Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2009, Article ID 302919, 7 pages
doi:10.1155/2009/302919

Research Article

One-Step Synthesis of Pd-M/ZnO (M=Ag, Cu, and Ni) Catalysts by γ-Irradiation and Their Use in Hydrogenation and Suzuki Reaction

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Received 2 October 2008; Revised 23 December 2008; Accepted 27 January 2009

Recommended by Sherine Obare

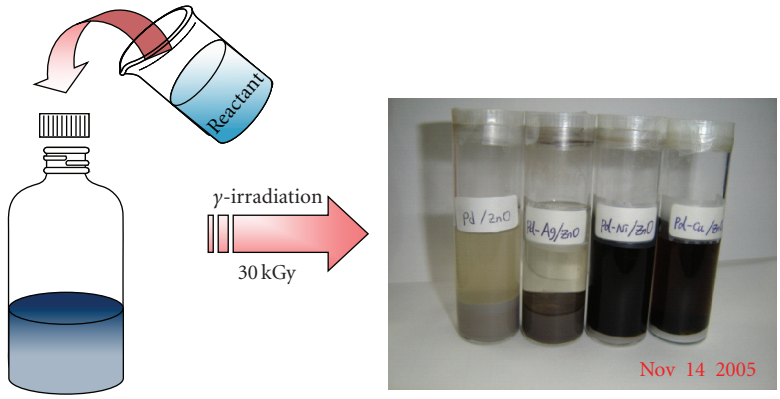
ZnO-supported Pd, Pd-Ag, Pd-Cu, and Pd-Ni catalysts (Pd-M/ZnO) were prepared in MeOH/H_2O mixture (4/1, v/v-%) by γ-irradiation at room temperature. Small mono- and bimetallic nanoparticles were loaded on the surface of ZnO nanopowder as confirmed with TEM, TEM-EDXS, XRD, and ICP-AES data. The catalytic efficiency against Pd-M/ZnO was determined in hydrogenation and Suzuki reaction and compared with the commercial Pd/C catalyst. The Pd-Ag/ZnO showed the highest catalytic efficiency in the Suzuki reaction.

1. Introduction

Palladium catalysts are used in cross-coupling reaction (e.g., Suzuki, Heck reaction, Sonogashira, etc.). While homogeneous palladium catalysts are not used in industrial application because of the difficulty in separating and recycling for the catalysts. Many heterogeneous palladium catalysts have been made for recycling mainly by immobilizing palladium onto inorganic supports or polymers [1–5]. Palladium nanoparticles, colloidal palladium species, and polymer-incarcerated palladiums have been also reported as recycling catalysts [6, 7]. However, they often suffer from problems such as low catalytic efficiency, degradation, the leaching of the metal species, and a difficult synthetic procedure.

Palladium catalyzed Heck or Suzuki C–C forming reactions using aryl bromides as one of the substrates are among the most versatile reactions for organic synthesis, since they are compatible with a large variety of functional groups. Many palladium complexes have been investigated as homogeneous catalysts and many supported palladium complexes as heterogeneous catalysts for these reactions. An extensive range of reaction conditions have been explored and literature on this subject has very recently been reviewed [8]. In a previous paper [9], carbon-supported monometallic Pd and bimetallic Pd-M (M=Ag, Ni, and Cu) nanoparticles were synthesized by γ-irradiation at room temperature without reducing agents. The prepared Pd/C and Pd-M/C catalysts were applied as catalyst in C–C coupling reaction (specially, Suzuki and Heck reactions) in EtOH and in acetonitrile, respectively. The Pd-Cu/C catalysts showed high catalytic efficiency in the Suzuki- and Heck-type reactions. However, the metallic nanoparticle based on Pd is mainly aggregated on carbon surface because carbon supporters have hydrophobic properties, while the metallic particles have hydrophilic properties. In order to increase dispersion of metallic nanoparticles, we selected hydrophilic property supporters.

