Cooperative Catalysis of Palladium Nanoparticles and Cobalt Oxide Support for Formylation of Aryl Iodides under Syngas Atmosphere

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Abstract

Formylation of aryl iodides proceeded effectively in the presence of palladium nanoparticles on cobalt oxide under a syngas atmosphere to afford aldehydes up to 91% yield. A cooperative effect between palladium nanoparticles and cobalt species derived from the support was integral to efficient transformation. Both palladium and cobalt were revealed to exist as zero valent metals after H₂ treatment from X-ray absorption near edge structure and X-ray diffraction spectra. The catalyst could be reused at least 7 times without significant loss of activity.

Keywords

Heterogeneous catalyst, Palladium nanoparticles, Cobalt oxide, Cooperative catalysis, Formylation

1. Introduction

The palladium-catalyzed carbonylation of aryl halides provides a versatile organic transformation mechanism for the preparation of carbonyl compounds [1]. Among the possible carbonylation products generated from this type of reaction, aldehydes are an important class of materials that are key intermediates in pharmaceuticals, agrochemicals, dyes, and perfumery. Several electrophilic aromatic substitution reactions classes, such as the Gattermann–Koch, Vilsmeier–Haack, Reimer–Tiemann and Duff reactions, have been employed to prepare aromatic aldehydes [2,3]. However, these reactions are sensitive to the electronic effects of substrate substituents, which can have a significant influence on regioselectivity and the reactivity rate. In addition, strongly acidic or basic conditions are generally required, thus narrowing the range of suitable substrates on the basis of the tolerance of their functional groups. An alternative route to aldehyde products proceeds via formylation of organolithium or organomagnesium compounds, which can be generated from aryl halides, with various formylating reagents such as *N,N*-dimethylformamide or *N*-formylpiperidine [4–7], but these methods suffer from competing reactions of substrate functional groups with the highly reactive organometallic reagents. Promisingly, the palladium-catalyzed formylation of aryl halides under a CO atmosphere, originally reported by Heck in 1974 [8], offers a more compatible procedure. Although an elevated CO pressure and reaction temperature were essential in the seminal report, the conditions could be improved by

inclusion of various hydride sources in the reaction mixture [9–15]. Beller and co-workers reported an industrially applicable system containing $\text{Pd}(\text{OAc})_2$ and $\text{P}(\text{1-adamantyl})_2n\text{Bu}$ (cataCXum[®]A) [16–18]. Although these modifications do improve on the practical limitations of the reaction, appropriate and efficient heterogeneous catalysts have not yet been developed for the process, and only one example of an immobilized Pd–phosphine complex [19] is described in the literature.

Recently, we developed an effective catalyst system comprising gold nanoparticles and a cobalt oxide support ($\text{Au}/\text{Co}_3\text{O}_4$) that may be used as an alternative to homogeneous dicobalt octacarbonyls under a syngas (CO/H_2) atmosphere [20–25]. Generally, oxide-supported catalysts can be prepared by simple methods from inorganic salts, which does not include multistep organic synthesis, thus inexpensive bulk supply is possible. Part of the cobalt oxide support is reduced to $\text{Co}(0)$ by spillover hydrogen arising from the effects of Au nanoparticles. The reduced metal binds CO to form a cobalt carbonyl equivalent. Pd nanoparticles display similar spillover properties as those described for Au nanoparticles, and are therefore expected to play dual roles as a Pd catalyst and a co-catalyst for promotion of the reduction of a cobalt oxide support. Hidai and co-workers reported carbonylation reactions employing a combination of a homogeneous Pd catalyst and metal carbonyls [26–30]. We anticipated that $\text{PdO}/\text{Co}_3\text{O}_4$ would act as a suitable catalyst for the formylation of aryl halides under conditions that are free of external hydride and additional ligands.

