

Study on Biochar as Desulfurizer for Fuel Cell System Running on Biogas

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Study on Biochar as Desulfurizer for Fuel Cell System
Running on Biogas

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Abstract

Production of biogas (the mixture of CH_4 and CO_2) from local biomass wastes and its utilization should be more promoted especially in rural areas or in agricultural sector to practice local energy and material productions for local consumption. Highly efficient biogas power generation with solid oxide fuel cell (SOFC) is expected to become a core technology for realizing this circulation, in which biogas purification, especially the removal of trace H_2S , will be an important factor. For wider dissemination of SOFC, a process to obtain an excellent desulfurizer made from locally available material is required. In this point of view, this study focused on the biochar (BC), a carbon-based material obtained by heat treatment of biomass in an oxygen-free condition (pyrolysis).

In Chapter 2, BCs were produced from bamboo (BB) and rice husk (RH), labeled BBBC and RHBC, respectively. For these BCs subjected to the steam or the ammonia (NH_3 gas) treatment, H_2S adsorption tests were performed, and breakthrough capacity of H_2S (q_0) and total H_2S adsorption capacity (q) were evaluated. For both BCs, steam and ammonia treatments were effective to increase q_0 and q , however for the RHBC intense steam treatment must be avoided so as not to expose silica on the surface which negatively affects the H_2S absorption ability.

Ammonia treatment changes the surface chemistry of biochar by N-doping to form nitrogen functional groups such as pyridinic-, pyrrolic- and graphitic-N. The presence of pyridinic-N promoting the formation of oxygen radicals (O^*) on the surface has been proven to be crucial to increase q_0 and q . By the ammonia treatment of RHBC at 900°C , q_0 and q increased by 30- and 4-fold, respectively, whereas these increases for BBBC were only 3- and 2-fold, respectively. Compared to BBBC, carbon in RHBC was more receptive to N-doping due to less basic surface, and the sulfate formation on the surface during H_2S adsorption, which has adverse effect on the adsorption capacity, was more mitigated. Although the ammonia treatment of BC resulted in the performance improvement of BC as a desulfurizer, unavailability of NH_3 gas must be taken into consideration especially in a rural area. Moreover, for further enhancement of q , the interaction between H_2S and N-doped surface must be moderately weakened, so that the utilization rate of micropores can be increased. Under this circumstance, one of the most promising approaches is the treatment of RHBC with NH_3 evaporated from digestate liquid discharged from a methane fermentation tank.

In Chapter 3, N-doping of RHBC was performed using two different methods. In the first method (N1 treatment), RHBC was heat-treated for 120 min at 900°C in flowing NH₃ gas (NH₃: 25vol%, N₂: 75vol%). This sample was labelled RHBC-N1. In the second method (N2 treatment), 10wt% NH₄⁺ aqueous solution was prepared to simulate the concentrated digestate liquid. Nitrogen carrier gas was bubbled through this solution at 30°C, and in the resulting gas flow with 15.7vol% NH₃ and 3.8vol% steam, RHBC was heat-treated at 850°C for 270 min. This sample was labelled RHBC-N2. Nitrogen contents doped on the surface of RHBC-N1 and -N2 were 3.69 and 2.52wt%, respectively, and the corresponding pyridinic-N contents were 2.29 and 1.31wt%, respectively. DFT calculation proved that among the N-doped sites on the biochar surface the pyridinic-N plays a crucial role to promote the formation of O* by donating electron from its lone pair to oxygen molecule to break the O-O bond. That is the reason why q_0 and q increased by 30- and 4-fold, respectively, by N1 treatment. Considerably larger q of RHBC-N2 (23.0 mgH₂S g-BC⁻¹) compared to RHBC-N1 (9.58 mgH₂S g-BC⁻¹) was due to less formation of sulfate on the surface during H₂S adsorption. Sulfate accumulation on the RHBC-N1 caused by the excess formation of oxygen radicals as a result of strong N-doping covered the micropore openings, leading to the lower q . For further improvement of q_0 and q of RHBC-N2, facilitating the diffusion of H₂S onto the biochar surface is indispensable. In this point of view, the powdered RHBC-N2 sample was formed into a sheet state. The paper-structured biochar labelled PS[RHBC-N2] exhibited q_0 and q of 8.71 and 96.1 mgH₂S g-BC⁻¹, respectively, comparable to commercial desulfurizer especially for q .

Although the performance of RHBC-N2 could be increased by adopting the paper-structured geometry, the H₂S adsorption ability of powdered sample, directly related to q_0 , must be more enhanced. To increase the surface affinity with H₂S, loading of nickel (Ni), which is well known as a material susceptible to sulfur poisoning in the field of catalyst chemistry, on the biochar surface was studied in Chapter 4. Ni was loaded on the RHBC-N2 by wet impregnation method using 0.1 M NiNO₃ solution. The dried sample was then heat treated at 500°C for 2 h in N₂ flow. The resulting sample was labelled RHBC-N2-Ni. In addition, to understand the effect of Ni-loading, the RHBC was first impregnated with the NiNO₃ solution, and then subjected to the N2 treatment. This sample was labelled RHBC-Ni-N2. RHBC-N2-Ni had q_0 and q of 6.95 and 75.4 mgH₂S g-BC⁻¹, respectively, which were 1.8 and 3.3-fold of RHBC-N2, respectively. The enhanced adsorption capacity results from the moderation of the O* formation effect of

pyridinic-N by the interaction with Ni, the adsorption ability of Ni itself, and the enlargement of micropore openings during Ni-loading process. If Ni is loaded on the RHBC prior to the N₂ treatment (RHBC-Ni-N₂), q_0 and q were significantly lowered to 1.13 and 15.3 mgH₂S g-BC⁻¹, respectively, because the Ni particles can catalyze the decomposition of NH₃ in the subsequent N₂ treatment to significantly restrain the N-doping on the biochar surface. Furthermore, these Ni particles without N-Ni bonding are easily coarsened and agglomerated.

RHBC-N₂-Ni was also made into a sheet state labelled PS[RHBC-N₂-Ni], which exhibited q_0 of 16.6 mgH₂S g-BC⁻¹ larger than those of PS[RHBC-N₂] and RHBC-N₂-Ni. This means only 10.8 kg of RHBC-N₂-Ni is needed to continuously obtain a H₂S free biogas from a biogas contaminated with 4 ppm H₂S for 100,000 h. The paper-structured biochar developed in this study is promising as a mechanically flexible desulfurizer, and practically applicable to the fine desulfurization of biogas containing several ppm H₂S for the SOFC operation fueled by biogas.

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CHAPTER I

Introduction

1.1. General background

A fuel cell is an energy conversion device that can convert chemical energy directly into electrical energy with high efficiency and low greenhouse gas (GHG) emissions [1]. Hydrogen gas (H_2), which can be obtained from various kinds of renewable energy, is the most prominent form of fuel for fuel cell operation. For realizing a decarbonized society, green H_2 (not blue and gray), must be utilized, and therefore the use of biomass waste as H_2 source is receiving a lot of attention. Via anaerobic fermentation of biomass waste, biogas, a mixture of CH_4 and CO_2 (Sec. 1.2), is produced, which is converted to syngas (the mixture of H_2 and CO) at high temperature (500-900°C) using a reforming catalyst [2–4].

When the humidified biogas is supplied to a reformer, steam reforming of methane (SRM, (1.1)), dry reforming of methane (DRM, (1.2)) and water-gas shift reaction (WGSR, (1.3)) take place as the major reactions to produce syngas [5].



A solid oxide fuel cell (SOFC) is an all solid state fuel cell operated at high temperature (600-900°C), which makes it more flexible in fuel selection. Even without a fuel reformer, in principle, syngas can be obtained within the Ni-based porous anode material (direct internal reforming (DIR) concept) due to its high temperature suitable for the endothermic reforming reactions and excellent catalytic activity of Ni for these reactions. The DIR concept can contribute to downsizing and cost reduction of SOFC module [6,7].

The energy conversion scheme of a biogas-fueled SOFC is described in Fig. 1.1. In general, as shown in Fig. 1.1a, humidified biogas is flowed into a reformer filled with reforming catalyst such as $Ru/\gamma-Al_2O_3$, and the resulting syngas is fed to the anode of the SOFC [8,9]. In the case of the DIR concept (Fig. 1.1b), within the anode, SRM, DRM, and electrochemical oxidations of H_2 and CO derived from SRM and DRM, reactions (1.4) and (1.5), respectively, simultaneously take place to generate electricity which eliminates the need for an external reformer [6,10]:

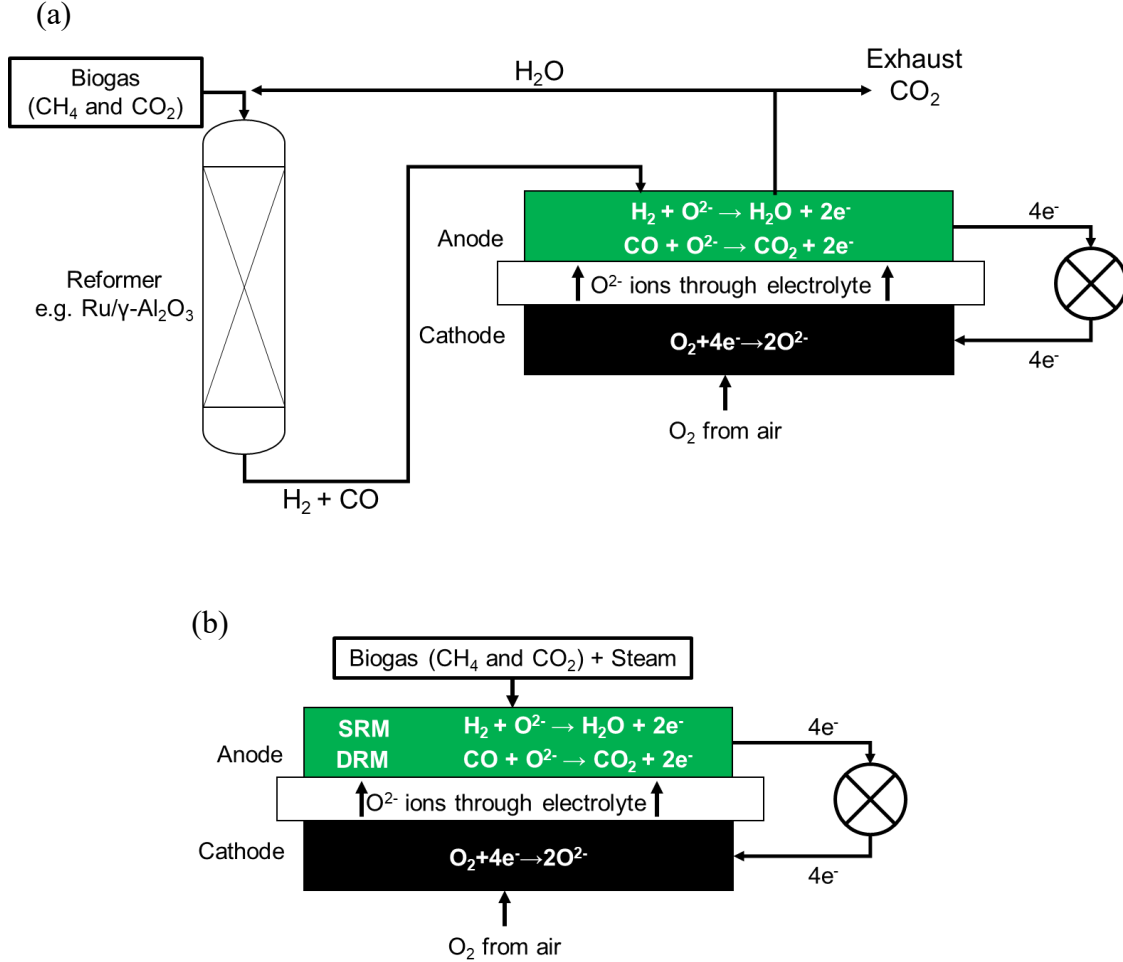


Figure 1.1: Energy conversion scheme of a biogas-fueled SOFC: (a) conventional type with external reformer; and (b) DIR concept.

In operating a biogas-fueled SOFC system, trace impurities, such as H_2S and siloxane, can poison the reforming catalyst [11–13] and subsequently the anode [14–16] to cause rapid degradation of the system performance when biogas purification unit for desulfurization and siloxane removal does not function well.

One of the object areas of this study, the Mekong Delta, Vietnam, where around 18 million people (approx. 20% of the national population) live, yields more than half of the nation's agricultural and fishery products. At present, the increasing amount of biomass wastes, such as agricultural residues and aquaculture sludge, and the serious proliferation of water hyacinth in agricultural waterways caused by eutrophication of

rivers have become major problems in the delta. Technologies for efficiently collecting and utilizing this biomass as dependable sources of renewable energy would help reduce the environmental load of this region.

Fig. 1.2 shows the concept of SOFC-integrated materials and energy circulation proposed in this study. Rice straw, water hyacinth and shrimp pond sludge are collected and supplied to a digester for biogas production based on anaerobic fermentation [17]. Biogas can be used as an alternative fuel for power generation. Shiratori *et al.* previously demonstrated in Ben Tre, Vietnam, that the sludge accumulated during shrimp farming can be used as a source of mesophilic methanogenic bacteria for the stable production of biogas, without heating and heat retention. The produced biogas is fed to a 1 kW SOFC system for power generation [18].

It is well-known that H_2S present in biogas at concentrations of 500–3,000 ppm [19] is a corrosive gas which can cause malfunction of engine systems [20,21], and therefore desulfurization is an indispensable process generally performed by using iron oxide pellets [18,19,22]. However, in SOFC operation, even after the process, if a trace H_2S (from sub ppm to several ppm) is still remaining in biogas, it can cause the deactivation of Ru-loaded catalyst for fuel reforming [9] and Ni at the cermet anode [16,23,24]. The preliminary research to evaluate the influence of H_2S poisoning on a reformer packed with 2wt% Ru/ γ - Al_2O_3 fueled by simulated biogas ($CH_4/CO_2 = 1.5$, $S/C = 2.7$) at $700^\circ C$ has revealed that even 1 ppm of H_2S strongly affects the catalytic activity of Ru/ γ - Al_2O_3 (10% decrease in the CH_4 conversion within 53 h), and Ru coarsening and agglomeration are more promoted with increasing H_2S concentration (a linear relationship between the degradation rate of CH_4 conversion and the decrease rate of specific surface area of Ru was confirmed.) [9]. To achieve practical operation of a biogas-fueled SOFC, either H_2S must be removed so that its concentration in biogas becomes less than 0.1 ppm [9], or H_2S -tolerant catalysts must be developed.

Although zeolite and activated carbon are usually applied for the second step desulfurization after the rough H_2S removal with iron oxide pellets [25,26], these adsorbents are not easily available in rural areas. For wider dissemination of SOFC, a process to obtain a high-performance desulfurizer made from locally available material is required. From this point of view, this study focused on the biochar, a carbon-based material derived from local biomass. On the other hand, regarding the social implementation of biogas-fueled SOFC, close attention must be paid to the circulation of materials such as the treatment of digestate liquid which contains over 2,000 ppm of NH_4^+ detrimental to the local ecosystem if discharged directly to the environment. By utilizing the digestate liquid as an alternative fertilizer, eutrophication of rivers and usage of

chemical fertilizer can be suppressed, and the proper circulation of nitrogen can be restored. However, the concentration of fertilizer component in the digestate liquid is not high enough and depends on the biomass feedstock, hindering the spread of biogas production technology.

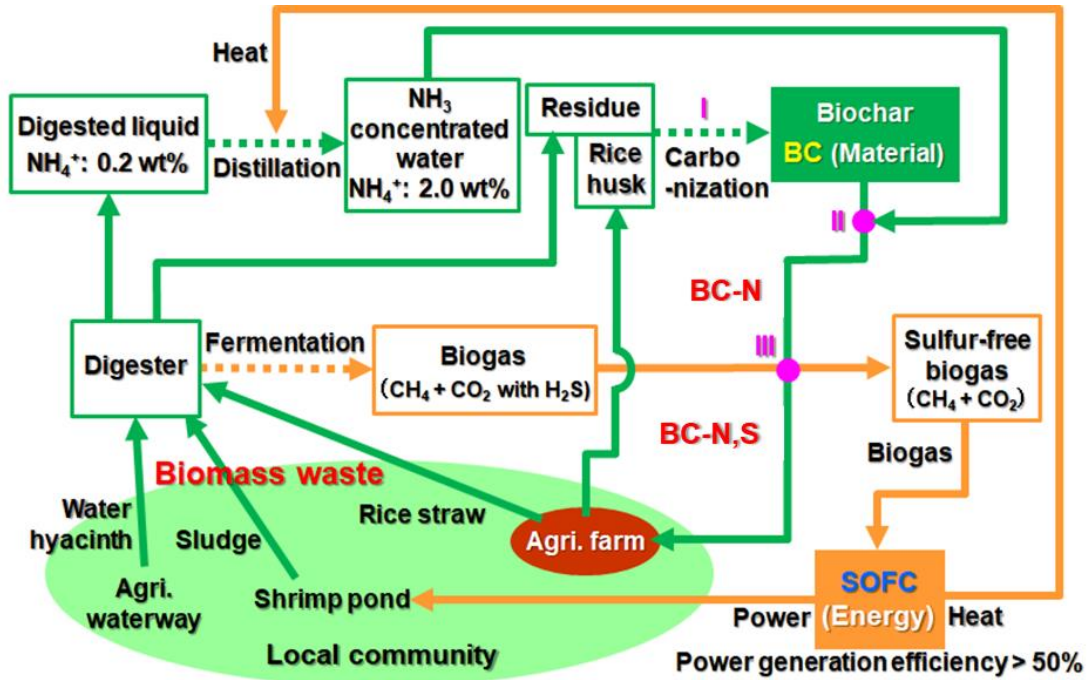


Figure 1.2: Concept of SOFC-integrated materials and energy circulation suitable for agricultural community [27].

As shown conceptually in Fig. 1.2, (I) biochar (BC), the main topic of this study, is produced from biomass feedstocks collected in a local community by carbonization. BC is a type of activated carbon which can be used as a remover of pollutants like heavy metals and acidic gases [28,29]. The adsorption capacity of BC depends not only on specific surface area but also on pore size distribution and surface chemistry such as pH and trace elements, and these parameters can differ greatly according to biomass feedstock [30]. Here, the properties of BC as a desulfurizer will be systematically studied by using different sources to understand a key parameter for getting higher adsorption ability. (II) The BC is treated at high temperature in a flow of NH_4^+ extracted from the digestate liquid by distillation technique using the exhaust heat of biogas-fueled SOFC to obtain a nitrogen doped BC (BC-N). (III) By the application of BC-N as a desulfurizer, N- and S-containing BC (BC-N,S) can be obtained simultaneously with a sulfur-free biogas for SOFC power generation. BC-N,S can be utilized as a solid fertilizer alternative to a chemical fertilizer, which is especially effective for the alkali soil.

1.2. Biogas

Biogas is obtained by the anaerobic fermentation of biomass wastes. It is a mixture of CH₄ (35–75%) and CO₂ (25–55%) with minor constituents such as H₂S, NH₃, CO, siloxanes, halocarbon and BTEX (benzene, toluene, ethyl benzene and xylenes) depending on the feedstock [5]. Biogas is expected to be an alternative fuel for suppressing greenhouse gas emission [31].

For the stable production of biogas, it is important to find a source of methanogenic bacteria indigenous to a local environment which is active at 35-37°C in the case of wet-type mesophilic fermentation [32].

1.2.1. Composition

Composition including impurities of biogas, produced by biochemical reaction, depends on the kind of feedstock and the production site with different climate condition. Major components and impurities of biogas are listed in Tables 1.1 and 1.2, respectively.

Table 1.1: Major components of biogas produced by wet-type mesophilic fermentation.

Place	Biomass type	CH ₄ / vol%	CO ₂ / vol%	N ₂ / vol%	O ₂ / vol%
Finland [33]	Landfill	52-57	40-43	-	-
	Wastewater	60-63	34-37	-	-
	Agriculture waste	55	44	-	-
USA [34]	Cow manure	±70.0	±20.0	±10.0	>0.50
	Food waste	±55.0	±35.0	±10.0	>0.50
	Landfill	±50.0	±20.0	±20.0	±5.00
Japan [35–37]	Sewage sludge	59.5	38.9	0.4	<0.1
	Municipal waste	56	44	-	-
	Wastewater	56	40	2.6	0.8

Table 1.2: Impurities of biogas produced by wet-type mesophilic fermentation.

Place	Biomass type	Sulfur / ppm	Halocarbon / ppm	BTEX / ppm	Siloxane / ppm
Finland [33]	Landfill	90-230	-	-	110-480
	Wastewater	<1-4	-	-	20-260
	Agriculture waste	300	-	-	-
USA [34]	Cow manure	0.80	0.10	0.14	0.0002
	Food waste	138.2	0.08	0.18	0.056
	Landfill	6.0	1.55	4.77	0.035
Japan [35–37]	Sewage sludge	480	-	-	12.6
	Municipal waste	500-2000	-	-	20-50
	Wastewater	<0.1	-	-	<1

1.2.2. Hydrogen sulfide (H₂S)

Hydrogen sulfide (H₂S) is a colorless toxic acidic gas with strong odor, which is harmful to human and animals if inhaled [38]. It is well-known that H₂S present in biogas in the concentration range from 500 to 10,000 ppm [19,39] is a corrosive gas which can cause malfunction of engine systems [20,21], and therefore desulfurization is an indispensable process generally performed by using iron oxide pellets as desulfurizer [18,19,22]. However, in SOFC operation, even after the process, if a trace H₂S (from sub ppm to several ppm) is still remaining in biogas, it can cause the deactivation of Ru-loaded catalyst for fuel reforming [9] and Ni for cermet anode [16,23,24], which are attributed to the irreversible changes, the coarsening and agglomeration of Ru and the formation of Ni₃S₂, respectively [9,40].

1.2.3. Desulfurization

To achieve practical level operation of a biogas-fueled SOFC, H₂S must be removed, so that its concentration in biogas becomes less than 0.1 ppm [9], or H₂S-tolerant reforming catalysts must be developed. As biogas upgrading techniques, a) absorption, b) adsorption, and c) membrane separation are commercially employed [39].

a) Absorption

Absorption is a process in which one material is being retained by another material, which relies on the difference in solubility of gaseous species in a solvent originated from van der Waals interaction (physical absorption) (see Fig. 1.3a) or chemical reaction (chemical absorption) (see Fig. 1.3b) [41]. Scrubbing is based on the physical absorption of a gaseous species in a solvent (water or an organic solvent). For example, H_2S and CO_2 are separated from biogas by flowing it into a vessel under the counter-flow of water during which H_2S and CO_2 are dissolved in the water while leaving other constituents [42]. As for the chemical absorption, a gaseous species such as H_2S is dissolved in an alkaline solution. Unlike physical absorption, after the H_2S is dissolved in the alkaline solution, it will then react with the alkaline salt to form a sulfur species that can be easily extracted from the solution [43]. This process shows higher absorption rate and efficiency than those of the physical absorption, however it leaves chemical waste [44].

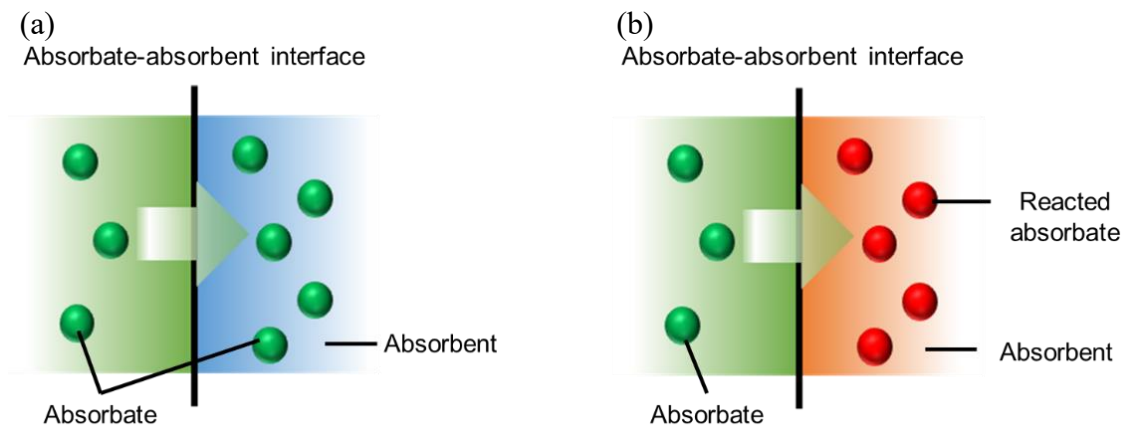


Figure 1.3: Schematic illustrations of (a) physical absorption and (b) chemical absorption.

b) Adsorption

Adsorption is a process in which adsorbate molecules adhere to the surface of a solid material (adsorbent) by either weak van der Waals force (physical adsorption) (see Fig. 1.5a) or strong chemical bonding (chemical adsorption) (see Fig. 1.5b) [41]. Most common is the pressure swing adsorption using a molecular sieve made from activated carbon, zeolite or other materials depending on the type of adsorbate [39,44]. This separation method is based on the differences in the affinities of adsorbates with an adsorbent. In the biogas upgrading, zeolite or activated carbon is usually applied as an adsorbent for the higher grade desulfurization [25,26] after the rough H_2S removal with iron oxide pellets.

c) Membrane separation

Membrane separation relies on the difference in permeability of gaseous species through a membrane (see Fig. 1.4). The process can be designed to be very simple, and highly efficient, if H_2S resistant membrane is developed. The current challenges of this technology are the high cost of membrane production and its selectivity [26].