On the other hand, the aromatic amines are of significant industrial importance because they are widely used as the intermediates for synthesis of dyes, pharmaceuticals, and agrochemicals [10]. Aromatic amines are generally prepared by the reduction of aromatic nitro compounds. Two general methods are used for the reduction of aromatic nitro compounds in industry: catalytic hydrogenation [11, 12] and stoichiometric reduction reaction [13–17]. The catalytic hydrogenation is a clean and convenient method for producing amine in high yield. However, little has been reported about synthesis of aromatic amine from aromatic nitro compound by using monometallic or bimetallic nanoparticles prepared by γ-irradiation, to our knowledge.



Scheme 1: Preparation procedure of Pd-M (M=Cu, Ni and Ag)/ZnO catalyst in MeOH-water mixture by using γ-irradiation. Reactants: CH_3OH (200 mL) and water (50 mL) as solvent, PVP as a stabilizer, palladium nitrate, silver nitrate, copper nitrate, and nickel nitrate, ZnO powder (10.0 g).

Herein, we described a simple method for preparing ZnO-supported Pd (Pd/ZnO) and Pd-M (M=Cu, Ni, and Ag) nanoparticles (Pd-M/ZnO) by γ-irradiation at room temperature without any reduction agents. The prepared Pd/ZnO and Pd-M/ZnO catalysts were characterized by TEM, TEM-EDXS, and ICP-AES spectroscopy. Furthermore, the catalytic efficiencies of the Pd/ZnO and Pd-M/ZnO catalysts were evaluated in hydrogenation and Suzuki reactions.

2. Experimental

2.1. Chemicals. $PdNO_3$, $CuNO_3$, $NiNO_3$, Iodobenzene, 2-iodothiophene, 4-iodobenzoic acid, phenyl boronic acid, and 4-nitrophenol were analytical reagent grade and supplied by Sigma-Aldrich Korea (Seoul, Korea). $AgNO_3$ was purchased from Kojima Chemicals Co., Ltd. (Japan). The ZnO nanopowder was obtained from Sunjin Chemical Co., Ltd. (Korea). The Poly (vinylpyrrolidone), PVP (molecular weight of 40 000), was purchased from Junsei Co. Ltd. (Japan). All the other chemicals were of reagent grade and used without further purification.

2.2. Radiolytic Synthesis of Pd-M/ZnO (M=Ag, Ni, and Cu) Catalysts. Scheme 1 shows the preparation procedure of Pd-M/ZnO catalysts by using γ-irradiation. The Pd-Ag/ZnO catalyst was prepared by the following procedure. First, $Pd(NO_3)_2$, $AgNO_3$, PVP as anchor agents, and ZnO nanopowder (10.0 g) as supporting material were dispersed in a mixed solution of MeOH-water (4/1, v/v-%). Next, nitrogen gas was bubbled through the solution for 30 minutes to remove the oxygen. The dispersed solution was then irradiated by the γ-ray from a Co-60 source under atmospheric pressure and ambient temperature. The total irradiation dose was 30 kGy (a dose rate = 1.0×10^4 Gy/hour). The Pd/ZnO, Pd-Ni/ZnO, and Pd-Cu/ZnO catalysts were also prepared by a similar method. After γ-irradiation, the reaction mixture was centrifuged at 1600 rpm for separation of the Pd-M/ZnO catalysts, which were then dried at 50°C in a vacuum oven for 6 hours.

Table 1: ICP data of Pd-M (M=Ag, Cu, Ni)/ZnO catalysts prepared by γ-irradiation.

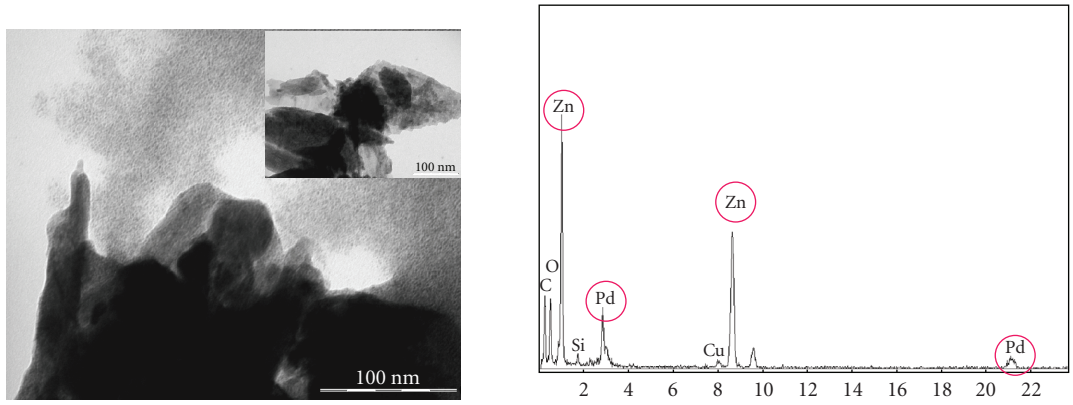
	Pd (%)	Ag (%)	Cu (%)	Ni (%)
Pd/ZnO	19.4			
Pd-Ag/ZnO	9.73	8.53		
Pd-Cu/ZnO	6.36		11.3	
Pd-Ni/ZnO	5.06			0.650

