CN)₂Cl₂ catalyzed the synthesis of *ortho*-aromatic sulfones using arylsulfonyl chlorides as sulfonyl sources. But the indicated C—S bond-forming process involving Pd^{0/II} or Pd^{II/IV} intermediates was not proposed explicitly. In 2015, Sun *et al.*^[16] reported that Pd(OAc)₂ catalyzed the *ortho*-sulfonylation of 2-aryloxypyridines and arylsulfonyl chlorides. They proposed the Pd^{II/IV} mechanism according to the references instead of other direct evidences.

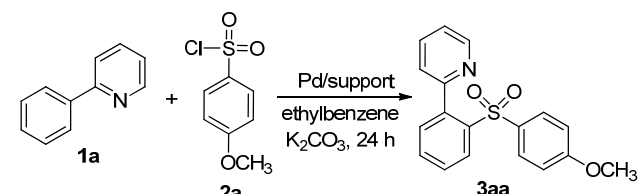
Based on our researches on the supported PdNPs catalyzed C—H activation reaction, we wished to gain some insight into catalytic properties of palladium catalyzed *ortho*-directed sulfonylation by means of XPS analysis. The XPS analysis of the supported palladium nanoparticle catalyst before and after reaction confirmed that there was not a redox cycle between Pd⁰ and Pd^{II}. The heterogeneity test and extensive Pd leaching suggested that the supported PdNPs catalyzed *ortho*-directed sulfonylation should proceed in a homogeneous catalytic cycle that began with Pd^{II}.

2 Results and discussion

The activity of the Pd/ γ -Al₂O₃ catalyst was first investi-

gated by the *ortho*-directed sulfonylation of 2-phenylpyridine (**1a**) with 4-methoxy-benzenesulfonyl chloride (**2a**) in ethylbenzene and the desired product **3aa** was isolated in 73% yield (Table 1, Entry 1). The catalytic activity of PdNPs was slightly lower than that of Pd(OAc)₂ (Table 1, Entry 2). The reaction proceeded smoothly over Pd/NiO ($w_{\text{Pd}}=3\%$), Pd/TiO₂ ($w_{\text{Pd}}=3\%$) and Pd/ZrO₂ ($w_{\text{Pd}}=3\%$) catalysts, while the obtained yields were much lower than that over Pd/ γ -Al₂O₃ ($w_{\text{Pd}}=3\%$) catalyst (Table 1, Entries 3~5). Moreover, the effect of different Pd loadings on the reaction was also examined, and Pd/ γ -Al₂O₃ ($w_{\text{Pd}}=3\%$) was the most effective catalyst (Table 1, Entries 6, 7). It was noteworthy that no reaction was observed in a blank experiment conducted with γ -Al₂O₃ powder instead of PdNPs under otherwise identical conditions (Table 1, Entry 8). Both an increase and decrease in the reaction temperature reduced the yield of 2-(2-(4-methoxyphenylsulfonyl)phenyl)pyridine (**3aa**) (Table 1, Entries 10, 11).

Table 1 Optimization of reaction conditions^a



Entry	Catalyst	Temp./°C	Yield/%
1	Pd/ γ -Al ₂ O ₃ ($w_{\text{Pd}}=3\%$)	125	73
2	Pd(OAc) ₂	125	75
3	Pd/NiO ($w_{\text{Pd}}=3\%$)	125	33
4	Pd/TiO ₂ ($w_{\text{Pd}}=3\%$)	125	52
5	Pd/ZrO ₂ ($w_{\text{Pd}}=3\%$)	125	56
6	Pd/ γ -Al ₂ O ₃ ($w_{\text{Pd}}=1\%$)	125	54
7	Pd/ γ -Al ₂ O ₃ ($w_{\text{Pd}}=5\%$)	125	61
8	γ -Al ₂ O ₃	125	0
10	Pd/ γ -Al ₂ O ₃ ($w_{\text{Pd}}=3\%$)	130	70
11	Pd/ γ -Al ₂ O ₃ ($w_{\text{Pd}}=3\%$)	115	65

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), catalyst (35 mg), K₂CO₃ (0.4 mmol), and ethylbenzene (2 mL) at 125 °C for 24 h. ^b Isolated yield.