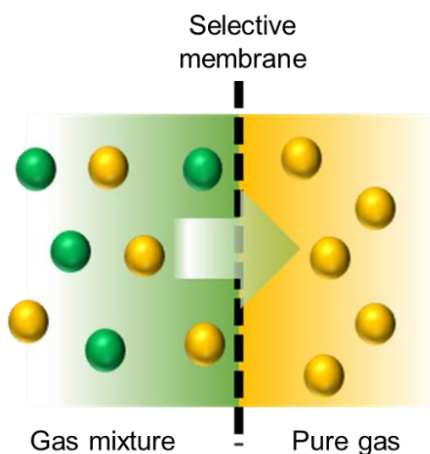


Figure 1.4: Schematic illustration of membrane separation of gas mixture.

1.3. Biochar

Biochar (BC) is an organic porous carbon material obtained by heat treatment of biomass in the O_2 -free condition (pyrolysis). BC can be used as a renewable fuel [45,46]. The applications of it to agriculture as soil amendment to increase nitrogen absorption and water retention abilities of the soil have also been reported [47–49]. BC is mainly composed of amorphous and graphitic carbons with aromatic carbons (more stable forms compared to those in the feedstock such as lignin) [50,51]. BC rich in alkaline minerals or reactive surface functional groups has been reported to be utilized for the removal of heavy metals and acid gases [28,52]. Depending on its source and treatment process, BC behaves not only as physical adsorbent whose adsorption capacity is governed by surface area and porosity, but also as chemical adsorbent which relies on the surface reaction [53], and in this case, surface modification by alkali addition, metal loading, or nitrogen (N)-doping becomes important to enhance the H_2S adsorption capacity [54,55].

1.3.1. Sources and composition

BC can be produced from wide variety of biomasses such as agricultural waste, forestry waste, manure, and so on. As listed in Table 1.3, chemical composition of BC varies significantly depending on its source [56–59].

Table 1.3: Compositions of BCs produced from various biomass feedstocks.

Feedstock	C / %	H / %	N / %	Ash / %	Ref.
Almond shells	87.9	2.50	1.32	17.3	[56]
Banana leaves	48.0	3.20	1.20	23.5	[57]
Wood chips	85.8	2.94	2.13	-	[58]
Cow manure	58.0	-	1.45	22.5	[59]

This study selected bamboo and rice husk as biomass feedstock. Bamboo, which is a woody biomass can grow on a poor soil, is one of the most promising biomass resources in terms of producibility. Bamboo has long been utilized for biofuel and biochar productions [60].

Rice husk is a non-woody biomass with high content of silica. Rice husk ash has been utilized for the production of concrete, and there is a growing interest about the utilization of rice husk biochar as an adsorbent [61].

1.3.2. Adsorption on biochar

In addition to the uses as a fuel or a soil amendment, BC is being researched widely as an adsorbent for the removal of organic and inorganic pollutants from wastewater [62,63] and atmospheric air [64]. The low price of BC is attractive for the practical application, however its adsorption behavior depending on feedstock makes the utilization more complex. The adsorption mechanism can be divided into two categories, a) physical and b) chemical adsorptions.

a) Physical adsorption

Physical adsorption (or physisorption) is the process to stabilize an adsorbate on the surface of an adsorbent with the enthalpy change of around 20 kJ mol^{-1} [65]. Physisorption which relies on weak van der Waals force between an adsorbate X and an adsorbent (see Fig. 1.5a) is affected by physical properties of adsorbent such as surface area and porosity [66,67]. As with composition, surface area and porosity of BC also

differ significantly with feedstocks. BC derived from a cellulose-rich biomass (e.g. rice husk) usually has microporous structure with average pore size diameter (d_p) less than 2 nm. Pyrolysis temperature is a crucial factor. Higher pyrolysis temperature results in larger d_p [50,68].

b) Chemical adsorption

Unlike physical adsorption, chemical adsorption (or chemisorption) relies on the reactive interaction between an adsorbate and an adsorbent with the enthalpy change of around 200 kJ mol^{-1} [65]. Chemisorption is more selective adsorption process than physisorption [66]. Fig. 1.5b describes the chemisorption mechanism of an adsorbate X on a chemical adsorbent. After adsorption on the surface of the adsorbent, X reacts with the surface elements to produce new species (A, B, and C).

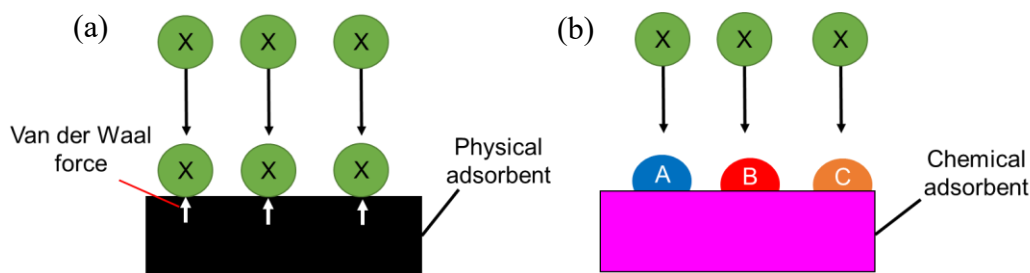


Figure 1.5: Schematic illustrations of (a) physisorption and (b) chemisorption of adsorbate X on an adsorbent.

On the surface of BC, randomly oriented polyaromatic clusters, heteroatomic surface functional groups, and mineral matters which determine the acidity (or basicity) are existing [53]. Among these surface functional groups of BC, oxygen and nitrogen functional groups are most influential to determine the surface acidity/basicity [69–71]. Minerals in BC are usually present as carbonate, oxide, or phosphate of Na, Mg, Mn, K, Ca, and other non-metal mineral such as silica (SiO_2). Alkali and alkaline earth metal compounds can provide basic sites in BC that play an important roles in the chemisorption of heavy metals such as Cd, Pb, As, etc. and acidic gases such as SO_2 , CO_2 , H_2S , etc. [72,73].

1.3.3. Physical activation

Physical activation is a process to improve the physicochemical characteristics of biochar by means of a) gaseous, b) thermal, and c) ultrasound activation processes, or the combination of them [68].

a) Gaseous activation

A carbon-based material is oxidized above 700°C in the flow of an oxidizing agent, which brings about the change in surface structure by the gasification of the carbon surface of BC, leading to widening of pores and exposure of previously inaccessible pores. Steam is one of the major oxidizing agents, and steam activation can develop both mesopores and micropores with wider range of pore size distribution compared to other activating gases such as CO₂, ozone, and air. Steam can not only improve the structure of BC by the gasification of carbon through reaction (1.6) but also remove the products of incomplete combustion (e.g. acids, aldehydes, ketones or fine particulate matter of biomass) from the pores of BC [74–76].



Steam activation can also introduce more oxygen-containing surface functional groups on the BC surface [77], that can enhance the chemisorption ability of BC [68,78].

b) Thermal activation

For the complete carbonization of biomass, treatment temperature above 700°C or a longer treatment time is generally required [79]. Above 700°C, the graphite content increases with increasing the treatment temperature. BC is rarely processed at excessively high temperature to avoid the reduction of yield and surface area. Thus, lower temperature with longer treatment time is preferred. Most BCs produced at low temperature possess highly disordered and heterogenous carbon structure (combination of amorphous and graphitic structure) [80,81].

Thermal treatment of BC is often performed to modify not only the carbon structure but also the concentration of surface functional groups. Generally, carboxylic, phenol, and quinone groups of BC start to decompose at 250, 500 and 900°C, respectively. Above 900°C, most of oxygen surface functional groups are eliminated. Hence, thermal treatment in inert atmosphere is applied to selectively eliminate oxygen functional groups from the surface, thus reducing the acidity of the surface [82,83].

c) Ultrasound activation

Ultrasound-assisted surface modification of BC is a new emerging technology that can contribute to the cost reduction of BC production [68]. The effect of ultrasound activation on BC is based on the water splitting to form oxygen, hydroxyl and peroxy radical from water, which promote hydrogenation and hydroxylation of BC [84], leaching of minerals such as K, Mg, and Ca from inner structure of BC [85], and shearing of thin graphite layers from the BC [86]. Ultrasound activated BC has been found to have higher gas capture capacity due to a 19-fold increase of internal surface area compared to untreated BC [87].

1.3.4. Chemical activation

Chemical activation is a process to modify the surface chemistry of biochar by doping elements or altering surface functional groups, though its mechanism is still not well understood [53]. As opposed to physical activation, carbonization and chemical activation processes can be performed in one step to achieve higher yield than physical activation. Lower process temperature compared to physical activation is also an advantage of the chemical process. However, hazardous chemical agents (such as H_2SO_4 and NH_3 gas) used in this process are discharged [88,89].

Chemical activation is generally performed by impregnating a biomass feedstock with a chemical agent followed by heat treatment. Chemical activation of biochar can be classified as: a) acidic/basic modification; b) sulfonation; c) nitrogen doping; and d) metal loading [53].

a) Acidic/basic modification

By using an activation agent such as steam or acidic/basic solution, oxygen-containing functional groups are introduced on the surface of biochar.

Acidic modification

Acidic agents, such as phosphoric acid [90], nitric acid [91], hydrochloric acid [92], and hydrogen peroxide [93], can catalyze the dehydration and the elimination reaction occurring upon pyrolysis, suppress tar formation and lower pyrolysis temperature.

Basic modification

Basic agents, such as KOH [94], NaOH [95], and ZnCl_2 [96], can modify the surface to be more alkaline. The basic site, functioning as an electron donor, will aid in the adsorption of an adsorbate acting as electron acceptor.

b) Sulfonation

Sulfuric acid is a highly corrosive mineral acid usually applied as catalyst in various chemical processes. However, efficient separation and neutralization processes to remove hazardous waste are required. On the other hand, the sulfonate-doped biochar is a promising material to realize a more environmentally-friendly and simple process substituting for the use of sulfuric acid. The sulfonation process is performed by submerging the biochar in a sulfonate-containing reagent followed by washing and heat treatment [53,97].

c) Nitrogen doping (N-doping)

Nitrogen doping is a process to introduce nitrogen functional groups to the surface of biochar generally by using (I) ammonia (NH_3) and (II) amino group-containing reagent, or (III) the combination of nitration and reduction [53].

A popular method is the N-doping using NH_3 , which is usually started with a pre-oxidation process to increase the number of oxygen-containing groups where N-doping is expected to easily take place, because the graphitic surface of biochar is not so reactive to NH_3 [98].

Nitrogen functional groups introduced to the surface of biochar in the NH_3 flow at high temperature of 500-700°C are pyridinic-N, pyrrolic-N, imine, amine, and amide group [99,100]. Formation scheme of pyridinic-N in biochar is described in Fig. 1.6. Nitrogen-containing groups can introduce structural defects with electron transfer capabilities that could activate the adsorbed oxygen or surface oxygen to create oxygen radicals (O^*) [101,102].

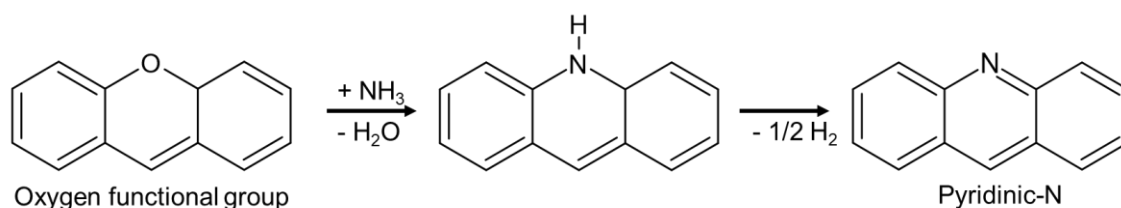


Figure 1.6: Formation of pyridinic-N at the site of oxygen functional group by the NH_3 treatment of biochar [103].

H_2S adsorption on the surface of N-doped carbon is explained based on the dissolution of H_2S in the water film on the surface (reaction (1.7)) followed by oxidation with O^* to form elemental sulfur (reaction (1.8)) [102,104].



Reactive O* on the surface of biochar can promote the chemisorption process of H₂S by consuming hydrosulfide ion (HS⁻) to form sulfur [105]. Among the N-doped sites, pyridinic-N is reported to most catalyze the formation of O* [101].

d) Metal loading

Impregnation of biochar with a precursor solution containing metal ions is applied for increasing its adsorption capacity, because a metal or a metal compound loaded on the surface of biochar has high affinity with an adsorbate [106]. By way of example, the metal-loading on carbon can promote the oxygen reduction reaction (ORR) due to increase in the amount of surface oxygen [107]. By selecting a suitable metal precursor, the surface pH can also be controlled [108].

The impregnation method is usually performed by mixing a biochar with a metal salt solution followed by thermal treatment [109,110]. Cu, Mg, and Fe have been reported to be effective for the enhancement of the adsorptions of mercury [106], NH₃ [108], and arsenic [111], respectively.

In the case of H₂S adsorption, various metals have been proven to be effective. For example, Zn in the form of ZnO is used as a desulfurizer in H₂ production from fossil resources. 0.25 g of ZnO was reported to be able to reduce the H₂S concentration from 100 ppm to 1 ppm for 9 h at 250°C [112]. Other example is the Cu-loaded rice husk biochar (16wt% Cu) attached to an electric fan to purify indoor toxic pollutant gases such as trimethylamine and H₂S [113]. Their experiment showed that it can purify 0.1 m³ of air mixed with 400 ppm H₂S in 15 min. These investigations indicate that the mechanism of adsorption enhancement is peculiar to each combination of loaded-metal and adsorbate.

1.4. Objectives

The purpose of this study is to develop a desulfurizer derived from local biomass resources through the systematic investigations on the H₂S adsorption behavior for the surface-modified biochars, focusing mainly on bamboo and rice husk as feedstocks.

Among various surface modification techniques to improve H₂S adsorption capacity of biochar, ammonia treatment (N-doping) and metal (Ni)-loading are selected, because the target of this study is rural areas of developing countries, where digestate liquid discharged from a biogas production plant (methane fermentation tank) is available as a convenient and sustainable source of NH₃ for N-doping to biochar, and Ni is quite susceptible to a trace H₂S to lose its catalytic activity for fuel reforming, showing high affinity of H₂S with Ni, and this metal, commonly used as the anode of SOFC, can be recycled from the spent SOFC. In the course of this study, synergetic effect of N-doping and Ni-loading will be discussed.

In order to evaluate the feasibility of biochars developed in this study as a desulfurizer, these performances will be compared to the reported desulfurizers listed in Table 1.4.

As shown in Fig. 1.2, the biochar-based desulfurizer to be developed will be applied for the purification of biogas, which is used for the fuel cell power generation in a rural area, contributing to the Sustainable Development Goals (SDGs), especially for “7. Affordable and clean energy”, “12. Responsible consumption and production”, and “13. Climate action” [114].

Aiming at achieving the H₂S adsorption capacity comparable to commercial desulfurizers, the powdered biochar samples are formed into a sheet state by the paper-making process using ceramic fibers to enhance the accessibility of adsorbate (H₂S) on the surface of adsorbent (biochar) [115]. The resulting “paper-structured biochar”, which is mechanically flexible and easily mounted into an adsorbent vessel, is expected to be practically applied in a real system as an easily affordable desulfurizer.

Table 1.4: H₂S adsorption capacities of the commercial and the reported desulfurizers.

Product name	SSA / m ² g ⁻¹	V_{mic} / 10 ⁻⁷ m ³ g ⁻¹	q_0 / mg H ₂ S g-BC ⁻¹	q / mg H ₂ S g-BC ⁻¹	Ref.
Chemviron Carbon ¹⁾	930	3.8	1.3	8	[116]
CECA 13X ²⁾	700	2.6	46	177	[117]
SBA-15 ³⁾	950	13.1	0.54	1.09	[118]
IRMOF-3 ⁴⁾	2200	-	10.6	15.4	[119,120]

1) Coconut-based activated carbon manufactured by Chemviron Ltd. (Commercial)

2) 13X zeolite manufactured by Arkema S.A. (Commercial)

3) Molecular sieve made from Pluronic P123 and TEOS in HCl

4) Zinc-based metal-organic framework, a Zn impregnated N-doped carbon made by dissolving NH₂-BDC (carbon precursor) and Zn(NO₃)₂ in DMF

All desulfurizers were tested in dry condition at ambient temperature. Chemviron carbon and CECA13x were tested using 80 ppm H₂S at 4000 mL min⁻¹ for 10 g adsorbent. SBA-15 was tested using 4000 ppm H₂S at 100 mL min⁻¹ for 1.0 g adsorbent. IRMOF-3 was tested using 0.1 ppm H₂S at 100 mL min⁻¹ for 0.25 g adsorbent.

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CHAPTER II

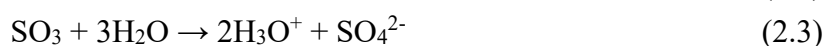
Feasibility of Biochar as a Desulfurizer

2.1. Introduction

The H₂S adsorption capacity of biochar (BC) depends not only on specific surface area but also on pore size distribution and surface chemistry such as pH and trace elements, and these parameters can differ greatly depending on the biomass feedstock [1,2].

Steam treatment of carbon materials at high temperature produces micropores and mesopores on the surface by the gasification of carbon expressed as reaction (1.6). Steam activation also increases the alkalinity of biochar by reducing the amount of acidic surface functional groups, thus helping the adsorption of H₂S [3].

NH₃ treatment of biochar at high temperature can dope nitrogen or create nitrogen functional groups on the surface of biochar [4]. One of such reactions is the formation of pyridinic-N as shown in Fig. 1.6. Nitrogen-containing groups can introduce structural defects with electron transfer capabilities that could activate the adsorbed oxygen or surface oxygen to create oxygen radicals [5,6]. H₂S adsorption on the surface of N-doped carbon has been explained based on the dissolution of H₂S in the water film on the surface followed by oxidation with oxygen radicals to form elemental sulfur [6,7] as expressed by reactions (1.7) and (1.8). A high amount of oxygen radicals can cause further oxidation of HS⁻ to form sulfur oxides (SO_x) and sulfate as follows:



2.2. Objective

Here, the properties of BC as a desulfurizer will be systematically studied by using different biomass feedstocks, bamboo and rice husk. The effects of steam and NH₃ treatments on the H₂S adsorption capacity of BC will be discussed focusing on the changes in surface morphology and chemistry to understand the key parameters for improving the performance.

2.3. Experimental

2.3.1. Biochar preparation

Bamboo (BB) (*Phyllostachys bambusoides*) and rice husk (RH) from Japonica rice (*Oryza sativa* subs. Japonica) were collected from the Itoshima area of Fukuoka prefecture. Bamboo was firstly chopped to pieces of roughly 0.5 cm x 1 cm as shown in Fig 2.1a, while rice husk was used without any pre-treatment (Fig. 2.1b). The collected biomasses were first dried at 100°C in an oven for 24 h. The dried sample (3.5 g) was put in an alumina tube and heated to 500°C at a rate of 10°C min⁻¹ in 50 mL min⁻¹ N₂ flow, then left at this temperature for 120 min for pyrolysis, followed by natural cooling to room temperature to obtain biochar (BC) (Fig 2.1c). The produced BC was then powdered and stored in a glass flask. BB- and RH-derived BCs were labeled as BBBC and RHBC, respectively.



Figure 2.1: Pictures of (a) bamboo chip and (b) rice husk used in this study. (c) is the biochar produced from rice husk.

2.3.2. Biochar treatments

a) Steam treatment

2.0 g of BC was placed into an alumina tube and heated to 850, 1,000 or 1,150°C at a rate of 10°C min⁻¹ in 94.5 mL min⁻¹ N₂ flow. Then, 100 µL min⁻¹ of distilled water was supplied to the tube by a liquid pump, with 94.5 mL min⁻¹ N₂ flow as a carrier gas (15vol% steam) for 90, 180 or 270 min, followed by natural cooling to room temperature in 94.5 mL min⁻¹ N₂ flow. The steam activated samples are labeled BBBC-S and RHBC-S with different treatment conditions of A-E, as listed in Table 2.1.

b) NH₃ treatment

2.0 g of BC was placed in an alumina tube and heated to 500 or 900°C at a rate of 10°C min⁻¹, in 100 mL min⁻¹ N₂ flow. After reaching the desired temperature, the gas flow was switched to a mixture of 25 mL min⁻¹ NH₃ and 75 mL min⁻¹ N₂, then kept under this condition for 120 min, followed by natural cooling to room temperature in 100 mL min⁻¹ N₂ flow. The NH₃-treated samples are labeled BBBC-N and RHBC-N with different treatment temperatures of A and B as listed in Table 2.1.

Table 2.1: Identification label of the produced samples.

Sample name	BC type	Treatment type	Treatment Temp. / °C	Treatment time / min
BBBC-S-A	BB	Steam	850	90
BBBC-S-B	BB	Steam	1,000	90
BBBC-S-C	BB	Steam	1,150	90
BBBC-S-D	BB	Steam	850	180
BBBC-S-E	BB	Steam	850	270
BBBC-N-A	BB	NH ₃	500	120
BBBC-N-B	BB	NH ₃	900	120
RHBC-S-A	RH	Steam	850	90
RHBC-S-B	RH	Steam	1,000	90
RHBC-S-C	RH	Steam	1,150	90
RHBC-S-D	RH	Steam	1,000	180
RHBC-S-E	RH	Steam	1,000	270
RHBC-N-A	RH	NH ₃	500	120
RHBC-N-B	RH	NH ₃	900	120

2.3.3. Sample characterizations

The contents of volatile solids (VS) and non-volatile solids (ash) corresponding to organic and inorganic substances, respectively, were analyzed by thermogravimetry and differential thermal analysis (TG-DTA) (Thermoplus EVO2, Rigaku Co., Ltd., Japan). 10 mg of a sample was heated to 800°C at a rate of 10°C min⁻¹ in 20 mL min⁻¹ air flow, and kept for 120 min at this temperature, during which weight loss and amount of residue were analyzed.

The C, H and N contents in the samples were analyzed by a CHN coder (MT-5, Yanaco Analytical Instruments, Japan) and other elemental components were analyzed by

an energy dispersive X-ray fluorescence analyzer (XRF) (EDX-7000, Shimadzu, Japan).

For qualitative evaluation of the surface basicity of BC, 0.4 g of a sample was dispersed in 20 mL of distilled water, and stirred vigorously by magnetic stirrer for 24 h at RT. Then, the pH of the supernatant water of the suspension was measured by a pH meter (pH meter D-52, Horiba Ltd., Japan).

Specific surface area (SSA) of the biochar samples was measured by the nitrogen adsorption method (Belsorp-mini II analyzer, MicrotracBEL Corp., Japan), and the pore size distribution was evaluated by the MP and BJH methods.

The microstructure was investigated by field emission scanning electron microscopy (FESEM-S5200, Hitachi High-Technologies Corp., Japan) using an energy-dispersive X-ray spectrometry (EDX).

The crystal structure of the samples was analyzed by X-ray diffractometry (Rint-Ultima III diffractometer, Rigaku, Japan) with CuK α radiation at 40 kV and 40 mA in the 2 θ range from 10° to 90° at 0.4° min⁻¹.

The graphitization degree of the samples was analyzed by Raman spectroscopy (LABRAM ARAMIS, Horiba Ltd., Japan) in the wavelength region of 100–3,000 cm⁻¹ using a diode pumped solid state laser (532 nm wavelength, 50 mW power).

For near-surface analysis, quasi-surface-sensitive technique using X-ray photoelectron spectroscopy (XPS) was done at room temperature using a monochromated Al K α ($h\nu = 1,486.7$ eV) X-ray source operated at 5 mA and 15 kV (Kratos Axis Ultra, Shimadzu, Japan). All binding energies (BEs) were referred to the C1s line at 284.6 eV.

2.3.4. H₂S adsorption test

The apparatus for measuring H₂S adsorption was designed as shown in Fig. 2.2. The biochar sample was packed into a glass fixed-bed reactor tube with an inner diameter of 0.75 cm, which was used as the adsorbent vessel. In the case of pure biochar, 1.0 g of powdered sample was packed into the tube.

The tests were conducted at room temperature by flowing nitrogen gas containing 40 ppm H₂S at 50 mL min⁻¹ through the adsorbent vessel. The outlet gas was collected every 15 min in a 2.0 L gas bag (F2S sampling bag, Asone Co.), and the H₂S concentration was monitored using a gas analyzer (Biogas 5000, Geotechnical Instrument Ltd., UK).

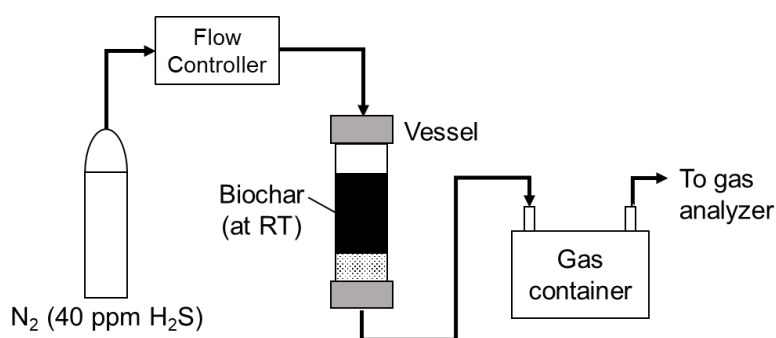


Figure 2.2: Apparatus used to evaluate the H₂S adsorption capacity of biochars.

Breakthrough is defined as the point at which the adsorbate starts to penetrate the column and 1 ppm of H₂S (the lower detection limit of Biogas 5000) is detected in the column effluent. After the breakthrough was reached, the gas was collected every 120 min in a 2.0 L plastic gas bag. The H₂S concentration was analyzed using two types of detector tubes with different measuring ranges of 1 to 40 ppm (4LK) and 0.25 to 120 ppm (4LL) (hydrogen sulfide detector tubes, Gastec Corporation, Japan). As shown in Fig. 2.3, the deviation of the measured H₂S concentration from the standard line was slight for all devices, showing the reliability of the measurements.