2. Experimental section

2.1 General remarks

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer. ^1H assignment abbreviations are the following; singlet (s), doublet (d), triplet (t), and multiplet (m). GC analysis was carried out using Agilent GC 6850 series II equipped with J&W HP-1 column (length 30 m, I.D. 0.32 mm). Column chromatography was performed on silica-gel (Kanto Chemicals, Silica gel 60N, spherical, neutral; particle size 40–100 μm). Formylation reactions were carried out using a 50 mL stainless steel autoclave reactor (Toyo Koatsu Co. Ltd.) with a glass tube equipped inside. High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations were performed by using JEOL JEM-3000F operating at 300 kV. Powder

X-ray diffraction (XRD) data were collected by Rigaku Multiflex X-ray diffractometer with Cu K α radiation. The contents of Pd and Co in the reaction mixtures were measured by using microwave plasma-atomic emission spectrometry (MP-AES) on Agilent 4100MP-AES system. TiO₂ was supplied from Catalysis Society of Japan, as Japan Reference Catalyst JRC-TiO-4. CeO₂ was purchased from Daiichi kigenso kagaku kogyo Co, Ltd. Co₂(CO)₈ (Kanto chemical Co, Inc) was sublimated under reduced pressure before use. All other reagents were used in commercial grade. The authentic samples of aldehydes **2** and reduced by-products **3** were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., Ltd., Kanto chemical Co, Inc., Nacalai tesque, Inc. and Sigma-aldrich, Inc.

2.2 Preparation of Co₃O₄

Co₃O₄ was prepared by precipitation method. A 200 mL aqueous solution of Co(NO₃)₂•6H₂O (5.8 g, 20 mmol) was poured into 200 mL of aqueous solution of Na₂CO₃ (2.8 g, 26 mmol). The aqueous mixture was stirred for 2 h at room temperature. The precipitate was washed with distilled water several times and dried at 100 °C for overnight. The obtained catalyst was calcined at 400 °C for 4 h.

2.3 Preparation of PdO/Co₃O₄ and other palladium heterogeneous catalysts

PdO/Co₃O₄ was prepared by impregnation method. Co₃O₄ (0.50 g, 2.1 mmol) were impregnated with Pd(NO₃)₂ (0.052 g, 0.22 mmol) aqueous solution and stirred for 30 min at room temperature. After impregnation, H₂O was removed by vacuum-freeze drying or evaporation. The obtained catalyst was dried at 100 °C for overnight and calcined at 400 °C for 4h. PdO/TiO₂ and PdO/CeO₂ were prepared by same method of PdO/Co₃O₄ except for using TiO₂ or CeO₂ instead of Co₃O₄, respectively.

2.4 Preparation of Au/Co₃O₄

Au/Co₃O₄ was prepared by coprecipitation method [20–25]. A 200 mL aqueous solution of HAuCl₄•4H₂O (0.42 g, 1.0 mmol) and Co(NO₃)₂•6H₂O (5.5 g, 19 mmol) was poured into 200 mL of aqueous solution of Na₂CO₃ (2.8 g, 26 mmol). The mixture was stirred for 2 h at room temperature. The precipitate was washed with distilled water several times and dried at 100 °C for overnight. The obtained catalyst was calcined at 400 °C for 4 h.

2.5 XAFS spectra of PdO/Co₃O₄

Pd K-edge and Co K-edge X-ray absorption fine structure (XAFS) measurements were carried out at BL14B2 of SPring-8 (Hyogo, Japan). The XAFS samples were ground with boron nitride in an agate mortar and made as pellets. The storage ring energy was 8 GeV with a typical current of 99.5 mA. Pd K-edge (24.3 keV) XAFS spectra of Pd/Co₃O₄, Pd foil, Pd(NO₃)₂ and PdO were measured using a Si(311) double crystal monochromator in transmission mode. Co K-edge (7.7 keV) XAFS spectra of Co foil, Co(NO₃)₂ and CoO were measured using a Si(111) double crystal monochromator in transmission mode. Ionization chambers were used to measure the intensity of the incident and transmitted X-rays and the Quick scan technique (QXAFS) was used in this measurement.

2.6 Typical procedure for formylation of aryl halides catalyzed by PdO/Co₃O₄ (Table 2)

The suspension of 5 wt% PdO/Co₃O₄ (20 mg, 1.6 mol% Pd atom and 47 mol% Co to substrate) in dioxane (1 mL) in a stainless autoclave attached a glass tube was stirred at 120 °C under H₂ atmosphere (2 MPa) for 2 h. After cooling to rt, aryl halide **1** (0.5 mmol), K₂CO₃ (0.5 mmol) and dioxane (1 mL) were added and stirred at 140 °C for 20 h under CO:H₂=3:1 atmosphere (4 MPa). The reaction mixture was analyzed by GC using tridecane (30 µL, 0.1 mmol) as an internal standard after filtration through celite to remove the catalyst. The products **2** and **3** were identified by comparison of the retention time of GC with the authentic samples. The aldehydes **2a–f** and **2h–k** were also characterized by ¹H and ¹³C NMR after chromatographic purifications. Other aldehydes were found to be difficult to isolate due to low yields and volatilities.

