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Highly Lewis-Acidic Pd(IV) Surface in Pd@SiO₂ Nanocatalysts for Hydroalkoxylation Reactions[†]

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Pd(IV) species, known to be critical intermediates in homogeneous catalysis, were successfully generated on the surface of Pd nanocatalysts by oxidation with iodobenzene dichloride (PhICl₂) or N-chlorosuccinimide (NCS). In particular, the Pd@SiO₂ yolk-shell nanocatalyst activated by PhICl₂ showed high reactivity and stability superior to the other Pd-based catalysts for hydroalkoxylation reactions even at 25 °C.

Well-defined nanostructured materials have emerged as a new class of heterogeneous catalysts, of which the reactivity and selectivity can be rationally modulated by their size, surface structure, and composition.¹⁻⁴ For instance, heterogeneous Pd species have been demonstrated to be effective catalysts in a variety of reaction systems,^{5,6} including C-C bond coupling^{7,8} and C-H bond functionalization reactions.⁹ Such efficient nanoscale heterogeneous catalysts are now classified as “nanocatalysts”.¹⁰⁻¹⁵ Among various designs of nanocatalysts, metal/metal oxide bicomponent systems, i.e. Pt@SiO₂ core-shell nanoparticles, could successfully mimic bifunctional heterogeneous catalysts, and exhibited remarkable stability in high temperature reactions.^{16,17} We have also introduced Ni@SiO₂ and Pd@SiO₂ yolk-shell nanostructures which, as highly active catalysts for hydrogen transfer and Suzuki coupling reactions, showed higher stability and reusability than homogeneous counterparts could achieve.^{18,19} However, active species of the nanocatalysts were limited to only a neutral state, metal(0),^{5-9,20} albeit that numerous catalytic reactions involved high-valent transition metals.²¹

Recently, Toste, Somojai, and coworkers disclosed a new concept of applying heterogeneous catalysts to known homogeneous catalytic reactions through generation of electrophilic surfaces on noble metal nanoparticles (NPs).²²⁻²⁴ They showed that π -bond activation reactions were efficiently promoted by Pt(II) or Pt(IV) species on the NP surface.²² It appeared that in a Pd surface more Lewis-acidic than Pd(II) could be generated such as Pd(IV) species. However, the existence of Pd(IV) species on the Pd NP surface is questionable because in homogeneous catalysis they are considered to be transient intermediates in Pd(II)-catalyzed C-H functionalization reactions.²⁵⁻²⁷ Thus, we have investigated the hydroalkoxylation reaction using Pd and Pd@SiO₂ yolk-shell nanocatalysts under oxidative conditions in order to identify the

actual active species on the surface. In the present study, we envisioned that (a) the Pd(IV) species were predominantly generated on the surface by the oxidation with PhICl₂; (b) the surface species were effectively modulated by the oxidation with N-chlorosuccinimide (NCS) and PhI(OAc)₂, which largely changed the catalytic activity; and (c) the Pd@SiO₂ nanocatalysts with surface oxidation were the only Pd catalysts active for the reactions at 25 °C.

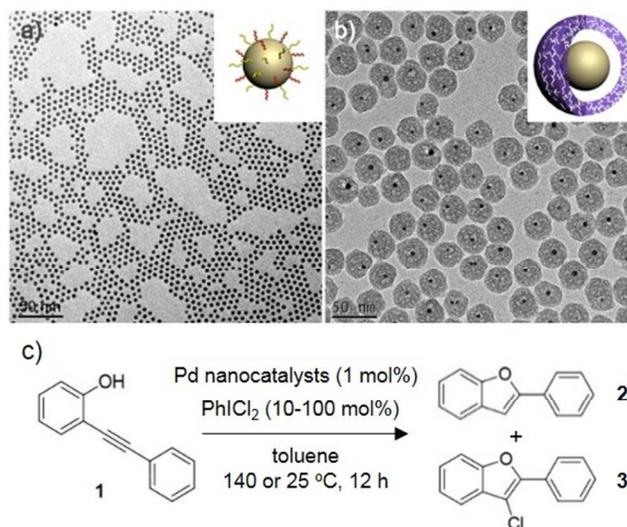


Fig. 1 TEM images of (a) Pd NPs and (b) Pd@SiO₂ yolk-shell nanocatalysts, and (c) a reaction scheme for hydroalkoxylation of 2-phenylethynylphenol (**1**) to **2** and electrophilic chlorination of **2** to **3** (see text).