2.3. Catalytic Test

2.3.1. Hydrogenation. For studying the catalytic efficiency for Pd and Pd-M/ZnO catalysts, the reaction mixtures were prepared with $NaBH_4$ (0.1 M) as hydrogen source and aromatic nitro compounds (0.01 M). Pd-M/ZnO catalysts (5 mg) were added in the prepared reaction mixture. The UV-visible spectra during reduction of aromatic nitro compounds using Pd-M/ZnO catalysts were recorded continuously. In order to compare the reduction of aromatic nitro compound, the standard aromatic amine compounds were also measured by UV-visible spectra.

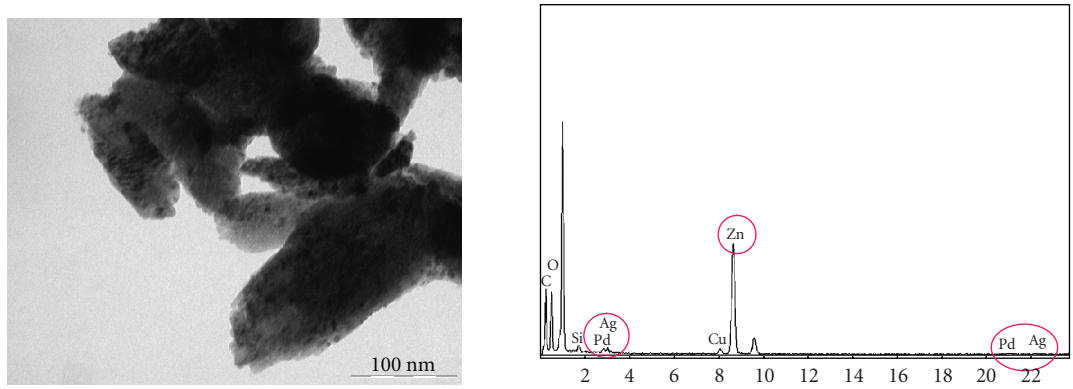
2.3.2. Suzuki Reaction. In a 100 mL three-necked flask, an aryl halide (3.0 mmol), phenyl boronic acid (6.0 mmol), Pd-M/ZnO catalyst (43.0 mg, ca. 4.0 mmol), and K_3PO_4 (12.0 mmol) were added in 50 mL EtOH. Three different types of aryl halides were tested. The mixture solution was reacted at 78°C for 3 hours under nitrogen atmosphere. In order to remove the Pd-M/ZnO catalyst, the reaction solution was filtered through a Whatman filter paper (no.2). The filtered solution was filtered again through 0.45 μm membrane filter (MFS-25 PVDF). Finally the solvent was evaporated. The yield was determined by HPLC with a ODS column.

2.4. Characterization. UV-visible spectra were measured by using a Shimadzu UV-160 digital spectrophotometer (Kyoto, Japan) in a 1 cm quartz cuvette. Field emission transmission electron microscopy (FE-TEM) images were collected at



(a) (b)

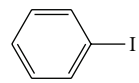
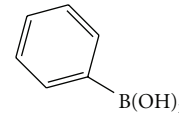
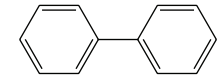
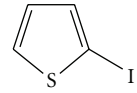
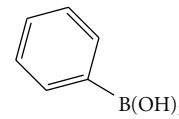
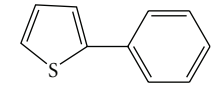
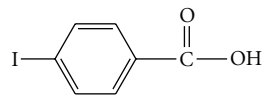
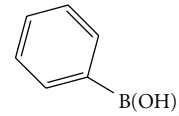
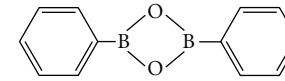
Figure 1: TEM images (a) and EDXS data (b) of the Pd/ZnO catalyst prepared by γ-irradiation.