Benzaldehyde (**2a**). ¹H NMR (CDCl₃, 400 MHz): δ 10.00 (s, 1H), 7.86 (d, *J* = 6.9 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 192.5, 136.5, 134.5, 129.8, 129.1.

p-Tolualdehyde (**2b**). ¹H NMR (CDCl₃, 400 MHz): δ 9.93 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 192.1, 145.6, 134.3, 129.9, 129.8, 21.9.

3,5-Dimethylbenzaldehyde (**2c**). ¹H NMR (CDCl₃, 400 MHz): δ 9.92 (s, 1H), 7.46 (s,

2H), 7.23 (s, 1H), 2.37 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 192.8, 138.8, 136.7, 136.3, 127.6, 21.1.

o-Tolualdehyde (**2d**). ^1H NMR (CDCl_3 , 400 MHz): δ 10.24 (s, 1H), 7.77 (d, $J = 7.3$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 7.3$ Hz, 1H), 2.65 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 192.9, 140.7, 134.2, 133.7, 132.1, 131.8, 126.4, 19.7.

p-Anisaldehyde (**2e**). ^1H NMR (CDCl_3 , 400 MHz): δ 9.85 (s, 1H), 7.81 (d, $J = 8.7$ Hz, 2H), 6.97 (d, $J = 9.2$ Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 191.0, 164.7, 132.1, 130.0, 114.4, 55.7.

m-Anisaldehyde (**2f**). ^1H NMR (CDCl_3 , 400 MHz): δ 9.95 (s, 1H), 7.42 (m, 2H), 7.36 (s, 1H), 7.15 (m, 1H), 3.83 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 192.2, 160.2, 137.9, 130.1, 123.6, 121.6, 112.1, 55.5.

p-Phenylbenzaldehyde (**2h**). ^1H NMR (CDCl_3 , 400 MHz): δ 10.05 (s, 1H), 7.95 (d, $J = 8.7$ Hz, 2H), 7.74 (d, $J = 6.4$ Hz, 2H), 7.63 (d, $J = 6.9$ Hz, 2H), 7.48 (t, $J = 7.3$ Hz, 2H), 7.41 (t, $J = 7.1$, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 192.0, 147.3, 139.8, 135.3, 130.4, 129.1, 128.6, 127.8, 127.5.

1-Naphthaldehyde (**2i**). ^1H NMR (CDCl_3 , 400 MHz): δ 10.38 (s, 1H), 9.24 (d, $J = 8.7$ Hz, 1H), 8.07 (d, $J = 8.2$ Hz, 1H), 7.96 (d, $J = 6.9$ Hz, 1H), 7.90 (d, $J = 8.7$ Hz, 1H), 7.68 (t, $J = 7.8$ Hz, 1H), 7.59 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 193.7, 136.8, 135.4, 133.8, 131.5, 130.6, 129.2, 128.6, 127.1, 125.0 (2C).

p-Chlorobenzaldehyde (**2j**). ^1H NMR (CDCl_3 , 400 MHz): δ 9.96 (s, 1H), 7.80 (d, $J = 8.7$ Hz, 2H), 7.49 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 191.0, 141.0, 134.8, 131.0, 129.5.

p-Fluorobenzaldehyde (**2k**). ^1H NMR (CDCl_3 , 400 MHz): δ 9.94 (s, 1H), 7.89 (t, $J = 7.1$ Hz, 2H), 7.19 (t, $J = 8.7$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 190.6, 166.6 (d, $J_{\text{C-F}} = 256$ Hz), 133.0 (d, $J_{\text{C-F}} = 2.8$ Hz), 132.3 (d, $J_{\text{C-F}} = 10$ Hz), 116.4 (d, $J_{\text{C-F}} = 23$ Hz).

2.7 Recycle experiments

After the initial experiment, the suspension was centrifuged to separate the solution from the insoluble materials. The clear supernatant was taken out and analyzed by GC after an addition of tridecane (30 μL , 0.1 mmol). The remaining solid was washed with dichloromethane and distilled water. This solid was dried at 100 $^\circ\text{C}$ for 4 h. The recovered catalyst was used for the next run of the formylation reaction by charging

with the same substrate and solvent.

