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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 H_2 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.

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 $Pd(OAc)_2$ and P(1-adamantyl)$_2$*n*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 (Au/Co_3O_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

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synthesis, thus inexpensive bulk supply is possible. Part of the cobalt oxide support is reduced to 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 PdO/Co_3O_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

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 nm). Column chromatography was performed on silica-gel (Kanto Chemicals, Silica gel 60 N, 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 Kα 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. TiO_2 was supplied from Catalysis Society of Japan, as Japan Reference Catalyst JRC-TiO-4. CeO_2 was purchased from Daiichi Kigenso Kagaku Kogyo Co., Ltd. $Co_2(CO)_8$ (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 Co_3O_4

Co_3O_4 was prepared by precipitation method. A 200 mL aqueous solution of $Co(NO_3)_2{\bullet}6H_2O$ (5.8 g, 20 mmol) was poured into 200 mL of aqueous solution of Na_2CO_3 (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/Co_3O_4 and other palladium heterogeneous catalysts

PdO/Co_3O_4 was prepared by impregnation method. Co_3O_4 (0.50 g, 2.1 mmol) were impregnated with $Pd(NO_3)_2$ (0.052 g, 0.22 mmol) aqueous solution and stirred for 30 min at room temperature. After impregnation, H_2O was removed by vacuum-freeze drying or evaporation. The obtained catalyst was dried at 100 °C for overnight and calcined at 400 °C for 4 h. PdO/TiO_2 and PdO/CeO_2 were prepared by same method of PdO/Co_3O_4 except for using TiO_2 or CeO_2 instead of Co_3O_4, respectively.

2.4. Preparation of Au/Co_3O_4

Au/Co_3O_4 was prepared by coprecipitation method [20–25]. A 200 mL aqueous solution of $HAuCl_4{\bullet}4H_2O$ (0.42 g, 1.0 mmol) and $Co(NO_3)_2{\bullet}6H_2O$ (5.5 g, 19 mmol) was poured into 200 mL of aqueous solution of Na_2CO_3 (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/Co_3O_4

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/Co_3O_4, Pd foil, $Pd(NO_3)_2$ 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, $Co(NO_3)_2$ and CoO were measured using a Si(1 1 1) 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/Co_3O_4 (Table 2)

The suspension of 5 wt% PdO/Co_3O_4 (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 H_2 atmosphere (2 MPa) for 2 h. After cooling to RT, aryl halide **1** (0.5 mmol), K_2CO_3 (0.5 mmol) and dioxane (1 mL) were added and stirred at 140 °C for 20 h under $CO:H_2 = 3:1$ 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 ^{13}C NMR after chromatographic purifications. Other aldehydes were found to be difficult to isolate due to low yields and volatilities.

Benzaldehyde (**2a**). ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.5, 136.5, 134.5, 129.8, 129.1.

p-Tolualdehyde (**2b**). ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.1, 145.6, 134.3, 129.9, 129.8, 21.9.

3,5-Dimethylbenzaldehyde (**2c**). ^1H NMR ($CDCl_3$, 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.