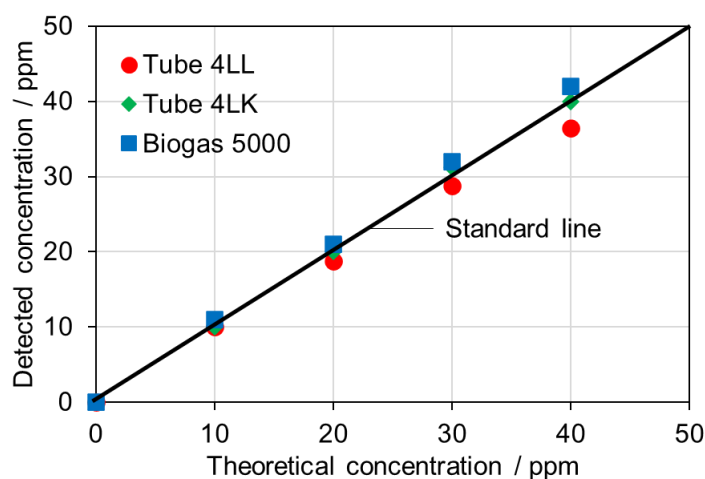


Figure 2.3: Validation of the measurement of H₂S concentration.

The adsorption curve to be measured is schematically shown in Fig. 2.4. The total H₂S adsorption capacity per gram of biochar (q), corresponds to the area above the adsorption curve (hatched area), was calculated using the following equation:

$$q = (\rho v/m) \int_0^t (C_0 - C) dt \quad (2.4)$$

where ρ is the density of H₂S gas, v is the volumetric flow rate, m is the adsorbent (biochar) mass, C_0 is the H₂S concentration at the inlet, and C is the H₂S concentration at the outlet at time t .

q is the amount of H₂S adsorbed in a sample until the H₂S concentration in the outlet gas reaches 40 ppm. Meanwhile, the breakthrough adsorption capacity (q_0), corresponding to the surface affinity with H₂S, was estimated from the area indicated by lateral stripes of Fig. 2.4.

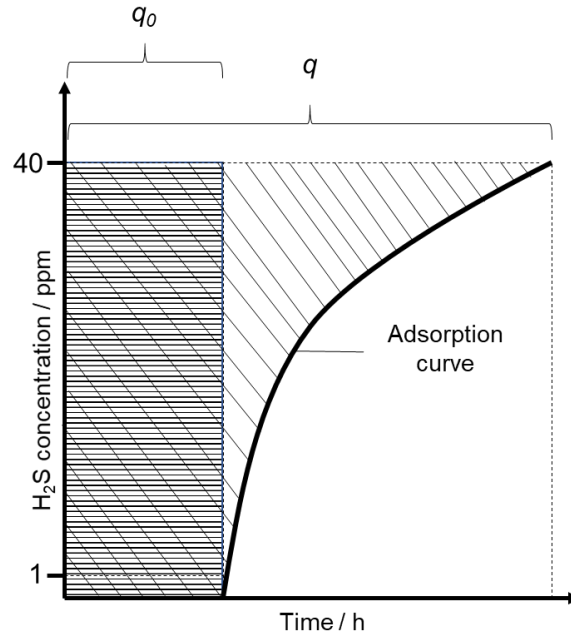


Figure 2.4: Example of an adsorption curve.

2.4. Results and discussion

2.4.1. Sample characterization

The TG profiles for BBBC and RHBC measured in the air flow are shown in Fig. 2.5. As listed in Table 2.2, the contents of volatile and non-volatile components (ash) were 91.8% and 8.2%, respectively, for BBBC, and 52.9% and 47.1%, respectively, for RHBC.

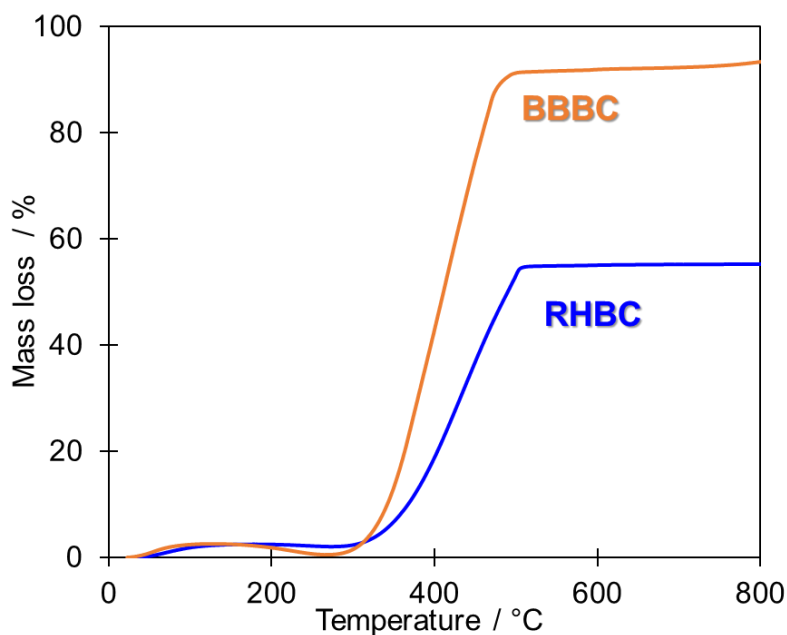


Figure 2.5: TG profiles for BBBC and RHBC measured in air flow.

In the XRD profiles of the biochars (Fig. 2.6a), a broad peak at around $2\theta = 22^\circ$ reflecting amorphous carbon (JCPDS card No. 22-1069) was observed [2]. In the diffraction patterns of the ashes of the biochars (Fig. 2.6b), for BBBC, a reflection of silica (SiO_2) in the amorphous phase ($2\theta = 23.5^\circ$) (JCPDS card No. 47-1144) was observed. On the other hand, for RHBC, reflections of SiO_2 ($2\theta = 21.5^\circ$) (JCPDS card No. 39-1425) are clearly observed, indicating that the non-volatile components were encapsulated by carbon, and especially in the case of RHBC, carbon existed on the stable SiO_2 .

Table 2.2: Chemical compositions of BBBC and RHBC.

BBBC				RHBC			
Overall		Ash ²⁾		Overall		Ash ²⁾	
Species	/ wt%	Species	/ wt%	Species	/ wt%	Species	/ wt%
C	82.4	SiO ₂	11.8	C	30.5	SiO ₂	87.0
N	0.50	K ₂ O	78.0	N	0.27	K ₂ O	11.0
H	2.98	CaO	0.85	H	1.28	CaO	0.99
O ¹⁾	5.92			O ¹⁾	20.9		
Ash	8.20			Ash	47.1		

- 1) Oxygen content was estimated from the difference between the compositions measured by CHN corder (contents of C, H, and N) and TG-DTA (organic content).
- 2) Ash composition was estimated from the elemental compositions analyzed by XRF and possible oxide formula.

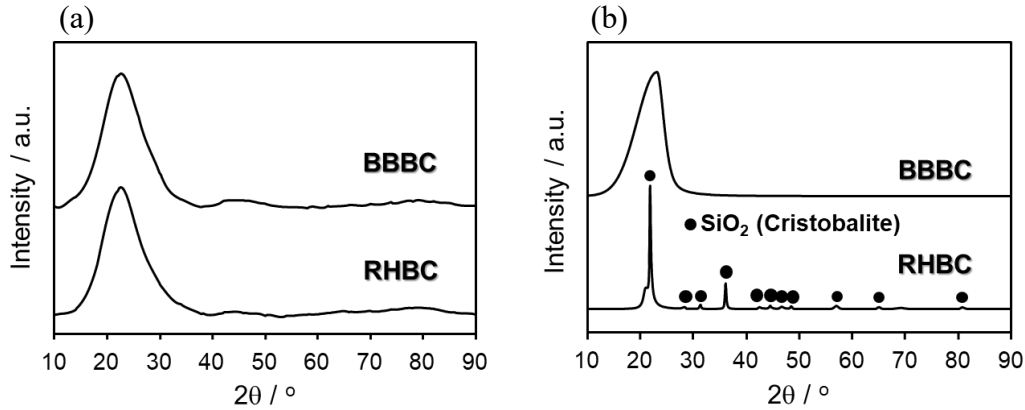


Figure 2.6: (a) XRD profiles of BBBC and RHBC and (b) the non-volatile components (ashes) in BBBC and RHBC.

FESEM-EDX images of BBBC and RHBC are shown in Fig. 2.7 and Fig. 2.8 respectively. Both BBBC and RHBC have a honeycomb-like pore structure (Figs. 2.7a and 2.8a). The honeycomb structure is expected to have a low pressure-drop in a gas flow, however the gas mixing may be poor inside the tubular macropores [8]. The magnified images (Figs. 2.7b and 2.8b) show the existence of smaller pores on the wall of the porous body [9]. The honeycomb structure of the biochar comes from the carbonization of xylem and phloem vessels of plant, which acts as water and nutrient conducting tissue [10]. In the EDX mapping (Figs. 2.7c and d, Figs 2.8c and d), only carbon was clearly detected, showing that mineral components (K₂O and SiO₂ are the major mineral components in BBBC and RHBC, respectively.) are covered by carbon.

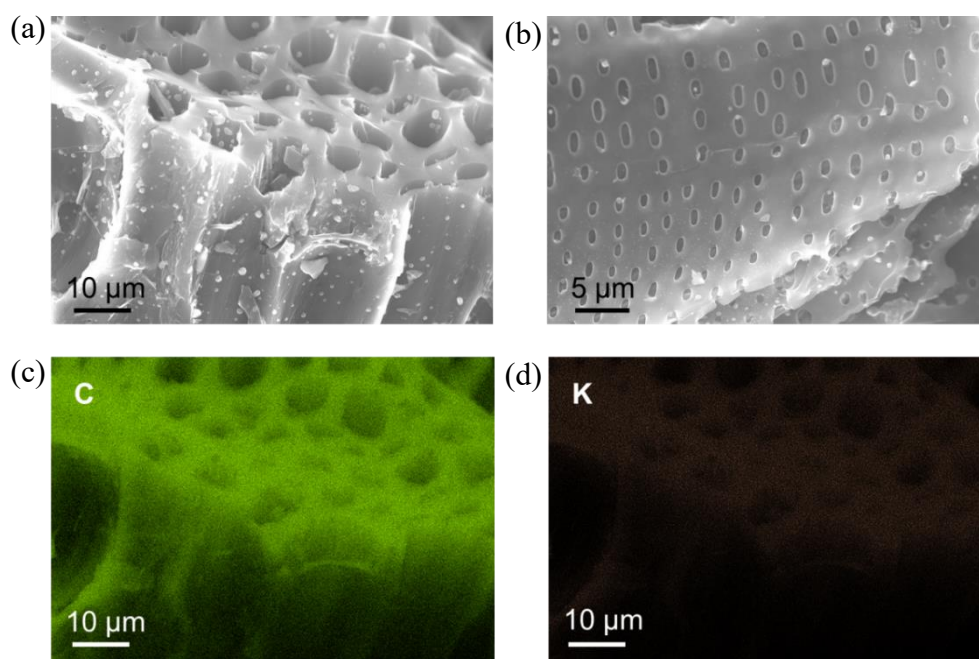


Figure 2.7: FESEM-EDX images of (a) BBBC and (b) the surface of the porous body of BBBC with the EDX mapping images of (c) C and (d) K, respectively, for the FESEM image of (a).

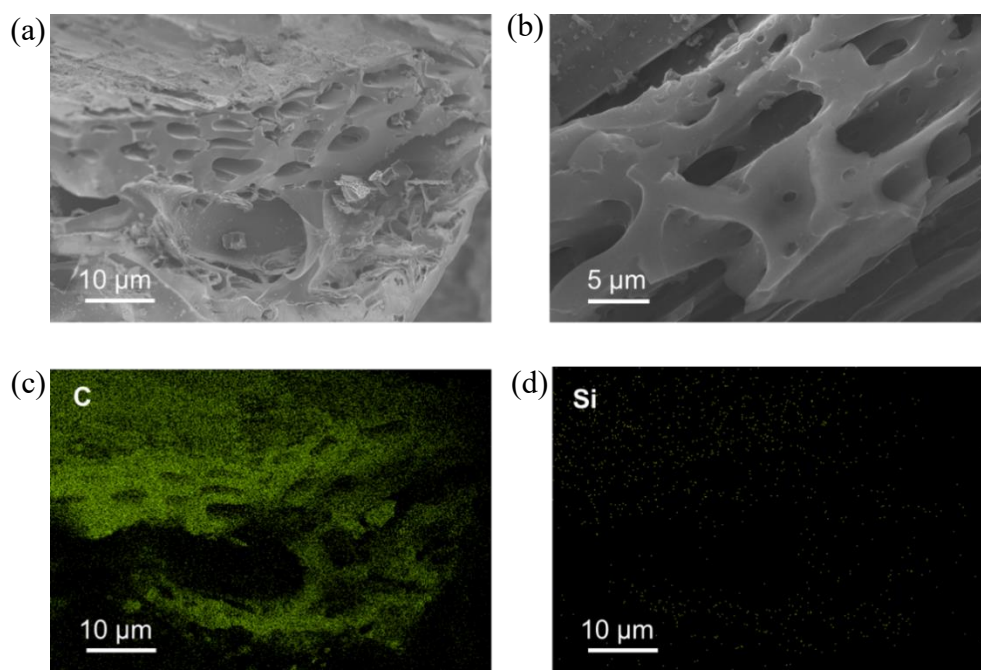


Figure 2.8: FESEM-EDX images of (a) RHBC and (b) the surface of the porous body of RHBC with the EDX mapping images of (c) C and (d) Si, respectively, for the FESEM image of (a).

The nitrogen adsorption-desorption isotherm for steam-treated samples are shown in Fig. 2.9. Both BBBC and RHBC had the characteristics of H4 loop [11] and showed high uptake at low relative pressure (p/p^0) which is associated with micropore fillings. On the other hand, steeper curves for RHBC at high p/p^0 indicate multilayer adsorption, which is detected in mesoporous materials.

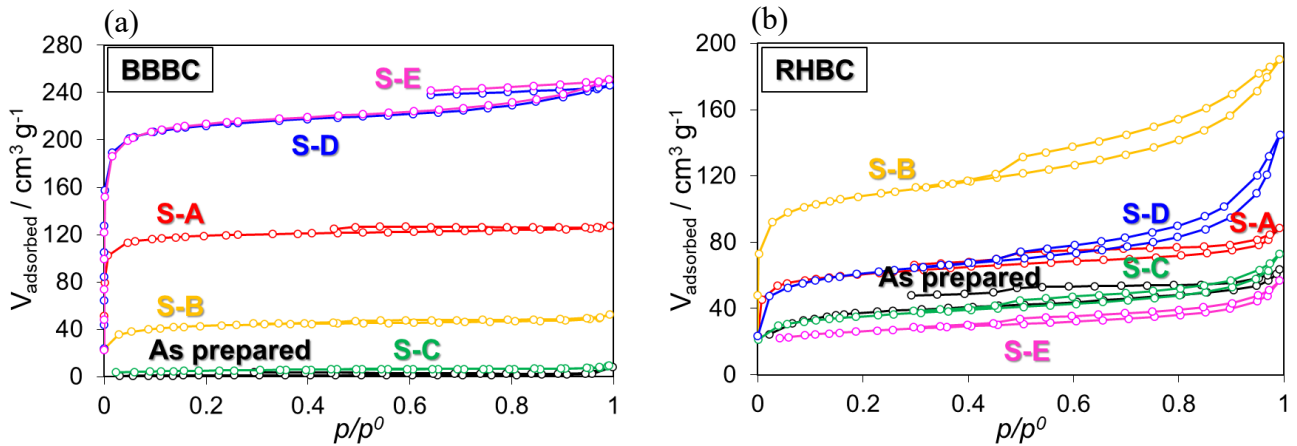


Figure 2.9: Nitrogen adsorption-desorption isotherms of the steam-treated (a) BBBC and (b) RHBC.

Characterization results for the as-prepared and the steam-treated (90 min) biochars at different temperatures are summarized in Table 2.3. The considerably low SSA of BBBC ($3.98 \text{ m}^2 \text{ g}^{-1}$) compared to RHBC ($146 \text{ m}^2 \text{ g}^{-1}$) suggests that the pyrolysis condition (120 min at 500°C in N_2 flow) was insufficient to complete the carbonization. However, in the case of RH, SiO_2 (one of the main components) may promote the pyrolysis of organic component as a support material, resulting in larger SSA.

Steam treatment increased the SSA and pH of biochars. The significant increase in SSA of BBBC ($3.98 \rightarrow 471 \text{ m}^2 \text{ g}^{-1}$ (BBBC-S-A)) means the completion of carbonization during steam treatment. The micropore volume also increased, showing the effectiveness of steam treatment for increasing potential adsorption sites by generating micropores. In terms of SSA and pore volume, the optimum steam treatment temperatures were 850 and $1,000^\circ\text{C}$ for BBBC (BBBC-S-A) and RHBC (RHBC-S-B), respectively. At a temperature higher than the optimum, the micropores collapsed, resulting in lower SSA and pore volume.

Alkaline mineral components in biochar, such as CaO and K_2O , result in high alkalinity of BBBC ($\text{pH}=10.3$) and RHBC ($\text{pH} = 9.59$) as listed in Table 2.3 [12]. Existence of the alkali oxides can help the adsorption of acidic gases such as H_2S [13].

The distortion or defects in the carbon structure detected as the D band in Raman spectra have been reported to provide active sites for the activation of oxygen promoting

the adsorption of H_2S according to reaction (1.8) [5]. Raman spectra for BBBC and RHBC are shown in Fig. 2.10 and Fig. 2.11, respectively. From these spectra, the ratio of the disordered band (D band at $1,350\text{ cm}^{-1}$) to the graphitic band (G band at $1,590\text{ cm}^{-1}$) in Raman spectra (I_D/I_G) were estimated and presented in Tables 2.3 and 2.4. I_D/I_G was the highest at the steam treatment temperature of $1,000^\circ\text{C}$ for both biochars, indicating the highest degree of disorder in the carbon structure.

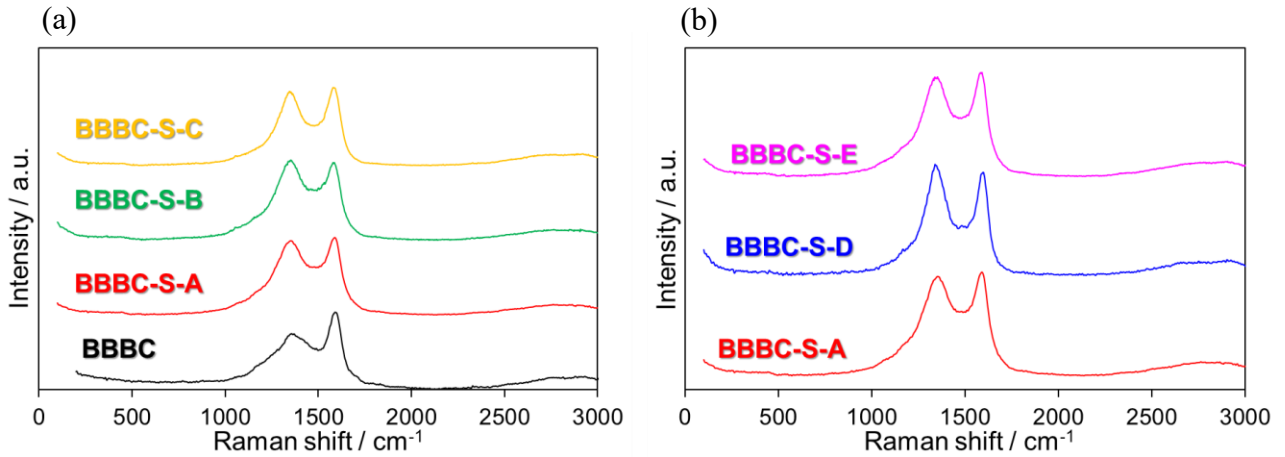


Figure 2.10: Raman spectra of the steam-treated BBBC samples with (a) different treatment temperatures and (b) different treatment times.

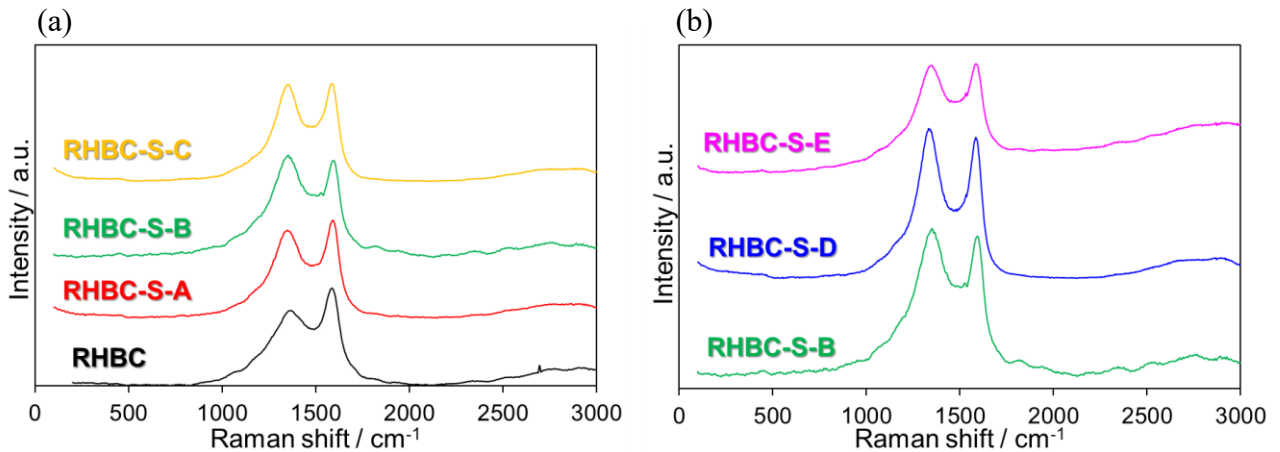


Figure 2.11: Raman spectra of the steam-treated RHBC samples with (a) different treatment temperatures and (b) different treatment times.

Table 2.3: Biochars steam-treated for 90 min at different temperatures.

Sample	SSA / $\text{m}^2 \text{g}^{-1}$	V_{tot} / $10^{-7} \text{m}^3 \text{g}^{-1}$	V_{mic} / $10^{-7} \text{m}^3 \text{g}^{-1}$	I_D/I_G	pH
BBBC	3.98	0.11	0.01	0.73	10.3
BBBC-S-A	471	2.03	1.99	0.96	11.4
BBBC-S-B	163	0.80	0.71	1.03	11.0
BBBC-S-C	176	0.14	0.09	0.95	12.0
RHBC	146	1.02	0.63	0.77	9.59
RHBC-S-A	227	1.37	0.98	0.90	10.7
RHBC-S-B	386	2.90	1.40	1.05	10.1
RHBC-S-C	40.2	0.49	0.02	0.99	10.1

Table 2.4: Biochar samples steam-treated for different times.

Sample	SSA / $\text{m}^2 \text{g}^{-1}$	V_{tot} / $10^{-7} \text{m}^3 \text{g}^{-1}$	V_{mic} / $10^{-7} \text{m}^3 \text{g}^{-1}$	I_D/I_G	pH
BBBC-S-A	471	2.03	1.99	0.96	11.4
BBBC-S-D	928	4.26	3.31	1.08	10.3
BBBC-S-E	842	4.02	3.34	0.96	11.4
RHBC-S-B	386	2.90	1.40	1.05	10.1
RHBC-S-D	155	1.68	0.68	1.07	10.3
RHBC-S-E	94.5	0.87	0.49	0.99	10.2

Table 2.4 shows the dependence on the steam treatment time at the optimum treatment temperatures in terms of SSA and micropores volume (850 and 1,000°C, for BBBC and RHBC, respectively). In terms of SSA, the optimum treatment times were 180 and 90 min for BBBC (BBBC-S-D) and RHBC (RHBC-S-B), respectively. For RHBC, the SSA decreased with increasing steam treatment time. Longer treatment time had a negative effect, possibly because the carbon on the surface of RHBC was etched by steam treatment, resulting in the exposure of SiO_2 with low SSA on the surface. BBBC-S-D and RHBC-S-B are good candidates as H_2S adsorbents, having the same level of I_D/I_G , 1.08 and 1.05, respectively.

