



Reduction of *p*-nitrophenol by magnetic Co-carbon composites derived from metal organic frameworks



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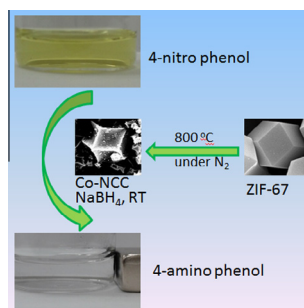
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HIGHLIGHTS

- Two types of magnetic Co-carbon composites are prepared from Co-based MOFs.
- Both composites are active in catalyzing the reduction of *p*-nitrophenol.
- N containing Co-carbon shows better performance in catalyzing the reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Two types of magnetic cobalt-carbon composites were synthesized via one-step calcination of cobalt-based metal organic frameworks (MOFs), ZIF-67 and $\text{Co}_3(\text{BTC})_3 \cdot 12\text{H}_2\text{O}$, and applied as catalysts in the reduction of *p*-nitrophenol by NaBH_4 . The MOFs precursors were respectively structured by using 2-methylimidazole (ZIF-67) and 1,3,5-benzenetricarboxylic acid ($\text{Co}_3(\text{BTC})_3 \cdot 12\text{H}_2\text{O}$) organic linkers. Calcination of ZIF-67 produced a Co-carbon composite containing N species (Co-NCC), while $\text{Co}_3(\text{BTC})_3 \cdot 12\text{H}_2\text{O}$ produced a simple Co-carbon composite (Co-CC). The prepared composites were characterized by a series of spectroscopic instruments and a surface analyzer. Raman spectra of the composites suggested carbons in both composites are present as graphitic oxide phases. Surface analyses indicated Co-NCC is highly porous with surface area of $298 \text{ m}^2 \text{ g}^{-1}$, and Co-CC has less porosity of $110 \text{ m}^2 \text{ g}^{-1}$. Both catalysts were active in catalyzing the reduction of *p*-nitrophenol to *p*-aminophenol, but Co-NCC exhibited much better performance to give pseudo-first-order rate constant 6.7 times greater than Co-CC, and robust reusability to complete five cycles of *p*-nitrophenol reduction with minimal loss of catalytic capability. The superior catalytic property of Co-NCC is attributed to the presence of N-moieties that provided additional reduction sites along with considerable porosity of the material.

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1. Introduction

Nitrophenols are persistent organic contaminants commonly found in various industrial effluents released from pesticides, plasticizers, dyes and pharmaceutical industries [1]. United State

Environmental Protection Agency (USEPA) has listed nitrophenols as “Priority Pollutants”, and regulated their concentrations in natural waters $<10 \text{ ng L}^{-1}$ [2]. Toxicological studies involving animal testing indicated, among the three isomeric nitrophenols, *p*-nitrophenol is more detrimental to cause various diseases including blood disorder, organ damages, and impairment of central nervous system [3]. Also, a trace amount of *p*-nitrophenol has shown high toxicity to green plants and aquatic organisms in

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surface waters [4]. Due to its highly polar characteristic, *p*-nitrophenol is highly soluble in water and likely to exhibit high bioavailability. Therefore, the presence of *p*-nitrophenol in water is of a significant environmental concern that could pose serious health threats to human and aquatic lives.

A number of methods have been used to address nitrophenol contamination in water, including adsorption [5], photo-degradation [6], microbial degradation [7], electro-coagulation [8], and electro-Fenton method [9]. However, these methods often suffer from various limitations such as low efficiency, high cost, long operating time, and longevity problems [10]. In a broad sense, conventional clean up techniques can be classified into two categories: (1) those aiming permanent removal of target contaminants, and (2) those aiming conversion of target contaminants into less or no toxic forms. In selection of remedial option for *p*-nitrophenol contaminated waters, techniques pertaining to the latter category would be desirable because *p*-aminophenol, the primary reduction product of *p*-nitrophenol, finds many industrial applications, especially as an essential intermediate in pharmaceutical industry [11].

Catalytic reduction involving noble metals such as Au, Ag, and Pd has been widely employed for reduction of water-borne contaminants. Recent researches have further advanced to non-noble metal catalysts such as CuFe_2O_4 , Co/SiO_2 , Cu/CuO/C , Ni/SiO_2 , and demonstrated their catalytic activity in contaminants reduction [12–14]. Apart from these metal-based catalysts, non-metallic catalysts such as N-containing carbon composites have been employed for catalytic reactions [15]. The incorporation of N atoms that possess excessive valence electrons generally increases the π -electron density in the carbon architecture, leading to improved electrical properties and surface reactivity [16]. These characteristics make them good catalytic materials for contaminants reduction. Conventionally, N-containing carbon composites are fabricated by chemical vapor deposition [17], segregation growth method [18], arc-discharge method [19], plasma or hydrazine hydrate treatment [20]. However, these methods have various limitations in their synthesis such as tedious multi-step procedures, high energy consumption, use of toxic chemicals (N_2H_4 , HCN, NH_3) as precursors, and poor chemical homogeneity [21].

