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Research Paper

UV-irradiation-mediated palladium nanoparticle catalytic system: Heck and decarboxylative coupling reactions

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ABSTRACT

This study has been undertaken to investigate the UV irradiation effect on catalytic activities in Pd-catalyzed cross coupling reactions. A Pd-TiO_2-CNT composite was prepared by a previously reported sol-gel method, whereby anatase TiO_2 and metallic Pd nanoparticles were deposited onto the surface of carbon nanotubes (CNTs). The average particle size of these nanoparticles was determined to be ~4.3 nm by transmission electron microscopy. The prepared Pd-TiO_2-CNT material was employed as a catalyst for the Heck and decarboxylative coupling reactions, and it showed higher catalytic activity in the presence of UV irradiation than in the absence of UV irradiation. The enhanced catalytic activity of this system can be explained by the increased nucleophilicity of Pd due to electron transfer from TiO_2 under UV irradiation.

1. Introduction

Palladium-catalyzed cross-coupling reactions are a powerful tool in synthetic organic chemistry for the preparation of useful building blocks for various fields including materials chemistry and pharmaceutical industry [1–5]. The catalytic activity of palladium complexes in the coupling reactions using aryl halide substrates is highly dependent on the nature of the ligands. It is well known that electron donating and sterically bulky ligands accelerate the rate-determining oxidation step of most cross-coupling reactions [6–13]. Based on this information, a number of novel ligands have been developed and applied in these reactions [14–20]. However, most of these ligands suffer from the drawback that they can be obtained only after multi-step synthetic procedures and even if some of them are commercially available, they are expensive.

Palladium nanoparticles have received significant attention in various metal-catalyzed transformations and cross-coupling reactions as recyclable and highly active catalysts [21–27]. However, they readily aggregate to form palladium black, a phenomenon that increases their size, makes them unstable, and decreases their catalytic performance. The difficult separation of Pd nanoparticles from the reaction products and the loss of catalytic activity upon reuse are some of the persistent problems encountered in their applications. One strategy for overcoming these limitations is to immobilize the catalyst nanoparticles on solid supports such as zeolites, active carbons, and carbon nanotubes (CNTs) [28–31].

Recently, deposition of noble metals (i.e. Au, Pt, Ag, and Pd) on n-type TiO_2 nanoparticles has attracted considerable attention due to the uniqueness of their combinatorial interfacial properties and functions which are otherwise not available to either of the single components. In fact, Pd deposition on anatase TiO_2 nanoparticles has been shown to enhance their catalytic activity in removal of organic pollutants and alcohol oxidation [32–35]. Although the role of the metal is not fully understood, the enhanced catalytic performance of such systems has been generally attributed to the formation of the Schottky barrier at the interface [36,37]. Under UV irradiation, the photo-induced electrons in the conduction band of TiO_2 can be effectively transferred to the metal nanoparticles because the Fermi level of the metal has lower energy than that of the conduction band of TiO_2 [38,39]. The charge separation induced by the metal suppresses the recombination of the photo-induced electrons and holes, which can enhance the photocatalytic performance. In addition, UV-induced organic transformations by transition-metal-catalysts have been reported [40]. Especially, Köhler et al. reported that the rate of Heck reaction was accelerated by UV- and Visible-Light-induced palladium(II) reduction [41].

Inspired by the above-mentioned studies, we prepared Pd-deposited TiO_2 nanoparticles by a sol-gel method and anchored them on carbon nanotubes (CNTs) that were used as a support in order to prevent aggregation. The resulting catalysts (Pd-TiO_2-CNT) possess some merits in Pd-catalyzed cross-coupling reactions under UV irradiation. First, the Pd nanoparticles were directly

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deposited on TiO_2, which enhanced the nucleophilicity of Pd. Second, the use of CNTs was favorable for reactant-product mass transportation. As a result, the resulting catalyst possessed an improved catalytic activity in the coupling reactions. In this work, the enhanced catalytic activity and stability of the Pd-TiO_2-CNT catalyst for Heck and decarboxylative coupling reactions carried out under UV irradiation has been studied experimentally. To the best of our knowledge, no examples of the effect of UV irradiation on catalytic activity in Pd-catalyzed cross-coupling reactions have been reported in literature till date.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Chemicals

Multi-walled CNTs were obtained from Carbon Nano Tech. Co. Ltd. (South Korea). Titanium tetra-*n*-butoxide ($Ti(OCH_2CH_2CH_2CH_3)_4$, 97%), and sodium tetrachloropalladate (Na_2PdCl_4, 98%) were purchased from Sigma-Aldrich (USA). All other reagents were of analytical grade and used as received without further purification. All aqueous solutions were prepared with Milli-Q deionized water (>18.2 MΩ cm) using the Direct Q3 system from Millipore (USA).

2.1.2. Preparation of the Pd-TiO_2-CNT catalyst

Pd-deposited TiO_2 nanoparticles were synthesized following a previously reported sol-gel method [42]. $Ti(OCH_2CH_2CH_2CH_3)_4$ (7 mL) was dissolved in 40 mL of anhydrous ethanol under vigorous stirring for 1 h. Subsequently, 20 mL of anhydrous ethanol containing 3 mL of concentrated HCl and 740 μL of DI water was slowly added to the solution of the Ti precursor over a period of 5 h with continuous stirring. The deposition of Pd on the surface of TiO_2 nanoparticles was accomplished via a simple reduction process. Na_2PdCl_4 ($\sim$4.0 mg mL^{-1}) was dissolved in distilled water and an ice-cold 0.1 M solution of $NaBH_4$ was added all at once with continuous stirring. The preparation of the Pd-TiO_2-CNT catalysts was carried out by dispersing an acid-treated CNT sample (300 mg) in 50 mL of anhydrous ethanol in an ultrasonic vibration bath for 20 min. The previously prepared Pd-TiO_2 solution (80 mL) was then added to the CNT solution and stirred for 24 h. Subsequently, the reaction mixture was subjected to centrifugation and after washing with absolute ethanol, it was vacuum dried at 40 °C overnight to obtain the desired Pd-TiO_2-CNT catalyst.