Pd NPs were synthesized by thermal decomposition of a Pd precursor, Pd(acac)₂, in the presence of oleylamine and trioctylphosphine.²⁸ The particles were spherical with an average particle diameter of 5.0 ± 0.3 nm (Fig. 1a). The Pd@SiO₂ yolk-shell structure was formed via the water-in-oil microemulsion method, and by partial dissolution of the silica shells under hydrothermal conditions. After heat treatment under H₂, the resulting yolk-shell structure showed an average diameter of 30 ± 2.6 nm, bearing Pd

cores with an average size of 5.1 ± 0.4 nm and large vacancies in the SiO_2 shells, identified in the transmission electron microscopy (TEM) image (Fig. 1b). The Pd and Pd@ SiO_2 NPs were treated in-situ with PhICl_2 , and used for hydroalkoxylation of 2-phenylethynylphenol (**1**) as shown in Fig. 1.

A survey of homogeneous and heterogeneous reactions at elevated temperature (140°C) was summarized in Table 1. Consistent with previous reports, homogeneous Pd(OAc)₂ and PdCl₂ only resulted in 10 and 7 % of 2-phenylbenzofuran (**2**), respectively (Table 1, entries 1 and 2). When we used heterogeneous Pd catalysts, Pd and Pd@ SiO_2 yolk-shell NPs, both catalysts were inactive in the absence of PhICl_2 . (Table 1, entries 3 and 5). However, in the presence of 25 mol% PhICl_2 , the Pd catalyst (1 mol%) successfully promoted the reaction with 100% conversion (Table 1, entries 4 and 6). In our experiments, we identified 3-chloro-2-phenylbenzofuran (**3**) as a side product (Fig. S1, ESI[†]) and demonstrated that the chlorination of **2** proceeded by reaction with PhICl_2 even without Pd catalysts, while no reaction took place between **1** and PhICl_2 (Fig. S2, ESI[†]). Thus, we could utilize the conversion of cyclization by combining the yields of **2** and **3**.

To investigate oxidants other than PhICl_2 for use in catalyst activation, PhI(OAc)_2 and N-chlorosuccinimide (NCS) were tested. Under the reaction conditions tested, PhI(OAc)_2 could not activate the Pd@ SiO_2 catalyst for the hydroalkoxylation reaction even when using a large amount (Table 1, entry 7). In contrast, NCS facilitated the Pd catalysts, Pd and Pd@ SiO_2 yolk-shell NPs to provide cyclized products as efficiently as PhICl_2 (Table 1, entries 8 and 9).

Table 1 Hydroalkoxylation of **1** using homogeneous and heterogeneous Pd catalysts at 140°C .^a

No	Catalyst (1 mol%)	Oxidant (X mol%)	Cyclization (%) (2 + 3) ^b	Conversion (%) (2 : 3) ^b
1	Pd(OAc) ₂	-	10	10:0
2	PdCl ₂	-	7	7:0
3	Pd NPs	-	0	-
4	Pd NPs	PhICl_2 (25)	100	80:20
5	Pd@ SiO_2	-	0	-
6	Pd@ SiO_2	PhICl_2 (25)	100	76:24
7	Pd@ SiO_2	PhI(OAc)_2 (100)	0	-
8	Pd NPs	NCS (25)	100	90:10
9	Pd@ SiO_2	NCS (25)	100	94:6

^aReactions in a sealed vial in toluene for 12 h. ^bDetermined by ¹H NMR.

X-ray photoelectron spectroscopy (XPS) is one of the most effective tools to identify the Pd species on heterogeneous surfaces.^{29,30} In the Pd NPs without treatment, the Pd 3d core-level lines were fitted with two main peaks, where the Pd 3d_{5/2} peak at 335.8 eV was assignable to the Pd(0) species (Fig. 2a). Remarkably, after the treatment with PhICl_2 , the major Pd 3d_{5/2} peak shifted to the higher binding energy at 338.2 eV, which could be assigned to the Pd(IV) species. This clear change indicated that the Pd surface oxidation by PhICl_2 mainly generated Pd(IV) species, not Pd(II). The oxidized surface was stable enough to conduct the measurement in air without significant degradation. The intensity of the Cl 2p_{3/2} peak at 199.0 eV was roughly correlated with that of the Pd peaks, revealing that the coordination of Cl atoms could stabilize high oxidation states of the surface atoms (Fig. S5, ESI[†]).²³

After stirring in toluene at 140°C for 1 h, the Pd(IV) fraction rapidly increased and reached the maximum value of 80%, along with an increase in the amount of PhICl_2 up to 1.2 equiv (Fig. 2c and Fig. S6, ESI[†]). This observation is surprising because stable organometallic Pd(IV) complexes have rarely been reported in homogeneous reactions,²⁵⁻²⁷ which is opposite from stable Pt(IV) species known to be active in many catalytic reactions.³¹ A prolonged treatment of PhICl_2 for 12 h significantly diminished the Pd(IV) fraction to 24% (Figure 2d and Fig. S7, ESI[†]), indicating that the highly electrophilic Pd(IV) species were slowly degraded into Pd(0) and Pd(II) species.³²

