



Synthesis of cobalt-impregnated carbon composite derived from a renewable resource: Characterization and catalytic performance evaluation



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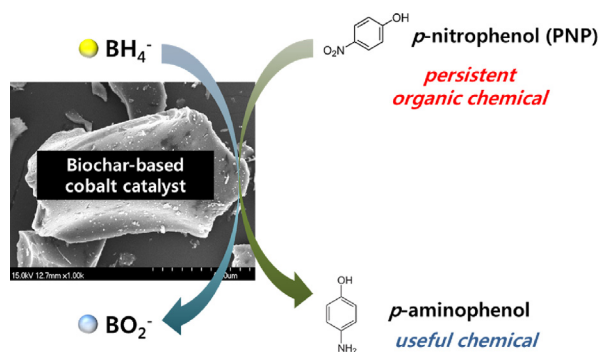
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HIGHLIGHTS

- Fabrication of nitrogen-doped Co-biochar derived from glucose (Co-NB).
- Homogeneous dispersion of metallic Co nanoparticles on the Co-NB surface
- Catalytic activity of Co-NB in converting *p*-nitrophenol into *p*-aminophenol
- Robust reusability of the Co-NB

GRAPHICAL ABSTRACT



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ABSTRACT

A novel nitrogen-doped biochar embedded with cobalt (Co-NB) was fabricated *via* pyrolysis of glucose pretreated with melamine (N donor) and Co(II). The Co-NB showed high catalytic capability by converting *p*-nitrophenol (PNP) into *p*-aminophenol (PAP) by NaBH_4 . The analyses of FE-SEM, TEM, BET, XRD, Raman, and X-ray photoelectron spectroscopy XPS of the Co-NB showed hierarchical porous structure (BET $326.5 \text{ m}^2 \text{ g}^{-1}$ and pore volume: $0.2403 \text{ cm}^3 \text{ g}^{-1}$) with well-dispersed Co nanoparticles (20–60 nm) on the N-doped graphitic biochar surface. The Co-NB showed higher PNP reduction capability compared to the Co-biochar without N-doping, achieving 94.3% removal within 4 min at 0.24 g L^{-1} catalyst dose and initial concentration of 0.35 mM PNP. Further conversion experiments under varying environmental conditions (*e.g.*, NaBH_4 concentration (7.5–30 mM), biochar dosage ($0.12\text{--}1.0 \text{ g L}^{-1}$), initial PNP concentration (0.08–0.17 mM)) were conducted in batch mode. The reusability of Co-NB was validated by the repetitive conversion experiments (5 cycles). The overall results demonstrated biochar potential as catalysts for environmental applications if properly designed.

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1. Introduction

Catalysts have been frequently utilized in various fields of chemistry, physics and biology due to their high reactivity and efficiency. However, there can be a considerable loss of catalytic activity resulting from

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particle aggregation and instability due to inherent high surface energy, especially in the homogenous catalyst system (Wang et al., 2017). To resolve this issue, efforts have been made to develop heterogeneous catalysts with improved recyclability and sustainability (Bennett et al., 2016; Joshi et al., 2016; Roschat et al., 2016). The use of heterogeneous catalysts to promote desired reactions for various applications such as organic synthesis, conversion to value-added products, and degradation of pollutants has received considerable attention (Hajduk et al., 2017; Y. Liu et al., 2017; J. Liu et al., 2017; Taifan and Baltrusaitis, 2016; Wang et al., 2014).

Many studies have been reported on the catalytic conversion of target chemicals using catalysts containing noble metals (Pt, Au, Ag, Rh, Ru, Pd, etc.) (Fang et al., 2017; Louie et al., 2017; Song et al., 2017). However, despite their high performances, noble metals-based catalysts are seldom used in scaled-up applications because of high cost and limited availability of the noble metals.

In recent, the potential utility of cobalt (Co) in triggering catalytic reactions has been examined as an alternative to the noble metals due to its low cost. For example, Hasan et al. (2016) fabricated a magnetic Co carbon composite *via* calcination of cobalt-based metal organic frameworks (MOFs) and demonstrated its catalytic capability in converting *p*-nitrophenol (PNP) into *p*-aminophenol (PAP), which is a useful chemical for pharmaceuticals, dyestuffs, and agrochemicals (Guo et al., 2016). In addition, Co-loaded polymers with hierarchical porous structures were prepared as a stable catalyst for PNP conversion into PAP (Zhao et al., 2016).

Carbon-based materials have gained much attention for use as support materials for catalytic metals to provide structural integrity and other desirable properties. For instance, activated carbon supports with high surface area and hierarchical porous structure have shown excellent conversion and selectivity in catalytic applications (Mouat et al., 2016; Si et al., 2017). Carbon materials prepared with renewable resources have been recently employed in the preparation of catalytic materials (Lee et al., 2017; Liu et al., 2016; Yao et al., 2016). Our previous work has used lignin as a carbon precursor to synthesize Co-biochar catalyst composite and validated its great catalytic performance in conversion of bromate (Cho et al., 2017). Xu et al. (2015) proposed environmentally benign method to prepare 3D porous graphene by converting waste papers mixed with a cobalt(II) complex. With such efforts, utilizing biomass- or biowaste-derived carbonaceous materials (*i.e.*, biochar) is evolving into a viable option in production of environmental catalysts. In addition, a good number of recent studies have explored the potential of biochar for the use in various catalytic/environmental applications (Dehkhoda and Ellis, 2013; Kastner et al., 2015; Mohan et al., 2014; Ren et al., 2014).