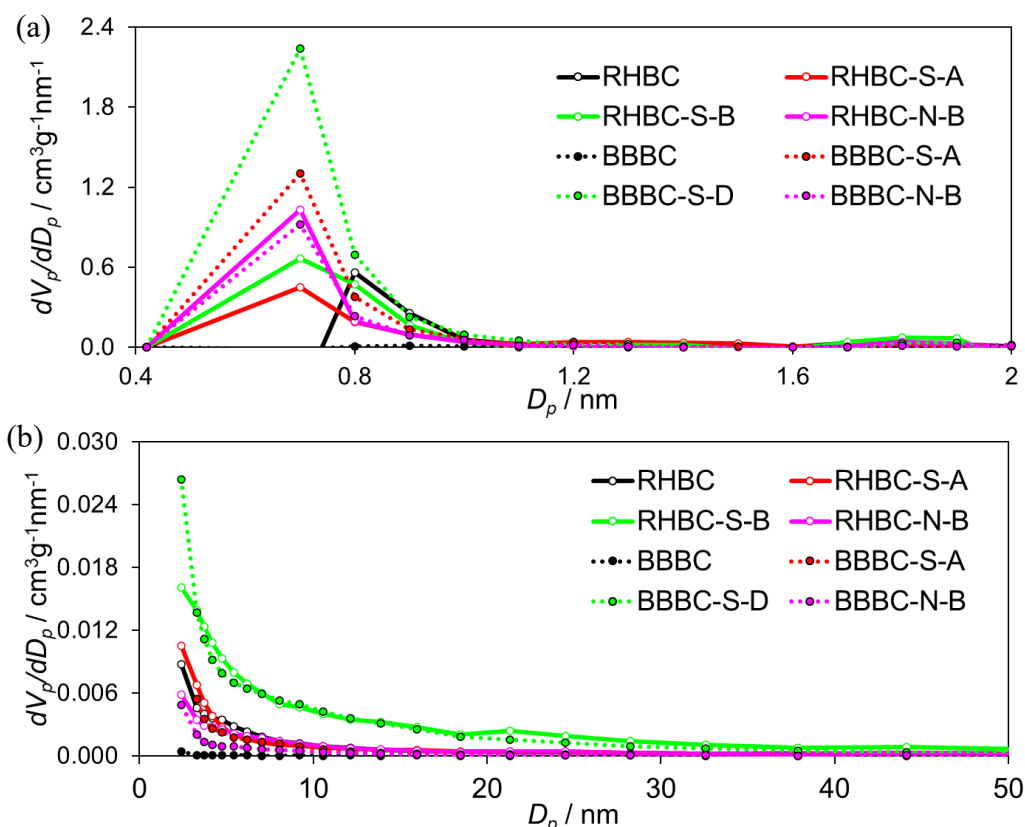


Figure 2.12: Pore size distributions of the prepared biochars: (a) micropores and (b) mesopores. V_p : pore volume, D_p : pore diameter.

Pore size distributions of the prepared biochars are shown in Figs. 2.12a and 2.12b for micropores and mesopores, respectively. The abundance of micropores was increased by steam treatment, however, in the case of RHBC, excessive steam treatment at 1,000°C was not effective. As shown in Figs. 2.13a and 2.13c, before steam treatment (RHBC), SiO₂ was mostly observed within the pores. After steam treatment at 1,000°C (RHBC-S-B), as shown in Figs. 2.13b and 2.13d, the carbon which covered the SiO₂ was gasified, and the SiO₂ was exposed on the surface resulting in lower SSA. The emergence of mesopores with pore size diameter of 21.3 nm by the intense steam treatment of RHBC at 1,000°C (RHBC-S-B) (see Fig. 2.12b), and the hysteresis at high p/p^0 region associated with mesoporous material (see Fig. 2.9b) may be caused by the gasification of the microporous carbon which leaves the nonporous SiO₂ exposed on the surface to reduce the porosity. Changes in the surface morphology of the biochars by the intense steam treatment are schematically illustrated in Fig. 2.14. The presence of a large amount of non-volatile contents (47.1%) in RHBC makes the intense steam treatment ineffective.

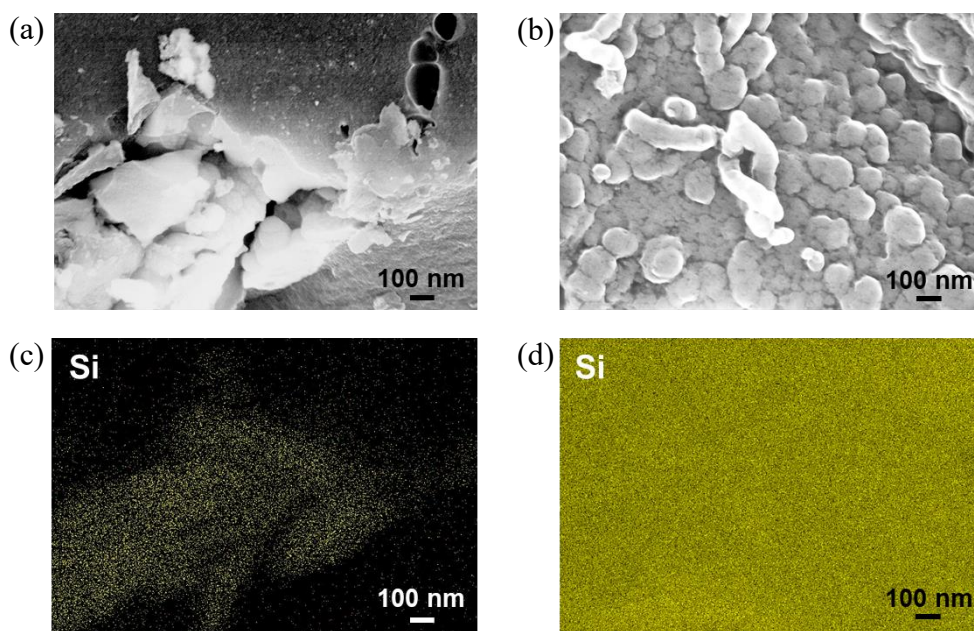


Figure 2.13: (a,b) FESEM and (c,d) Si mapping images of biochar surfaces. (a,c) the surface of RHBC showing SiO₂ in pores and (b,d) the surface of RHBC-S-B showing SiO₂ exposure.

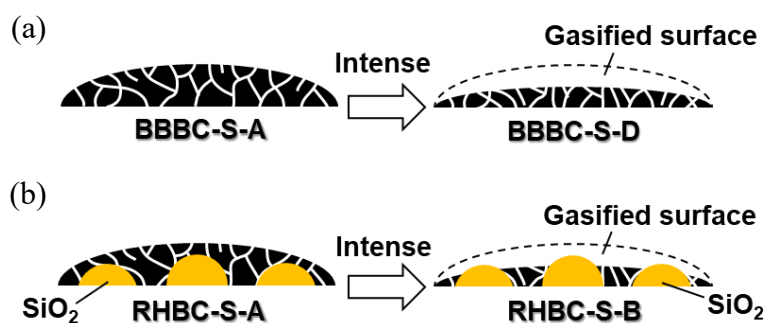


Figure 2.14: Schematic illustrations of the biochar surfaces showing the changes in morphology by the intense steam treatment; (a) BBBC and (b) RHBC.

Figure 2.15 shows the nitrogen adsorption-desorption isotherms for the NH₃-treated samples. Similar to the steam-treated samples (see Fig. 2.9), the NH₃-treated RHBC samples showed the characteristics of H4 loop (Fig. 2.15b) with steeper curve at high p/p^0 region compared to BBBC (Fig. 2.15a), indicating the presence of larger pores. In comparison to the steam-treated RHBC, the NH₃-treated RHBC showed a less steep curve, suggesting less etching by the NH₃ treatment, and therefore less SiO₂ exposure. Table 2.5 summarizes the change in surface morphology and chemistry due to ammonia treatment of BBBC and RHBC. With increasing NH₃ treatment temperature, the SSA,

pore volume, I_D/I_G estimated from Fig. 2.16 and pH all increased. However, NH_3 treatment of RHBC at 500°C lowered the SSA and pore volume. It has been stated in previous literature that NH_3 treatment at low temperature (450°C) can result in the incomplete decomposition of NH_3 . Nitrogen species present as amine ($-\text{NH}_2$) may be deposited on the surface of biochar and cause the blockage of micropores [7]. When the NH_3 treatment is performed at 900°C , N-doping, mainly pyridinic-N formation, was promoted for RHBC. However, surface N content did not increase for BBBC, probably due to more basic surface, which may repel NH_3 (a basic gas), limiting N-doping, although a small amount of pyridinic-N was formed [14]. After NH_3 treatment, both BBBC and RHBC had almost the same pore size distribution (see Fig. 2.12), and similar micropore volume. This means that NH_3 treatment was not influenced by the presence of SiO_2 , suggesting that the main function of NH_3 treatment is N-doping on the surface without SiO_2 exposure as schematically shown in Fig. 2.17.

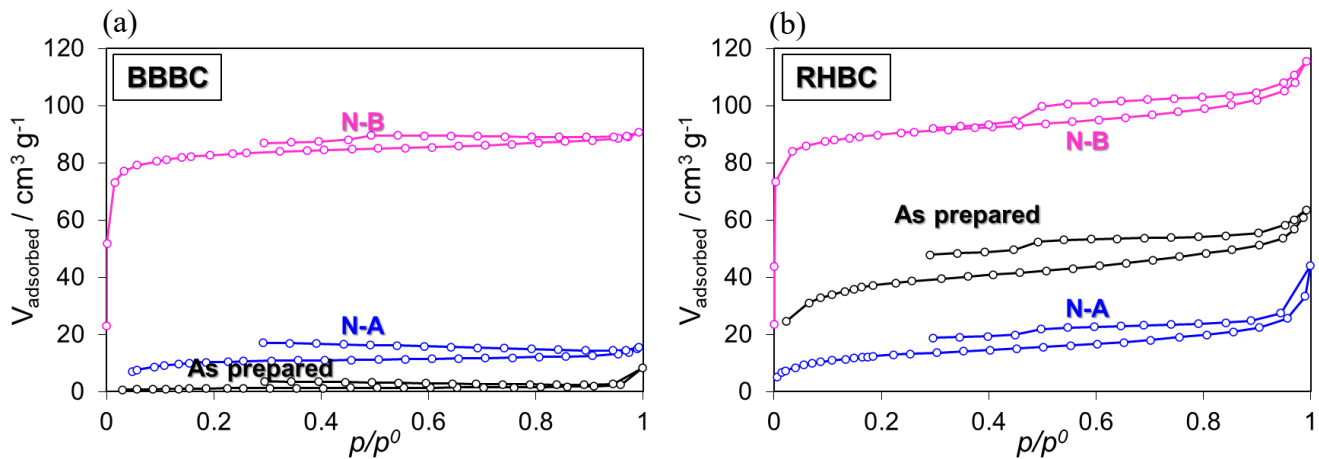


Figure 2.15: Nitrogen adsorption-desorption isotherms of the NH_3 -treated (a) BBBC and (b) RHBC.

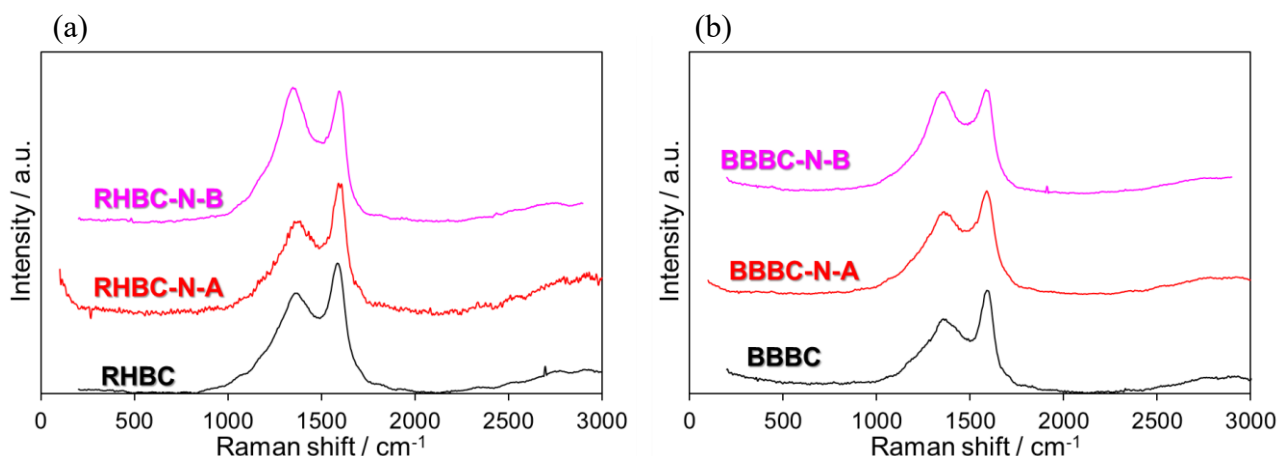


Figure 2.16: Raman spectra of the NH_3 -treated (a) BBBC and (b) RHBC samples with different treatment temperatures.

Table 2.5: Biochar samples NH_3 -treated for 120 min at different temperatures.

Sample	SSA / $\text{m}^2 \text{g}^{-1}$	V_{tot} / $10^{-7} \text{m}^3 \text{g}^{-1}$	V_{mic} / $10^{-7} \text{m}^3 \text{g}^{-1}$	Surface N / wt%	Pyridinic-N content / wt%	I_D/I_G	pH
BBBC	3.98	0.11	0.01	-	-	0.73	10.3
BBBC-N-A	35.4	0.23	0.17	1.97	-	0.80	10.8
BBBC-N-B	328	1.40	1.37	1.91	0.76	0.98	12.0
RHBC	146	1.02	0.63	-	-	0.77	9.59
RHBC-N-A	72.5	0.68	0.30	1.50	-	0.71	10.0
RHBC-N-B	354	1.78	1.43	3.69	2.29	1.03	10.3

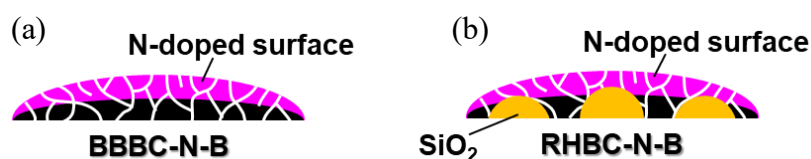


Figure 2.17: Schematic illustrations of the biochar surfaces showing the N-doping by the NH_3 treatment; (a) BBBC and (b) RHBC.

2.4.2. H_2S adsorption test

The results of the H_2S adsorption test are shown in Figs. 2.18a and 2.18b, for BBBC and RHBC, respectively. For BBBC, increasing the steam treatment time from 90 to 180 min led to a significant increase in breakthrough capacity, q_0 , and adsorption capacity, q (these values are listed in Table 2.6). This is attributed to the extension of the

mass transfer zone (MTZ) in the micropores [15]. As can be seen in the pore size distributions (Fig. 2.12a), the surface area of micropores was significantly increased by prolonging the steam treatment time (90 min $\rightarrow$ 180 min) as illustrated in Fig. 2.14a, and the resulting micropore area was considerably larger than that of the NH_3 -treated sample (BBBC-N-B). Meanwhile, q_0 of the NH_3 -treated sample was $6.90 \text{ mgH}_2\text{S g-BC}^{-1}$, higher than those of steam-treated samples (BBBC-S-A and BBBC-S-D), 2.51 and $4.00 \text{ mgH}_2\text{S g-BC}^{-1}$, respectively. The volume of micropores within BBBC-N-B was smaller than those within the steam-treated samples, and after breakthrough, the increase rate of H_2S concentration was faster than those of the steam-treated samples (see Fig. 2.18a). These results suggest that, unlike the steam-treated samples, the main adsorption sites of the NH_3 -treated sample exist in the surface region, and MTZ in the micropores is not well utilized due to strong interaction between H_2S and N-doped surface. To enhance q of the NH_3 -treated biochar, this interaction should be mildly suppressed so that sulfur species can diffuse well into the MTZ.

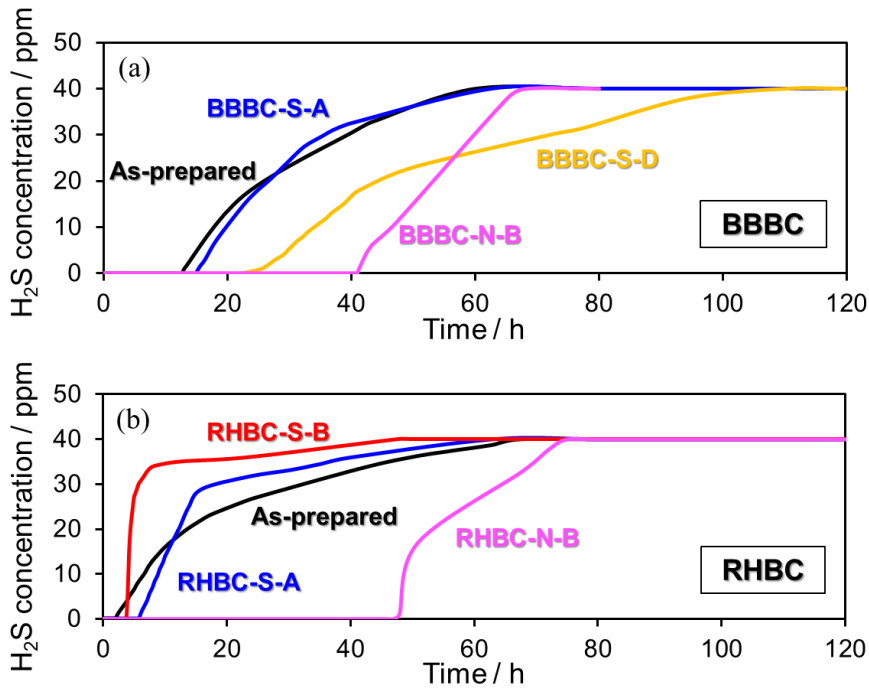


Figure 2.18: Results of H_2S adsorption test for (a) BBBC and (b) RHBC.

For RHBC, intense steam treatment at $1,000^\circ\text{C}$ (RHBC-S-B) is not a good way to increase q_0 and q due to the presence of a large amount of SiO_2 , which is exposed by the excessive steam etching (see Fig. 2.14b). The change in surface chemistry is more important for RHBC. Similar adsorption behaviors of BBBC-N-B and RHBC-N-B indicate that the doped N plays the main role in the H_2S adsorption. H_2S adsorption

behaviors on the surface of the prepared biochars are schematically summarized in Fig. 2.19.

Table 2.6: H₂S adsorption capacity of the prepared biochars.

Sample	q_0 / mgH ₂ S g-BC ⁻¹	q / mgH ₂ S g-BC ⁻¹	q / mgH ₂ S g-C ⁻¹
BBBC	2.18	4.83	5.86
BBBC-S-A	2.51	5.11	6.27
BBBC-S-D	4.00	9.24	11.3
BBBC-N-B	6.90	8.91	11.3
RHBC	0.27	2.54	5.32
RHBC-S-A	0.73	2.22	5.18
RHBC-S-B	0.67	1.38	3.22
RHBC-N-B	8.02	9.58	21.7

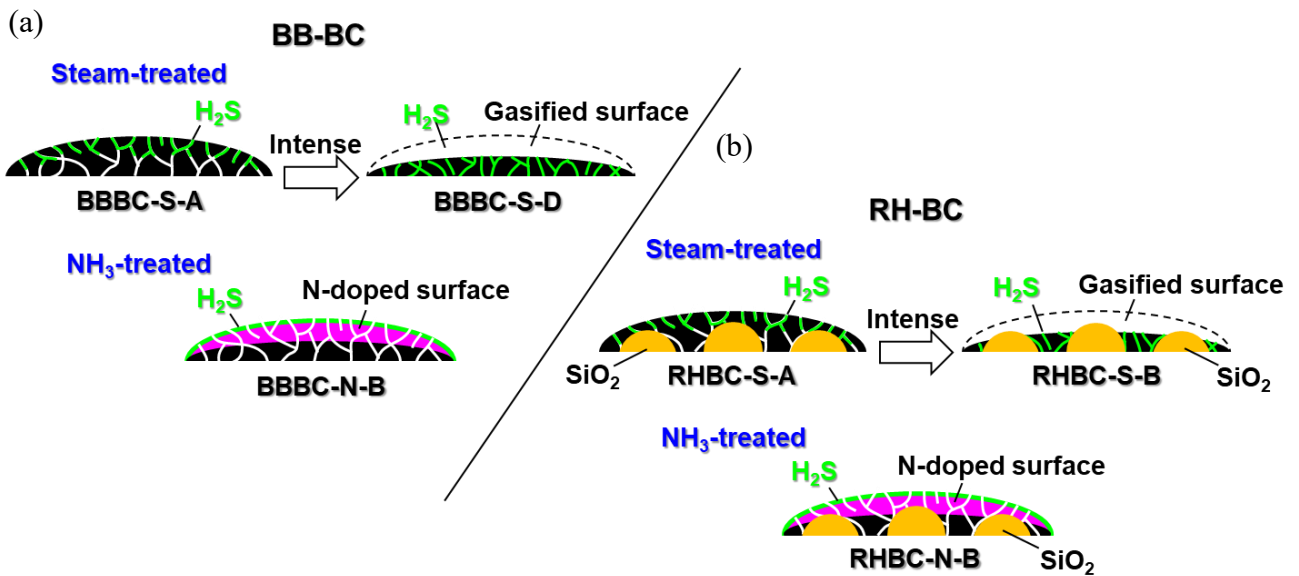


Figure 2.19: Schematic illustrations of the biochar surfaces to explain the H₂S adsorption behavior; (a) BBBC and (b) RHBC.

The surface chemistry of the NH₃-treated biochars was analyzed by XPS. Before the H₂S adsorption test (Figs. 2.20a and c), a high proportion of pyridinic-N (398 eV) [16], indicating N-doping at the edge and the defects of the carbon structure, was detected for both NH₃-treated biochars (BBBC-N-B and RHBC-N-B). Meanwhile, the peak of oxidized nitrogen (nitrate) (407.5 eV) [17] can be seen only for BBBC-N-B. Although the reason for the nitrate formation only on the surface of BBBC is not clear, considering

the existence of carboxylic species ($\text{O}-\text{C}=\text{O}$) on the surface of the pristine BBBC (see $\text{C}1\text{s}$ XPS spectrum of Fig. 2.21a), the alkaline components in BBBC (The surface of BBBC is more basic compared to RHBC as shown in Table 2.5.) can increase the surface affinity with O_2 and CO_2 which can oxidize the surface nitrogen such as pyridinic-N to nitrate [18].

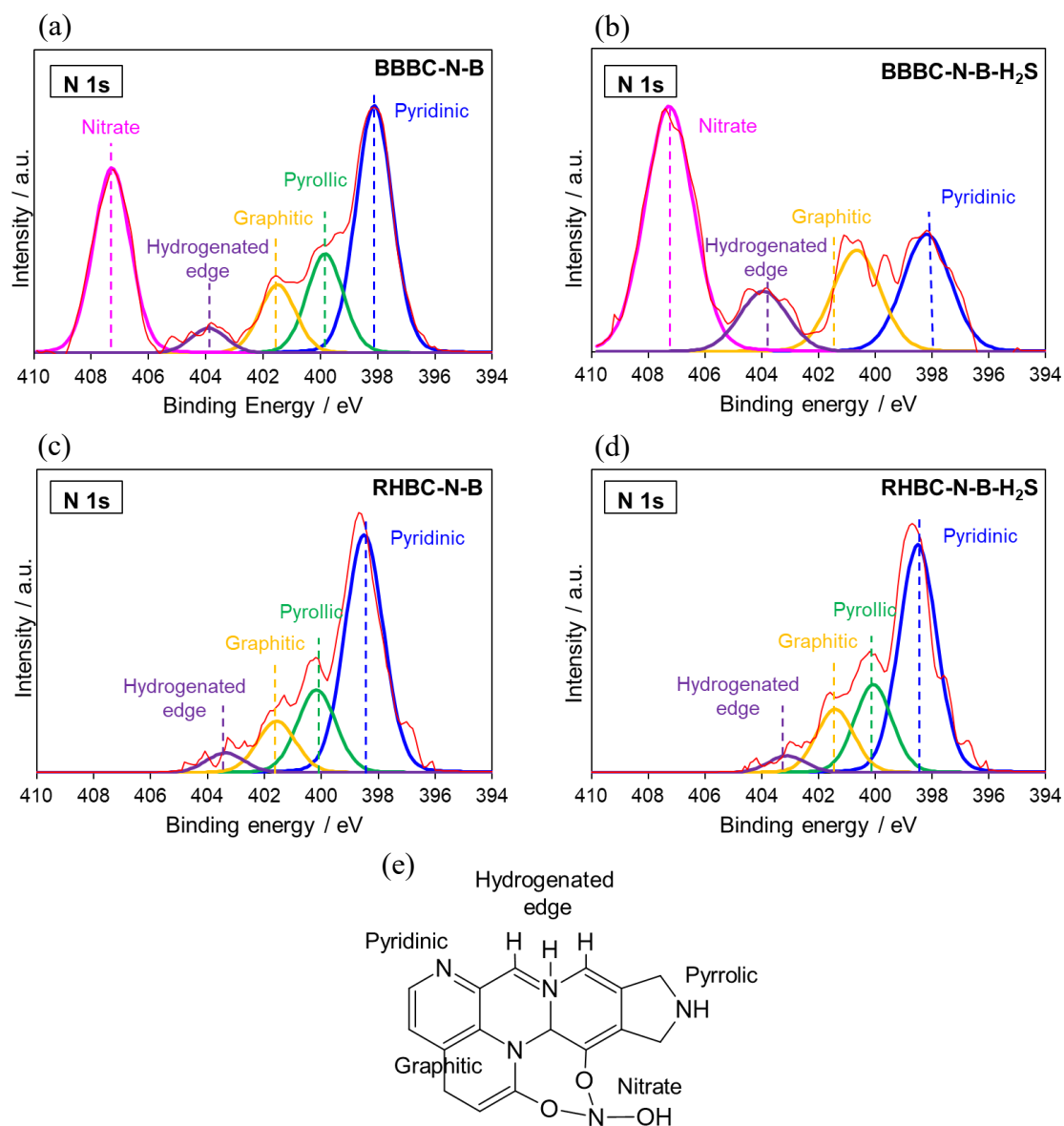


Figure 2.20: XPS $\text{N} 1\text{s}$ profiles for (a,b) BBBC-N-B and (c,d) RHBC-N-B; (a,c) before and (b,d) after the H_2S adsorption test. (e) is the schematic drawing of the nitrogen species doped on the surface detected by XPS. All spectra were obtained with 8 scans.