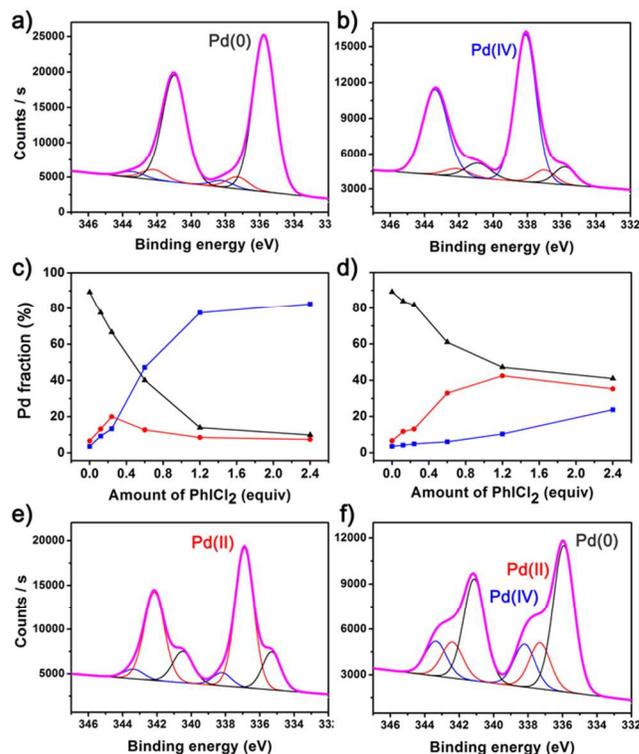


Fig. 2 XPS spectra of the Pd 3d level (pink) and deconvolution peaks of the Pd species, Pd(0) (black), Pd(II) (red), and Pd(IV) (blue); (a) for pristine Pd NPs and (b) for Pd NPs after treatment with PhICl_2 (2.4 equiv) at 140°C for 1 h; Fraction of the Pd species after treatment with variable amounts of PhICl_2 (c) for 1 h and (d) for 12 h; XPS spectra of the Pd 3d level for Pd NPs after treatment (e) with PhI(OAc)_2 (2.4 equiv) and (f) with NCS (2.4 equiv).

PhICl_2 is an excellent oxidant by which to generate the Pd(IV) species, but apparently, another oxidants need to be surveyed for their potential for expansion of reaction scopes. After treatment with PhI(OAc)_2 under the experimental conditions, the Pd 3d_{5/2} peak appeared at 337.0 eV, corresponding to the Pd(II) species (Fig. 2e). As shown in entry 7 of Table 1, no hydroalkoxylation reaction occurred, directly indicating that the Pd(II) species were not acidic enough to catalyse the reaction. In contrast, treatment with NCS generated Pd(IV) species in a significant fraction (18%), as determined by quantitative analysis (Fig. 2f). This elucidated the effective conversion into the products indicated in entries 8 and 9 of Table 1. In a homogeneous system, NCS successfully generated a stable Pd(IV) compound via oxidative addition to the Pd(II) center.³³

Table 2 Hydroalkoxylation of **1** using homogeneous and heterogeneous Pd catalysts at 25°C .^a

No	Catalyst (1 mol%)	PhICl ₂ (mol%)	Cyclization (%) (2 + 3) ^b	Conversion (%) (2:3) ^b
1	Pd(OAc) ₂	0	9	9:0
2	PdCl ₂	0	<1	-
3	Pd NPs	25	0	-
4	Pd@SiO ₂	25	100	78:22
5	Pd@SiO ₂	10	100	95:5
6 ^c	Pd@SiO ₂	10	0	-

^aReactions in a sealed vial in toluene for 12 h. ^bDetermined by ¹H NMR. ^cExcess surfactants were added.

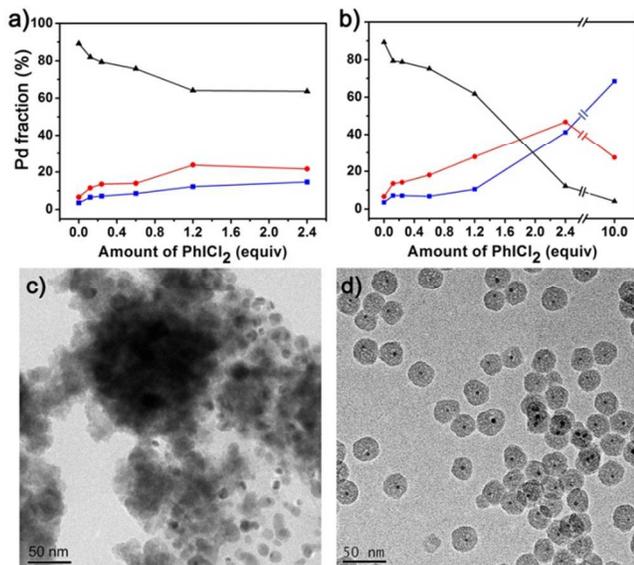


Fig. 3 Fraction of the Pd species, Pd(0) (black), Pd(II) (red), and Pd(IV) (blue), after treatment with variable amounts of PhICl₂ at 25 °C for (a) 1 h and (b) 12 h; TEM images of (c) Pd NPs and (d) Pd@SiO₂ yolk-shell catalyst recovered after the reactions of entries 4 and 6 in Table 1.