Glucose derived from the hydrolysis of cellulose is a common carbon source which has merits of low cost, easy access, and fast regeneration (Tian et al., 2016). Thus, glucose was chosen as a carbon support precursor for the synthesis of biochar-based Co catalyst. Recently, nitrogen (N) doping onto the catalysts has showed enhanced catalytic performances as compared to the catalysts without N-doping (Wang et al., 2015). Blending N-containing ligands with carbon precursor followed by pyrolysis is a facile method to provide N dopant to the catalyst, and therefore melamine that contains high amount of nitrogen was used as N donor in this work. The biochar was characterized by spectroscopic and surface analyses. The catalytic ability of the biochar was compared with that of the biochar without N doping. A series of PNP conversion experiments were performed under varying experimental parameters such as NaBH₄ concentration, composite dosage, and initial PNP concentration. The reusability of the biochar was also examined to demonstrate the longevity of catalytic ability of the biochar.

2. Experimental methods

2.1. Chemical reagents & materials

Cobalt chloride hexahydrate (CoCl₂·6H₂O, 99%), D-(+)-Glucose (C₆H₁₂O₆) and melamine (C₃H₆N₆, 99%) were obtained from Sigma

Aldrich, USA. *p*-Nitrophenol (PNP, C₆H₅NO₃, 99%) and sodium borohydride (NaBH₄) were purchased from Alfa Aesar, USA and Daejung Chemical, Korea, respectively. Solutions were prepared with ultrapure deionized distilled water (DDW, 18.2 MΩ cm⁻¹).

2.2. Synthesis of biochar catalyst

The mixture solution of Co/glucose/melamine was prepared by adding 1 g CoCl₂·6H₂O, 4 g glucose and 1 g melamine into 20 mL DDW. An alumina crucible was used as a sample container of the mixture solution. A tubular reactor (TR) with batch type was used for the synthesis of catalyst composites under ambient pressure. A stainless Ultra Torr Vacuum Fitting (Swagelok SS-4-UT-6-400) was used to connect quartz tubing (25.4 mm outer diameter and 610 mm length, Chemglass CGQ-0900T-13, USA). The N₂ gas (ultra-high purity) was obtained from AirTech Korea, and N₂ flow rate was manipulated by a mass flow controller (Brooks E Series, USA).

The synthesis procedure of N-doped Co-biochar (Co-NB) was as follows. The flow rate was controlled to 500 mL min⁻¹. The mixture solution was added to the alumina crucible, and carbonized at low temperature of 80 °C for 30 min. The carbonized solid was converted into biochar in the TR *via* pyrolysis. The starting temperature condition of pyrolysis process was 200 °C, and the temperature increased to 700 °C at the heating rate of 10 °C min⁻¹ within 50 min, and then held constant for 5 h. The resulting biochar were washed several times using DDW until visible suspended particles were completely removed and kept in a drying oven at 40 °C prior to use. For the synthesis of Co-biochar without N-doping (Co-B), the mixture solution of 5 g glucose and 1 g CoCl₂·6H₂O was used, and the synthesis procedure was the same as Co-NB synthesis.

2.3. Characterization of biochar catalyst

The morphology of Co-NB was characterized by a field emission scanning electron microscopy (FE-SEM, Hitachi S-4700, Japan). Transmission electron microscopy/energy dispersive spectroscopy (TEM/EDS, Jeol JEM-1400) was used to investigate the distribution of formed Co solid particles on the surface. The porosity and pore size distribution of the biochar were measured using a Brunauer-Emmett-Teller (BET) surface analyzer (Belsorp-mini II, Japan). X-ray powder diffraction (XRD, D8 Advance, Bruker-AXS) analysis was carried out to investigate the phase transformation of Co during pyrolysis with a Rigaku DMax-2500 diffractometer using CuKα radiation. Raman spectra were obtained with a Dimension P1 Raman spectroscopy (Lambda Solution Co., USA). Surface analysis of the composite was conducted using a theta probe angle-resolved X-ray photoelectron spectrometer (ARXPS) system equipped with the monochromatic Al Kα line (1486.7 eV).

2.4. PNP conversion experiments

PNP conversion experiments were performed using a standard quartz cuvette with 1 cm path length in the presence of excess amount of NaBH₄ at 25 ± 2 °C. First, 1 mL of 5 mM PNP solution was added into the cuvette containing 2 mL DDW, and subsequently 1 mL of 510 mM NaBH₄ solution was spiked into the solution, which immediately changed pale yellow solution to bright yellow. Then, 0.1 mL of the biochar suspension (10 mg mL⁻¹) was added into the cuvette, and the cuvette was introduced to UV-vis measurements. The absorbance of the solution was scanned at different intervals using a UV-vis spectroscopy (Hach DR/4000, USA). The conversion of PNP to PAP by Co-NB was examined under varying experimental parameters including NaBH₄ concentration (7.5–30 mM), composite dosage (0.12–1.0 g L⁻¹), and initial PNP concentration (0.08–0.17 mM). Lastly, the reusability of Co-NB was evaluated by running repetitive conversion cycles.

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