3. Results and discussion

3.1 Characterization of PdO/Co₃O₄ catalyst

The PdO/Co₃O₄ catalyst was prepared by an impregnation method using Co₃O₄ and Pd(NO₃)₂ as the Pd source. The valences of Pd and Co after air calcination and H₂ treatment were determined by X-ray absorption near edge structure (XANES) (Figs. 1 and 2) and X-ray diffraction (XRD) spectral analyses (Fig. 3). The spectrum of the Pd catalyst after calcination under air was virtually identical to that of PdO [Fig. 1, (a) and (c)]. H₂ treatment (2 MPa, 120 °C, 2 h) resulted in alteration of the spectrum to match that of Pd foil [Fig. 1, (d) and (e)]. These results indicate that Pd assumes a Pd(II) oxidation state after calcination and is subsequently reduced to Pd(0) by H₂ treatment. Along with the reduction of Pd(II), the H₂ treatment caused an alteration of the peaks at 7.727 and 7.710 keV, which were assigned to Co₃O₄ and Co(0), respectively (Fig. 2). This spectral change suggested a disappearance of Co₃O₄ and a formation of Co(0). The reduction of Co₃O₄ was also clearly observed by XRD analysis (Fig. 3).

Pd K-edge k^3 -weighted phase uncorrected radial structure function (RSF) for H₂-treated PdO/Co₃O₄ and Pd foil is shown in Fig. 4. Both H₂-treated PdO/Co₃O₄ [Fig. 4 (b), solid line] and Pd foil [Fig. 4 (a), solid line] displayed a characteristic peak at 2.46 Å which was assigned to Pd–Pd bonds. An absence of the peaks corresponding to Pd–O bonds indicated a complete reduction of PdO to Pd(0) during H₂ treatment. An additional analysis of the structure was performed by a fitting of the Fourier transformed Pd K-edge data. The EXAFS fit parameters are shown in Table 1. Whereas a theoretical RSF fitted well with an *R*-factor of 0.03% by considering not only Pd–Pd bond but Pd–Co bond as the first coordination shell (Table 1, entry 3), a *R*-factor of 4.56% was obtained by using only Pd–Pd bond (Table 1, entry 2). This result implied that a part of Pd was present as Pd–Co species. A similar analysis was also performed on Co (Fig. S1 and Table S1). In the case of Co, a theoretical RSF accorded with an experimental data with only consideration of Co–Co bond due to a low content of Pd against Co.

(Insert Figs. 1–4)

(Insert Table 1)

Fig. 5 shows high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of PdO/Co₃O₄ and Co₃O₄. Very few particles of Pd, which were indicated by white arrows, were identified after calcination under air, probably as a result of dispersion of undetectable particles [Fig. 5, (a)]. In contrast, H₂ treatment resulted in aggregation of Pd to form nano-sized particles [Fig. 5, (b)]. Most of the Pd nanoparticles had around 2–3 nm diameters with some exceptions.

(Insert Fig. 5)

3.2 Formylation of aryl halides catalyzed by PdO/Co₃O₄

Parameters for the optimization of the formylation reaction conditions are displayed in Table 2. 1,4-Dioxane gave the highest yield among all solvent candidates tested (Table 2, entries 1–6). Temperatures below 120 °C were deemed inadequate (Table 2, entries 7 and 8) and harsher conditions compromised the yield (Table 2, entry 9). The reaction demonstrated sensitivity to the partial pressures of CO and H₂ (Table 2, entries 10–12), illustrating the dependence of the CO insertion step and formation of the Co species on the respective gas pressures. Inorganic bases promoted reactivity more effectively than organic bases (Table 2, entries 13–15). Based on the outlined results, the conditions described in entry 1 of Table 2 were discerned as optimal.

(Insert Table 2)

The scope of substrates suited to PdO/Co₃O₄-catalyzed formylation reactions was examined (Table 3). Substrates bearing an electron-donating group gave moderate to good yields, except in the case of **2g** (Table 3, entries 1–6). Certain organic bases (Table 2, entries 14 and 15) functionalized with an N donor atom exerted a negative influence on the reaction yield. Hydrogenated by-products, corresponding to **3**, remained dominant when substrates bore an electron-withdrawing group (Table 3, entries 9–14), as observed for the conversion of 3-iodopyridine to pyridine (Table 3, entry 15). Under the described conditions, bromobenzene did not react at all, possibly as a result of its comparatively reduced propensity to undergo oxidative addition (Table 3, entry 16). As

expected from this result, *p*-bromiodobenzene afforded *p*-bromobenzaldehyde **2r** as a major product (Table 3, entry 17).