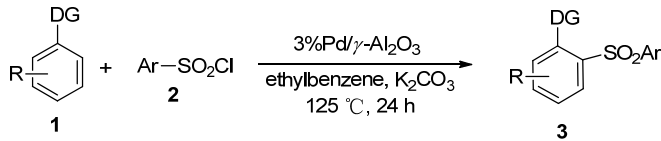
The scope of the method of synthesizing a broad range of sulfones was investigated with a variety of arylsulfonyl chlorides and 2-phenylpyridine derivatives under the optimized reaction conditions, and the results were shown in Table 2. The initial investigations were focused on the *ortho*-directed sulfonylation of 2-phenylpyridine (**1a**) with various arylsulfonyl chlorides (Table 2, Entries 1~8). To our delight, various substituted arylsulfonyl chlorides were successfully converted to the corresponding sulfones in moderate yields. Our experiment indicated that the arylsulfonyl chlorides bearing electron-withdrawing groups on the aromatic ring gave lower yields than others and 4-nitrobenzenesulfonyl chloride (**2e**) led to the lowest yield of the corresponding sulfone (**3ae**). 4-*tert*-Butylbenzene-sulfonyl chloride (**2d**) which bears an electron-donating group afforded the desired product 2-(2-(4-*tert*-butylphenylsulfonyl)phenyl)-pyridine (**3ad**) in the best yield of 78% (Table

2, Entry 3). In addition, 2-naphthalenesulfonyl chloride (**2f**) and 1-naphthalenesulfonyl chloride (**2g**) as well as benzenesulfonyl chloride performed the sulfonylation reaction to give the corresponding sulfones in moderate yields (Table 2, Entries 5, 6). Apart from aromatic sulfonyl chloride, the methodology was also successful in converting heteroaromatic sulfonyl chloride to the corresponding products (Table 2, Entries 7, 8). The sulfonylation of 2-(*p*-tolyl)pyridine (**1b**) with 4-*tert*-butylbenzenesulfonyl chloride (**2d**) were investigated, and the desired product was isolated in moderate yields (Table 2, Entry 9). Using 1-phenyl-1*H*-pyrazole (**1c**) as a substrate resulted in desired 1-(2-(4-*tert*-butylphenylsulfonyl)phenyl)-1*H*-pyrazole (**3cd**) albeit in com-

paratively lower yield (Table 2, Entry 10).

In order to get information on the valence state of Pd on the surface of the catalyst, the fresh and used (after 1st cycle) Pd/ γ -Al₂O₃ ($w_{\text{Pd}}=3\%$) catalysts were tested by XPS analysis (Figure 1a, 1e). The XPS signal appeared at binding energies for 335.11 eV of Pd 3d_{5/2} and 340.36 eV of Pd 3d_{3/2} over fresh catalyst and 336.71 eV of Pd 3d_{5/2} and 342.01 eV of Pd 3d_{3/2} over used catalyst. Obviously, the Pd 3d_{3/2} binding energy observed in the XPS spectrum of the Pd/Al₂O₃ is shifted by *ca* +1.60 eV revealing a full oxidation of the Pd atoms. 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}, re-

Table 2 Substrate scope of *ortho*-directed sulfonylation^a

									
Entry	1	2	Product	Yield ^b /%	Entry	1	2	Product	Yield ^b /%
1	1a	2b	3ab	51	6	1a	2g	3ag	29
2	1a	2c	3ac	48	7	1a	2h	3ah	55
3	1a	2d	3ad	78	8	1a	2i	3ai	57
4	1a	2e	3ae	18	9	1b	2d	3bd	73
5	1a	2f	3af	43	10	1c	2d	3cd	28

^a Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), Pd/ γ -Al₂O₃ ($w_{\text{Pd}}=3\%$, 35 mg), K₂CO₃ (0.4 mmol), ethylbenzene (2 mL), 125 °C, 24 h. ^b Isolated yield.