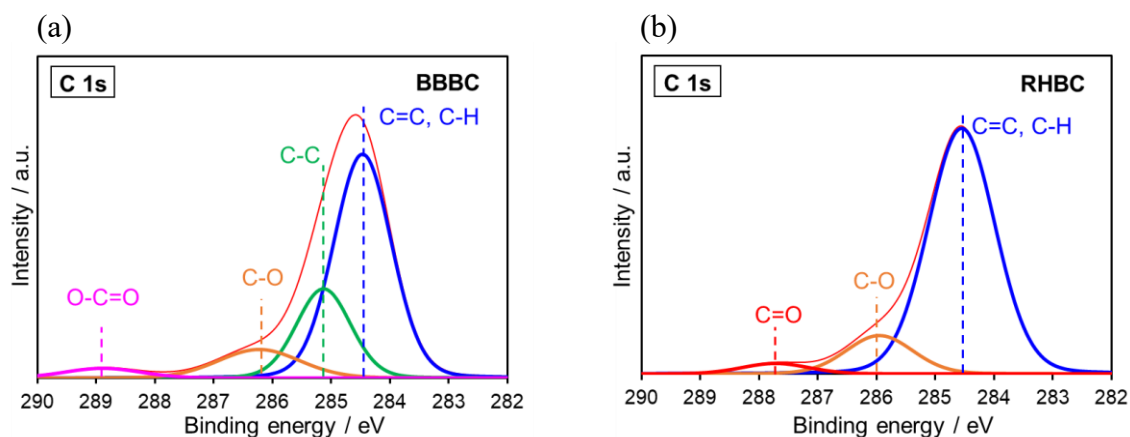


Figure 2.21: XPS C 1s profiles for (a) as-prepared BBBC and (b) as-prepared RHBC. All spectra were obtained with 8 scans.

The pyridinic-N site has stronger interaction with sulfur species compared to the other N-doped sites such as nitrate sites (to be discussed in Chapter 3), and therefore the pyridinic/nitrate ratio should be as high as possible in order to develop an excellent H₂S adsorbent.

As shown in Fig. 2.22, for both NH₃-treated biochars, BBBC-N-B and RHBC-N-B, after the H₂S adsorption test, peaks assigned to sulfur (~164 eV) and oxidized sulfur (sulfate) (~168 eV) [19,20] appeared. The sulfate peak was more pronounced for BBBC-N-B. This would be due to more alkaline surface confirmed by the pH measurement (Table 2.5), which can promote the adsorption of the acidic H₂S on the surface (mainly pyridinic-N site), resulting in the accumulation of sulfur followed by its oxidation with the surface oxygen [5]. Then, the sulfate would cover the pyridinic-N site to reduce the pyridinic-N peak as shown in Fig. 2.20b. In the case of RHBC-N-B, even after the H₂S adsorption test, the pyridinic-N peak was still strong. As indicated in Table 2.6, when the H₂S adsorption capacity of biochar, q , per weight of carbon is considered, the adsorption capacity of RHBC-N-B was twice that of BBBC-N-B, which would be due to the higher content of pyridinic-N on the surface of the carbon.

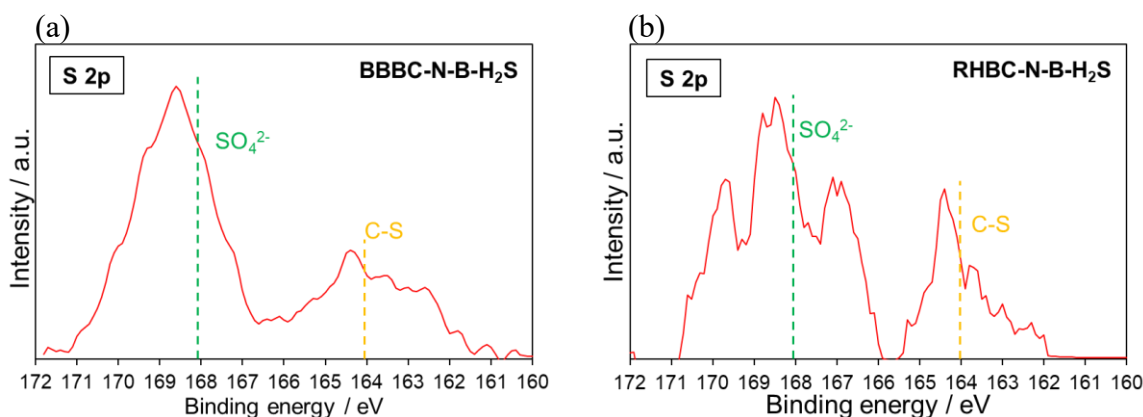


Figure 2.22: XPS S 2p profiles for (a) BBBC-N-B and (b) RHBC-N-B after the H₂S adsorption test. All spectra were obtained with 8 scans.

As mentioned above, the challenge is to enhance the utilization rate of MTZ by a milder N-doping. In addition, for N-doping, the use of pure ammonia gas is not realistic in terms of availability especially in a rural area. Utilization of digestate liquid containing over 2,000 ppm of NH₄⁺ as the ammonia source is an attractive approach to solve the above two issues simultaneously.

2.4.3. Comparison with commercial desulfurizers

H₂S adsorption capacities of the biochars of this chapter together with the commercial and the reported desulfurizers are summarized in Table 2.7. The steam-treated sample, BBBC-S-D, had higher q_0 and q than those of Chemviron carbon and SBA-15 with similar SSAs. More basic surface of BBBC-S-D (pH = 10.3) may have better affinity with H₂S compared to Chemviron carbon (pH = 9.40) and SBA-15 composed only of silica (pH < 7).

In spite of smaller surface area, the NH₃-treated biochars (BBBC-N-B and RHBC-N-B) exhibited higher q_0 and q than those of the commercial activated carbon (Chemviron carbon), indicating the importance of surface chemistry rather than surface area. Main components of CECA 13x are Al₂O₃, Fe₂O₃, MgO, etc. at 85wt%. Even though CECA 13x has lower SSA compared to the other desulfurizers, it exhibited considerably larger q_0 and q , showing the positive effect of alkali components.

As shown in Table 2.7, q_0 and q of BBBC increased 2- and 3-fold, respectively, when subjected to the NH₃ treatment, indicating the enhancement of surface affinity with H₂S by N-doping. On the other hand, 30- and 4-fold increases, respectively, were confirmed for RHBC. This larger increase rate comes from the higher N-doping level

compared to BBBC with more basic surface. Among the prepared biochars in this chapter, RHBC-N-B exhibited largest q_0 and q . In the next step of this study aiming at maximizing the H₂S adsorption capacity of biochar, deeper discussions on the effect of N-doping are made focusing on RHBC.

Table 2.7: H₂S adsorption capacities of the biochars of this chapter together with the commercial and the reported desulfurizers.

Product name	SSA / m ² g ⁻¹	V_{mic} / 10 ⁻⁷ m ³ g ⁻¹	q_0 / mg H ₂ S g-BC ⁻¹	q / mg H ₂ S g-BC ⁻¹	Ref.
BBBC	3.98	0.01	2.18	4.83	This study
BBBC-S-D	928	4.26	4.00	9.24	This study
BBBC-N-B	328	1.37	6.90	8.91	This study
RHBC	146	0.63	0.27	2.54	This study
RHBC-S-B	386	2.90	0.67	1.38	This study
RHBC-N-B	354	1.43	8.02	9.58	This study
Chemviron Carbon ¹⁾	930	3.8	1.3	8	[21]
CECA 13X ²⁾	700	2.6	46	177	[22]
SBA-15 ³⁾	950	13.1	0.54	1.09	[23]
IRMOF-3 ⁴⁾	2200	-	10.6	15.4	[24,25]

1) Coconut-based activated carbon manufactured by Chemviron Ltd. (Commercial)

2) 13X zeolite manufactured by Arkema S.A. (Commercial)

3) Molecular sieve made from Pluronic P123 and TEOS in HCl

4) Zinc-based metal-organic framework, a Zn impregnated N-doped carbon made by dissolving NH₂-BDC (carbon precursor) and Zn(NO₃)₂ in DMF

All desulfurizers were tested in dry condition at ambient temperature. Chemviron carbon and CECA13x were tested using 80 ppm H₂S at 4000 mL min⁻¹ for 10 g adsorbent. SBA-15 was tested using 4000 ppm H₂S at 100 mL min⁻¹ for 1.0 g adsorbent. IRMOF-3 was tested using 0.1 ppm H₂S at 100 mL min⁻¹ for 0.25 g adsorbent.

2.5. Conclusions

It was revealed that the biochar prepared in this study has a potential to be utilized as a H₂S adsorbent, when compared to commercial desulfurizers such as Chemviron carbon and SBA-15. To maximize its adsorption ability, modification of the surface morphology and chemistry must be investigated. This study revealed that steam and ammonia treatments effectively increased the breakthrough capacity of H₂S (q_0) and the total H₂S adsorption capacity (q) of the bamboo- and rice husk-derived biochars, abbreviated as BBBC and RHBC, respectively. As for the RHBC, intense steam treatment must be avoided so as not to expose SiO₂ on the surface which negatively affects the enhancement of H₂S absorption ability. NH₃ treatment, which can affect the change in surface chemistry (to form pyridinic-N sites) rather than surface morphology, was considerably effective to increase the q of the biochars, however, for further enhancement of q , the interaction between H₂S and N-doped surface must be controlled to increase the utilization rate of MTZ in the micropores.

One of the promising approaches is the treatment with low-concentration NH₃ evaporated from digestate liquid to perform mild N-doping on the surface. As mentioned in Chapter 1, digestate liquid can be used as a source of NH₃ for the treatment of biochars to produce biomass-derived H₂S adsorbent. Furthermore, the N-doped biochar spent as a desulfurizer can be used as a N- and S-containing fertilizer for crop cultivation.

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CHAPTER III

Enhancement of the H₂S Adsorption Capacity of Biochar by NH₃ Treatment

3.1. Introduction

In Chapter 2, heat treatment of biochar in NH₃ gas to dope nitrogen (N) was proven to be a more effective method for the enhancement of the H₂S adsorption capacity (q_0 and q) compared to steam treatment. However, in rural areas, the use of pure NH₃ gas is not a viable approach in terms of cost and availability.

Biogas is produced by the anaerobic fermentation of biowaste. In this process, a large amount of digestate liquid is discharged, which is sometimes used as a liquid fertilizer [1]. This contains ammonium ions (NH₄⁺) with a concentration of 0.15–0.7 wt%, depending on the type of biomass feedstock [2]. If the digestate liquid is concentrated to 10wt% NH₄⁺, for example, via distillation and/or electrodialysis, it could be utilized as a convenient and sustainable source of NH₃ for N-doping of biochar.

3.2. Objective

For rice husk biochar (RHBC), the effect of N-doping via high temperature treatment with NH₃ evaporated from NH₄⁺ aqueous solution (N2 treatment) is studied and compared with the method using NH₃ gas from a cylinder (N1 treatment). Formation mechanism of oxygen radicals is studied by DFT calculation to find out the main nitrogen functional group affecting H₂S adsorption. Then, feasibility of the N-doped RHBC by N2 treatment (RHBC-N2) as a desulfurizer is assessed.

3.3. Experimental

3.3.1. Production and N-doping of biochar

Rice husk obtained from Japonica rice (*Oryza sativa* subs. Japonica) was collected from the Itoshima area of Fukuoka prefecture in Japan. This was first dried at 100°C for 24 h in air. Then, 3 g of dried rice husk was pyrolyzed at 500°C under flowing N₂ gas (50 mL min⁻¹) for 120 min, to produce rice husk biochar (RHBC). N-doping of RHBC was performed using two different methods. In the first method, 2 g of RHBC was heat treated for 120 min at 900°C in flowing NH₃ and N₂ (25:75vol%) with a total flow rate of 100 mL min⁻¹ (Fig. 3.1a). This sample is labelled RHBC-N1. In the second method, an NH₄⁺ solution was prepared with a concentration of 10wt% to simulate concentrated digestate liquid. Carrier gas (N₂) was bubbled through this solution at 100 mL min⁻¹ at 30°C (Fig. 3.1b), and the resulting gas flow is calculated to have an NH₃ content of 15.7vol% and a water content of 3.8vol%. Then, 2 g of RHBC was heated treated in this NH₃-rich gas at 850°C for 270 min. This sample is labelled RHBC-N2.

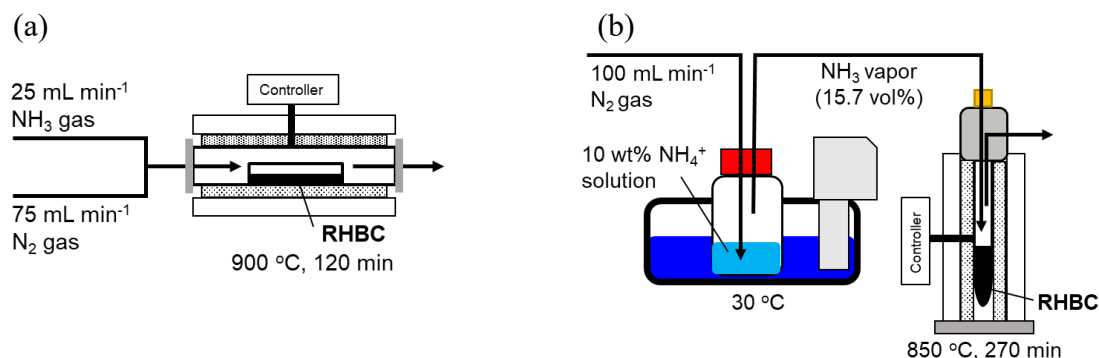


Figure 3.1: Schematic illustration of different methods to dope rice husk biochar with nitrogen: (a) using NH₃ gas from a cylinder, and (b) using N₂ gas bubbled through a 10wt% NH₄⁺ solution, simulating digestate liquid.

3.3.2. Fabrication of a paper-structured biochar

Paper-structured biochar was prepared using a paper-making process based on the dual polymer retention system [3]. First, 6 g of ceramic fiber (75wt% SiO₂-25wt% CaO(+MgO), Ibiden Ltd., Japan) was dispersed in 1 L of distilled water. Then, 15 g of a 2wt% solution of cationic polymer (poly(diallyldimethylammonium chloride, Sigma-

Aldrich LCC, USA) was mixed into the slurry and stirred for 3 min, followed by the addition of 6 g of biochar (either RHBC or RHBC-N2) and stirred for a further 3 min. Subsequently, 16.3 g of a 0.2wt% solution of anionic polymer (acrylamide-co-acrylic acid, Fujikasui Engineering Co., Ltd.) was mixed in and stirred for a further 3 min.

The resulting slurry was filtrated to obtain a wet-state paper-like sheet with a diameter of 16 cm. This was pressed at 350 kPa for 3 min and dried at 100°C overnight. The dried paper was cut into small pieces with a diameter of 15 mm. These pieces were then heat-treated at 800°C for 5 h under flowing nitrogen (50 mL min⁻¹) to remove the organic components and form the ceramic fiber network. The resulting paper-structured biochars are herein labelled as PS[RHBC] and PS[RHBC-N2].

3.3.3. Sample characterization

The specific surface area (SSA) was measured via the nitrogen adsorption method (Belsorp-mini II analyzer, MicrotracBEL Corp., Japan), and the pore size distribution was evaluated via the MP micropore analysis method.

Microstructures were investigated by field emission scanning electron microscope (FESEM-S5200, Hitachi High-Technologies Corp., Japan) using an energy-dispersive X-ray spectrometer (EDX).

For near-surface analysis, quasi-surface-sensitive technique using X-ray photoelectron spectroscopy (XPS) was done at room temperature using a monochromated Al K α ($h\nu = 1,486.7$ eV). X-ray source was operated at 5 mA and 15 kV (Kratos Axis Ultra, Shimadzu, Japan). All binding energies (BEs) were referred to the C1s line at 284.6 eV.

3.3.4. Hydrogen sulfide (H₂S) adsorption test

Details of the H₂S adsorption test were described in Sec. 2.3.4.

3.3.5. DFT calculation

Density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) [4–6]. The Perdew-Burke-Ernzerhof (PBE) [7] exchange-correlation functional was employed based on the projector-augmented wave (PAW) method [6]. The cutoff energy of the plane wave basis was set to 400 eV following previous study [8]. Firstly, 4 x 4 graphene sheet was constructed and optimized using 5 x

5 x 1 Monkhorst-Pack k-points mesh. Also, the spin polarization was considered. Pseudopotentials with valence states of C ($2s^2, 2p^2$), N ($2s^2, 2p^3$), S ($3s^2, 3p^4$), O ($2s^2, 2p^4$), and H (1s) were used in the calculations. All ionic positions were optimized by a conjugate gradient method until the forces on each ion were below 10^{-2} eV/Å. Electronic energy was converged to 10^{-6} eV. The graphene structurally optimized by the above process showed 1.426 Å as a length of C-C bond, which was in good agreement with previous results [9–11]. Then, N-doped structures containing pyridinic-, pyrrolic-, or graphitic-N were made in the graphene sheet. To calculate the van der Waals (vdW) interaction between the graphene sheet and oxygen molecule (O_2), Tkatchenko-Scheffler method was applied [8,12]. To discuss the stability of O_2 on pyridinic-N, pyrrolic-N, or graphitic-N, the interaction energy (E_{int}) was estimated for each N-doped site. E_{int} for the pyridinic-N can be expressed as follows,

$$E_{\text{int}} = E_{O_2+\text{pyridinic-N}} - (E_{\text{pyridinic-N}} + E_{O_2}) \quad (3.1)$$

where $E_{O_2+\text{pyridinic-N}}$, $E_{\text{pyridinic-N}}$, and E_{O_2} are the electrostatic potentials of pyridinic-N with adsorbed O_2 , pyridinic-N, and O_2 , respectively [13]. The negative value of the interaction energy indicates that O_2 can be adsorbed on the pyridinic-N [14].

3.4. Results and discussion

3.4.1. Structure of N-doped biochar

The SSAs of the prepared biochar samples are summarized in Table 3.1, as measured by nitrogen adsorption. The SSA of the as-prepared RHBC was $146 \text{ m}^2\text{g}^{-1}$. After NH_3 treatment (RHBC-N1), the total pore volume (V_{tot}) and the micropore volume (V_{mic}) increased significantly, resulting in an increase in SSA to $354 \text{ m}^2\text{g}^{-1}$. This increase is caused by partial gasification (NH_3 etching) [15,16]. After NH_3 treatment using the simulated digestate liquid (RHBC-N2) the SSA and porosity did not significantly change compared to as-prepared RHBC. This may be because the NH_3 vapor (15.7vol% NH_3) in N2 treatment was unable to change the carbon structure as drastically as N1 treatment with 25.0vol% NH_3 gas.

The nitrogen (N) contents on the near-surface estimated from the XPS survey profiles shown in Fig. 3.2 are summarized in Table 3.1. N was not detected on the surface of the pristine RHBC. After NH_3 treatment (RHBC-N1), this increased to 3.69wt%, confirming that NH_3 treatment is a suitable method for N-doping. Using the simulated digestate liquid (RHBC-N2) results in a nitrogen content of 2.52wt%. N-doping has been shown to produce nitrogen functional groups on the surface by substituting oxygen bound on the carbon surface [17]. The decreases in the near-surface O from 19.2wt% to 15.7wt% and 16.9wt% for N1 and N2 treatments, respectively, indicate this substitution. The lower near-surface O content of RHBC-N1 compared to RHBC-N2 also indicates the higher degree of nitrogen-doping of the N1 treatment.

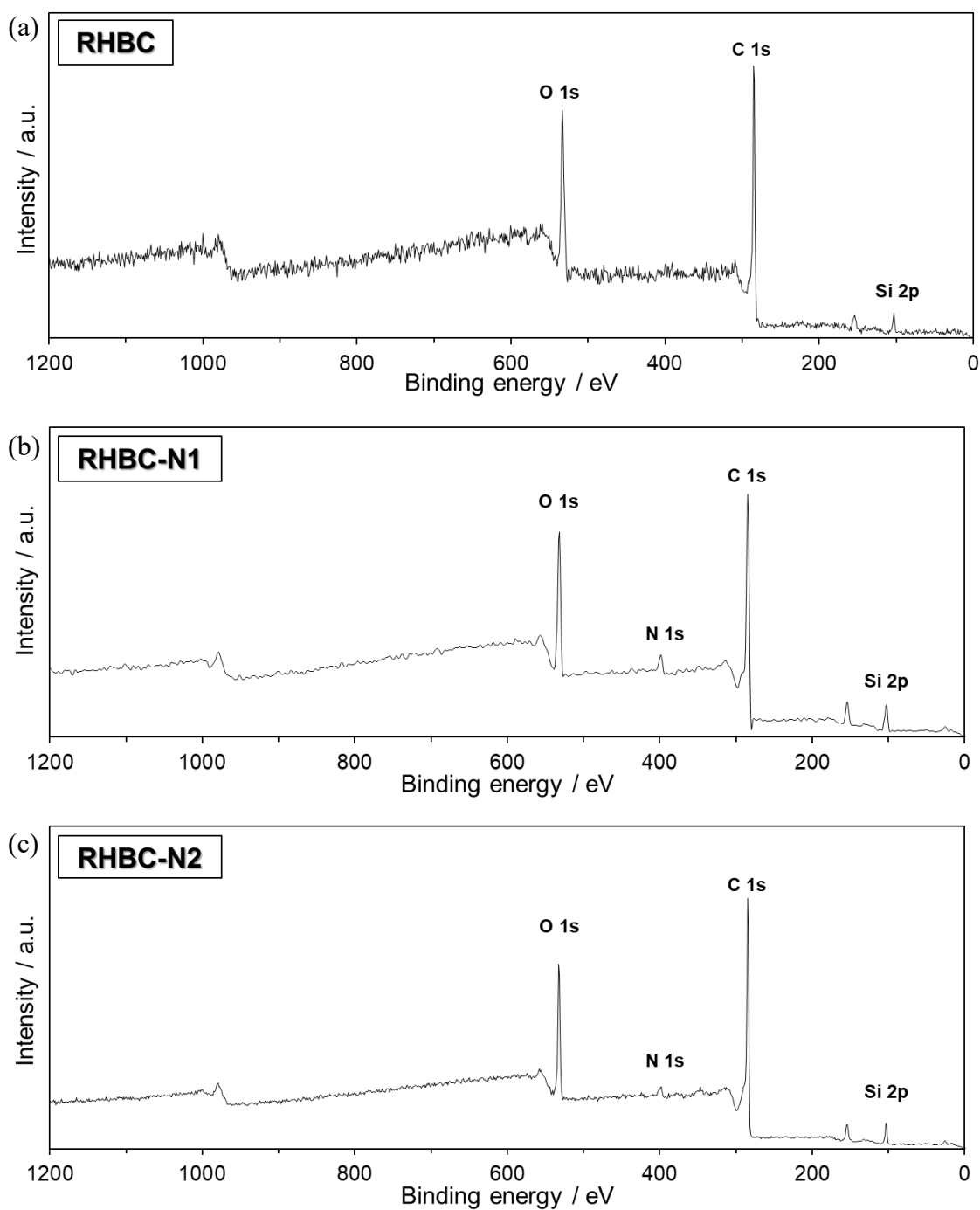


Figure 3.2: XPS survey profiles (4 scans) for: (a) RHBC, (b) RHBC-N1, and (c) RHBC-N2.

Table 3.1: Results of the BET measurement and the XPS quantification of surface element for the RHBC samples before the H₂S adsorption test.

Sample	SSA / m ² g ⁻¹	V_{tot} / 10 ⁻⁷ m ³ g ⁻¹	V_{mic} / 10 ⁻⁷ m ³ g ⁻¹	Near- surface N / wt%	Near- surface O / wt%	Pyridinic-N content / wt%
RHBC	146	1.02	0.63	-	19.2	-
RHBC-N1	354	1.78	1.43	3.69	15.7	2.29
RHBC-N2	170	1.02	0.68	2.52	16.9	1.31

The XPS N 1s spectra for the biochar samples are summarized in Fig. 3.3, and deconvoluted into contributions from pyridinic-, pyrrolic-, and graphitic-N nitrogen sites, as illustrated in Fig. 3.3 [18,19]. The high temperature NH₃ treatment produces thermally stable nitrogen groups, pyridinic- (dominant), pyrrolic-, and graphitic-N [20,21]. RHBC-N1 has much higher pyridinic content (2.29wt%) than RHBC-N2 (1.31wt%) due to higher concentration of NH₃ and slightly higher treatment temperature. The higher pyridinic-N content will make the surface of RHBC-N1 more active for chemically adsorbing H₂S.

