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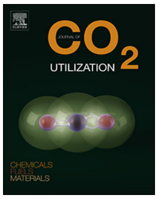

One step fabrication of carbon supported cobalt pentlandite (Co_9S_8) via the thermolysis of lignin and Co_3O_4

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ABSTRACT

This work proposed a new method for one step fabrication of carbon supported (biochar) Co_9S_8 composite via the thermo-chemical process of cobalt oxide (Co_3O_4) and lignin under CO_2 atmosphere. A series of pyrolysis were conducted in N_2 and CO_2 environment, and their thermal degradation behaviors were characterized. The thermogravimetric analysis tests revealed that CO_2 did not affect physical aspects of the thermal degradation. However, the influence of CO_2 on chemical aspects governing the thermal degradation mechanisms was apparent. As an example of it, carbon supported (biochar) Co_9S_8 composite was only generated in CO_2 environment. The surface morphology and structural matrix of biochar generated from CO_2 environment was characterized using various spectroscopic instruments, which confirmed the formation of Co_9S_8. The formation of Co_9S_8 was highly affected by the pyrolytic parameters such as temperature and duration for isothermal run. Furthermore, use of CO_2 as the reaction medium provided an effective way for modifying pore structure of biochar. More importantly, the formation of highly porous structure and Co_9S_8 in the presence of CO_2 imparted strong catalytic capability. The reaction kinetics of *p*-nitrophenol (PNP) reduction using CO_2-700 °C and CO_2-760 °C biochar was 9×10^{-3} and $18 \times 10^{-3}\,s^{-1}$, respectively, of which performance was superior to other catalytic materials in the literature. Lastly, the successive PNP reduction tests revealed the invulnerable catalytic capability up to 10 PNP reduction cycles. Thus, all experimental findings in this study suggests that Co_9S_8 could be synthesize from the waste materials and CO_2. Moreover, Co_9S_8 could be employed as an effective catalyst in the environmental applications.

1. Introduction

The electrocatalytic oxygen evolution reaction (OER) has been extensively conducted over the last few decades because OER is one of the central reactions in the realm of electrochemistry [1–4]. Accordingly, many catalysts have been synthesized and the catalytic effectiveness has been evaluated to improve under the different electrolyte environments [1–5]. Despite the fact that rutile-type RuO_2 and IrO_2 were identified as an effective OER catalyst in both acidic and alkaline electrolyte, their commercial implementation has not been established due to their high cost and scarcity [6–8]. To circumvent these problems, exploiting effective, earth-abundant, and non-noble metal-based OER catalysts have gained great attention [9–13]. Recently, a number of transition-metal-based compounds and their derivatives have emerged as attractive catalyst candidates for OER application [2,5,9–13]. Especially, cobalt sulfide materials, such as Co_3S_4, CoS_2, Co_9S_8, $Co_{1-x}S$, and Co_xS_y, have gained attention as OER electrocatalysts owing to their wide stoichiometric composition and good stability [14–17]. Among them, Co_9S_8 has been demonstrated to be a promising candidate for OER electrocatalyst due to its excellent redox capability [18–20].

Indeed, the electrocatalytic performance of Co_9S_8 suffers from complicated synthetic procedures and low yield [9,12,14–18]. The structural property such as morphology is also a key factor to determine the catalytic activity of Co_9S_8 [9,12,14–18]. Accordingly, to maximize the catalytic capability of Co_9S_8 while preventing its aggregation, porous carbon materials including graphene, multiwall carbon nanotube, and carbon nanosheets are commonly being used as a carbon support [9,10,12–14,16,15–18]. However, incorporation of Co_9S_8 into carbon matrix is often technically challenging. Therefore, it is highly desirable to fabricate carbon supported Co_9S_8 through a single thermo-chemical step such as pyrolysis because char (i.e., carbon rich substance) is inevitably generated from the pyrolysis process [21]. For example, pyrolysis is a thermo-chemical process to reform the carbon distribution into three pyrogenic products (oil, syngas, and char), and