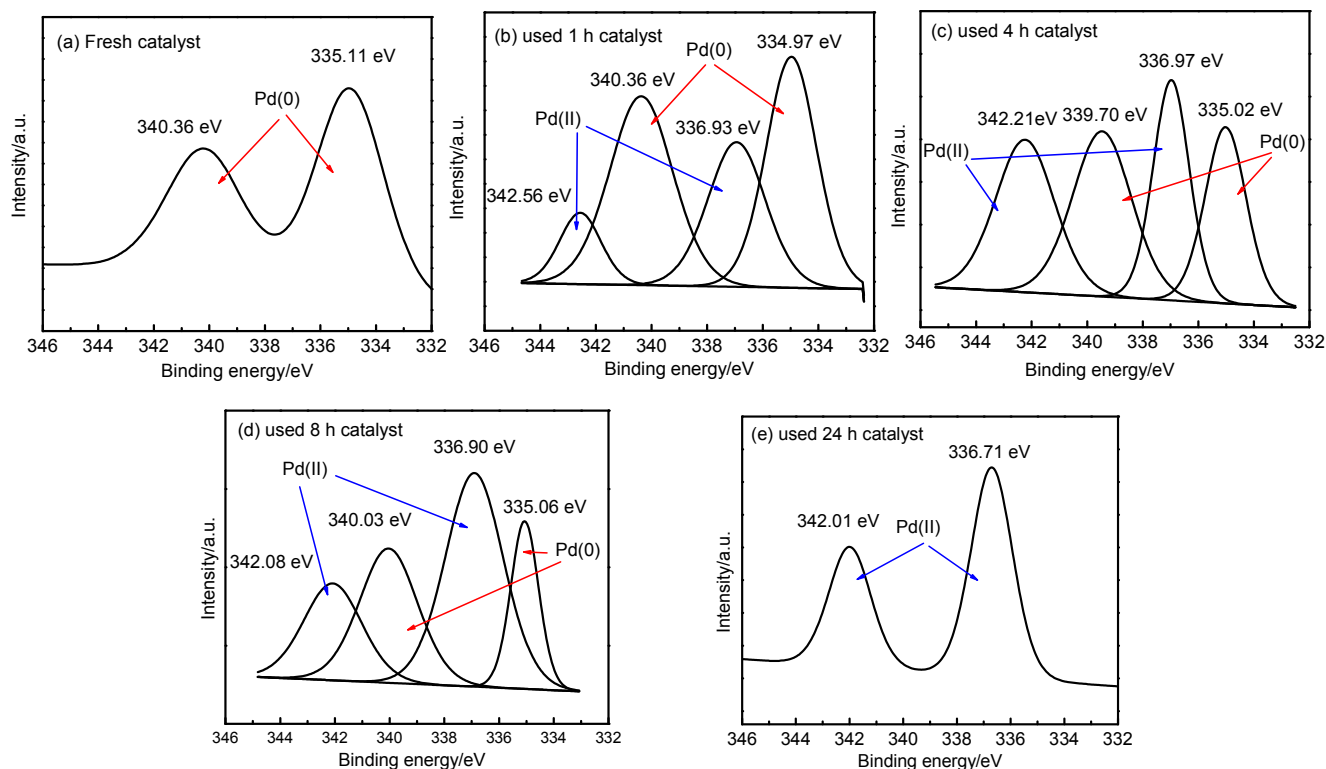


Figure 1 XPS spectra of fresh and used Pd/ γ -Al₂O₃ ($w_{\text{Pd}}=3\%$) (after reaction different times)

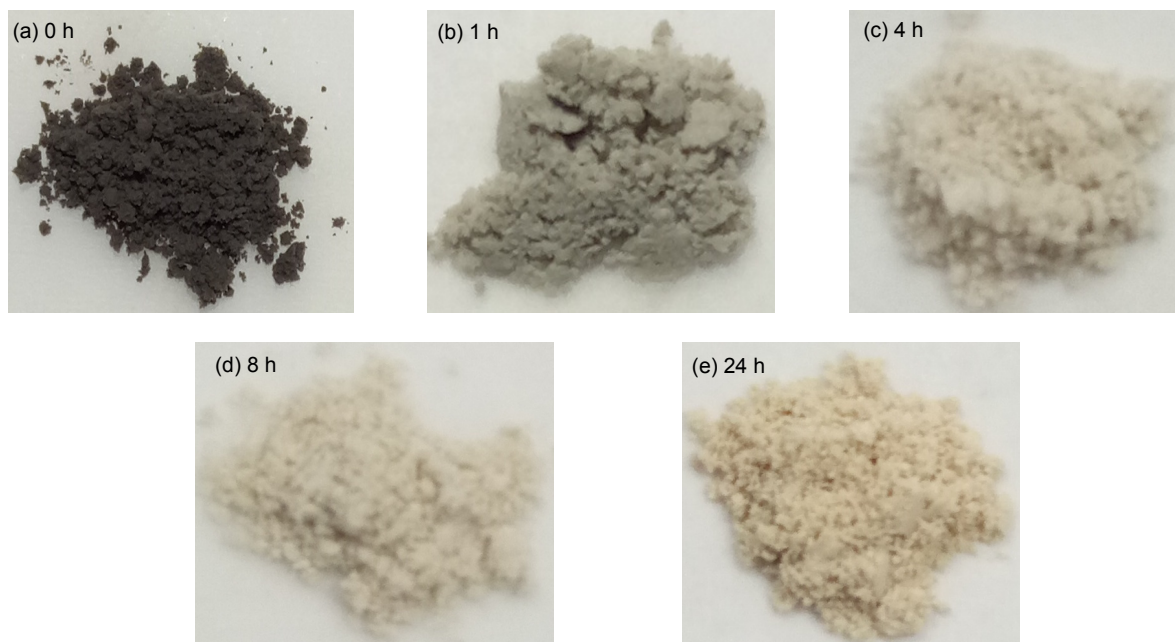


Figure 2 Photos of fresh and used Pd/ γ -Al₂O₃ ($w_{\text{Pd}}=3\%$) (after reaction different times)

spectively. While the values of Pd^{II} are 336.70 eV of Pd 3d_{5/2} and 342.00 eV of Pd 3d_{3/2}, respectively.^[17] These results showed that the supported metallic PdNPs were fully oxidized to divalent Pd species after reaction 24 h. Aim to get more detail process about the full oxidation of the Pd atoms, the catalysts after reaction for different times were isolated and detected by XPS. As shown in Figure 1, the co-existence of Pd⁰ and Pd^{II} was observed in the XPS

