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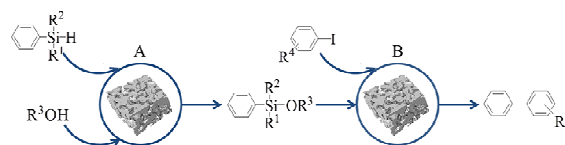
Zhiwen Li, Sha Lin, Lisha Ji, Zhonghua Zhang, Xiaomei Zhang,* Yi Ding*

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ARTICLE TYPE

Nanoporous Palladium Catalyzed Silicon-Based One-Pot Cross-Coupling Reaction of Aryl Iodides with Organosilanes

Zhiwen Li,[a] Sha Lin,[a] Lisha Ji,[a] Zhonghua Zhang,[b] Xiaomei Zhang*[a] and Yi Ding*[ab]

One-pot cross-coupling of aryl iodides with organosilanes is realized in excellent yield by utilizing dealloyed nanoporous palladium as a sustainable and heterogeneous catalyst. The reaction is completed under mild conditions and the catalyst
10 **can be reused for several times without evident loss of its catalytic activity.**

One-pot synthesis is particularly desirable in synthetic chemistry and chemical engineering, because it dramatically simplifies the processing by avoiding separation and purification of reaction
15 intermediates.[1-2] Nanostructured catalysts have been found to play critical roles in these reactions due to their unique structural properites.[3-5] As a result, great efforts have been made to seek new nanocatalysts and develop the related catalytic systems that are highly effective and sustainable for one-pot reaction.

20 The metal-catalyzed carbon–carbon cross-coupling reaction is among the most crucial transformations in synthetic chemistry.[6-7] The silicon-based cross-coupling reaction, as a burgeoning method, has received increasing interest due to its low toxicity, high chemical stability, and broad availability.[8-10] To date, a
25 variety of silicon coupling reagents have been developed, including organo(alkoxy)silanes,[11-12] organosilanols[13-15] and so on.[16-19] Among them, introduction of OH or OR groups into these silicon coupling reagents is believed to play an important role in the transformation of the carbon-silicon bond of the silicon
30 coupling reagents to the carbon-carbon bond of the cross-coupling products. However, traditional methods to synthesize these compounds are often difficult and toxic.[21-24] Although recent investigations have revealed some facile routes to fabricate the silicon coupling reagents [organo(alkoxy)silanes and
35 organosilanols] by oxidation of organosilanes with ROH (water or alcohols),[25-26] these compounds still need to be purified before they are used for the following silicon-based cross-coupling reaction. Taking green and sustainable concept into consideration, development of an atom-economical and environmentally
40 attractive one-pot catalytic system is a good choice for such silicon-based cross-coupling reaction, particularly in which normal organosilanes could be used as starting materials.

Dealloyed nanoporous metals are a new class of monolithic heterogeneous catalysts, which have shown attractive catalytic
45 properties such as high activity, selectivity, stability and recyclability in some important organic reactions in recent years.[27-28] For example, nanoporous gold (np-Au or NPG) showed excellent behaviour in oxidation and hydrogenation reactions,[29-32] while nanoporous silver (np-Ag) exhibited
50 particular selectivity when used as catalysts for gas-phase oxidation of alcohols.[33] As homogeneous palladium complex catalysts are widely used for cross-coupling reactions, the development of novel heterogeneous palladium catalysts is highly desired as they can be readily separated and recycled. Recently,
55 nanoporous palladium (np-Pd) was reported to have high activity towards Suzuki and Heck type cross-coupling reactions.[34-35] Considering that palladium nanoparticle catalyst was capable of realizing selective oxidation of organosilanes to organosilanols or organo(alkoxy)silanes.[36-37] So we conjecture if np-Pd could be a
60 prospective catalyst to combine the oxidation of organosilanes by ROH (water or alcohols) with silicon-based cross-coupling reaction and realize the direct synthesis of aryl-aryl products in one-pot, which to our knowledge has never been realized before.
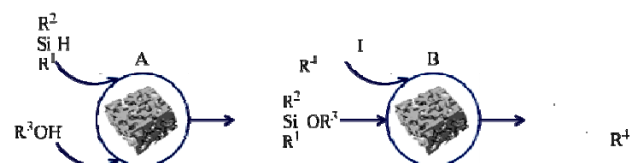
65 **Scheme 1** Schematic representation of silicon-based cross-coupling reaction. Cycle A: Oxidation of organosilanes; Cycle B: C-C cross-coupling reaction.