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the pore structure is intrinsically developed during the pyrolysis process [22,23]. In addition, considering the fact that Co_9S_8 exhibits a high redox potential [9,15–18], it is also pertinent to expand its practical use toward the diverse environmental applications. More preferably, using waste material for carbon support for Co_9S_8 offers the benefits in sustainability since the term of "*sustainability*" is profoundly contingent on how and/or where we procure carbon sources without environmental burdens [24–27]. Among various candidates for a carbon substrate, employing lignin as an initial feedstock for carbon supported Co_9S_8 is an optimistic approach because the global generation of lignin is estimated as 70 million tons per year, and lignin from the Kraft process contains a substantial amount of sulfur (approximately 2 wt.%) as a constituent [28–31].

Carbon distribution toward three pyrogenic products (oil, syngas, and char) is highly dependent upon pyrolytic conditions (i.e., heating rate and temperature) and pyrolytic reaction media [22,23]. In other words, the morphology of char is greatly influenced by the pyrolytic conditions and pyrolytic reaction media [32,33]. In these respects, this study placed great emphasis on the mechanistic role of pyrolytic reaction media. To this end, the influence and CO_2 on the fabrication of carbon supported Co_9S_8 was mainly investigated. For an in-depth understanding, the thermolysis of Co-impregnated lignin in N_2 and CO_2 was characterized thermo-gravimetrically. Moreover, char from the thermolysis of Co-impregnated lignin in N_2 and CO_2 was characterized to confirm the formation of carbon supported Co_9S_8 using various analytical instruments. Lastly, to evaluate its capability as an environmental redox catalyst, reduction experiments with of *p*-nitrophenol (PNP) were performed.

2. Materials and methods

2.1. Sample preparation and chemical reagents

Kraft lignin (Lot # 471003, average molecular weight of ~10,000) was purchased from Sigma-Aldrich (St. Louis, USA) and the sulfur content in the lignin was 2 wt.% (dry basis). Cobalt oxide (Co_3O_4) (Lot #: 32122-1501) was purchased from JUNSEI (Tokyo, Japan). Sodium borohydride ($NaBH_4$, > 98% purity) (Lot #: S2094) was purchased from SAMCHUN Chemical (Pyeongtaek, Korea). PNP (*p*-nitrophenol) ($C_6H_5NO_3$, > 99% purity) (Lot #: A14376) was purchased from Alfa Aesar (England). The solid phases of lignin and Co_3O_4 were homogenized with a mass ratio of 20. The homogenized sample was dried at 80 °C for 24 h. The ultra-high purity grade (> 99.999 purity) of N_2 and CO_2 was obtained from *AirTech* Korea (Seoul, Korea).

2.2. Thermo-gravimetric analysis (TGA) test

The thermal degradation of the homogenized sample (mixture of lignin and Co_3O_4) was characterized using a Netzsch TGA analyzer (STA 449 F5 Jupiter, Germany). The sample loading on the TGA unit was 10 ± 0.02 mg and the flow rate of purge gas (i.e., N_2 or CO_2) was set as 70 mL min^{-1}. The flow rate of purge gas was controlled by the imbedded mass flow controllers (MFCs) equipped in the TGA unit. The TGA test was conducted at a heating rate of 10 °C min^{-1} from 30 °C to the target temperature (760 or 800 °C), and then the target temperature (760 or 800 °C) was isothermally maintained for 120 min. All TGA tests were conducted in triplicates.