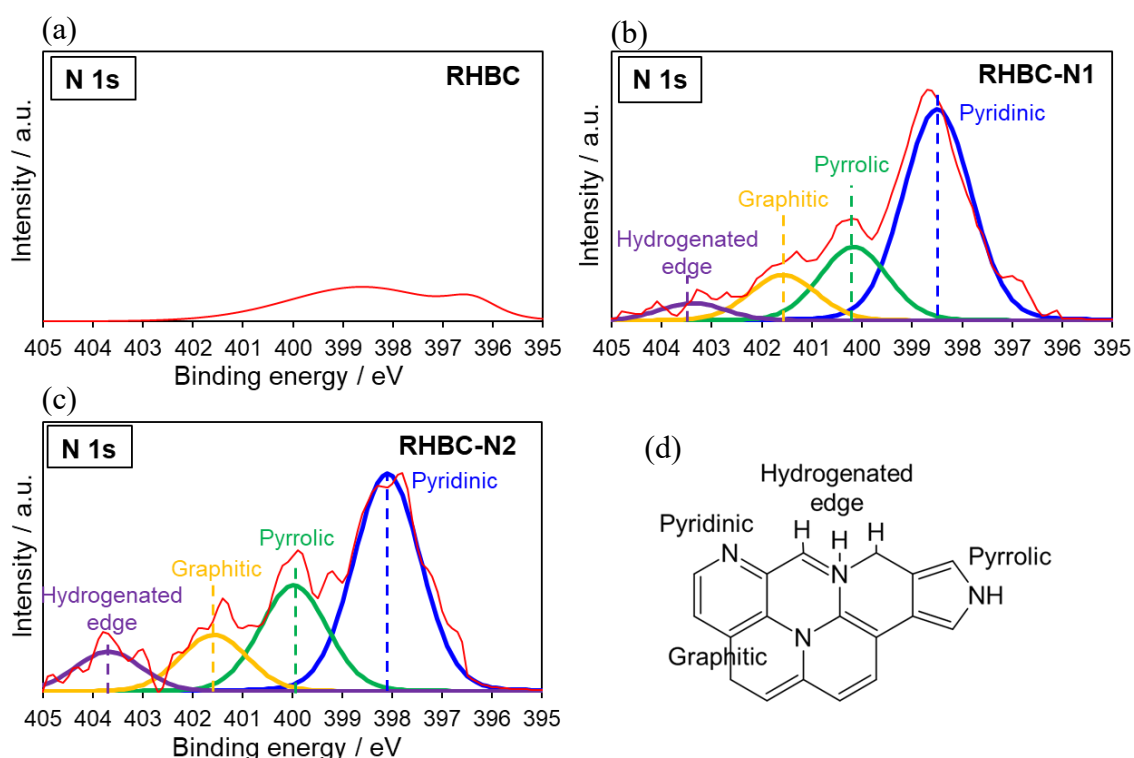


Figure 3.3: XPS N1s profiles for: (a) RHBC (8 scans), (b) RHBC-N1 (8 scans), (c) RHBC-N2 (16 scans), and (d) schematic of the main nitrogen species.

3.4.2. DFT calculations

The sulfur adsorption process (i.e. H₂S removal from a gas stream) can be described by reactions (1.7) and (1.8). A higher concentration of O* on the surface of carbon is expected to assist the reaction. It has been shown in this study that when nitrogen is doped into the carbon phase of biochar, pyridinic-N, pyrrolic-N, and graphitic-N were produced. Among these, it has been reported that pyridinic-N most promotes the formation of O* which can contribute to the promotion of oxygen reduction reaction (ORR) on the Pt-based electrocatalysts of fuel cells. As for the nitrogen-doped biochar, however, the H₂S adsorption mechanism is still not fully understood [22,23]. O₂ in the atmosphere or in the testing gas stream is considered to be an origin of O*. O₂ adsorption on graphene type structures has been reported [13]. For the formation of O*, the O-O bonds need to be broken, which is achieved by donating two more electrons to the degenerate π -molecular orbital in the oxygen molecule [24]. Pyridinic-N in the graphene structure has two unpaired electrons in the sp² hybridization orbitals, which could contribute to the dissociation of the O-O bond of the approached O₂ [25,26]. To prove this phenomenon, the following DFT simulations were performed.

Table 3.2: Interaction energy (E_{int}) between O₂ and N-doped graphene structure estimated by DFT.

Energy / eV					Interaction energy / eV	Distance of O-O bond / Å
	Initial position of O ₂	O ₂ on graphene structure	O ₂ only	Graphene structure		
Pyridinic-N	C adjacent to doped-N	-258.58	-9.85	-248.02	-0.71	1.23
	Doped-N	-260.98	-9.85	-248.02	-3.12	Broken
Pyrrolic-N	C adjacent to doped-N	-279.47	-9.85	-267.63	-2.00	1.44
	Doped-N	-279.47	-9.85	-267.63	-2.00	1.57
Graphitic-N	C adjacent to doped-N	-292.18	-9.85	-280.89	-1.45	1.32
	Doped-N	-292.21	-9.85	-280.89	-1.48	1.28

After the simulated graphene structures with pyridinic-, pyrrolic-, and graphitic-N moieties were optimized for the respective N-doped structures, an O₂ molecule was placed on the doped-N site or on the carbon adjacent to the doped-N site to compare their final configurations. The negative interaction energies shown in Table 3.2 indicate that O₂ molecule can adsorb on the graphene structure for all cases. O₂ tended to adsorb more readily on the doped-N sites than on the adjacent carbon atom. The stability of the O₂ molecule adsorbed on these nitrogen-doped graphene structures was in the order of graphitic-N < pyrrolic-N < pyridinic-N. As shown in Fig. 3.4, except for on pyridinic-N sites, the O₂ molecule remained near its initial position without decomposition. However, if the O₂ molecule was placed on the pyridinic-N site, it decomposed, and the resulting oxygen atoms were adsorbed onto the carbon atoms in the pyridinic chain, as shown in Fig. 3.4a. This result indicates that two electrons (i.e. a lone pair) from the pyridinic-N site were supplied to the O₂ molecule, and that the O-O bond was stretched and finally broken, as the origin of the O* species. The DFT calculation has confirmed the importance of pyridinic-N for H₂S adsorption and the justification of the reactions (1.7), (1.8), and (2.1)-(2.3) as the basis of the H₂S adsorption.

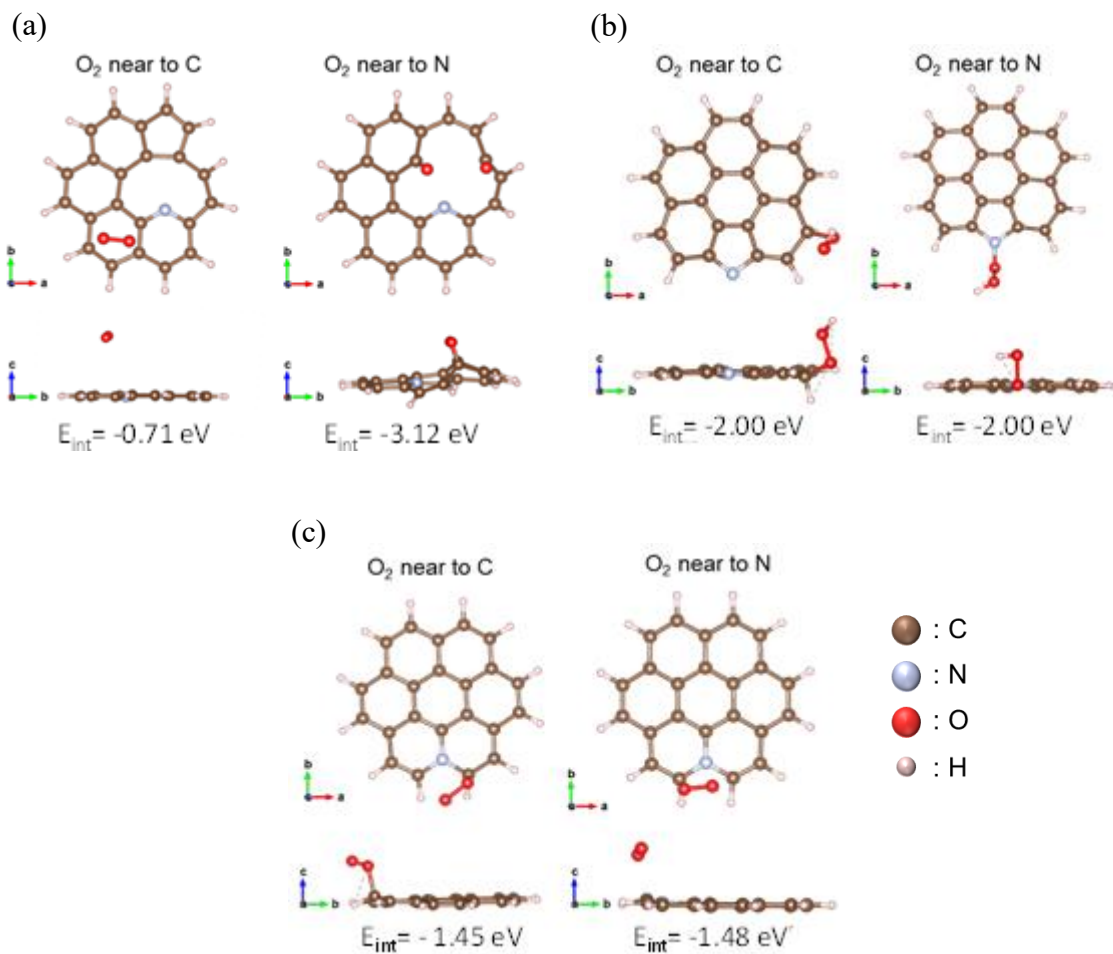


Figure 3.4: Optimized configurations for the adsorption of O_2 on (a) pyridinic-, (b) pyrrolic-, and (c) graphitic-N.

3.4.3. H_2S adsorption on powdered biochar

The H_2S adsorption results for the powdered biochar samples measured under the gas hourly space velocity (GHSV) of $1,579 \text{ hr}^{-1}$ are shown in Fig. 3.5. The breakthrough capacity (q_0) and the total adsorption capacities (q) calculated from the breakthrough curve using Equation (2.4) are summarized in Table 3.3.

As-prepared RHBC with the smallest SSA ($146 \text{ m}^2\text{g}^{-1}$) had the lowest breakthrough capacity ($0.27 \text{ mgH}_2\text{S g-BC}^{-1}$), mainly attributed to the insufficient surface alkalinity and the lack of surface N, that is fewer O^* sites that can assist H_2S adsorption. RHBC-N1 has the largest breakthrough capacity ($8.02 \text{ mgH}_2\text{S g-BC}^{-1}$), due to its highest pyridinic-N content on the near-surface (2.29wt%) (Table 3.1), resulting in enhanced affinity with H_2S , as confirmed by the DFT calculations in the previous section. Due to

this high affinity combined with large SSA, the rate of reaction in equation (1.8) is relatively fast. The q_0 of RHBC-N2 (3.96 mgH₂S g-BC⁻¹) was only around half that of RHBC-N1 (Table 3.3) attributed to the lower content of pyridinic-N on the near-surface (1.31wt%) as well as lower SSA (170 m²g⁻¹) (Table 3.1).

Meanwhile, q of as-prepared RHBC (2.54 mgH₂S g-BC⁻¹) is again the lowest of all the biochar samples. The value for RHBC-N1 is about 4 times larger (9.58 mgH₂S g-BC⁻¹), again attributed to the existence of pyridinic-N sites and the enhanced porosity (Table 3.1). However, in this case, q of RHBC-N2 (23.0 mgH₂S g-BC⁻¹) is the highest despite having lower nitrogen content and lower porosity compared to RHBC-N1. The reasons for this are elaborated upon in the following paragraphs.

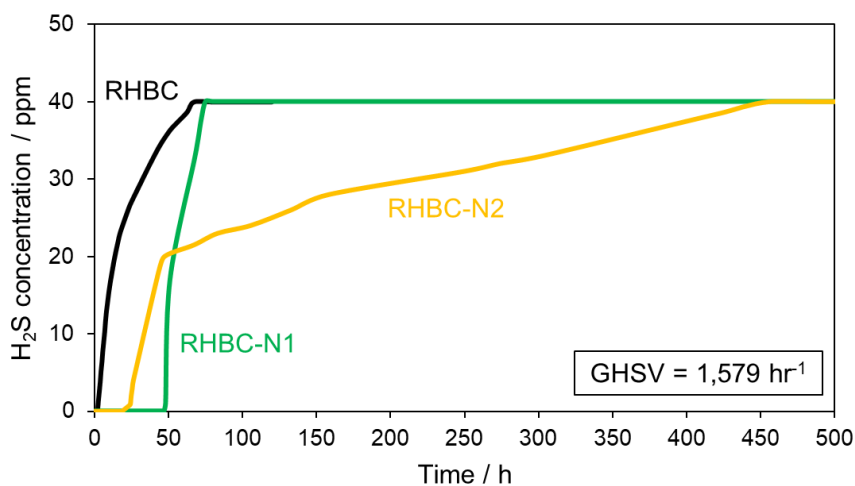


Figure 3.5: Results of H₂S adsorption tests for the powdered RHBC samples.

Table 3.3: Breakthrough H₂S adsorption capacity (q_0) and total H₂S adsorption capacity (q) of the powdered and the paper-structured RHBC samples.

Sample		q_0 / mgH ₂ S g-BC ⁻¹	q / mgH ₂ S g-BC ⁻¹
Powdered	RHBC	0.27	2.54
	RHBC-N1	8.02	9.58
	RHBC-N2	3.96	23.0
Paper-structured	PS[RHBC]	1.30	14.7
	PS[RHBC-N2]	8.71	96.1

To gain more insight into the adsorption mechanism, and the differences in capacity between the samples, XPS S 2p profiles were measured on RHBC-N1 and RHBC-N2, after H₂S adsorption tests (Fig. 3.6).

In the case of RHBC-N1, a relatively high proportion of sulfate species (~ 168 eV) is observed compared to sulfur species (~ 164 eV) [27,28]. The presence of sulfates is attributed to the high proportion of pyridinic-N, namely O*, which can oxidize HS⁻ to form sulfate as expressed by reactions (2.1)-(2.3).

Meanwhile, for RHBC-N2, a higher proportion of C-S bonds (~ 164 eV) is observed compared to sulfate species (~ 168 eV) [29]. This is attributed to the lower proportion of pyridinic-N and associated O* species, suppressing sulfate formation.

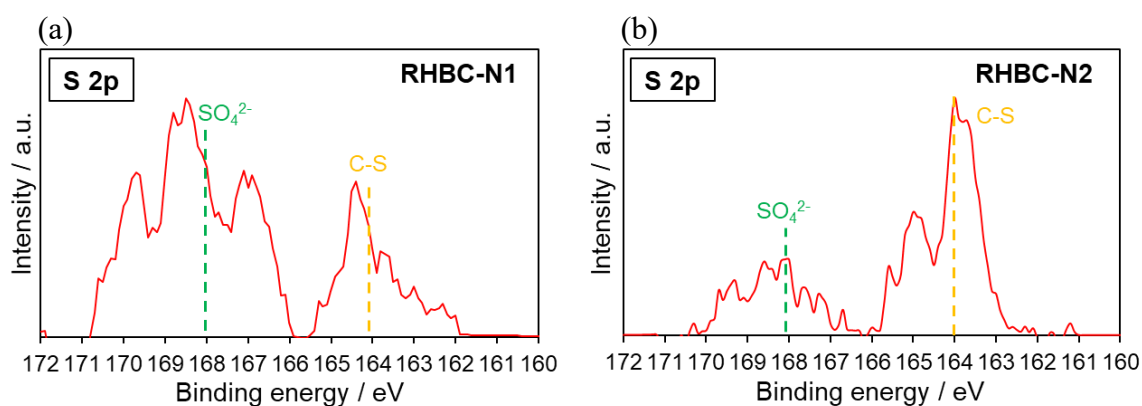


Figure 3.6: XPS profiles for S 2p after the H₂S adsorption tests (see Fig. 3.5); (a) RHBC-N1 (8 scans) and (b) RHBC-N2 (32 scans).

The SSA, pore volume and near-surface sulfur (S) contents after the H₂S adsorption test are summarized in Table 3.4. The near-surface S content after the H₂S adsorption estimated from the XPS profiles measured in the vacuum condition (see Fig. 3.7) indicates the retention of sulfur species. S could not be detected on the surface of the spent RHBC. The near-surface S content of the spent RHBC-N1 was only 1/7 of the spent RHBC-N2, even though the q of RHBC-N1 was about half that of RHBC-N2. The S peak of Fig. 3.7b was shifted to higher binding energy side compared to that in Fig. 3.7c due to higher content of sulfate in RHBC-N1 compared to RHBC-N2 as confirmed in Fig 3.6. This indicates that sulfate adsorbed on the surface of RHBC-N1 are more easily detached from the surface under vacuum conditions compared to the case of RHBC-N2.

Table 3.4: Results of the BET measurement and the XPS quantification of near-surface S content for the RHBC samples after the H₂S adsorption test.

Sample	SSA / m ² g ⁻¹	V_{tot} / 10 ⁻⁷ m ³ g ⁻¹	V_{mic} / 10 ⁻⁷ m ³ g ⁻¹	Near-surface S / wt%
RHBC	11.3	0.27	0.01	-
RHBC-N1	270	1.44	1.11	0.37
RHBC-N2	16.1	0.33	0.01	2.51

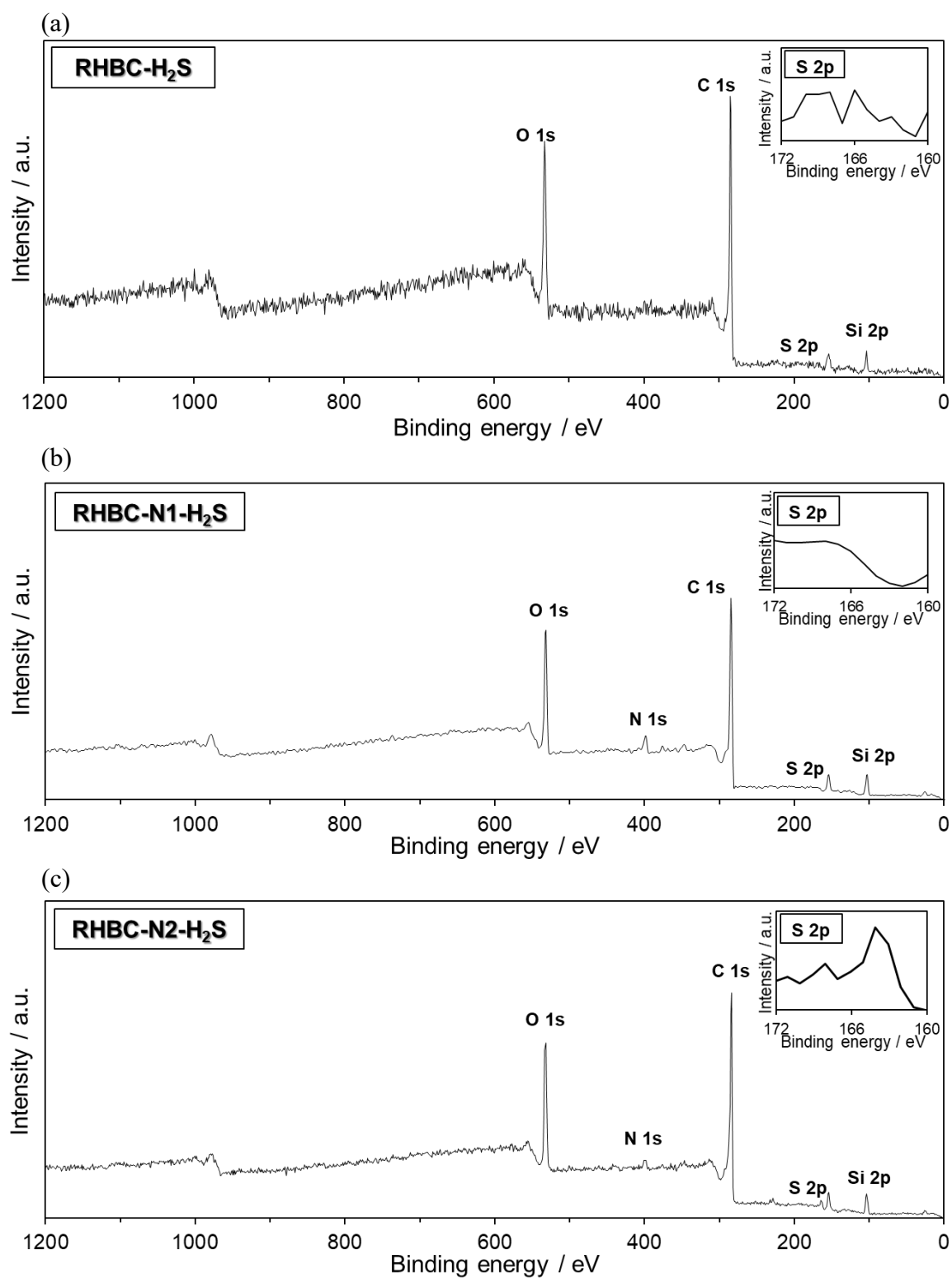


Figure 3.7: XPS survey profiles (4 scans) after the H_2S adsorption tests (see Fig. 3.6); (a) RHBC; (b) RHBC-N1; and (c) RHBC-N2. Inset is the focus of S 2p.

The pore size distributions of RHBC, RHBC-N1 and RHBC-N2 before and after H₂S adsorption tests are shown in Fig. 3.8. Before the adsorption test, among the tested samples, RHBC-N1 had the highest proportion of micropores. After the H₂S adsorption test, there is only a small decrease in the fraction of accessible micropores. This indicates that the utilization rate of micropores in this sample for H₂S adsorption is relatively low. From the comparison between the values listed in Tables 3.1 and 3.4, it is clear that RHBC and RHBC-N2 lost almost all of their micropore volume after H₂S adsorption, whereas RHBC-N1 lost only around 20%, indicating that the adsorbed sulfur did not well penetrate into the micropores of RHBC-N1. As shown in Fig. 3.6, the dominant sulfur species on the spent RHBC-N1 was sulfate resulting from the higher content of O*. The low retention of sulfur species of RHBC-N1 under the vacuum condition is probably derived from the sulfate species existing outside the micropores.

However, in the case of RHBC-N2, before the H₂S adsorption test, the proportion of micropores is lower than for RHBC-N1, as reflected in the lower surface area and pore volume (Table 3.1). After the H₂S adsorption test, the proportion of micropores in RHBC-N2 is dramatically decreased. Even under vacuum conditions, the adsorbed sulfur (C-S) does not easily desorb. This suggests that the micropores are almost completely filled with adsorbed sulfur species, corresponding to high micropore utilization rate, and providing an explanation for the higher measured total adsorption capacity despite the lower SSA and pore volume.

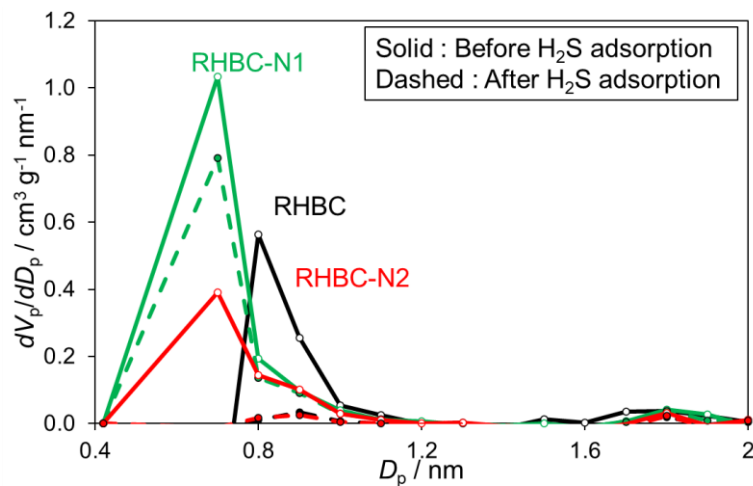


Figure 3.8: Pore size distributions of RHBC, RHBC-N1 and RHBC-N2 before and after H₂S adsorption tests (see Fig. 3.6), obtained from nitrogen adsorption/desorption isotherms using the MP method. V_p is the pore volume and D_p is the pore diameter.

The proposed reason for the difference in adsorption behavior between RHBC-N1 and RHBC-N2 is described schematically in Fig. 3.9. For RHBC-N1, the higher abundance pyridinic-N sites result in a high proportion of O* species on the surface (as confirmed by XPS). These promote the formation of sulfur via H₂S adsorption. However, it is proposed that the formation rate of sulfur is higher than the diffusion rate into the micropores, resulting in an accumulation of sulfur on the surface. This accumulated sulfur is then further oxidized to form sulfate, as observed by XPS after adsorption tests. This sulfate prevents subsequent diffusion of sulfur into the micropores, limiting the total H₂S adsorption capacity. This is consistent with the fact that this sample has the highest breakthrough capacity, but low total adsorption capacity. In short, the micropores are not well utilized as adsorption sites in this case.

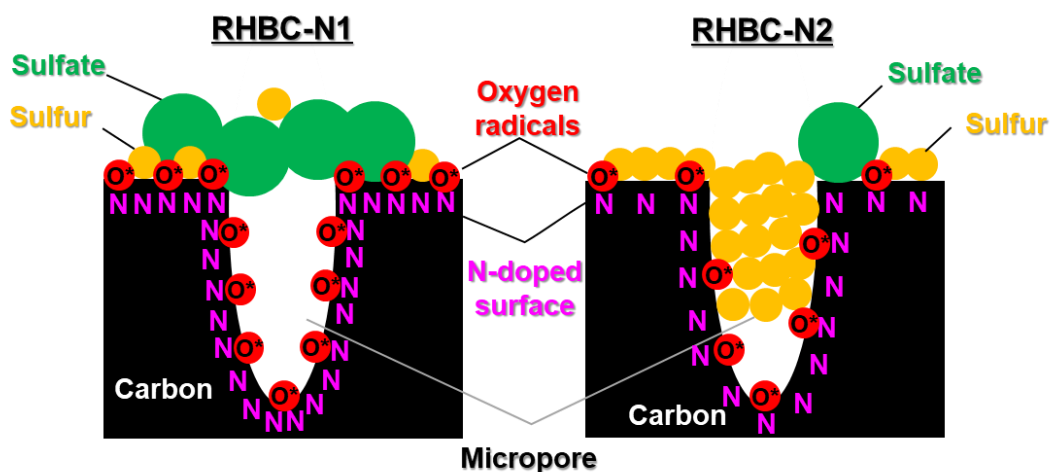


Figure 3.9: Schematic illustration explaining the difference in H₂S adsorption behavior between RHBC-N1 and RHBC-N2.

On the other hand, the total adsorption capacity of RHBC-N2 is double that of RHBC-N1, despite the lower nitrogen content. In this case, it is proposed that lower nitrogen content leads to a lower abundance of O* species on the surface. This keeps the sulfur formation rate below the diffusion rate, meaning that diffusion of sulfur into the micropores can occur unhindered by sulfate formation. This is confirmed by the low sulfate content observed by XPS and the low micropore volume after H₂S adsorption tests. This is consistent with the low breakthrough capacity and the high total H₂S adsorption capacity.