(Insert Table 3)

3.3 Mechanistic studies on PdO/Co₃O₄ catalyzed formylation of aryl halides

Catalysts employing other types of nanoparticles and oxide supports were also examined. Pd nanoparticles demonstrated reactivity with 1-iodonaphthalene, regardless of the type of oxide support present (Table 4, entries 1 and 2). However, the formation of hydrogenated **3i** took precedence over the sought transformation. In the case of PdO/CeO₂, an electron donating character of Ce³⁺ which was formed by a reduction of CeO₂ with the aid of Pd [31,32] may play a part to enhance a reactivity of Pd. An alteration of the supported nanoparticles from Pd to Au resulted in complete loss of activity (Table 3, entry 3). A combination of PdO/TiO₂ and homogeneous Co₂(CO)₈ dramatically improved the yield of **2i**, implicating HCo(CO)₄ generated from Co₂(CO)₈ [26–30]. Although Co₂(CO)₈ did not catalyze the formylation of iodobenzene under conditions of 70 °C and CO/H₂ (1:1, 10 MPa) in an earlier report [26], a small amount of **2i** was produced at 140 °C in the presence of CO/H₂ (3:1, 4 MPa) (Table 4, entry 5). The results indicate that cooperative catalytic processes involving Pd nanoparticles and Co species are important in the formylation of 1-iodonaphthalene.

(Insert Table 4)

The authors speculate that an intermediary Pd–Co bimetallic species may offer a synergistic catalytic effect between Pd and Co. On the basis of previous reports and the experimental results described herein, a catalytic mechanism for PdO/Co₃O₄-catalyzed formylation is proposed, as depicted in Scheme 1. Initially, Ar–X adds to Pd(0) oxidatively. Insertion of CO proceeds rapidly as a result of the promoting effect of the Pd–Co system [33], forming an acyl–Pd bond. In this process, migration of aryl and acyl groups between Pd and Co centers is important for the efficient CO insertion [33]. Transfer hydrogenation and reductive elimination result in the formation of an aldehyde product, with concomitant liberation of Pd–Co species. The true catalytic cycle may be complicated by generation of other intermediates, such as an aryl–Co species formed

via a reductive elimination pathway from the Ar–Pd–Co complex, or a direct oxidative addition of Ar–X to Co(0).

(Insert Scheme 1)

3.4 Recycle experiment

Fig. 6 reveals the recyclability of the PdO/Co₃O₄ catalyst, for which similar yields of **2i** and **3i** were observed in up to seven recycle runs. In order to examine the metal-leaching attributes of the reaction, a new run using fresh catalyst was interrupted after 2 h and analyzed by GC to clarify the extent of conversion (32% of **2i** and 10% of **3i**). The catalyst and K₂CO₃ were removed from the reaction mixture by filtration, with subsequent heating of the filtrate in the presence of K₂CO₃ and syngas over an extended period. After 18 h, the resulting mixture was reanalyzed, and 37% of **2i** and 12% of **3i** were ascertained. Given that both Pd and Co mediate catalysis (Table 4, entries 2 and 5), it remained unclear as to whether Pd or Co or a combination of the two metals was responsible for the slight increase in the product yields. A content of Pd and Co in the post-reaction solution after the standard work-up was revealed to contain no leached Pd and 0.15% of total Co by a measurement of microwave plasma atomic emission spectrometry. In a recent literature example describing C–C bond-forming reactions, Pd nanoparticles were observed to behave in the capacity of a reservoir of soluble active species [34–37] and a heterogeneous catalyst [38,39]. Additional evidences are necessary in order to make firm assertions about the nature of the active species.

(Insert Fig. 6)

4. Conclusions

A novel catalytic system, composed of Pd nanoparticles and a Co₃O₄ support, is proposed for the formylation of aryl iodides. The supported Pd nanoparticles play dual roles as a Pd catalyst and a co-catalyst for the formation of cobalt-carbonyl-like species. A cooperative effect between Pd and Co species was deemed significant to the efficiency of the formylation process.