In the present work, we demonstrate for the first time that nanoporous palladium is a highly effective and sustainable
70 catalyst toward one-pot cross-coupling of aryl iodides with organosilanes (Scheme 1). With this nanostructured green catalyst, organosilanols or organo(alkoxy)silanes were first obtained via oxidation of organosilanes with ROH (water or alcohols). And within the same reaction system, these products
75 could further react with aryl iodides, generating the aryl-aryl coupling products in excellent yield. The catalyst could be recycled several times without evident loss of its catalytic activity.
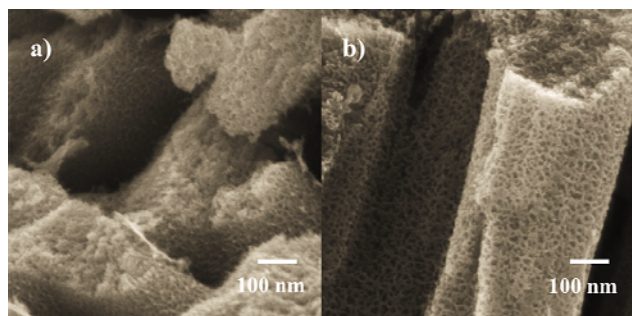
Fig. 1 SEM images of dealloyed np-Pd a) before catalytic reaction and b) after being used for five times.

Nanoporous palladium used in the present was obtained by selective leaching of aluminium from a $Al_{77}Pd_{23}$ (at.%) alloy foil using 10 wt % sodium hydroxide solution for 6 h at room temperature. The morphology of this nanomaterial was characterized by scanning electron microscopy (SEM). As shown in Figure 1a, the ligaments and pores are formed uniformly across the entire np-Pd and their diameter is around 5-10 nm. Compared with the size of np-Pd (30–60 nm) made by dealloying $Pd_{30}Ni_{50}P_{20}$ which has been used in Suzuki reactions,[34,35] the size of nanopore obtained here is much smaller, which suggests its potential of having higher catalytic activity.

Table 1. Oxidation of organosilanes by using np-Pd as the catalyst.

$$R_{(4-n)}SiH_n + n\ ROH \xrightarrow{\text{np-Pd}} R_{(4-n)}Si(OR)_n + n\ H_2$$

$$1 \qquad\qquad\qquad\qquad\qquad 2$$

Entry[a]	$R_{(4-n)}SiH_n$	ROH	t [h]	$R_{(4-n)}Si(OH)_n$	Yield [%]
1	Me₂PhSiH **1a**	H_2O	3	Me₂PhSiOH **2a**	98
2	Me₂PhSiH **1a**	CH_3OH	3	Me₂PhSiOCH₃ **2aa**	95
3	Me₂PhSiH **1a**	C_2H_5OH	3	Me₂PhSiOC₂H₅ **2aaa**	95
4	Ph₂SiH₂ **1b**	H_2O	2	Ph₂Si(OH)₂ **2b**	85
5	Ph₃SiH **1c**	H_2O	4	Ph₃SiOH **2c**	90
6	Et₃SiH **1d**	H_2O	3	Et₃SiOH **2d**	95
7	Bu₃SiH **1e**	H_2O	3	Bu₃SiOH **2e**	95
8	PhSiH₃ **1f**	CH_3OH	4	PhSi(OCH)₃ **2f**	95
9	PhSiH₃ **1f**	C_2H_5OH	4	PhSi(OC2H₅)₃ **2ff**	95

a) Reactions were performed using np-Pd (30 mg), **1** (1.0 mmol), ROH (0.2 mL) in 1.5 mL of THF at room temperature.