3.4.4. Paper-structured biochar for practical application

With the aim of maximizing the total H₂S adsorption capacity of nitrogen-doped biochar, whilst improving the compatibility with practical applications, the powdered samples were formed into a porous ceramic composite using the paper-making process described in Sec. 3.3.2 (see Fig. 3.10a). The resulting “paper-structured biochar” (PS[RHBC]) are mechanically flexible and can therefore easily be mounted into the adsorbent vessel. As shown in Figs. 3.10b-d, the biochar was dispersed into the network of silica-calcia based ceramic fibers, and the space between the fibers is several tens of micrometers, allowing effective gas diffusion.

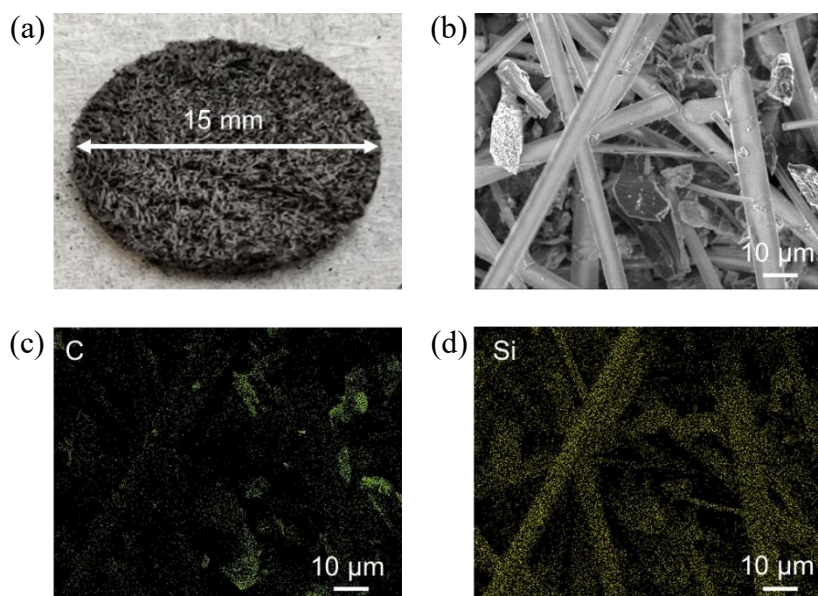


Figure 3.10: Paper-structured biochar (PS[RHBC]) prepared in this study: (a) photograph, (b) FESEM image showing the microstructure, and EDX map for (c) carbon and (d) silicon.

The results of the H₂S adsorption test for the PS[RHBC] and PS[RHBC-N₂] paper-structured samples are shown in Fig. 3.11. From these adsorption curves, the breakthrough H₂S adsorption capacity and the total H₂S adsorption capacity per gram of biochar are calculated and listed in Table 3.3. The breakthrough capacity of PS[RHBC] (1.30 mgH₂S g-BC⁻¹) was significantly higher than that of the unsupported RHBC (0.27 mgH₂S g-BC⁻¹). Similarly, the breakthrough capacity of PS[RHBC-N₂] (8.71 mgH₂S g-BC⁻¹) was higher than that of the unsupported RHBC-N₂ (3.96 mgH₂S g-BC⁻¹). The total H₂S adsorption capacity also dramatically increased by the dispersion of the biochars in

the ceramic fiber network, 2.54 and 14.7 mgH₂S g-BC⁻¹ for RHBC and PS[RHBC], respectively, and 23.0 and 96.1 mgH₂S g-BC⁻¹ for RHBC-N2 and PS[RHBC-N2], respectively. This significant increase in uptake is attributed to decrease in the GHSV from 1,579 h⁻¹ for the powdered biochar samples, to 514 h⁻¹ for the paper-structured samples. This results in higher solid/gas contact efficiency.

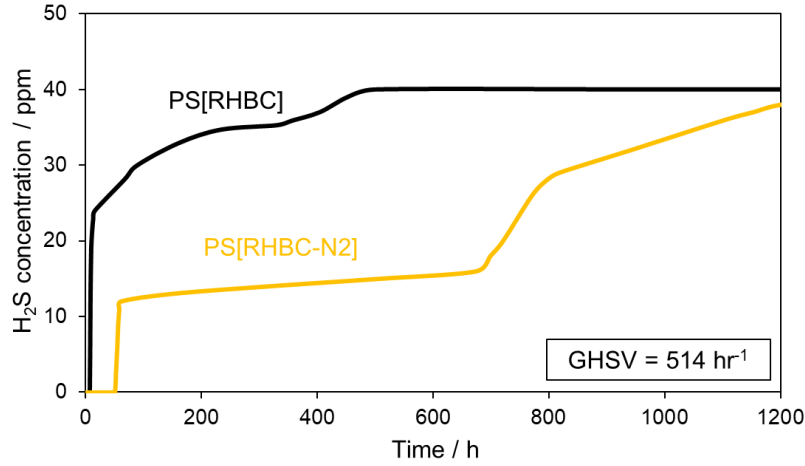


Figure 3.11: H₂S adsorption tests for the paper-structured RHBC samples.

3.4.5. Viability of nitrogen-doped biochar as a desulfurizer for SOFCs

The nitrogen-doped biochar developed in this study is intended to be used for the second step of biogas desulfurization before being supplied to an SOFC. Using the results obtained above, the mass (M_{BC}) of biochar required for 100,000 h operation for a 1 kW SOFC was estimated using the following equation:

$$Desulfurizer\ lifetime = \frac{q M_{BC}}{V_{biogas} C_{H_2S} \rho_{H_2S}} \quad (3.2)$$

where V_{biogas} is the flow rate of the biogas, C_{H_2S} is the concentration of H₂S in the biogas, and ρ_{H_2S} is the density of H₂S, 1.36 kg Nm⁻³.

In a biogas-fueled SOFC demonstration reported by Shiratori *et al.* [30], biogas passed through a desulfurizing tower packed with 40 kg of iron oxide pellets, resulting in a concentration of $C_{H_2S} = 4$ ppm. This was supplied at $V_{biogas} = 0.33$ Nm³ h⁻¹ to the SOFC system resulting in 1 kW of power generation. For continuous supply of H₂S-free biogas to the SOFC, the breakthrough capacity ($q_o = 3.96$ mgH₂S g-BC⁻¹) can be used, corresponding to a mass of 45 kg. If the adsorption capacity of powdered biochar RHBC-

N₂ is fully utilized ($q = 23.0 \text{ mgH}_2\text{S g-BC}^{-1}$), the required mass is estimated to be 7.8 kg. By using the paper-structured biochar (PS[RHBC-N₂]) ($q_o = 8.71 \text{ mgH}_2\text{S g-BC}^{-1}$), the mass needed for H₂S-free operation for 100,000 h drops to 20.5 kg, and if the adsorption capacity ($q = 96.1 \text{ mgH}_2\text{S g-BC}^{-1}$) is fully utilized, the mass needed will further drops to 1.87 kg. These estimations indicate the clear viability of using paper-structured nitrogen-doped biochar as a desulfurizer for biogas-fueled SOFC systems, as well as the feasibility of using digestate liquid as an alternative source of NH₃.

3.4.6. Comparison with commercial desulfurizers

Performance of the N-doped biochars discussed in this chapter as desulfurizer is compared with the commercial and the reported desulfurizers in Table 3.5. RHBC-N₂ showed remarkably large q_o and q compared to Chemviron Carbon (mainly used for the desulfurization of diesel fuel) despite the quite lower SSA and V_{mic} , suggesting the importance of surface chemical composition over porosity in H₂S adsorption. The performance of RHBC-N₂ was further increased by dispersing it in the ceramic fiber network (PS[RHBC-N₂]), while still far inferior to CECA 13X (mainly used for the desulfurization of natural gas). IRMOF-3 is the material based on the N-doped carbon. Its q_o larger than that of RHBC-N₂ indicates the better surface affinity with H₂S probably due to the presence of zinc in its structure. [31]. To enhance the value of RHBC-N₂ as a desulfurizer, that is, to produce H₂S-free biogas as long as possible by its application, q_o of RHBC-N₂ must be further increased. For this purpose, metal loading on the N-doped biochar is studied in the next chapter.

Table 3.5: H₂S adsorption capacities of the biochars of this chapter together with the commercial and the reported desulfurizers.

Product name	SSA / m ² g ⁻¹	V_{mic} / 10 ⁻⁷ m ³ g ⁻¹	q_0 / mg H ₂ S g-BC ⁻¹	q / mg H ₂ S g-BC ⁻¹	Ref.
RHBC-N2	170	0.68	3.96	23.0	This study
PS[RHBC-N2]	-	-	8.71	96.1	This study
Chemviron Carbon ¹⁾	930	3.8	1.3	8	[32]
CECA 13X ²⁾	700	2.6	46	177	[33]
SBA-15 ³⁾	950	13.1	0.54	1.09	[34]
IRMOF-3 ⁴⁾	2200	-	10.6	15.4	[31,35]

1) Coconut-based activated carbon manufactured by Chemviron Ltd. (Commercial)

2) 13X zeolite manufactured by Arkema S.A. (Commercial)

3) Molecular sieve made from Pluronic P123 and TEOS in HCl

4) Zinc-based metal-organic framework, a Zn impregnated N-doped carbon made by dissolving NH₂-BDC (carbon precursor) and Zn(NO₃)₂ in DMF

All desulfurizers were tested in dry condition at ambient temperature. Chemviron carbon and CECA13x were tested using 80 ppm H₂S at 4000 mL min⁻¹ for 10 g adsorbent. SBA-15 was tested using 4000 ppm H₂S at 100 mL min⁻¹ for 1.0 g adsorbent. IRMOF-3 was tested using 0.1 ppm H₂S at 100 mL min⁻¹ for 0.25 g adsorbent.

3.5. Conclusions

Biochar (BC) was prepared by the pyrolysis of rice husk (RH) for utilizing as a sustainable H₂S adsorbent for biogas-fueled SOFCs. The effect of nitrogen (N)-doping to rice husk biochar (RHBC) on the H₂S adsorption capacity was investigated via high temperature NH₃ treatment using different methods. Using pure NH₃ gas is not always feasible in rural locations, so digestate liquid containing ammonium ions was investigated as an alternative. As such, RHBC samples were doped with nitrogen either using NH₃ gas from a cylinder, or by bubbling nitrogen carrier gas through an aqueous NH₄⁺ solution.

N-doping was confirmed to be effective in increasing the total H₂S adsorption capacity (q), because the formed pyridinic-N sites, which promote the formation of oxygen radicals (O*), can catalyze the conversion of H₂S to S. Counterintuitively, higher N-doping levels resulted in lower adsorbent capacity. This was attributed to the promotion of sulfate formation, resulting in a lower micropore utilization rate.

For practical applications, a flexible paper-structured biochar was fabricated by dispersing biochar in a network of ceramic fibers. This resulted in almost a 4-fold increase in the total H₂S adsorption capacity, attributed to the lowered gas hourly space velocity, i.e. improved interaction between the H₂S gas and the biochar surface. These materials therefore meet the requirements for practical application in the second desulfurization step for supplying H₂S-free biogas to a SOFC. For 100,000 h continuous operation of 1 kW SOFC, it was calculated that just 20.5 kg of N-doped biochar would be required to obtain H₂S-free biogas from the biogas contaminated with 4 ppm H₂S.

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CHAPTER IV

Enhancement of the H₂S Adsorption Capacity of Biochar by Ni Loading

4.1. Introduction

In Chapter 3, it was revealed that for the enhancement of H₂S adsorption capacity of rice husk biochar (RHBC), the use of digestate liquid as NH₃ source (N₂ treatment) is good way due to the availability of ammonia in rural area and the large total adsorption capacity (q) of the produced sample (RHBC-N₂) at 23.0 mg H₂S g-BC⁻¹. However, one drawback of the RHBC-N₂ is the low breakthrough capacity (q_0) at 3.96 mg H₂S g-BC⁻¹ compared to RHBC-N₁ treated with NH₃ gas which is 8.02 mg H₂S g-BC⁻¹. Thus, a further study to increase q_0 is needed.

Metal loading on the surface of biochar by wet impregnation is considered to be effective [1,2], because a metal loaded on the surface can increase the affinity with adsorbate [3]. Adsorption ability strongly depends on the metal/adsorbate combination [3–6]. In this study, to enhance the H₂S adsorption ability of biochar (q_0), Ni was selected, because in the field of catalyst engineering, it is well-known that catalytic activity of Ni for fuel reforming is strongly affected by a trace H₂S, showing high affinity of H₂S with Ni, and this metal, commonly used as the anode of SOFC, can be recycled from the spent SOFC.

4.2. Objective

Through the characterizations of Ni-loaded RHBCs and the evaluations of their q_0 and q , the effect of Ni-loading on the H₂S adsorption is studied. In the course of this study, the synergetic effect of N-doping and Ni-loading is discussed. A simple kinetic study is also performed to evaluate the rate of reaction in H₂S adsorption.

4.3. Experimental

4.3.1. Biochar production

Rice husk (RH) of Japonica rice (*O. sativa* subs. Japonica) was collected from Itoshima City in Fukuoka Prefecture, Japan. This was first dried at 100°C for 24 h. Then, 3 g of dried RH was pyrolyzed at 500°C under flowing nitrogen (50 mL min⁻¹) for 120 min, to produce rice husk biochar (RHBC).

4.3.2. Nitrogen (N)-doping

10wt% NH₄⁺ solution (Fujifilm Wako Pure Chemical Corporation, Japan) simulating the concentrated digestate liquid was used as a nitrogen source. As shown in Fig. 4.1, carrier gas (N₂) was bubbled through this solution with 100 mL min⁻¹ at 30°C, which is calculated to have an ammonia content of 15.7vol% and a steam content of 3.8vol%. In this NH₃-rich gas flow, 2 g of RHBC was heat-treated at 850°C for 270 min. The resulting sample is labelled RHBC-N2.

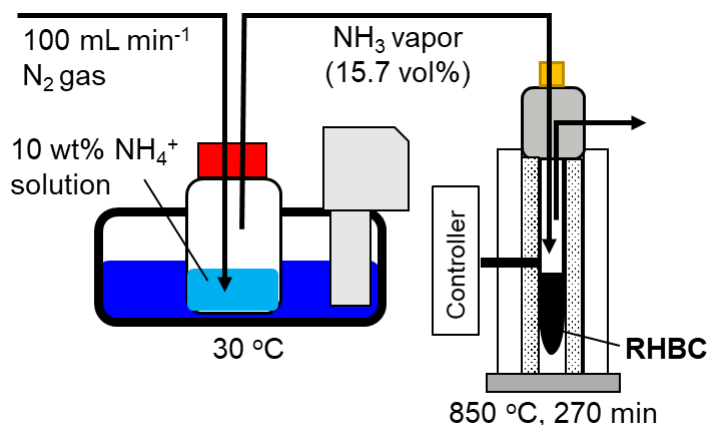


Figure 4.1: Schematic illustration of the setup for N-doping in biochar using NH₄⁺ aqueous solution simulating concentrated digestate liquid.

4.3.3. Ni-loading

1.17 g of NiNO₃·6H₂O (Kishida Chemical Co., Ltd., Japan) was mixed with 40 mL distilled water to prepare a 0.1 M NiNO₃ solution, in which 1.50 g of RHBC-N2 was added and stirred using magnetic stirrer for 24 h. The resulting suspension was then dried

at 80°C in a drying oven in air overnight to slowly evaporate water for better diffusion of Ni particles into the RHBC pores. Subsequently, excess NiNO₃ was washed off using distilled water, and the sample was dried again at 100°C in air overnight, followed by the heat-treatment at 500°C for 2 h under O₂-free atmosphere (50 mL min⁻¹ N₂ flow). The resulting Ni-loaded sample was denoted as RHBC-N2-Ni. For the comparison, RHBC-Ni-N2 was prepared, for which Ni was loaded first, followed by N-doping.

4.3.4. Fabrication of paper-structured biochar

Paper-structured biochar was prepared using a paper-making process based on the dual polymer retention system [7]. First, 6 g of ceramic fiber (75wt% SiO₂-25wt% CaO(+MgO), Ibiden Ltd., Japan) was dispersed in 1 L of distilled water. Then, 15 g of a 2wt% solution of cationic polymer (poly(diallyldimethylammonium chloride, Sigma-Aldrich LCC, USA) was mixed into the slurry and stirred for 3 min, followed by the addition of 6 g of biochar (RHBC-N2-Ni) and stirred for a further 3 min. Subsequently, 16.3 g of a 0.2 wt% solution of anionic polymer (acrylamide-co-acrylic acid, Fujikasui Engineering Co., Ltd.) was mixed in and stirred for a further 3 min.

The resulting slurry was filtrated to obtain a wet-state paper-like sheet with a diameter of 16 cm. This was pressed at 350 kPa for 3 min and dried at 100°C overnight. The dried sheet was cut into small pieces with a diameter of 15 mm. These pieces were then heat-treated at 800°C for 5 h under flowing nitrogen (50 mL min⁻¹) to remove the organic components and form the ceramic fiber network. The resulting paper-structured biochar sheets are herein labelled as PS[RHBC-N2-Ni].

4.3.5. Sample characterization

The specific surface area (SSA) was measured via the nitrogen adsorption method (Belsorp-mini II analyzer, MicrotracBEL Corp., Japan), and the pore size distribution was evaluated via the MP micropore analysis method. Microstructure was investigated by transmission electron microscope with energy dispersive X-ray spectroscopy (TEM-EDX; JEM-ARM200F, JEOL Ltd., Japan).

The amount of Ni-loading was measured as follows. 3.0 mg of Ni-loaded RHBC was dissolved in aqua regia, followed by the evaporation process at 130°C until the

precipitate remains, which was then dissolved in 20 mL distilled water. Using the resulting solution, Ni amount was measured by inductively-coupled plasma atomic emission spectrometry (ICP-AES; ICPE-9000; Shimadzu Corp., Japan).

For near-surface analysis, quasi-surface-sensitive technique using X-ray photoelectron spectroscopy (XPS) was done at room temperature using a monochromated Al K α ($h\nu = 1,486.7$ eV) X-ray source operated at 5 mA and 15 kV (Kratos Axis Ultra, Shimadzu, Japan). All binding energies (BEs) were referred to the C1s line at 284.6 eV.

4.3.6. H₂S adsorption test

Details of the H₂S adsorption test were described in Sec. 2.3.4.

4.4. Results and discussion

4.4.1. Structure of Ni-loaded biochar

In Chapter 2, it was shown that the SSA of RHBC increased by the NH_3 treatment due to the changes in carbon structure brought by the nitrogen etching caused by partial NH_3 gasification to dope nitrogen functional groups on the carbon surface [8]. As for the N_2 treatment, due to the low concentration of NH_3 in the gas flow, the increases in SSA and V_{micro} were not so pronounced. However, as shown in Table 4.1, these values were increased by the subsequent Ni-loading (RHBC- N_2 -Ni). However, those of RHBC-Ni- N_2 were significantly smaller compared to the pristine RHBC.

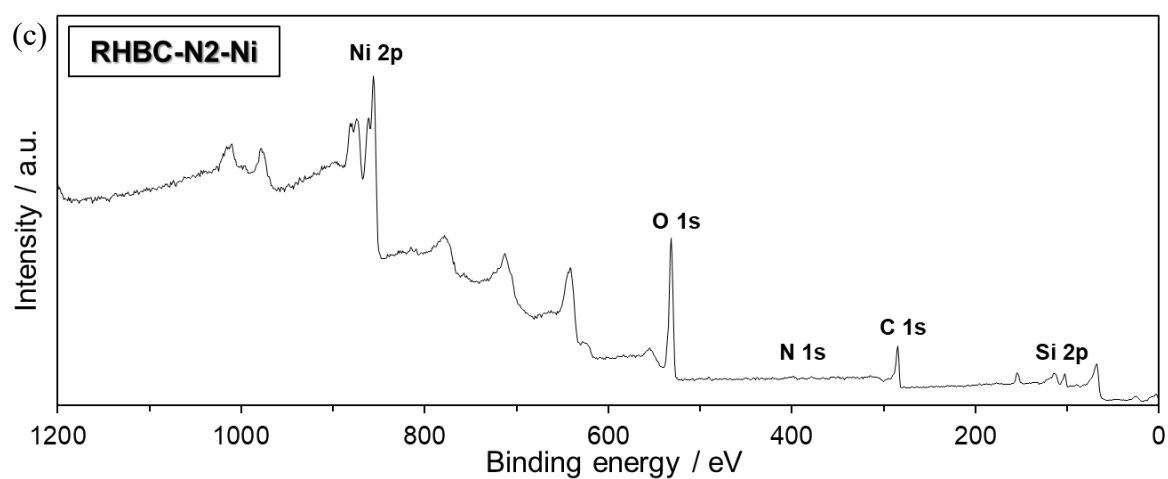
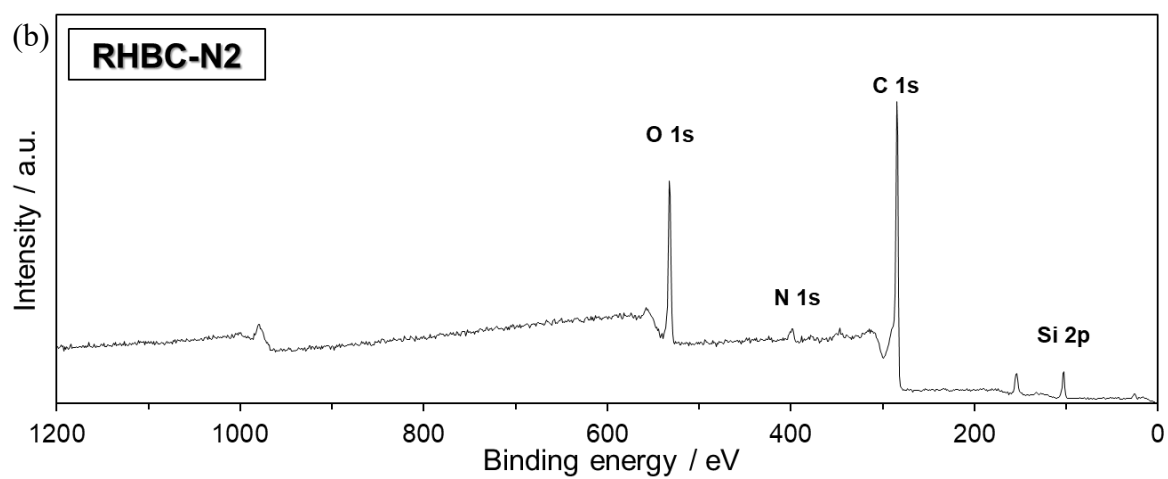
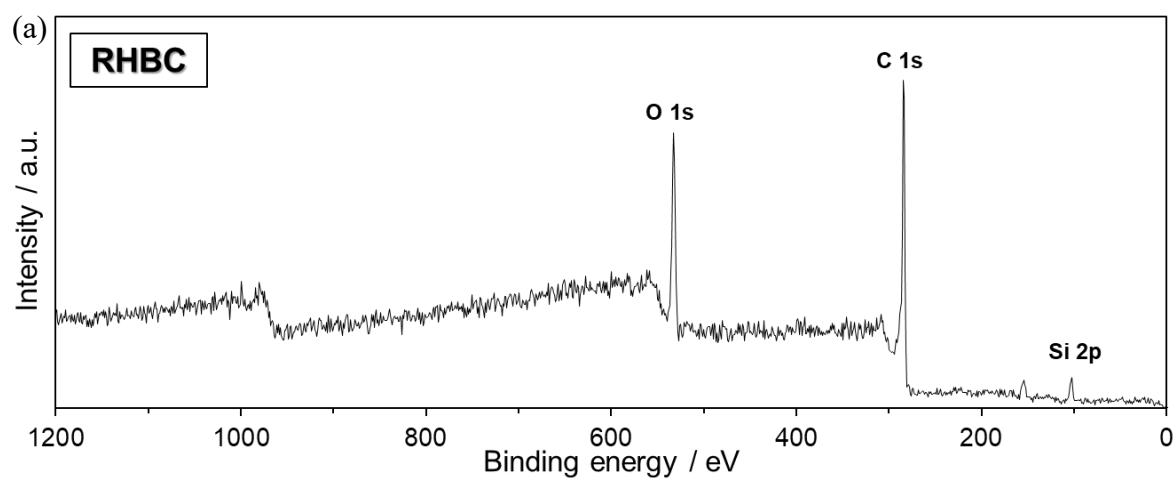
Table 4.1: Results of the surface analysis for the Ni-loaded RHBCs.

Sample	SSA / m^2g^{-1}	V_{mic} / $10^{-7} \text{ m}^3 \text{ g}^{-1}$	Content on the near-surface* / wt%		
			O	N	Pyridinic-N
RHBC	146	0.63	19.2	-	-
RHBC- N_2	170	0.68	16.9	2.52	1.31
RHBC- N_2 -Ni	260	0.99	30.9	0.89	0.32
RHBC-Ni- N_2	119	0.36	20.8	0.08	0.03

*Measured by XPS

Near-surface contents of the samples estimated by the XPS survey profiles shown in Fig. 4.2 are listed in Table 4.1. During the NH_3 treatment, NH_3 reacts with the carbon and the oxygen functional groups on the surface. N is substituted for O in aromatic ring to mainly produce pyridinic-N sites. Due to this substitution, O content near the surface decreased as shown in Table 4.1 [9,10]. SSA and V_{micro} are increased by the NH_3 etching, which also can increase the electron exchange activity of the carbon surface to be more reactive [11,12]. As discussed in Chapter 3, two electrons (i.e. a lone pair) of the pyridinic-N atom are supplied to the O_2 molecule, and that the O-O bond was stretched and finally broken, as the origin of the oxygen radicals (O^*).

