



Supported palladium hydroxide-catalyzed intramolecular double C–H bond functionalization for synthesis of carbazoles and dibenzofurans



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ABSTRACT

Metal oxide-supported palladium hydroxide ($\text{Pd}(\text{OH})_2/\text{MO}_x$) catalysts enabled the oxidative intramolecular couplings of diarylamines to carbazoles and diarylethers to dibenzofurans via double aryl C–H bond functionalizations with molecular oxygen as the sole oxidant. While supported PdO, Pd, and palladium acetate catalysts showed poor catalytic activities, supported $\text{Pd}(\text{OH})_2$ exhibited remarkably high catalytic activity. Among supported $\text{Pd}(\text{OH})_2$ catalysts, $\text{Pd}(\text{OH})_2/\text{ZrO}_2$ was found to be an efficient catalyst in terms of catalytic activities and selectivities for the synthesis of carbazoles and dibenzofurans.

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1. Introduction

Transition metal-catalyzed C–C bond formation reactions are particularly important reactions in fine chemical syntheses, and many reactions have been established by using organic halides and organometallic compounds such as Suzuki, Heck, and Negishi coupling reactions [1]. Although these methods can be utilized for versatile substrates under mild reaction conditions, large amounts of inorganic wastes are produced from these reactions. Over the past decades, to avoid the use of activated aryl halides, direct transformation of C–H bonds into C–C bonds has received significant attention [2].

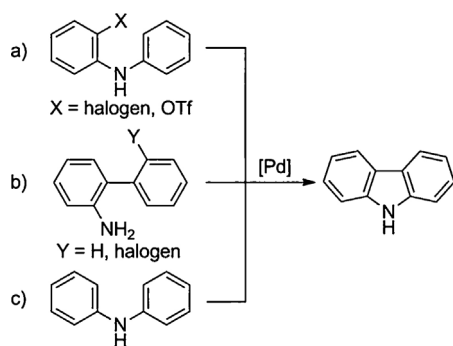
Carbazoles can be found in biologically active alkaloids [3] and are important compounds owing to photorefractive, photoconductive, hole-transporting, and light-emitting properties [4,5]. Although carbazole is produced by distillation of coal tar in industry, only small amounts can be obtained. To establish efficient processes for synthesizing carbazoles is of great interest, and several methods have been investigated in laboratories.

Representative synthetic protocols involving C–C or C–N bond formations are depicted in Scheme 1: (a) intramolecular coupling of C–X (X=halogen, triflate) and C–H bonds [6–10], (b) intramolecular C–N bond formation in [1,1'-biphenyl]-2-amine [11–14], and (c) intramolecular coupling of two C–H bonds of diphenylamine [15–20]. To avoid the use of aryl halides, Scheme 1b or c is more desirable. In C–H/N–H coupling (Scheme 1b), protecting groups are generally required at the nitrogen atom. Matsubara and co-workers reported the synthesis of carbazole from unprotected [1,1'-biphenyl]-2-amine over Pd/C [14]. However, high temperatures of over 250 °C are required. Since diphenylamine is readily available, the transformation of diphenylamine to carbazole (Scheme 1c) can be regarded as the most attractive route for carbazole synthesis. Moreover, water is a sole by-product when molecular oxygen can be utilized as an oxidant for the reaction.

The intramolecular oxidative coupling of two C–H bonds of diphenylamine to carbazole has been mainly studied using homogeneous palladium catalysts such as $\text{Pd}(\text{OAc})_2$ [15–20]. Although O_2 can be used as an oxidant, stoichiometric oxidant such as Ag_2O [18] or co-catalyst such as $\text{Cu}(\text{OAc})_2$ [20] have still been used. C–X/C–H coupling over heterogeneous catalysts has been reported using polymer-supported Pd nanoparticles (NPs) [21], $\text{Pd}(\text{OH})_2/\text{C}$ [22], and colloidal Pd NPs [23]. However, C–H/C–H bond coupling is limited [24,25]. Yin and co-workers reported

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Scheme 1. Synthetic methods of carbazole by C–H bond functionalization.

that heterogeneous carbon-supported Pd-polyoxometalate (POM) catalysts promoted the coupling of aryl C–H bond with sp^2 C–H bond of electron-deficient alkenes [24]. POM was responsible for high catalytic activity of Pd(II) species and worked as re-oxidation catalysts for Pd(0) species in the catalytic cycle. Direct aryl C–H/aryl C–H coupling over heterogeneous catalysts has been limited to the synthesis of 2,2'-bipyridines from pyridine derivatives [25].

In this work, we demonstrated that $\text{Pd}(\text{OH})_2/\text{ZrO}_2$ efficiently catalyzed the synthesis of carbazoles from diphenylamines using O_2 as the sole oxidant without the aid of re-oxidation catalysts. Dibenzofuran and its derivatives are also important chemicals, but examples are scarce compared to those for carbazole synthesis [15]. The intramolecular coupling of diphenylethers to obtain dibenzofurans was also studied using supported $\text{Pd}(\text{OH})_2$ catalysts.