We first studied np-Pd's activity toward the selective oxidation of organosilanes. For this reaction, both acetone and tetrahydrofuran (THF) are suitable solvent. Considering that THF is more suitable for the subsequent silicon-based cross-coupling reaction, it was selected as the solvent for this reaction. The dimethylphenylsilane (**1a**) was tested first with 0.2 mL water in the presence of 30 mg np-Pd at room temperature. After 3 h, dimethylphenylsilanol (**2a**) was obtained with 98% yield (entry 1, Table 1). Substitution of water with methanol and ethanol would generate the corresponding organosilyl ethers dimethylphenylmethoxylsilane (**2aa**) and dimethylphenylethoxylsilane (**2aaa**), again in high yield (entry 2, 3). We then explored different substrates. As shown in Table 1, both aromatic and aliphatic organosilanes could be activated and the reaction typically finished in a few hours, indicating the high activity of np-Pd toward the oxidation of organosilanes. Ph₃SiH, Et₃SiH, and Bu₃SiH containing one H atom, were oxidized to the corresponding organosilanols or organo(alkoxy)silanes with one OH or OR group (entry 5-7). PhSiH₃ containing three H atoms could also be effectively oxidized to the corresponding PhSi(OCH₃)₃ (**2f**), and PhSi(OCH₂CH₃)₃ (**2ff**), respectively (entry 8, 9).

We then investigated np-Pd's activity toward silicon-based cross-coupling reaction. Taking follow-up one-pot reaction into consideration, the equivalent amount catalyst and the same solvent were used. Dimethylphenylmethoxylsilane was chosen as nucleophilic coupling partner to react with 1.5 mmol 4-iodotoluene and three equivalent amount tetrabutylammonium fluoride (TBAF, used as base) at 80 °C. After reacting for 3 h at this temperature, 4-methyl-bipheny as the cross-coupling product was obtained (55% yield). Similar with dimethylphenylmethoxylsilane (**2aa**) activated by one methoxyl, dimethylphenylsilanol (**2a**) activated by one hydroxyl also gave the cross-coupling product with 75% yield. In comparison with **2a** and **2aa**, phenyltrimethoxylsilane (**2f**) activated by three methoxyl groups exhibited perfect activity. The reaction time was distinctly shortened and the corresponding 4-methyl-bipheny was obtained almost quantitatively. These results indicated that the heterogeneous np-Pd was a suitable catalyst for silicon-based cross-coupling reaction and also notably implied the positive effect of OR on the activity of organosilanes.
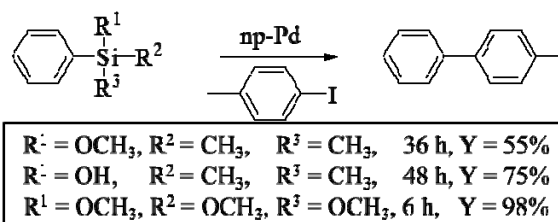
Scheme 2 Np-Pd catalyzed the silicon-based cross-coupling reaction.

The above experimental observations have demonstrated that np-Pd was active for organosilane oxidation and silicon-based cross-coupling reaction individually. We then came up with an idea of realizing these two reactions in one system, i.e., one-pot synthesis of aryl-aryl coupling product from aryl iodides and organosilanes. Based on the above optimized experimental conditions, the reaction was initiated with phenylsilane (**1f**) and 0.2 mL methanol in 1.5 mL THF solvent at room temperature. When no obvious bubbles emerged, 4-iodotoluene and 3 mmol TBAF were added into the system without changing the reaction vessel except that the reaction temperature was elevated to 80 °C. After reacting at this temperature for 6 h, 4-methyl-bipheny was obtained in 91% yield, indicating the higher activity of np-Pd toward the one-pot cross-coupling of aryl iodides with organosilanes. We then examined the substrate generality under the same reaction conditions. Aryl iodides derivatives containing both electron-donating and electron-withdrawing group were explored. As shown in Table 2, the coupling of aryl iodides

containing an electron-withdrawing group (nitro, hydroxy and acetyl) produced relatively lower efficiencies, (38-62% yields, entry 4-6). However, for aryl iodides containing an electron-donating group on the aromatic ring such as methyl, methoxyl and fluoro could couple with phenylsilanetriol smoothly and gave the corresponding products with high yields (91-95%, entry 1-3).

Table 2. The one-pot cross-coupling reaction of aryl iodides with organosilanes.