2.2. Characterization of catalysts

Transmission electron microscopy (TEM) images were obtained with a Tecnai-F20 system operating at 200 kV. In preparation for the electron micrographs, the samples were dispersed in ethanol ($\sim$1.0 wt% solid content) using an ultrasound bath and a drop of this suspension was deposited on a carbon-coated copper grid. X-ray diffraction (XRD) analysis was performed by X'Pert-Pro X-ray diffractometer utilizing Cu K_α radiation (λ = 1.5406 Å) as the X-ray source. Data were collected at room temperature in the 10–85° range at increments of 0.05°. An X-ray photoelectron spectroscopy (XPS) analysis was performed in an ultra-high vacuum by using a VG Multilab 2000 spectrometer employing a non-monochromatic Mg Kα (1253.6 eV) source and a spherical section analyzer.

2.3. Pd-TiO_2-CNT-catalyzed heck and decarboxylative coupling reactions under UV-irradiation

2.3.1. Heck reaction

In a quartz vessel, Pd-TiO_2-CNT (12.5 mg, 0.002 mmol), 4-iodotoluene (21.8 mg, 0.1 mmol), *n*-butylacrylate (14.3 μL, 0.1 mmol), and triethylamine (28 μL, 0.2 mmol) in DMF (1 mL) were mixed together and stirred under UV irradiation at 50 °C for 12 h. Eight UV lamps (Hg-lamp, PL-S 9W/20 BLB, Philips) of 18 cm length and a wavelength centered at 365 nm were employed as the light source and placed above the solution. The distance between the light source and the vessel was $\sim$10 cm. Subsequently, the reaction mixture was washed with water and extracted with ethyl acetate. Naphthalene was added as an internal standard to the resulting mixture, and the conversion of aryl halides and the product yields were calculated.

2.3.2. Scale up of the heck reaction

General procedure of the Heck reaction sample was scaled up to 0.7 mmol scale for isolation using a quartz vessel, Pd-TiO_2-CNT (87.6 mg, 0.014 mmol), 4-iodotoluene (152.6 mg, 0.7 mmol), *n*-butylacrylate (100.4 μL, 0.7 mmol) and triethylamine (195.1 μL, 1.4 mmol) in DMF (4 mL) were mixed together and stirred under UV irradiation at 50 °C for 12 h. Eight UV lamps (Hg-lamp, PL-S 9W/20 BLB, Philips) of 18 cm length and a wavelength centered at 365 nm were employed as the light source and placed above the solution. The distance between the light source and the vessel was $\sim$10 cm. Subsequently, the reaction mixture was washed with water and extracted with ethyl acetate. The combined extracts were dried with anhydrous $MgSO_4$ and the solvent was removed in vacuo. Product was isolated by silica gel column chromatography.

2.3.3. Decarboxylative coupling reaction

To a quartz vessel, Pd-TiO_2-CNT (87.6 mg, 0.014 mmol), iodobenzene (78.3 μL, 0.7 mmol), phenylpropiolic acid (122.7 mg, 0.84 mmol), and DBU (209.4 μL, 1.4 mmol) in DMSO (4 mL) were added and stirred under UV irradiation at 80 °C for 12 h. The reaction mixture was washed with water and extracted with diethyl ether. A known amount of the internal standard (naphthalene) was added to the resulting mixture, and the conversion of aryl halides and the product yields were determined. Product was isolated by silica gel column chromatography.

3. Results and discussion

Fig. 1 shows a typical TEM image of the Pd-TiO_2-CNT catalyst in which the nanoparticles were uniformly dispersed over the surface of the CNTs. Smaller and highly dispersed nanoparticles were significantly abundant than larger aggregated ones. The average particle size was $\sim$4.3 nm. The corresponding EDX spectrum contained peaks corresponding to the C, O, Pd, and Ti that confirmed the presence of Pd and Ti species on the CNTs.

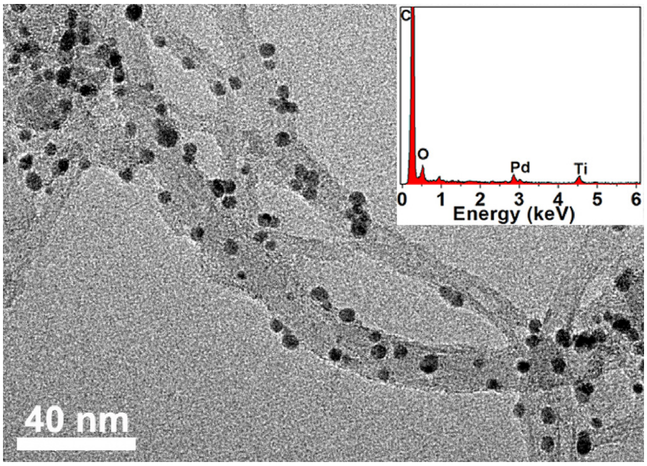

Fig. 1. TEM image of Pd-TiO_2-CNT and the corresponding EDX spectrum (inset).