2.3. Biochar fabrication using a batch-type tubular reactor (TR)

A batch-type tubular reactor (TR) was constructed using a quartz tubing (Chemglass CGQ-0900T-13). The dimension of the TR was 25.4 mm outer diameter and 0.6 m length. Stainless Ultra Torr Vacuum Fitting (Swagelok SS-4-UT-6-600, USA) was used. The sample loading at the center of the TR was 10 ± 0.02 g, and the flow rate of purge gas (N_2 or CO_2) was set as 500 mL min^{-1}. A mass flow controller (5850 series E, Brooks Instrument, USA) was used to control the flow rate of purge gas. A temperature programming tubular furnace (RD 30/200/11, Nabertherm, USA) was used as an external heating source. The pyrolytic temperature condition was the same as the TGA test. During the pyrolysis process, the temperature deviation was maintained less than ± 3 °C.

2.4. Characterization of biochar

Surface area (Brunauer–Emmett–Teller: BET) and pore size distribution (Barrett–Joyner–Halenda: BJH) of biochar was measured using a BELSORP-mini II (MicrotracBEL, Japan). Phase transformation and crystallinity of biochar generated in N_2 and CO_2 at the different temperatures were determined using X-ray diffractometer (XRD, D8 Advance, Bruker-AXS) with Cu-Kα radiation and LynxEye position sensitive detector. High performance X-ray photoelectron spectrometer (HPXPS) system with microfocused monochromated Al-Kα (1486.6 eV) was used to investigate surface elemental composition and their atomic bond. The magnetic property of the sample was determined using alternating gradient magnetometer (MicroMag 2900 Series).

2.5. PNP reduction using biochar

Prior to the experimental work, the stock solutions for PNP and $NaBH_4$ were prepared as 0.68 and 250 mM, respectively. Catalytic reduction of PNP in the presence of biochar (from pyrolysis of the mixture of lignin and Co_3O_4 in N_2 and CO_2 at the different temperatures) was carried out in a 4 mL quartz cuvette. The biochar (4 mg) was added in the cuvette, followed by addition of 2 mL distilled water. Then, 1 mL of $NaBH_4$ solution (250 mM) and 1 mL of PNP solution (0.68 mM) were separately added into the cuvette. The concentration change of PNP was monitored at time-designated intervals using a UV–vis spectrometer (UV-1800, SHIMADZU, Japan). The detection limit for PNP was 0.16 mg L^{-1} (1.15 μM).

3. Results and discussion

3.1. Characterization of the thermolysis of the mixture of lignin and Co_3O_4 in N_2 and CO_2

The thermolysis of the mixture of lignin and Co_3O_4 in N_2 and CO_2 was characterized thermo-gravimetrically, and the representative TGA results were presented in Fig. 1. TGA tests were conducted at a heating rate of 10 °C min^{-1} from 30 °C to the final target temperature (760 and 800 °C), followed by isothermal run for 120 min at the target temperature.

Fig. 1a demonstrates that the thermolytic behavior of the mixture of lignin and Co_3O_4 in N_2 and CO_2 is nearly identical before the initiation of the Boudouard reaction ($C + CO_2 \rightleftharpoons 2CO$) [22,23]. In detail, mass decay of the mixture of Co_3O_4 in N_2 and CO_2 (< 730 °C) is nearly the same. This observation signifies that the influence of reaction medium (CO_2) on the physical aspects governing the onset and end temperature for the thermolysis of the mixture of lignin and Co_3O_4 in N_2 and CO_2 is negligible. This interpretation is well consistent with the DTG curved in Fig. 1b. For example, the DTG curves (< 730 °C) from the N_2 and CO_2 environment are nearly the same. However, at the temperature regime (> 730 °C) in Fig. 1a, the more mass decay is accomplished in the CO_2 environment, and mass decay attributed to the Boudouard reaction is fully saturated after 16 min of the isothermal run at 800 °C. Therefore, this observation is in good agreement with the general thermolysis behavior induced by the Boudouard reaction because the Boudouard reaction is thermodynamically favorable at temperatures higher than 720 °C [22,23]. The initiation of Boudouard reaction at 730 °C implies no catalytic effects arising from Co_3O_4 since the initiation temperature of the Boudouard reaction from the thermolysis of lignin in the CO_2 environment was 730 °C in our previous work [22]. Furthermore, no