spectra of catalysts after reaction 1, 4 and 8 h. However, according to the area integral, the fraction of Pd^{II} in total metal species increased continuously in the reaction progress and after reacting 8 h Pd^{II} had occupied a dominant position. It suggested that Pd⁰ could continuously be oxidized to Pd^{II}, but Pd^{II} was not reduced to Pd⁰ in the reaction process. After reacting 24 h, Pd⁰ disappeared. Meanwhile, the corresponding continuously changes of catalyst colours

were also detected (Figure 2). This was opposite to the XPS study result of Pd/ γ -Al₂O₃ catalyzed *ortho*-directed CDC reaction in our previous work.^[18] Hence, it is fairly probable that there is not a redox cycle between Pd⁰ and Pd^{II} in the *ortho*-directed sulfonylation reaction and Pd^{II} may be served as catalytic centre.

Then, the possibility of recycling the oxidized PdNP catalyst in the model reaction was examined (Figure 3). The divalent supported PdNPs could be recycled 3 times, although the catalytic performance of the PdNPs declined apparently after every once recycle. This further confirmed the hypothesis that the Pd-catalyzed *ortho*-directed sulfonylation reaction was performed via a catalytic cycle that began with Pd^{II} instead of Pd⁰.

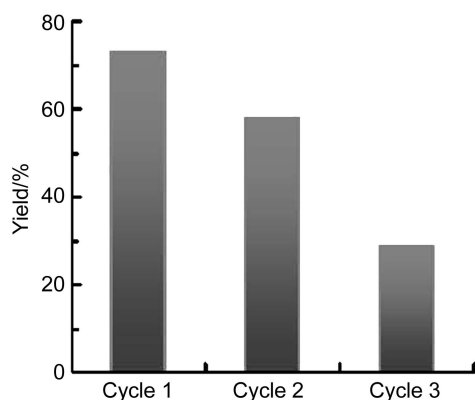


Figure 3 Recyclability of catalyst

The dispersed states of Pd⁰ and Pd^{II} NPs on the support were detected by the transmission electron microscopic (TEM). As shown in Figure 4, the Pd⁰ NPs are distributed

evenly on the γ -Al₂O₃ surface, and the mean diameters of the PdNPs are 3.20 nm in fresh catalyst. However, after 1st cycle, larger aggregated particles with a mean particle size estimate as 10.54 nm was detected. Likewise, after 3th cycle, the aggregation of PdNPs was much more serious. This indicated that without Pd⁰ served as reservoirs, Pd^{II} hard to reassemble into small sized PdNPs on the supporter surface. The aggregation of metal NPs during the catalysis processes results in a significant decrease of activity.^[19]

The amounts of Pd loading in the samples were determined by atomic absorption spectrophotometer (AAS), and the Pd content of the fresh catalyst was approximately 3% (Table 3). We did note a continuously decrease in the Pd content after being cycles 3 times, which confirmed that there was the extensive Pd leaching of Pd/ γ -Al₂O₃ in the sulfonylation reaction.^[20] Apparently, it could decrease the catalytic activity on the basis of available Pd of the catalyst.

In order to prove whether the present sulfonylation reaction proceeded with heterogeneous catalyst or homogeneous catalyst, the hot filtration test of the model reaction mixture was executed and GC data was given in Table 4. The conversion of **1a** and turn over frequency (TOF) value indicated that after filtration the substrate turnover did not cease, instead the reaction can continuously proceed. This result indicated that oxidized Pd^{II} species, which served as catalytic active centre, extensively leached into solution from higher order aggregated Pd species, including Pd⁰ and Pd^{II} NPs, and the *ortho*-directed sulfonylation should proceed in a homogeneous manner. Combined with the AAS results of fresh and used catalysts (Figure 1), we consider