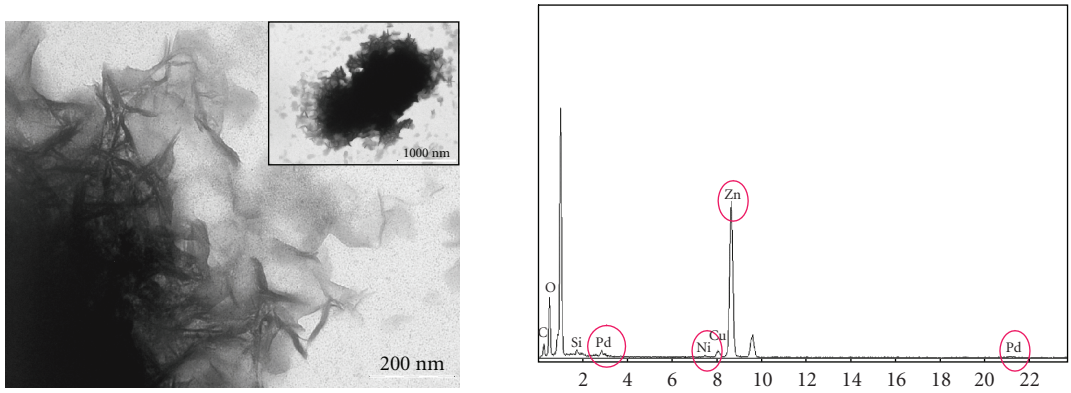


(a) (b)

Figure 2: TEM images (a) and EDXS data (b) of the Pd-Ag/ZnO catalyst prepared by γ-irradiation.

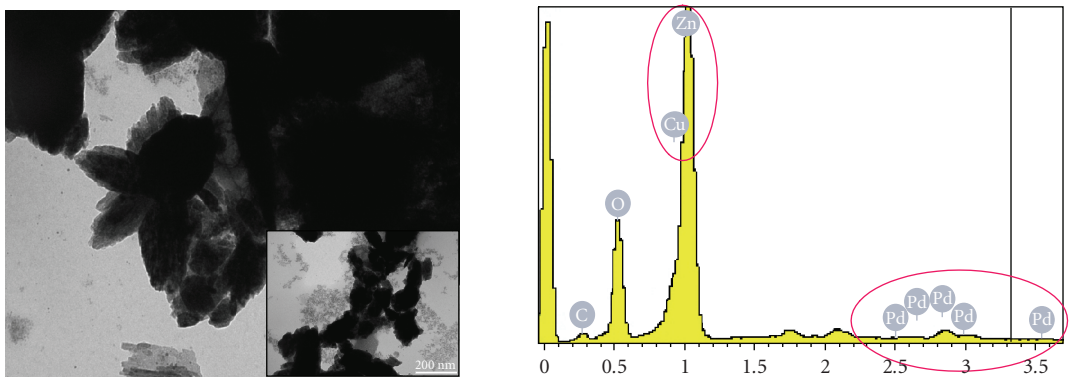
Table 2: Catalytic efficiency of Pd-M/ZnO catalysts in Suzuki reaction. Reaction conditions: Pd-M/ZnO catalysts (0.4 mmol), aryl halide (3 mmol), boronic acid (6 mmol), K_3PO_4 (12 mmol), in EtOH (50 mL), at 78°C, for 3 hours, yield obtained from HPLC data.