In the last decade, nanostructured materials have received much attention because of their great potentials in different applications such as energy storage or conversion [22], environmental remediation [23], and catalysis [24]. Moreover, instead of single-component nanostructured materials, collective assemblies of nanomaterials comprising active nanomaterial dispersed on solid supports or nano composites are gaining increasing interests for more elaborate and versatile applications [25,26]. A recent milestone in the development of nano-porous materials is metal organic frameworks (MOFs). MOFs are new classes of highly crystalline porous materials [27,28]. Several desirable properties, such as high porosity, tunable pore architecture, ability to impart specific functionalities or active species without altering the framework topology, have turned them into very promising materials for a wide range of applications such as adsorption [29], gas storage/separation [30], catalysis [31], and fuel purification [32]. Beside these direct applications, MOFs have been used as a template or platform to prepare highly porous carbonaceous materials [33]. Liu et al. prepared highly porous carbonaceous material using MOF-5 as a template and farfural alcohol as carbon precursors [34]. More recently, direct carbonization of MOFs (without additional carbon source) has also been reported to prepare MOF-derived metal or metal oxide-carbon composites [13,35]. These metal-carbon composites can be synthesized in a simple process and showed promising performance as catalysts or absorbents.

In this study, two Co-based MOFs, ZIF-67 (ZIF: zeolite imidazole framework, cobalt linked by 2-methylimidazole [36]) and

$\text{Co}_3(\text{BTC})_3 \cdot 12\text{H}_2\text{O}$ (Cobalt linked by 1,3,5-benzenetricarboxylic acid [37]), were prepared and subsequently heat-treated under N_2 atmosphere to prepare Co-carbon composites. The calcination of ZIF-67 produces N-containing carbon composites as imidazole linker turns into N-moieties upon heat treatment. The composite from ZIF-67 is expected to exhibit different functionality from the other composite in the catalytic reactions due to the presence of N-moieties, as documented in recent studies by Li et al. [38,39]. The prepared composites were characterized using a series of spectroscopic instruments and a surface analyzer. The composites were used as catalysts for reduction of *p*-nitrophenol by NaBH_4 . A series of experiments, including the effect of NaBH_4 concentration, kinetics of *p*-nitrophenol reduction, and reusability of the catalyst, were carried out to demonstrate the catalytic capability of the composites.

2. Experimental methods

2.1. Materials

p-nitrophenol ($\text{C}_6\text{H}_5\text{NO}_3$, 99%), 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 99%), 1,3,5-benzenetricarboxylic acid ($\text{C}_9\text{H}_6\text{O}_6$, 98%) and commercial cobalt powder (–400 mesh, 99.8%) were obtained from Alfa Aesar, USA. Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, >97%), sodium borohydride (NaBH_4 , extra pure), methanol (CH_3OH , 99.5%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.9%), hydrochloric acid (HCl, 37%), N, N-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, >99.5%), and activated carbon were purchased from Daejung chemical, South Korea.

2.2. Synthesis of ZIF-67

ZIF-67 was synthesized according to the procedure by Shao et al. [40] with a minor modification. In brief, 16 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 32 mmol 2-methylimidazole were completely dissolved in 200 mL methanol and then, two solutions were mixed and stirred for 5 min at room temperature. After stirring, the mixture was aged for 24 h to allow precipitation of solid products. Finally, the purple solid precipitates were collected by filtration, washed three times with ethanol, and dried for 12 h at 100 °C.

2.3. Synthesis of $\text{Co}_3(\text{BTC})_3 \cdot 12\text{H}_2\text{O}$

A 10 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 5 mmol 1,3,5-benzenetricarboxylic acid were taken in a 100 mL beaker, and 60 mL mixed solvent (N,N-dimethylformamide:ethanol:water = 1:1:1, v/v) was added. After stirring for 1 h, the solution was transferred into a 100 mL Teflon-lined vessel, placed in an electric oven and heated at the 85 °C for 20 h. After cooling, the mauve crystals were washed several times with water and ethanol, and finally dried in air.

2.4. Synthesis of Co-carbon composites

The synthesized ZIF-67 was taken in an alumina crucible, which was placed in a tubular reactor for thermal treatment. A 610 mm long quartz tubing with 25.4 mm outer diameter (Chem glass CGQ-0900T-13) was used as a tubular reactor. The ZIF-67 was heated at a temperature 800 °C for 4 h using a split-hinged furnace (AsOne, Japan). The heating rate was 5 °C min^{-1} and an S-type thermocouple was used to monitor the temperature. The N_2 gas flow rate was fixed at 500 mL min^{-1} using a Brooks mass flow controller (5850 series E), and a computer-aided control system by LabVIEW (National Instrument, USA) was employed to control the total procedure. After cooling to room temperature, a black powder was obtained and the product was named as N-containing Co-carbon composites (Co-NCC). A similar procedure

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