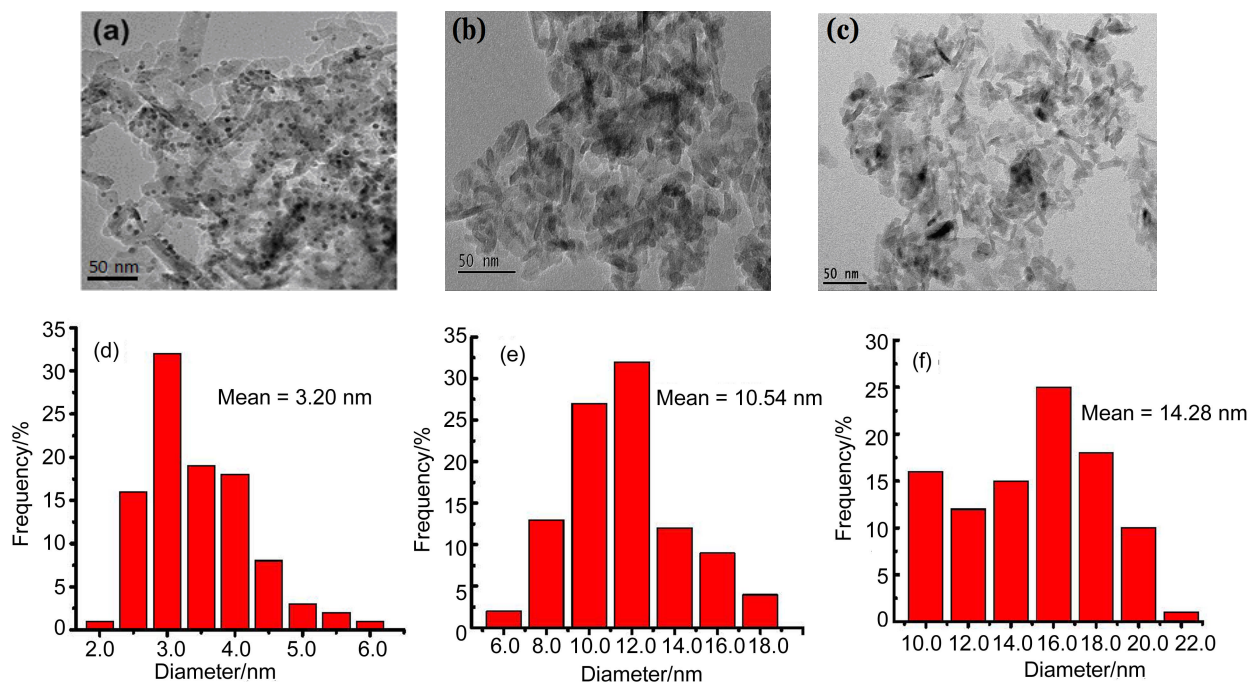


Figure 4 TEM images of fresh (a), after 1th cycle (b) and after 3th cycle (c) Pd/ γ -Al₂O₃ ($w_{\text{Pd}}=3\%$), and the PdNPs size distributions of fresh (error range: ± 0.25 nm) (d), after 1th cycle (Error range: ± 1.0 nm) (e) and after 3th cycle (Error range: ± 1.0 nm) (f) catalysts, respectively

Table 3 Characterization results of AAS of different Pd/ γ -Al₂O₃ catalysts

Sample	Pd loading w/%	Pd leaching rate/%
3% Pd/ γ -Al ₂ O ₃ (fresh)	3.01	
3% Pd/ γ -Al ₂ O ₃ (after 1th cycle)	2.36	—22
3% Pd/ γ -Al ₂ O ₃ (after 3th cycle)	0.51	—83

Table 4 The results of the hot filtration test

Time/h	Conversion ^a /%	TOF
0	0	
2	27.9	2.81
4 (after hot filtration)	68.0	6.86

^a GC data.

that the release of Pd is concomitant with recapture Pd at the catalyst surface, but releasing much more than recapturing.

Based on the experiment results and references, the homogeneous manner manifold using Pd^{II} as active centre was proposed (Scheme 1). First, Pd⁰ NPs was oxidized to Pd^{II} species and leaching into reaction solution at reaction temperature. Simultaneously, Pd^{II} species was recaptured by supporter and aggregated to Pd^{II} NPs, so the fraction of Pd^{II} in total metal species increased continuously as the reaction progress. Instead of Pd⁰ NPs, the leached Pd^{II} species served as the true catalytic centre and performed the *ortho*-directed sulfonylation reaction by homogeneous manner. A Pd^{IV} intermediate **II** via oxidative addition of sulfonyl chloride to the cyclopalladated intermediate **I** was proposed in the palladium catalyzed *ortho*-directed sulfonylation.

2 Conclusion

In summary, the mechanism of supported palladium nanoparticles catalyzed *ortho*-directed sulfonylation has been researched by means of heterogeneous approach (the XPS analysis of catalysts). After reaction 24 h, the supported metallic PdNPs were fully oxidized to divalent Pd species. It confirms that there is not a redox cycle between Pd⁰ and

Pd^{II} in the *ortho*-directed sulfonylation reaction. This is opposite to the XPS study result of Pd/ γ -Al₂O₃ catalyzed *ortho*-directed CDC reaction in our previous work. The experiment results indicated that the oxidized Pd^{II} species, which served as catalytic active centre, extensively leached into solution from higher order aggregated Pd species, including Pd⁰ and Pd^{II} NPs, and drive the *ortho*-directed sulfonylation reaction. The practicality of this heterogeneous approach for mechanism study may inspire further studies on the other palladium catalyzed C—H activation reaction.