Entry	Catalysts	Yield (%)	Aryl halede	Boronic acid	Product
1	Pd/C	99.5			 GC-mass data; 7.8 min, MW = 154
2	Pd/ZnO	99.0			
3	Pd-Ni/ZnO	99.2			
4	Pd-Cu/ZnO	99.1			
5	Pd-Ag/ZnO	100			
6	Pd/C	95.6			 GC-mass data; 8.3 min, MW = 160
7	Pd/ZnO	96.9			
8	Pd-Ni/ZnO	97.1			
9	Pd-Cu/ZnO	98.0			
10	Pd-Ag/ZnO	98.3			
11	Pd/C	37.0			 GC-mass data; 16.4 min, MW = 207
12	Pd/ZnO	38.0			
13	Pd-Ni/ZnO	42.8			
14	Pd-Cu/ZnO	44.7			
15	Pd-Ag/ZnO	40.4			



(a) (b)

Figure 3: TEM images (a) and EDXS data (b) of the Pd-Ni/ZnO catalyst prepared by γ-irradiation.



(a) (b)

Figure 4: TEM images (a) and EDXS data (b) of the Pd-Cu/ZnO catalyst prepared by γ-irradiation.

200 kV using a Hitachi HF-2000 TEM equipped with a field emission source. An energy dispersive X-ray spectrometer (EDXS) attached to the Hitachi HF-2000 TEM was used to analyze the chemical composition of the samples. FE-TEM specimens were prepared by placing microdrops of colloid solution on a carbon film supported on copper grids. The elemental analysis of the catalysts was performed by an Ultima-C Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Jobin-Yvon Co. USA).

3. Results and Discussion

3.1. Characterization of Pd-M/ZnO Catalysts Prepared by γ-irradiation. Figure 1 shows the TEM image and the EDXS data of the Pd/ZnO catalysts. The TEM image clearly shows the Pd particles are successfully loaded on the surface of the ZnO nanopowder. The presence of Pd is also seen in the TEM-EDXS spectrum. The formation of Pd nanoparticles from the metal ions can be explained by the following equation. In an aqueous solution, hydrated electrons were generated by γ-irradiation (see (1)):

$$H_2O \longrightarrow e_{aq}^{-}, H_3O^{+}, H^{\cdot}, H_2, {}^{\cdot}OH, H_2O_2. \quad (1)$$

The Pd ions are reduced by the hydrated electrons to form metallic Pd (Pd^0) (see (2)), which are aggregated to form more stable Pd particles (Pd_{agg}) (see (3)):

$$e_{aq}^{-} + Pd^{2+} \longrightarrow Pd^0, \quad (2)$$

$$nPd^0 \longrightarrow Pd^2 \longrightarrow Pd_n \longrightarrow Pd_{agg}. \quad (3)$$

In (3), n is the number of aggregated Pd^0 and Pd_{agg} is the aggregate in the final stable state.

Figure 2 shows a typical TEM image and the EDXS data of the Pd-Ag/ZnO catalysts. The TEM image and TEM-EDXS data inform that the Pd-Ag alloy particles were formed on the surface of ZnO by γ-irradiation. In Figures 3 and 4, the TEM and TEM-EDXS data were shown for Pd-Ni/ZnO and Pd-Cu/ZnO catalysts, respectively. It is seen in both figures that the Pd-M bimetallic nanoparticles are again successfully loaded on the surface of the ZnO nanopowder. It is noted that the loaded amount of the Pd-Ni/ZnO catalysts (shown in Figure 3) was smaller than that of the other particles. In order to determine the amounts of the metallic nanoparticles, an elemental analysis was performed on the nanoparticles using ICP-AES, and the results are shown in Table 1. The Pd content in Pd-Ni/ZnO (5.06%) is much lower than that in Pd/ZnO (19.4%), Pd-Ag/ZnO (9.73%), and Pd-Cu/ZnO