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References

- [1] A. Brennfürher, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* 48 (2009) 4114–4133.
- [2] L. Kürti, B. Czákó, *Strategic Applications of Named Reactions in Organic Synthesis*, Elsevier Academic Press, Burlington, MA, 2005.
- [3] Z. Wang, *Comprehensive Organic Name Reactions and Reagents*, Wiley-Interscience, 2009.
- [4] G. D. Hartman, W. Halczenko, B. T. Phillips, *J. Org. Chem.* 50 (1985) 2427–2431.
- [5] J. G. Smith, P. W. Dibble, R. E. Sandborn, *J. Org. Chem.* 51 (1986) 3762–3768.
- [6] G. A. Olah, M. Arvanaghi, *Angew. Chem. Int. Ed. Engl.* 20 (1981) 878–879.
- [7] G. A. Olah, L. Ohannesian, M. Arvanaghi, *J. Org. Chem.* 49 (1984) 3856–3857.
- [8] A. Schoenberg, R. F. Heck, *J. Am. Chem. Soc.* 96 (1974) 7761–7764.
- [9] V. P. Baillargeon, J. K. Stille, *J. Am. Chem. Soc.* 105 (1983) 7175–7176.
- [10] I. Pri-Bar, O. Buchman, *J. Org. Chem.* 49 (1984) 4009–4011.
- [11] V. P. Baillargeon, J. K. Stille, *J. Am. Chem. Soc.* 108 (1986) 452–461.
- [12] Y. Ben-David, M. Portnoy, D. Milstein, *J. Chem. Soc., Chem. Commun.* (1989) 1816–1817.
- [13] T. Okano, N. Harada, J. Kiji, *Bull. Chem. Soc. Jpn.* 67 (1994) 2329–2332.
- [14] I. Carelli, I. Chiarotto, S. Cacchi, P. Pace, C. Amatore, A. Jutand, G. Meyer, *Eur. J. Org. Chem.* (1999) 1471–1473.
- [15] L. Ashfield, C. F. J. Barnard, *Org. Pro. Res. Dev.* 11 (2007) 39–43.
- [16] S. Klaus, H. Neumann, A. Zapf, D. Strübing, S. Hübner, J. Almena, T. Riermeier, P. Groß, M. Sarich, W.-R. Krahner, K. Rossen, M. Beller, *Angew. Chem. Int. Ed.* 45 (2006) 154–158.

- [17] A. Brennführer, H. Neumann, S. Klaus, T. Riermeier, J. Almena, M. Beller, *Tetrahedron* 63 (2007) 6252–6258.
- [18] A. G. Sergeev, A. Spannenberg, M. Beller, *J. Am. Chem. Soc.* 130 (2008) 15549–15563.
- [19] M.-Z. Cai, H. Zhao, J. Zhou, C.-S. Song, *Synth. Commun.* 32 (2002) 923–926.
- [20] X. Liu, M. Haruta, M. Tokunaga, *Chem. Lett.* 37 (2008) 1290–1291.
- [21] A. Hamasaki, X. Liu, M. Tokunaga, *Chem. Lett.* 37 (2008) 1292–1293.
- [22] X. Liu, B. Hu, K. Fujimoto, M. Haruta, M. Tokunaga, *Appl. Catal. B: Environ.* 92 (2009) 411–421.
- [23] X. Liu, M. Tokunaga, *ChemCatChem* 2 (2010) 1569–1572.
- [24] A. Hamasaki, A. Muto, S. Haraguchi, X. Liu, T. Sakakibara, T. Yokoyama, M. Tokunaga, *Tetrahedron Lett.* 52 (2011) 6869–6872.
- [25] X. Liu, A. Hamasaki, Y. Yamane, S. Aikawa, T. Ishida, M. Haruta, M. Tokunaga, *Catal. Sci. Technol.* 3 (2013) DOI: 10.1039/c3cy00336a.
- [26] Y. Misumi, Y. Ishii, M. Hidai, *J. Mol. Catal.* 78 (1993) 1–8.
- [27] Y. Misumi, Y. Ishii, M. Hidai, *Chem. Lett.* 23 (1994) 695–698.
- [28] Y. Misumi, Y. Ishii, M. Hidai, *Organometallics* 14 (1995) 1770–1775.
- [29] Y. Misumi, Y. Ishii, M. Hidai, *J. Chem. Soc. Dalton Trans.* (1995) 3489–3496.
- [30] Y. Ishii, M. Hidai, *Catal. Today* 66 (2001) 53–61.
- [31] C. Binet, A. Jadi, J.-C. Lavalley, M. Boutonnet-Kizling, *J. Chem. Soc. Faraday Trans.* 88 (1992) 2079–2084.
- [32] A. Badri, C. Binet, J.-C. Lavalley, *J. Chem. Soc. Faraday Trans.* 92 (1996) 1603–1608.
- [33] A. Fukuoka, S. Fukagawa, M. Hirano, N. Koga, S. Komiya, *Organometallics* 20 (2001) 2065–2075.
- [34] N. T. S. Phan, M. Van Der Sluys and C. W. Jones, *Adv. Synth. Catal.*, 2006, 348, 609
- [35] J. G. de Vries, *Dalton Trans.* (2006) 421–429.
- [36] L. D. Pachón, G. Rothenberg, *Appl. Organometal. Chem.* 22 (2008) 288–299.
- [37] A. Balanta, C. Godard, C. Claver, *Chem. Soc. Rev.* 40 (2011) 4973–4985.
- [38] P. J. Ellis, I. J. S. Fairlamb, S. F. J. Hackett, K. Wilson, A. F. Lee, *Angew. Chem. Int. Ed.* 49 (2010) 1820–1824.
- [39] A. F. Lee, P. J. Ellis, I. J. S. Fairlamb, K. Wilson, *Dalton Trans.* 39 (2010)