3 Experimental

3.1 Catalyst preparation

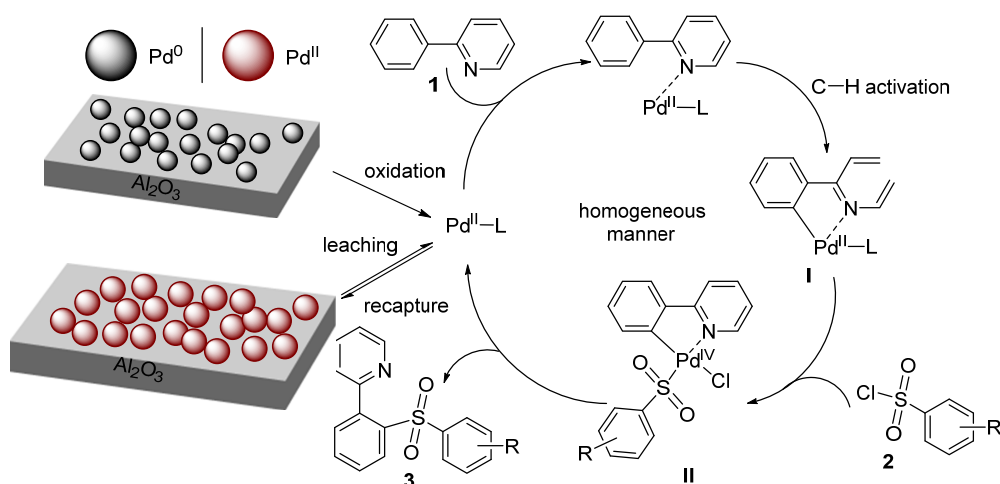
The PdNPs on γ -Al₂O₃ and other supports were prepared by a modified impregnation-reduction method.^[18]

3.2 Catalyst characterization

The TEM images were recorded on a JEM-2100 transmission electron microscope employing an accelerating voltage of 200 kV. The samples were suspended in ethanol and dried on holey carbon-coated Cu grids. The X-ray photoelectron spectroscopy (XPS) was recorded on a Kratos Amicus of British equipped with taper anode Mg K α radiation. The C1s hydrocarbon peak at 284.60 eV was used as an internal standard for the correction of binding energies. The Pd content was determined by the Z-8000-type polarized Zeeman atomic absorption spectrophotometer (AAS) of Hitachi company. The Au sensitive wavelength is 242.8 nm. GC-MS analysis was detected on a Thermo DSQ-II with a DB-5 column. Thin layer chromatography (TLC) was performed on pre-coated silica gel GF254 plates.

3.3 Activity test

The reaction was conducted in a 25 mL of oven-dried reaction tube. 2-Phenylpyridine (**1a**) sulfonylation with 4-methoxy benzenesulfonyl chloride (**2a**) was used as the model reaction. In a typical reaction, catalyst (35 mg), 2-phenylpyridine (30 μ L, 0.20 mmol), 4-methoxy benzenesulfonyl chloride (123.6 mg, 0.60 mmol), K₂CO₃ (2

**Scheme 1** Plausible reaction mechanism

equiv.) and ethylbenzene (2.0 mL) were added into the reaction tube. The resulting solution was stirred at 125 °C for 24 h in an oil bath. All the products were confirmed by comparison with the previously reported ¹H NMR and ¹³C NMR data.

2-(2-(4-Methoxyphenylsulfonyl)-phenyl)-pyridine (**3aa**):^[21] Yield 73% (47.5 mg). White solid, m.p. 128.2~129.8 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.42 (d, *J*=4.8 Hz, 1H), 8.31 (d, *J*=7.6 Hz, 1H), 7.75 (td, *J*=7.7, 1.5 Hz, 1H), 7.64~7.54 (m, 3H), 7.36 (dd, *J*=11.4, 5.1 Hz, 3H), 7.28 (d, *J*=8.5 Hz, 1H), 6.77 (d, *J*=8.9 Hz, 2H), 3.80 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ: 163.0, 156.8, 148.5, 140.0, 135.6, 132.9, 132.8, 132.0, 130.3, 130.0 (2C), 128.9, 128.7, 126.0, 122.6, 113.9 (2C), 55.6; MS (ESI) *m/z*: 326.05 [M+H]⁺.

2-(2-(4-Methylphenylsulfonyl)-phenyl)-pyridine (**3ab**):^[22] Yield 51% (31.5 mg). White solid, m.p. 107 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.38 (d, *J*=4.3 Hz, 1H), 8.32 (d, *J*=7.5 Hz, 1H), 7.73 (t, *J*=7.3 Hz, 1H), 7.6~7.57 (m, 2H), 7.54 (d, *J*=7.8 Hz, 1H), 7.39~7.30 (m, 3H), 7.28~7.23 (m, 1H), 7.10 (d, *J*=8.0 Hz, 2H), 2.34 (s, 3H).