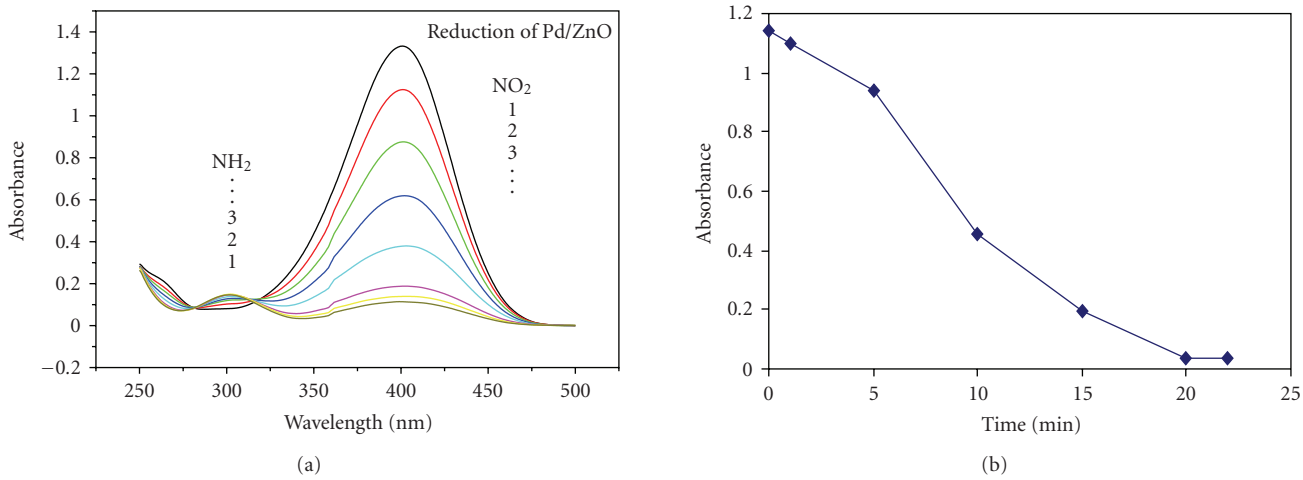


Figure 5: UV-Vis spectra (a) of the reduction of 4-NP and absorbance versus time plot (b) of the reduction of 4-nitrophenol by Pd/ZnO catalyst.

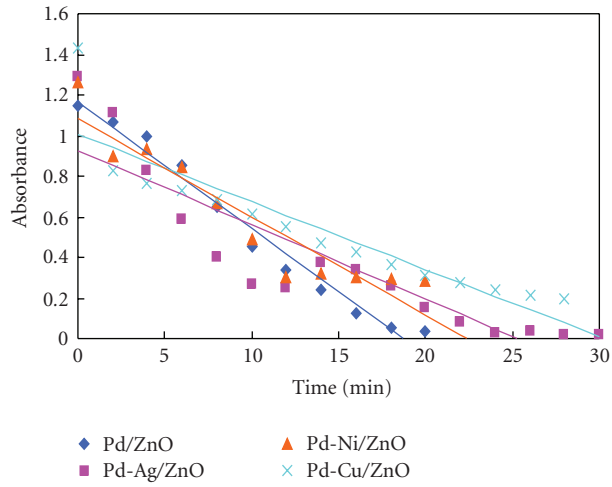


Figure 6: Absorbance versus time plot of reduction of 4-nitrophenol by Pd-M/ZnO catalysts.

(6.36%). Also, the Ni content in Pd-Ni/ZnO (0.65%) is much lower than the Ag content in Pd-Ag/ZnO (8.53%) and the Cu content in Pd-Cu/ZnO (11.3%). The results shown in Table 1 confirm that a lesser amount of Pd-Ni/ZnO nanoparticles was formed than other nanoparticles. Belloni et al. [18–20] published that the control of the conditions for the synthesis of the metallic nanoparticle and alloy clusters. He concluded that the reduction of the respective metal ions should be related to the radiation dose, time, and concentration of metal ions.

3.2. Catalytic Efficiency of Pd-M/ZnO Catalysts. The ZnO-supported Pd and Pd-M nanoparticles prepared in this study can be applied as a catalyst in hydrogenation. Figure 5 shows the UV-Vis spectra (a) and absorbance versus time plot (b) of the reduction of 4-nitrophenol by Pd/ZnO catalysts. It has been observed that the intensity at 400 nm due to nitro group peak was decreased, while the intensity at 290 nm due to amine group peak was increased. This means the formation of 4-aminophenol. Pradhan et al. [21] published about the reduction of nitro group on 4-nitrophenol by using sodium borohydride as a hydrogen source in the presence of the Pt-Ni nanoparticle as catalyst. Figure 6 exhibited that the absorbance versus time plot during reduction of 4-nitrophenol using Pd and Pd-M/ZnO (M=Ag, Ni, and Cu) catalysts. This data shows reduction process of 4-nitrophenol on Pd-M/ZnO monitored by UV-Visible spectroscopy. The order of catalytic efficiency for Pd-M/ZnO catalysts was as follows: Pd/ZnO > Pd-Ni/ZnO > Pd-Cu/ZnO > Pd-Ag/ZnO. In a previous paper [22], we also prepared the PVP stabilized Pd colloids by γ-irradiation in aqueous solution without additional reducing agent. The Pd colloid was used as catalysts for the reduction of 2-, 3-, 4-nitrophenol, 2,4,6-trinitrotoluene, and 4-nitrobenzo-15-crown in aqueous solution at room temperature. However, Pd colloid could not be recycled, while these Pd-M/ZnO catalysts could be recycled.