2. Experimental

2.1. Materials

Palladium chloride (PdCl_2) was purchased from Tanaka Kikin-zoku KK. and used as received. Reagent grades $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was purchased from Kanto Kagaku Chemical. Carbon supported Pd catalysts, 10 wt% Pd/C and 20 wt% $\text{Pd}(\text{OH})_2/\text{C}$ were purchased from Sigma–Aldrich. All commercial starting materials and reagents were used as received. For the scope of substrate, 4-chlorodiphenylamine was synthesized according to the literature [26]. Al_2O_3 , TiO_2 (P-25), ZrO_2 (RC-100), and CeO_2 , were supplied by Wako Pure Chemical, Mizusawa Chemicals, Nippon Aerosil Co., Ltd., Daiichi Kigenso Kagaku Kogyo, and Shin-Etsu Chemical Co., Ltd., respectively.

2.2. Catalyst preparation

Metal oxide-supported $\text{Pd}(\text{OH})_2$ catalysts ($\text{Pd}(\text{OH})_2/\text{MO}_x$) were synthesized according to the literature [27] with minor modifications. Palladium chloride (PdCl_2) (177 mg) was dissolved in distilled water (1000 mL) containing 2 mL of conc. HCl. The pH of the solution was adjusted to 10 by adding 1.0 M NaOH aqueous solution. The metal oxide support (1.0 g) was added to the solution at 70 °C. The pH of the solution was adjusted to 10 by adding 1.0 M NaOH aqueous solution, if necessary. The suspension was cooled to room temperature and stirred at room temperature for 24 h. The solid was filtered, washed with water, and then dried in air at 100 °C for 12 h.

For the preparation of 20 wt% $\text{Pd}(\text{OH})_2/\text{ZrO}_2$, PdCl_2 (417 mg) was dissolved in an aqueous solution of conc. HCl (10 mL) and distilled water (240 mL). The solution was warmed to 60 °C and the pH of the solution was adjusted to 8.0 by adding 0.1 M NaOH aqueous solution. Then, the support (1.0 g) was added to the

solution and the suspension was stirred at 70 °C for 1 h. The solid was filtered, washed with water, and then dried in air at 70 °C overnight.

10 wt% PdO/ZrO_2 was prepared by impregnation followed by calcination in air at 300 °C for 4 h. 20 wt% Pd/ZrO_2 and 20 wt% PdO/ZrO_2 catalysts were prepared from 20 wt% $\text{Pd}(\text{OH})_2/\text{ZrO}_2$ treated in a flow of H_2 at 300 °C for 4 h and calcination in air at 300 °C for 4 h, respectively.

2.3. Characterization

High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations were performed using JEOL JEM-ARM200F operating at 200 kV at the research laboratory for high vacuum electron microscopy (HVEM), Kyushu University. Palladium contents in the catalysts and leaching of palladium into the reaction solutions were analyzed by microwave plasma-atomic emission spectrometry (MP-AES) by Agilent, 4100 MP-AES. The reaction solution was filtered to remove solid catalysts and the concentration of Pd in filtrate was analyzed by MP-AES. Fourier transform infrared (FT-IR) spectra of catalysts were obtained by JASCO FT-IR 6100 with an attenuated total reflection (ATR) accessory equipped with a single reflection ZnSe.

X-ray absorption fine structure (XAFS) measurements were performed at BL14B2 beamline of SPring-8 (Hyogo, Japan) [28,29]. The XAFS samples were ground with boron nitride in an agate mortar and were compacted into pellets. Pd K-edge (24.3 keV) XAFS spectra were measured using a Si(311) double crystal monochromator in transmission mode. Ionization chambers were used, and the quick scan technique (QXAFS) was used in these measurements. The spectral analysis was performed using the XAFS analysis software, Athena [30]. The extraction of the extended X-ray absorption fine structure (EXAFS) oscillation from the spectra, normalization by edge-jump, and Fourier transformation were performed using the Athena software.

Conversions and product yields were analyzed by gas chromatography (GC) using Agilent GC 6850 Series II equipped with FID and a J&W HP-1 column (0.25 μm thickness, 0.25 mm I.D., 30 m) using tridecane as an internal standard. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer at 400 and 100 MHz, respectively and were shown in Supplementary data. ^1H assignment abbreviations are the following: singlet (s), doublet (d), triplet (t), and multiplet (m). Analytical thin-layer chromatography (TLC) was performed with Merck, TLC silica gel 60 F_{254} plates. Column chromatography was performed on silica gel (Kanto Chemicals, Silica gel 60 N, spherical, neutral, particle size 40–100 μm). Recycling preparative HPLC was performed on Japan Analytical Industry Co., Ltd., LC-908. Elemental analyses were carried out at the center of elementary analysis, Kyushu University.

2.4. General procedure for intramolecular oxidative coupling

To an autoclave was charged with diphenylamine (1 mmol), 10 wt% $\text{Pd}(\text{OH})_2$ catalyst (50 mg, Pd 5 mol%), solvent (3.0 mL), and a magnetic stirring bar. The autoclave was purged and filled with O_2 until the pressure reached 0.25 MPa. The reaction mixture was stirred at 100 °C for 12 h. After the reaction, the mixture was filtered, and the filtrate was analyzed by GC using tridecane as an internal standard. Intramolecular oxidative couplings of diarylamines and diarylethers were also performed in a similar manner. Characterization and NMR charts of the isolated compounds were listed in the supplementary data.

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