2-(2-Phenylsulfonylphenyl)-pyridine (**3ac**):^[21] Yield 48% (28.3 mg). Slightly yellow solid, m.p. 90~91.6 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.35 (dd, *J*=7.6, 1.2 Hz, 2H), 7.72 (td, *J*=7.7, 1.7 Hz, 1H), 7.63 (m, *J*=15.1, 7.5, 1.5 Hz, 2H), 7.52 (d, *J*=7.8 Hz, 1H), 7.48~7.42 (m, 3H), 7.37 (dd, *J*=7.3, 1.4 Hz, 1H), 7.31 (dd, *J*=8.7, 7.0 Hz, 2H), 7.28~7.22 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ: 156.6, 148.5, 141.3, 140.8, 139.3, 135.6, 133.2, 132.8, 132.1, 129.2, 128.7, 128.6 (2C), 127.6 (2C), 125.9, 122.6; MS (ESI) *m/z*: 296.05 [M+H]⁺.

2-(2-(4-*tert*-Butylphenylsulfonyl)-phenyl)-pyridine (**3ad**): Yield 78% (54.8 mg). Colorless viscous oil. ¹H NMR (500 MHz, CDCl₃) δ: 8.39~8.29 (m, 2H), 7.75~7.68 (m, 1H), 7.66~7.57 (m, 2H), 7.54 (d, *J*=7.8 Hz, 1H), 7.39~7.33 (m, 3H), 7.31~7.25 (m, 2H), 7.23 (dd, *J*=7.1, 5.2 Hz, 1H), 1.27 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ: 156.6, 156.5, 148.5, 140.6, 139.7, 138.1, 135.5, 133.1, 132.0, 128.9, 128.7, 127.5 (2C), 126.0, 125.7 (2C), 122.5, 35.1, 31.0 (3C). Anal. calcd for C₂₁H₂₁NO₂S: C 71.77, H 6.02, N 3.99; found C 71.64, H 6.07, N 4.05; MS (ESI) *m/z*: 352.23 [M+H]⁺.

2-(2-(4-Nitrophenylsulfonyl)-phenyl)-pyridine (**3ae**): Yield 18% (12.2 mg). Yellow solid, m.p. 121.4~123.6 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.38 (d, *J*=4.4 Hz, 1H), 8.03~7.96 (m, 2H), 7.64 (t, *J*=7.6 Hz, 1H), 7.58 (d, *J*=7.7 Hz, 1H), 7.53~7.48 (m, 5H), 7.46~7.40 (m, 1H), 7.22~7.15 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ: 154.0, 150.6, 149.6, 146.1, 140.1, 136.1, 133.6, 131.7, 130.3, 129.4 (2C), 128.3, 125.1, 124.1, 123.8 (2C), 122.3; MS (ESI): Anal. calcd for C₁₇H₁₂N₂O₄S: C 59.99, H 3.55, N 8.23; found C 60.10, H 3.57, N 8.15; MS (ESI) *m/z*: 341.15 [M+H]⁺.

2-(2-(2-Naphthylsulfonyl)-phenyl)-pyridine (**3af**):^[21] Yield 43% (29.7 mg). White solid, m.p. 111.6~114.9 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.41 (dd, *J*=6.3, 2.8 Hz, 1H), 8.15 (d, *J*=4.5 Hz, 1H), 7.92 (s, 1H), 7.80 (dd, *J*=

14.4, 8.4 Hz, 2H), 7.76~7.68 (m, 2H), 7.66~7.56 (m, 3H), 7.56~7.48 (m, 3H), 7.35 (dd, *J*=5.9, 2.8 Hz, 1H), 7.17 (dd, *J*=7.0, 5.2 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ: 156.6, 148.3, 140.9, 139.30, 138.0, 135.5, 134.9, 133.2, 132.1, 131.8, 129.5, 129.3, 129.2, 129.1, 128.9, 128.8, 127.9, 127.3, 125.9, 122.7, 122.7; MS (ESI) *m/z*: 346.17 [M+H]⁺.

2-(2-(1-Naphthylsulfonyl)-phenyl)-pyridine (**3ag**): Yield 29% (20.0 mg). Viscous oil. ¹H NMR (500 MHz, CDCl₃) δ: 8.48 (d, *J*=7.7 Hz, 1H), 8.24~8.17 (m, 2H), 7.92 (d, *J*=8.1 Hz, 1H), 7.82 (d, *J*=8.0 Hz, 1H), 7.69~7.57 (m, 4H), 7.50~7.40 (m, 3H), 7.30 (d, *J*=7.2 Hz, 1H), 7.22~7.12 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ: 156.1, 148.6, 140.4, 140.0, 135.3, 135.1, 134.6, 133.9, 133.0, 132.1, 129.9, 128.9, 128.7, 128.4, 128.3, 128.1, 126.7, 126.0, 124.0, 123.7, 122.5; Anal. calcd for C₂₁H₁₅NO₂S: C 73.02, H 4.38, N 4.06; found C 73.11, H 4.36, N 4.05; MS (ESI) *m/z*: 346.21 [M+H]⁺.