The ZnO-supported Pd and Pd-M nanoparticles prepared in this study can also be applied in Suzuki reactions as catalyst. Table 2 shows the catalytic efficiencies (measured by the reaction yield) of Pd/ZnO and Pd-M/ZnO catalysts in three different Suzuki reactions. The reaction yield was determined by an HPLC with an ODS column, with MeOH as the mobile phase, and a UV/VIS detector set at 254 nm. As shown in Table 2, in the first reaction, the catalytic efficiency (measured by the yield of product, 2-phenylthiophene) decreases in the order of Pd-Ag/ZnO > Pd-Cu/ZnO > Pd-Ni/ZnO > Pd/ZnO. However, C-C coupling formation was not formed at no. 11–15 in Table 2, whereas the biboronic compound was mainly obtained. Figure 7 shows HPLC and GC/Mass data obtained for the reactants and the products of biphenyl compound in Suzuki reactions. There are two important factors, such as catalytic efficiency and recycling, in catalytic reaction. Figure 8 show the recycling results of Pd-Ag/ZnO catalysts in the Suzuki reaction. The product yield of 2-phenylthiophene was 98.9% in the first reaction.

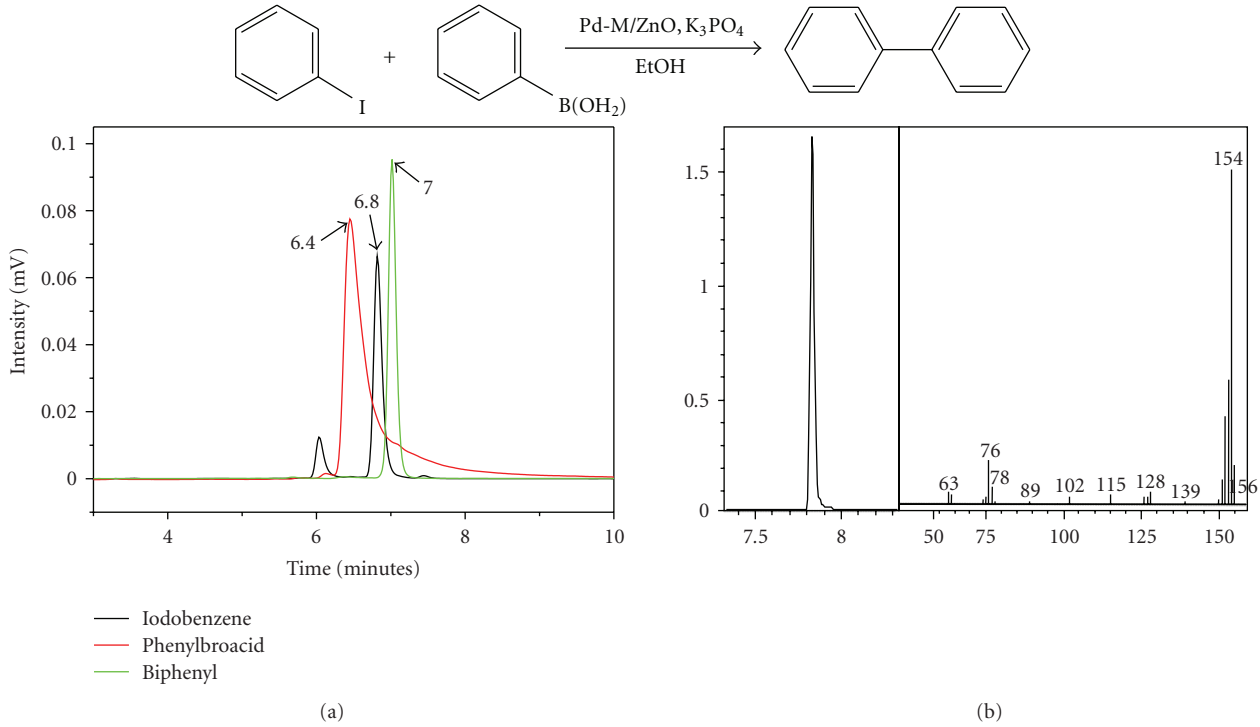


Figure 7: HPLC chromatograms of standard (a) and GC/Mass spectra (b) of biphenyl compound.

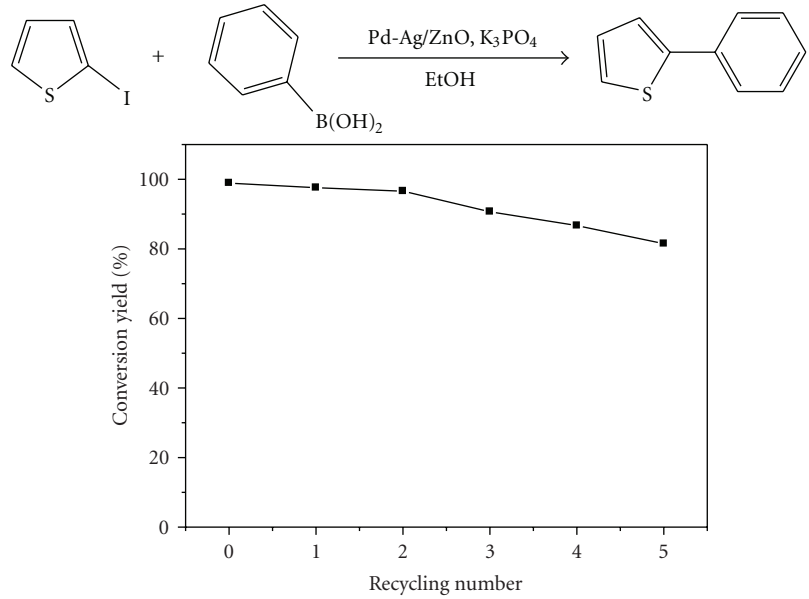


Figure 8: Recycling results of Pd-Ag/ZnO catalyst.

After the fifth recycling, the yield was 81.5%. These results indicate that the ZnO supported Pd and Pd-M nanoparticles prepared by γ-irradiation were good catalysts in the Suzuki reaction.