At elevated temperature (140 °C) in toluene, the Pd and Pd@SiO₂ yolk-shell NPs exhibited similar activities. However, at 25 °C, only the Pd@SiO₂ catalyst with PhICl₂ was remarkably active for the hydroalkoxylation reaction. The homogeneous Pd(OAc)₂ and PdCl₂ catalysts yielded 9% and trace amounts of products, respectively (Table 2, entries 1 and 2). While 1 mol% Pd NPs with 25 mol% of PhICl₂ did not yield any products at 25 °C, distinctively, 1 mol% Pd@SiO₂ yolk-shell NPs with 25 mol% PhICl₂ exhibited complete conversion (Table 2, entries 3 and 4). Moreover, the product selectivity increased to 95:5 for 2:3 when the amounts of PhICl₂ were reduced to 10 mol% (Table 2, entry 5). XPS analysis showed that oxidation of the catalyst surface by PhICl₂ at 25 °C for 1 h, was not as effective as that at 140 °C, by which significant amounts of Pd(II) species were generated on the surface (Fig. 3a). However, prolonged treatment by PhICl₂ (10 equiv) for 12 h successfully provided Pd(IV) as a major species (69%, Fig. 3b, and Fig. S8, ESI†). Although Pd(IV) species were effectively generated at 25 °C, the Pd NPs were inactive. In contrast, all the surfactants in the Pd@SiO₂ catalyst were perfectly removed by heat treatment at 500 °C under a flow of H₂, while the catalyst structure was stable against particle agglomeration due to the protective SiO₂ shell.³⁴ Thus, only the surfactant-free Pd@SiO₂ catalyst was effective at 25

°C. As expected, the addition of surfactants to the Pd@SiO₂ catalyst completely eliminated its catalytic activity (Table 2, entry 6).

Another advantage of the Pd@SiO₂ yolk-shell catalyst is high stability after reaction. After the treatment with PhICl₂ at 140 °C (Table 1, entry 4), the Pd NPs were severely agglomerated and formed large clusters (Fig. 3c). In contrast, the Pd@SiO₂ catalysts activated with PhICl₂ were very stable without any structural deformation after the reaction at 140 °C for 12 h (Table 1, entry 6, and Fig. 3d).

The hydroalkoxylation reactions by the Pd@SiO₂ catalyst proceeded in a heterogeneous way. The negative effect of the surfactants on the Pd@SiO₂ yolk-shell catalyst (Table 2, entry 6) indicated that the reaction actually occurred on the heterogeneous Pd surface. To gain more evidence of this, the catalyst was filtered after the reaction in entry 6 of Table 1, and the filtrates were analysed by ICP-OES (inductively coupled plasma-optical emission spectrometer). Pd species were undetected at the detection limit of the measurement (0.003 ppm), revealing that the catalysts were very stable against leaching during the reaction. The Pd@SiO₂ catalyst could be recycled six times by a simple decantation procedure, and was used for hydroalkoxylation reaction without a significant decrease of activity (Fig. S3, ESI†).

In summary, the Pd and Pd@SiO₂ nanocatalysts generated Pd(IV) as the primary surface species by oxidation with PhICl₂. The Pd(IV) species were highly active for the hydroalkoxylation reaction of **1**, and the activity was even higher than that of the homogeneous Pd catalysts. Two products, **2** and **3**, were identified, which were selectively yielded by using different amounts of PhICl₂. The catalyst surface was also activated to form Pd(IV) by the addition of NCS, leading to high activity of the hydroalkoxylation reaction, whereas Pd(OAc)₂ formed primarily Pd(II) on the surface, which was not efficient for the reaction. In particular, the Pd@SiO₂ yolk-shell catalyst exhibited remarkable activity, higher than those of other homogeneous and heterogeneous catalysts at 25 °C, with the additional advantage of excellent stability. Consequently, by the combination of appropriate activation reagents, this type of nanocatalyst system bearing various metal NPs should be applicable for a wide range of valuable organic reactions. Such combinations should provide excellent stability, high levels of activity, and superior selectivity to homogeneous systems.

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†Electronic Supplementary Information (ESI) available: Experimental, XPS, and ¹H NMR spectra of **1**, **2**, and **3**. See DOI: 10.1039/c000000x/

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