



Contribution of pyrolytic gas medium to the fabrication of co-impregnated biochar

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ABSTRACT

Co-impregnated biochars were fabricated by pyrolysis of spent coffee grounds (SCG) or glucose as carbon (C) sources under N₂ and CO₂. The formed biochar samples were characterized with FE-SEM, TEM/EDS, XRD, TGA, Raman, XPS, and BET, and further used as catalytic medium for the reduction of *p*-nitrophenol in the presence of NaBH₄. The physicochemical characteristics of biochar significantly changed with the types of C precursor and flow gas stream. The biochar from pyrolysis of SCG under N₂ gas stream showed good dispersion of Co nanoparticles (10–20 nm) in carbon matrix as compared to that produced under CO₂ stream, but BET surface area was very small (4.5 m² g⁻¹) due to pore blockage by thermal degradation products. SCG-derived biochar formed in the presence of CO₂ possessed highly porous structure due to CO₂-assisted C volatilization. In contrast, for glucose-derived biochar, significant reduction in porosity of biochar occurred with excess devolatilization of C under CO₂ conditions, while the pyrolysis under N₂ flow produced porous biochar. These contrasting results demonstrated the significance of structure crystallinity and thermal degradability of C precursors. The catalytic performance of biochar was better correlated with the external surface area rather than microporosity.

1. Introduction

Metal-impregnated composites have gained increasing attention as catalytic media in a variety of industrial and environmental applications such as oxygen reduction [1], organic chemicals synthesis [2], photocatalytic decomposition [3], and chemical reduction [4]. Preparation of such solid catalysts commonly involves impregnation of noble metals (Pd, Pt, Rh, Ru etc.) onto organic/inorganic supporting materials [5,6]. However, high cost and scarcity of the noble metals often limit their expansion in scaled-up or practical applications [7]. To resolve this issue, researchers have investigated the potential utility of non-noble metals (Co, Ni, Cu, Mn etc.) as alternative catalysts [8,9].

Co has been widely applied to industrial and chemical processing applications, and its catalytic ability has been well reported [10–12]. For instance, a core-shell catalyst consisting of metallic Co core and amorphous Co oxide shell showed good catalytic capability in electrolysis for H₂ production [13]. A nitrogen (N)-doped Co-carbon composite efficiently catalyzed oxygen reduction [14]. Also, Co-based metal-

organic framework (MOF) catalysts significantly improved the conversion of acetylene to vinyl chloride in the production of plastics [15]. In environmental applications, Co-based composites have been utilized for the catalytic reduction of toxic *p*-nitrophenol (PNP) to non-toxic *p*-aminophenol (PAP) [16]. The catalytic reduction of PNP to PAP is also of practical significance because PAP is an important ingredient used for the production of dyes, pharmaceuticals, and chelating agents [17]. Hasan et al. [18] fabricated Co-carbon composites from Co oxide-melamine mixture, and demonstrated their catalytic capabilities in PNP reduction to PAP.

Several types of materials have been utilized as a supporting matrix for Co particles (metallic Co or Co oxides) including zeolite [19], silica [20], layered double hydroxide (LDH) [21], MOF [22], carbon nanotube [23], fullerene [24], and reduced graphene oxides [25]. Their primary functions are to provide active surface sites for metal dispersion and to help to control the particles size and shape, thereby enhancing catalytic performance of Co. Besides the investigations of the supporting materials, several other factors (Co particle size formed,

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nitrogen existence, and annealing temperature) have been studied to improve the catalytic activity of Co-based catalysts [14,23]. For example, the plasma-assisted method was found to be very effective in enhancing the catalytic activity by modifying the morphology and chemical composition of the catalyst precursors [26]. N-doped Co-carbon composites fabricated by using urea and melamine showed enhanced catalytic performances compared to non-treated composites [27–29]. Pereira et al. [28] also suggested that pyrolysis temperature is one of the key factors to improve catalytic capability of N-doped Co-carbon composite. However, the effects of pyrolytic gas as a reaction medium on the material properties and catalytic ability of the carbon composite have not been fully investigated.

Due to the increasing public recognition for environmental sustainability, research efforts have been made to switch the renewable materials (*i.e.*, biomass) as a carbon precursor for catalysis [30–32]. The use of biomass offers environmental merits. Biochar, a low-density charred material, can be produced by pyrolyzing biomass feedstocks under anoxic conditions and temperatures of 300–1000 °C [33,34]. For instance, glucose has been widely used as a carbon source for solid catalysts due to its low cost and easy accessibility [35–37]. Moreover, there have been increasing efforts to utilize biomass wastes as carbon precursors [38]. Global generation of spent coffee grounds (SCG) has gradually increased [39], and SCG has a great potential for producing value-added products because it contains high concentration (> 90%) of renewable organic components (*i.e.*, cellulose, hemicellulose, lignin, and others) [40,41]. In this sense, both glucose and SCG are a feasible option to synthesize carbon based catalyst in that they are inexpensive and renewable carbon resources.

Our recent work [31] has shown that Co-impregnated biochar can be prepared using lignin as a raw material through pyrolysis. One of the important findings was that using CO₂ as a reaction medium led to greater catalytic capability of the produced biochar than using N₂. This observation signifies the importance of pyrolytic gas medium in catalyst production. It is noteworthy that the thermal degradation behavior of lignin-free biomass (*i.e.*, cellulose or hemicellulose) and lignin-containing biomass can be different [42], due to a high portion of aromatics in lignin, which could differentiate the catalytic properties of the produced biochar.