4. Conclusion

The Pd/ZnO and Pd-M/ZnO catalysts (M=Ag, Cu, and Ni) were one-pot synthesized by γ-irradiation in an MeOH-water mixture without a reducing agent. TEM, TEM-EDXS, and ICP-AES data showed that the Pd and Pd-M (M=Ag, Cu, and Ni) nanoparticles were successfully loaded on the surface of the ZnO nanopowder. The catalytic efficiencies of the Pd-M/ZnO catalysts were examined in hydrogenation and Suzuki reactions. In hydrogenation of 4-nitrophenol, the catalytic efficiency of Pd and Pd-M/ZnO catalysts was similar. In the Suzuki reactions, the catalytic efficiency (measured by the yield of the product) decreases in the order

of Pd-Ag/ZnO > Pd-Cu/ZnO > Pd-Ni/ZnO > Pd/ZnO. In comparison of the catalytic efficiency between Pd-M/ZnO and the commercial Pd/C catalyst, the catalytic efficiency of Pd and Pd-M/ZnO catalysts prepared by γ-irradiation was higher than that of the commercial Pd/C. The heterogeneous Pd-M/ZnO catalysts prepared by γ-irradiation can be used for carbon-carbon coupling reactions such as Still-, Heck-, and Sonogashira-reactions.

Acknowledgment

This research was supported by the Nano R&D Program (M10803001311-08M0300-31110) and the National Nuclear Technology Program (M20802000206-08B0200-20610) through the Korea Science and Engineering Foundation funded by the Ministry of Science & Technology.

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