Entry	1	R³OH	R⁴	t_1+t_2 [h]	4	Yield / %
1			CH₃	10	**4a**	91
2			OCH₃	12	**4b**	96
3		CH₃OH	F	8	**4c**	95
4			COCH₃	20	**4d**	62
5			NO₂	10	**4e**	38
6			OH	20	**4f**	45
7			CH₃	10	**4a**	90
8		C₂H₅OH	OCH₃	12	**4b**	95
9			F	10	**4c**	95
10			COCH₃	20	**4d**	60
11			CH₃	70	**4a**	76
12		H₂O	OCH₃	26	**4b**	82
13			F	24	**4c**	47
14			COCH₃	24	**4d**	20
15			CH₃	40	**4a**	50
16		CH₃OH	OCH₃	26	**4b**	67
17			F	24	**4c**	45
18			COCH₃	16	**4d**	50

a) Reactions were performed using np-Pd (30 mg), **1** (1.0 mmol), ROH (0.2 mL) in 1.5 mL of THF at room temperature for 2 h. Then aryl iodides (1.5 mmol) and TBAF (3 mmol) were added and the mixture were elevated to 80 ºC.

The reusability of np-Pd was also tested. As np-Pd holds a macroscopic dimension with nanoscale feature size, it can be easily separated by simple filtration and reused without further purification except washing it with water and THF. As shown in Table 3, no significant loss of the catalytic activity was observed (entry 1–5) after np-Pd was reused for four additional times. Figure 1b is the SEM image of the recovered catalyst after five uses. Compared to the fresh one (Figure 1a), no evident change in porous morphology and feature dimension was observed. This is markedly different from dealloyed nanoporous gold (np-Au) and silver (np-Ag) catalysts in other reaction systems as quite severe structural coarsening was often observed for these materials.[28]

To clarify whether np-Pd catalyst has been leached into the reaction mixture or not, we carried out the following experiments. After 4-iodotoluene was added into the reaction system of phenylsilane and methanol under the standard conditions, the reaction was carried out for 3 h and then the catalyst was separated from the reaction mixture by filtration. Under this condition the conversion of 4-iodotoluene reached 50% by HPLC analysis. The first half of the filtrate remained at this temperature without catalyst for additional 3 h and 7% further consumption of 4-iodotoluene was observed. In comparison, if we added the catalyst into the residual filtrate, the conversion of 4-iodotoluene could reach 95% after 3 h. We then separated out the catalyst and analyzed the solution by inductivity coupled plasma atomic emission spectroscopy (ICP-AES). Results showed that the leaching of palladium was lower than the detection limits (< 0.02 ppm). These results are consistent with previous observations by Tanaka and coworkers who used np-Pd for Suzuki reactions.[30-31] Although our present results can't exclude the possibility of Pd leaching, the majority of the catalytic activity seemed to originate from the catalytic np-Pd itself.

Table 3. Reusability of np-Pd for silicon-based one-pot cross-coupling reaction.

Entry	Catalyst	t1+t2 [h]	Yield %
1	fresh	15	91
2	reused 1	15	92
3	reused 2	15	90
4	reused 3	15	90
5	Reused 4	15	90

a) Reactions were performed using np-Pd (30 mg), **1f** (1.0 mmol), MeOH (0.2 mL) in 1.5 mL of THF at room temperature for 2 h. After that reactions were performed adding 4-Iodotoluene (1.5 mmol), TBAF (3 mL 1 M in THF) at 80 ºC.

Conclusions

In conclusion, we reported a noteworthy feature of dealloyed np-Pd catalyst for one-pot cross-coupling reaction of aryl iodides with organosilanes. Based on the experimental observations of np-Pd's activity in catalyzing organosilane oxidation with ROH (water or alcohols) and silicon-based cross-coupling reaction, we realized a one-pot synthesis from aryl iodides and organosilanes to produce directly the aryl-aryl coupling products in excellent yield. The results described here not only represent the first report of dealloyed nanoporous metals used in one-pot reaction but also are helpful to promote the development of new sustainable processes for clean and efficient one-pot green synthesis.

Acknowledgements

Notes and references

ᵃ Center for Advanced Energy Materials & Technology Research (AEMT), and School of Chemistry and Chemical Engineering, Shandong

University, Jinan 250100, China. Fax: (+86) 531-88366513; E-mail:
yding@sdu.edu.cn; zhangxiaomei@sdu.edu.cn
ᵇ Key Laboratory for Liquid-Solid Structural Evolution and Processing of
Materials, Ministry of Education,Shandong University, Jinan 250061,
5 *China.*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant
10 to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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