10473–10482.

Figure captions

Fig. 1 Pd K-edge XANES spectra of (a) PdO, (b) Pd(NO₃)₂, (c) PdO/Co₃O₄ (air calcination), (d) PdO/Co₃O₄ (H₂ treatment), and (e) Pd foil.

Fig. 2 Co K-edge XANES spectra of (a) Co₃O₄, (b) CoO, (c) Co(NO₃)₂, (d) PdO/Co₃O₄ (air calcination), (e) PdO/Co₃O₄ (H₂ treatment), and (f) Co foil.

Fig. 3 X-ray diffraction patterns of (a) PdO/Co₃O₄ (air calcination) and (b) PdO/Co₃O₄ (H₂ treatment). The patterns of (c) Co₃O₄ and (d) Co are shown based on JCPDS data.

Fig. 4 Pd K-edge k^3 -weighted phase uncorrected radial structure functions (RSFs) for (a) Pd foil and (b) PdO/Co₃O₄ (H₂ treatment). Solid and dashed lines indicate experimental RSFs and theoretical RSFs, respectively.

Fig. 5 HAADF-STEM images of (a) PdO/Co₃O₄ after air calcination (400 °C, 4 h), (b) PdO/Co₃O₄ after H₂ treatment (2 MPa, 120 °C, 2 h in 1,4-dioxane), and (c) Co₃O₄. Pd nanoparticles are indicated by white arrows.

Fig. 6 Recycle use of PdO/Co₃O₄ catalyst for the formylation of 1-iodonaphthalene.

Scheme 1 Possible mechanism for PdO/Co₃O₄-catalyzed formylation of haloarenes.

Table 1 EXAFS fit parameters for H₂-treated PdO/Co₃O₄ (k^3 : $\Delta k = 2.5\text{--}13.5 \text{ \AA}^{-1}$ and $\Delta R = 1.6\text{--}2.8 \text{ \AA}$)

Entry		Shells	CN ^a	$R \text{ (\AA)}^b$	$\sigma^2 \text{ (\AA}^2)^c$	$R_{\text{factor}} \text{ (\%)}^d$
1	Pd foil	Pd–Pd	12 ^e	2.743 ± 0.002	0.0059 ± 0.0002	0.08
2	H ₂ -PdO/Co ₃ O ₄ ^f	Pd–Pd	8.92 ± 3.84	2.718 ± 0.016	0.0079 ± 0.0020	4.56
3	H ₂ -PdO/Co ₃ O ₄ ^g	Pd–Pd	6.67 ± 2.09	2.727 ± 0.015	0.0072 ± 0.0017	0.03
		Pd–Co	2.03 ± 2.06	2.535 ± 0.079	0.0078 ± 0.0085	

^a First shell coordination number. Intrinsic loss factor, $S_0^2 = 0.884$ (Pd–Pd from Pd foil data) and $S_0^2 = 0.884$ (Pd–Co from Pd foil data).

^b Bond length.

^c Debye–Waller factor.

^d Goodness-of-fit index.

^e Coordination number was fixed as that of an fcc lattice.

^f Fitting was performed using the model that the first coordination atoms are all Pd atoms.

^g Fitting was performed using the model that the first coordination atoms are Pd and Co.