In the present work, a series of N-doped Co-biochar (SCG and glucose derived) was synthesized by pyrolyzing under N₂ or CO₂ flowing, and used for PNP reduction. The resulting catalysts were characterized with various spectroscopic and surface analyses. Insights into the influence of flow gas on the characteristics and catalytic activity of catalyst were discussed.

2. Experimental section

2.1. Chemical reagents and materials

Sodium borohydride (NaBH₄) and PNP (C₆H₅NO₃, 99%) were obtained from Daejung Chemical, Korea. Cobalt chloride hexahydrate (CoCl₂·6H₂O, 99%), glucose (C₆H₁₂O₆, ≥ 99%), and melamine (C₃H₆N₆, 99%) were purchased from Sigma Aldrich, USA. The SCG samples (< 150 μm) were stored at 40 °C in a dry-oven prior to the biochar synthesis procedures. The components of SCG (total organic carbon: 89 wt.%) were 9 wt.% cellulose, 13.8 wt.% galatan, 23.4 wt.% mannan, 12.9 wt.% protein and 29.8 wt.% lignin [43]. The ultrahigh purity (*i.e.*, 99.999%) N₂ and CO₂ gases were purchased from International Industry Gas Co, Korea.

2.2. Fabrication of biochar

The fabrication methods of N-doped Co-biochar samples were as follows (Fig. 1). The SCG was pretreated with CoCl₂ and melamine by modifying the preparation procedure reported in our previous studies [31,44]. In brief, a CoCl₂/melamine aqueous solution was prepared by

mixing 1 g of melamine and 1 g of CoCl₂·6H₂O (molar ratio of melamine to Co = 2.13) into 50 mL distilled deionized water (DDW). Subsequently, 5 g of SCG (SCG/Co weight ratio = 20) was added into the aqueous solution followed by drying at 80 °C for 120 min. The dried samples were stored in a dry-oven at 60 °C for 24 h. For the preparation of Co/glucose/melamine mixture, 1 g of CoCl₂·6H₂O salt was completely dissolved in the 25 mL DDW containing 1 g of melamine (melamine/Co molar ratio = 2.13) and 5 g of glucose (glucose/Co weight ratio = 20), and the solution was transferred into an aluminum crucible. The aqueous solution was dried at 80 °C for 120 min to remove the water and the dried sample was kept in a dry-oven at 60 °C for 24 h.

The as-prepared sample (3 ± 0.3 g) was carbonized via pyrolysis under N₂ or CO₂ atmosphere, in which the temperature was increased from 200 to 700 °C with a heating rate of 10 °C min⁻¹ and held at 700 °C for 2 h. A batch-type tubular reactor (TR) was used in the pyrolysis under ambient pressure. A 25.4 mm 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) to supply the gas stream. The TR was placed in a temperature program module-equipped tube furnace (Wisetherm, Korea). The flow gas rates were maintained at 500 mL min⁻¹ using a mass flow controller (Brooks, 6850E series, USA). The resulting solids were stored in a N₂-purged desiccator. The N-doped biochar catalysts derived from SCG and glucose were denoted as NSB and NGB, respectively. According to the flow gas, N₂ or CO₂ was also denoted after the sample name.

2.3. Characterization of biochar

The morphologies of fabricated biochar were analyzed using a field-emission scanning electron microscopy (FE-SEM, Jeol JSM-7401 F). The morphological characteristics of particles within the internal surfaces were probed by a transmission electron microscope/energy dispersive X-ray spectroscopy (TEM/EDS, Jeol JEM-1400). The specific surface area and pore volume of the biochar were analyzed with a Brunauer-Emmett-Teller (BET) surface analyzer (Belsorp-mini II, Japan) using N₂ adsorption-desorption isotherm/Barrett-Joyner-Halenda (BJH) curves. The BET surface area (SA) was calculated by the obtained adsorption isotherm; the external SA was obtained by *t*-plot method; the micropore SA was calculated by subtracting the external SA from the BET SA. Thermogravimetric analysis (TGA) was conducted in air condition with a Mettler Toledo TGA/DSC Star System (Mettler, Switzerland) to explore the fractions of inorganic/organic substances present in the carbonized samples. The total flow rate was set at 150 mL min⁻¹. Each TGA test was performed with 10 ± 0.1 mg of sample, and conducted at a heating rate of 5 °C min⁻¹ from 25 to 793 °C. X-ray powder diffraction (XRD, D8 Advance, Bruker-AXS) analysis was performed to identify the transformed Co phase after the pyrolysis using CuKα radiation. The Raman spectra of the N-doped Co-biochar samples were obtained with visible (633 nm) excitation (Dimension P1 Raman spectroscopy, Lambda Solution Co., USA). Elemental compositions of the composite surface was conducted using a theta probe angle-resolved X-ray photoelectron spectrometer (ARXPS, ESCALAB 250, ThermoScientific) system equipped with the monochromatic Al Kα line (1486.7 eV).

2.4. Catalytic activity test

The catalytic reduction of PNP to PAP by aqueous NaBH₄ in the presence of Co-impregnated biochar samples was carried out at room temperature (25 ± 2 °C) using a UV quartz cuvette (5 mL, 12.5 mm wide and 45 mm high). The experiments were conducted by modifying the experimental procedure of Hasan et al. [45] First, 0.1 mL of 5 mM PNP solution was mixed with 2.1 mL DDW in the cuvette, and then 0.2 mL of freshly prepared NaBH₄ solution (510 mM) 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

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