2-(2-(Thiophene-2-sulfonyl)-phenyl)-pyridine (**3ah**):^[21] Yield 55% (33.1 mg). White solid, m.p. 100.4~102.4 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.53 (d, *J*=4.5 Hz, 1H), 8.29 (m, *J*=7.9, 1.2 Hz, 1H), 7.76 (td, *J*=7.7, 1.7 Hz, 1H), 7.65 (td, *J*=7.5, 1.3 Hz, 1H), 7.60 (dd, *J*=7.8, 1.4 Hz, 1H), 7.59~7.54 (m, 2H), 7.40 (dd, *J*=7.4, 1.3 Hz, 1H), 7.31 (m, *J*=7.5, 4.9, 0.9 Hz, 1H), 7.28 (dd, *J*=3.8, 1.3 Hz, 1H), 6.92 (dd, *J*=4.9, 3.9 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ: 156.8, 148.5, 142.9, 140.7, 140.2, 135.8, 134.1, 133.8, 133.3, 132.1, 129.1, 128.9, 127.2, 125.7, 122.8; MS (ESI) *m/z*: 302.12 [M+H]⁺.

2-(2-(5-Chloro-thiophene-2-sulfonyl)-phenyl)-pyridine (**3ai**): Yield 57% (38.2 mg). White solid, m.p. 133.3~136.2 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.60 (d, *J*=4.7 Hz, 1H), 8.26 (dd, *J*=8.0, 0.8 Hz, 1H), 7.79 (td, *J*=7.7, 1.7 Hz, 1H), 7.67 (td, *J*=7.5, 1.1 Hz, 1H), 7.60 (td, *J*=7.9, 1.2 Hz, 1H), 7.55 (d, *J*=7.8 Hz, 1H), 7.42 (dd, *J*=7.5, 1.0 Hz, 1H), 7.35 (dd, *J*=7.1, 5.3 Hz, 1H), 7.15 (d, *J*=4.1 Hz, 1H), 6.78 (d, *J*=4.1 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ: 156.9, 148.5, 140.9, 140.8, 139.8, 139.6, 136.0, 133.5 (2C), 132.1, 129.4, 129.1, 126.6, 125.4, 122.9. Anal. calcd for C₁₅H₁₀ClNO₂S₂: C 53.65, H 3.00, N 4.17; found C 53.70, H 3.03, N 4.08; MS (ESI) *m/z*: 336.05 [M+H]⁺.

2-(2-(4-*tert*-Butylphenylsulfonyl)-4-methylphenyl)-pyridine (**3bd**): Yield 73% (53.3 mg). White solid. m.p. 175.0~177.0 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.32 (d, *J*=4.7 Hz, 1H), 8.19 (s, 1H), 7.71 (td, *J*=7.7, 1.7 Hz, 1H), 7.54 (d, *J*=7.8 Hz, 1H), 7.45 (d, *J*=7.7 Hz, 1H), 7.40~7.35 (m, 2H), 7.33~7.28 (m, 2H), 7.26 (d, *J*=7.7 Hz, 1H), 7.24~7.20 (m, 1H), 2.52 (s, 3H), 1.29 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ: 156.7, 156.3, 148.4, 139.3, 139.0, 138.2, 137.8, 135.5, 133.7, 132.0, 129.2, 127.5 (2C), 126.1, 125.6 (2C), 122.3, 35.1, 31.0 (3C), 21.3; Anal. calcd for C₂₂H₂₃NO₂S: C 72.30, H 6.34, N 3.83; found C 72.11, H 6.33, N 3.89; MS (ESI) *m/z*: 366.14 [M+H]⁺.

1-(2-(4-*tert*-Butylphenylsulfonyl)-phenyl)-1*H*-pyrazole (**3cd**): Yield 28% (19.0 mg). Colorless viscous oil. ¹H NMR (500 MHz, CDCl₃) δ: 8.40 (dd, *J*=7.6, 1.8 Hz, 1H), 7.93 (d, *J*=2.4 Hz, 1H), 7.70~7.61 (m, 2H), 7.41 (d, *J*=1.5 Hz, 1H), 7.38~7.30 (m, 5H), 6.40 (t, *J*=2.1 Hz, 1H), 1.28 (s,

9H); ^{13}C NMR (126 MHz, CDCl_3) δ : 157.2, 140.8, 138.9, 137.6, 136.7, 134.4, 134.1, 130.3, 129.6, 129.2, 127.4 (2C), 125.8 (2C), 106.4, 35.1, 31.0 (3C). Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$: C 67.03, H 5.92, N 8.23; found C 67.08, H 5.93, N 8.19; MS (ESI) m/z : 341.13 $[\text{M}+\text{H}]^+$.

3.4 Catalyst recycle experiment

After each reaction cycle, the solvent, substrate, and products were removed by centrifugation; the separated catalyst was washed thoroughly with 0.1 mol/L 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.

3.5 Hot filtration test

The hot filtration test was applied by filtering the model 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** and TOF. Then the filtered reaction solution continued to react for 2 h under normal conditions, and was detected by GC again.^[18]

Supporting Information The ^1H NMR and ^{13}C NMR spectra of the products. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn>.

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