Table 2 Optimization of the PdO/Co₃O₄ catalyzed formylation^{a,b}

<div><div><div><div><div> </div><div>1a (0.5 mmol)</div></div><div><div>5 wt% PdO/Co₃O₄ (1.6 mol% Pd, 47 mol% Co) CO/H₂ (4 MPa) Base (1 equiv.) Solvent (2 mL) 20 h</div><div> </div></div></div><div>2a</div></div></div>					
Entry	Solvent	Base	Temp. (°C)	CO:H ₂	Yield ^c (%)
1	1,4-dioxane	K ₂ CO ₃	140	3:1	73
2	THF	K ₂ CO ₃	140	3:1	29
3	cyclohexane	K ₂ CO ₃	140	3:1	27
4	benzene	K ₂ CO ₃	140	3:1	51
5	EtOAc	K ₂ CO ₃	140	3:1	37
6	1,2-DCE	K ₂ CO ₃	140	3:1	7
7	benzene	K ₂ CO ₃	100	3:1	trace
8	benzene	K ₂ CO ₃	120	3:1	33
9	benzene	K ₂ CO ₃	160	3:1	12
10	1,4-dioxane	K ₂ CO ₃	140	7:1	40
11	1,4-dioxane	K ₂ CO ₃	140	4:1 (5 MPa)	46
12	benzene	K ₂ CO ₃	120	1:2	11
13	1,4-dioxane	CS ₂ CO ₃	140	3:1	44
14	1,4-dioxane	Et ₃ N	140	3:1	10
15	1,4-dioxane	pyridine	140	3:1	0

^a Conditions: 5 wt% PdO/Co₃O₄ (20 mg, 1.6 mol% Pd and 47 mol% Co to iodobenzene), iodobenzene (102 mg, 0.5 mmol), base (0.5 mmol, 1 equiv.), solvent (2 mL).

^b The catalyst was treated at 120 °C under H₂ (2 MPa) for 2 h in the reaction solvent (1 mL) prior to the reaction.

^c Determined by GC using tridecane as an internal standard.

Table 3 Substrate scope for the PdO/Co₃O₄ catalyzed formylation^{a,b}

<div>5 wt% PdO/Co₃O₄ (1.6 mol% Pd, 47 mol% Co) CO/H₂ (3:1, 4 MPa) K₂CO₃ (1 equiv.) 1,4-dioxane (2 mL) 140 °C, 20 h</div> <div> </div> <div>1 (0.5 mmol) 2 3</div>				
Entry	Substrate	Product	Yield ^c (%)	
			2	3
1		2b	58	7
2		2c	71	6
3		2d	58	8
4 ^d		2e	90	0
5		2f	57	16
6		2g	14	4
7		2h	52	14
8		2i	77	20
9		2j	60	20
10		2k	91	7
11		2l	31	38
12		2m	8	45

13		2n	0	56
14		2o	0	84
15		2p	19	62
16		2a	0	0
17		2q	39	17

^a Conditions: 5 wt% PdO/Co₃O₄ (20 mg, 1.6 mol% Pd and 47 mol% Co to substrate), **1** (0.5 mmol), K₂CO₃ (69 mg, 0.5 mmol, 1 equiv.), 1,4-dioxane (2 mL), CO/H₂ (3:1, 4 MPa).

^b The catalyst was treated at 120 °C under H₂ (2 MPa) for 2 h in 1,4-dioxane (1 mL) prior to the reaction.

^c Determined by GC using tridecane as an internal standard.

^d The reaction was carried out at 160 °C.

Table 4 The formylation of 1-iodonaphthalene with various catalysts^a

Entry	Catalyst	Yield ^b (%)	
		2i	3i
1 ^c	5 wt% PdO/TiO ₂ (5 mol% Pd)	2	28
2 ^c	5 wt% PdO/CeO ₂ (5 mol% Pd)	38	40
3 ^c	11 wt% Au/Co ₃ O ₄ (48 mol% Co)	0	0
4 ^{c,d}	5 wt% PdO/TiO ₂ (5 mol% Pd)	47	22
	+ Co ₂ (CO) ₈ (2 mol%)		
5 ^d	Co ₂ (CO) ₈ (2 mol%)	19	4

^a Conditions: **1i** (127 mg, 0.5 mmol), K₂CO₃ (69 mg, 0.5 mmol, 1 equiv.), 1,4-dioxane (2 mL), CO/H₂ (3:1, 4 MPa).

^b Determined by GC using tridecane as an internal standard.

^c The catalysts were treated at 120 °C under H₂ (2 MPa) for 2 h in 1,4-dioxane (1 mL) prior to the reaction.

^d Co₂(CO)₈ was purified by sublimation under reduced pressure just prior to use.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Scheme 1