The Ni-loaded samples had higher O content compared to the samples without Ni loading. This difference may come from the susceptibility of Ni to oxidation, and also from the residue of the Ni precursor containing oxygen ($\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$).



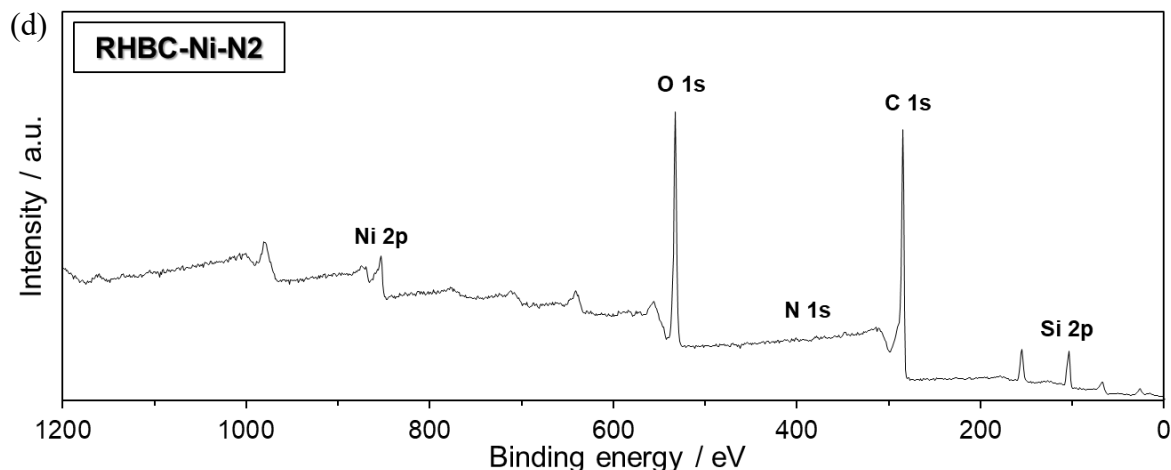


Figure 4.2: XPS survey profiles (4 scans) for: (a) RHBC; (b) RHBC-N2; (c) RHBC-N2-Ni; and (d) RHBC-Ni-N2.

The contents of N and corresponding pyridinic-N on the surface of RHBC-N2-Ni evaluated by XPS were significantly lower than RHBC-N2. Wang *et al.* reported that the defect site surrounded by three pyridinic-N atoms can be a stable receptor for Ni atom as described in Fig. 4.3 [13]. This N-Ni bonding not only can prevent Ni from coarsening and agglomerating, but also make the pyridinic-N less active for the formation of oxygen radicals.

If Ni is loaded on the RHBC prior to the NH_3 treatment (RHBC-Ni-N2), the Ni particles can catalyze the decomposition of NH_3 in the subsequent NH_3 treatment to significantly suppress the N-doping on the biochar surface [14]. Furthermore, these Ni particles without N-Ni bonding are easily coarsened and agglomerated [15].

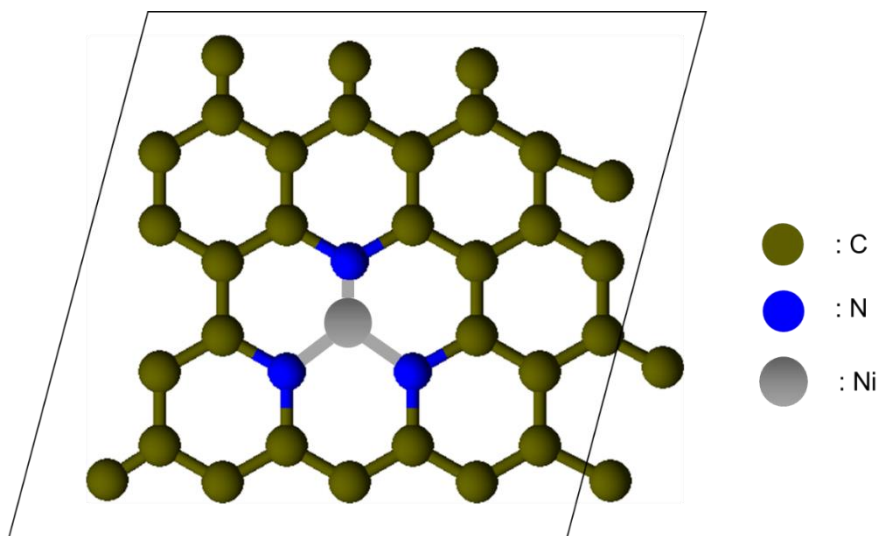


Figure 4.3: Illustration of the carbon structure after the N-doping followed by the Ni-loading, showing Ni incorporation at the defect sites surrounded by three pyridinic-N atoms.

N 1s spectra of XPS are shown in Fig. 4.4. For RHBC-N2 (Fig. 4.4a), pyridinic-, pyrrolic- and graphitic-N were detected as main components, showing the N-doping on the surface [16,17]. In the previous DFT calculation (Chapter 3), pyridinic-N has been proven to promote the formation of O* that can contribute to the increase in H₂S adsorption. As shown in Fig. 4.4b, nitrate formation was prominent in RHBC-N2-Ni compared to RHBC-N2, indicating the residue of the Ni precursor containing oxygen even after the heat-treatment in N₂ flow.

On the other hand, O content in RHBC-Ni-N2 was comparable to the pristine RHBC (see Table 4.1), indicating that oxygen-containing Ni precursor was completely reduced by the subsequent NH₃ treatment to form Ni metal particles.

The peak at around 400 eV in the N 1s spectrum of RHBC-N2-Ni (see Fig. 4.4b) may reflect the bonding of Ni with the doped N as shown in Fig. 4.3 [17]. On the other hand, high level of noise shown in the N 1s spectrum of RHBC-Ni-N2 corresponds to the low amount of nitrogen in the near-surface, indicating the failure of N-doping. In the N2 treatment to prepare RHBC-Ni-N2, Ni loaded on the pristine RHBC possibly catalyzed the NH₃ decomposition to prevent N-doping on the carbon surface.

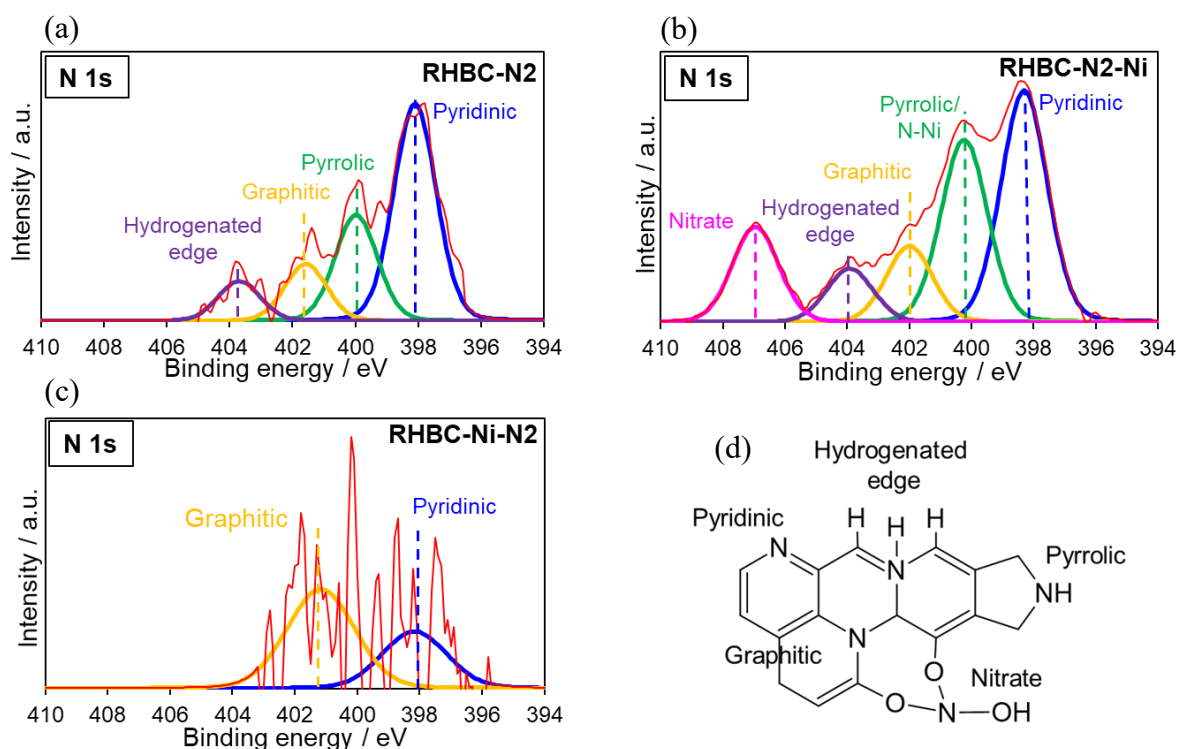


Figure 4.4: XPS N 1s profiles for (a) RHBC-N2 (16 scans), (b) RHBC-N2-Ni (16 scans), and (c) RHBC-Ni-N2 (32 scans) with (d) schematic drawing of the nitrogen species detected by XPS.

In the Ni 2p_{3/2} profiles of RHBC-N2-Ni (Fig. 4.5a), the oxidized Ni species such as NiO (854.3 eV) and Ni(OH)₂ (856.3 eV) [18] appeared as main components resulting from the Ni loading subsequently performed by NH₃ treatment. Although the binding energy of Ni-N could not be clearly defined, some studies suggested that it exists at slightly higher binding energy than Ni metal due to the effect of N. Thus, it can be assumed that it overlapped with NiO peak in the case of RHBC-N2-Ni [19,20]. Ni metal (852.6 eV) was slightly present, which was formed during the heat-treatment in N₂ flow at 500°C after the impregnation process using NiNO₃·6H₂O solution.

As shown in Figs. 4.5b, the Ni composition in RHBC-Ni-N2 was quite different from RHBC-N2-Ni. For RHBC-N2-Ni, nickel oxide was successfully loaded on the surface of the material. Meanwhile, for RHBC-Ni-N2, in the N₂ treatment after the Ni-loading, the NH₃ gas evaporated from the NH₄⁺ aqueous solution reduced the nickel oxide to form metallic Ni.

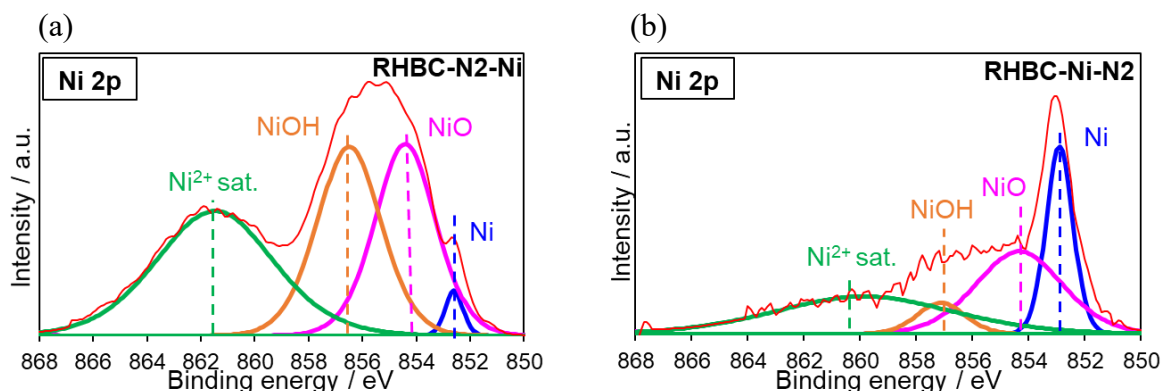


Figure 4.5: XPS Ni 2p_{3/2} profiles (8 scans) for (a) RHBC-N2-Ni and (b) RHBC-Ni-N2.

Table 4.2 shows the amount of Ni-loading measured by ICP-AES and the weight ratio of Ni near the surface to the total near-surface elements estimated by XPS. Although the amounts of Ni-loading for RHBC-N2-Ni and RHBC-Ni-N2 were the same level, Ni content near the surface of RHBC-N2-Ni evaluated by the wide scan of XPS shown in Fig. 4.2 was considerably higher than that of RHBC-Ni-N2. Bulk (7.32wt%) $\leq$ Near-surface (13.4wt%) for RHBC-N2-Ni suggests the considerably better dispersion of Ni particles on the surface than RHBC-Ni-N2 with Near-surface (0.94wt%) $\leq$ Bulk (7.47wt%).

Table 4.2: Ni content in the Ni-loaded samples.

Sample	Ni loading* / wt%	Near-surface Ni ** / wt%
RHBC-N2-Ni	7.32	13.4
RHBC-Ni-N2	7.47	0.94

*measured by ICP-AES

**measured by XPS

When an N-doped sample is loaded with Ni (RHBC-N2-Ni), atomic level incorporation of Ni at the pyridinic-N site of the carbon structure can take place during heat-treatment as described in Fig. 4.3 [13], resulting in well-dispersion of Ni nanoparticles as can be seen in the high-resolution TEM-EDX image (Fig. 4.6a).

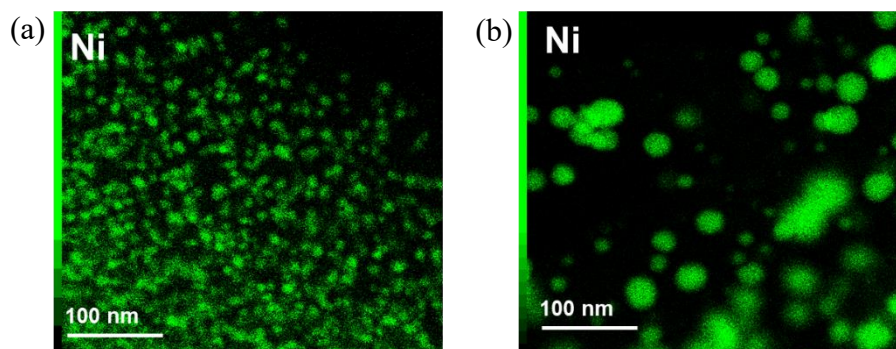
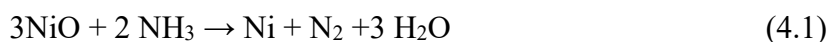


Figure 4.6: High-resolution TEM-EDX images of Ni particles loaded on (a) RHBC-N2-Ni and (b) RHBC-Ni-N2.

On the other hand, when as-prepared biochar was loaded with Ni without prior N-doping (RHBC-Ni-N2), the dispersion of Ni particle became worse than RHBC-N2-Ni as shown in Fig. 4.6b because of no atomic level interaction with the biochar surface. In the subsequent NH_3 treatment, the loaded Ni (oxidated state) was reduced to metallic state (see Fig. 4.5b) expressed as reaction (4.1). Once the Ni metal particles are formed, they can catalyze the decomposition of NH_3 to form H_2 and N_2 (reaction (4.2)). As a result, NH_3 is not well utilized for N-doping in RHBC, which is supported by the significantly low N content in RHBC-Ni-N2 (Table 4.1).



4.4.2. H_2S adsorption capacity of the prepared biochars

H_2S adsorption curves measured for the prepared biochars are shown in Fig. 4.7. The breakthrough capacity (q_0) and total adsorption capacity (q) estimated from these curves are listed in Table 4.3. The pristine RHBC had the lowest q_0 and q of 0.27 and 2.54 $\text{mgH}_2\text{S g-BC}^{-1}$, respectively. The lowest capacity of RHBC is attributed to the untreated surface having low affinity with H_2S and low porosity. q_0 corresponding to breakthrough time, showing the affinity of the biochar surface with H_2S , increased to 3.96 $\text{mgH}_2\text{S g-BC}^{-1}$ by N-doping (RHBC-N2), and further increased to 6.95 $\text{mgH}_2\text{S g-BC}^{-1}$ by the subsequent Ni-loading (RHBC-N2-Ni).

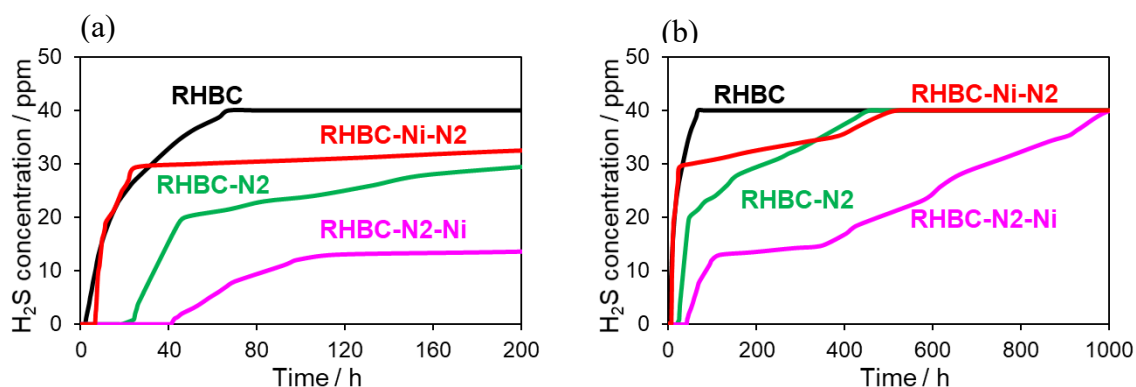


Figure 4.7: Results of H₂S adsorption tests for the RHBC-based samples; (a) focused on the initial stage within 200 h and (b) whole plots to estimate q .

Table 4.3: Breakthrough capacity (q_0) and total adsorption capacity (q) of the tested biochar samples.

Sample	q_0 / mgH ₂ S g-BC ⁻¹	q / mgH ₂ S g-BC ⁻¹
RHBC	0.27	2.54
RHBC-N2	3.96	23.0
RHBC-N2-Ni	6.95	75.4
RHBC-Ni-N2	1.13	15.3

S 2p profiles measured after the H₂S adsorption tests (Fig. 4.8) shows that various sulfur species are existing on the surface of the Ni-loaded samples (Figs. 4.8c and d), whereas only organic sulfide (C-S (~164 eV)) and sulfate (SO₄²⁻ (~168 eV)) were detected on the surface of RHBC-N2 (Fig. 4.8b). Formation of C-S indicates the H₂S adsorption following reactions (1.7) and (1.8), and SO₄²⁻ is the product of further oxidation by excess O* following reactions (2.1)-(2.3). If N is strongly doped, more pyridinic-N sites are formed on the biochar surface, that increase the concentration of O* resulting in the accumulation of sulfate to cover the micropore openings [21–23].

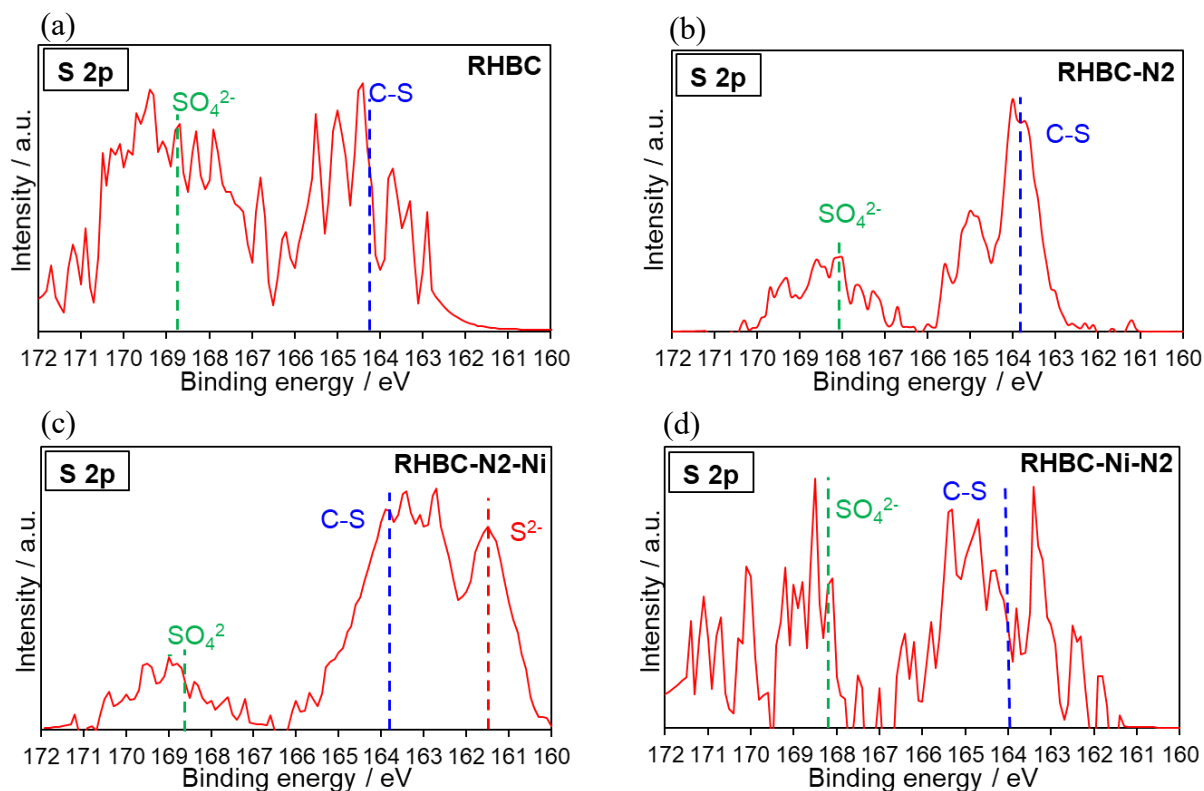


Figure 4.8: XPS S 2p profiles after H₂S adsorption tests for (a) RHBC (8 scans), (b) RHBC-N2 (32 scans), (c) RHBC-N2-Ni (16 scans), and (d) RHBC-Ni-N2 (32 scans).

Remarkable increases of q_0 and q by Ni-loading on RHBC-N2 can be explained as follows. In addition to the adsorption reaction promoted by O* (reactions (1.8) and (2.1)), Ni species dispersed on the biochar surface can act as strong adsorption sites as expressed by reactions (4.3)-(4.5) [24,25].



For RHBC-N2-Ni, as shown in Fig. 4.8c, sulfur species other than C-S and SO₄²⁻ were detected. The peak appeared at 161.7 eV was assigned as S²⁻ which corresponds to NiS [22].

RHBC-Ni-N2 showed quite low adsorption capacity, q_0 and q of only 1.13 and 15.3 mg H₂S g-BC⁻¹, respectively. In the S 2p spectrum of RHBC-Ni-N2 (Fig. 4.8d), noise

was strongly accentuated, indicating the low amount of adsorbed sulfur species. The main reasons are the significantly low content of pyridinic-N (see Table 4.1) and the coarsening of Ni metal particles (see Fig. 4.6b).

The higher H₂S adsorption capacity of RHBC-N2-Ni ($q = 75.4 \text{ mg H}_2\text{S g-BC}^{-1}$) than that of RHBC-N2 ($q = 23.0 \text{ mg H}_2\text{S g-BC}^{-1}$) may come from the higher utilization rate of micropores. The Ni-loading at the pyridinic-N sites may moderate the electron donating function of the pyridinic-N to form O*. This modification can prevent S from oxidizing to SO₄²⁻ that can cover the micropore openings. Moreover, as shown in Fig. 4.9, by Ni-loading on RHBC-N2, pore size distribution was shifted to larger side to facilitate the diffusion of sulfur species inside the micropores, and the Ni particles loaded on the inner wall of micropores further promotes the diffusion into the pore. During heat-treatment in N₂ flow after the impregnation process, the produced Ni metal particles may catalyze the gasification of carbon to enlarge the micropores [26]. To the contrary, RHBC-Ni-N2 with smaller SSA, smaller pore size, poor Ni dispersion and larger Ni particle size had terribly low adsorption capacity.

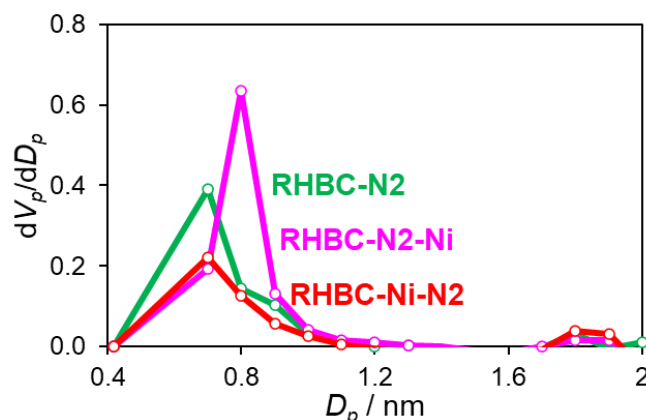


Figure 4.9: Pore size distributions of the prepared biochar samples, obtained from nitrogen adsorption/desorption isotherms using the MP method. V_p is the pore volume and D_p is the pore diameter.

Adsorption behavior of H₂S on the surface of the prepared biochars can be summarized as Fig. 4.10. As discussed before, H₂S adsorption on N-doped biochar is dominated by the O* induced by pyridinic-N. As shown in Fig. 4.10a, sulfur, the product of the reaction between O* and HS⁻, can enter the micropore. When Ni is loaded on the

N-doped surface, the strong interaction between pyridinic-N and Ni makes Ni particles finer. The finely distributed Ni on both outer and inner surfaces of the carbon may promote the diffusion of sulfur deep into the micropore as shown in Fig. 4.10b to considerably increase q . On the other hand, as shown in Fig. 4.10c, the surface loaded with Ni followed by the NH_3 treatment doesn't have sufficient amount of N. The resulting low interaction of the Ni with the surface cannot prevent Ni from agglomerating. The coarsened Ni can block the substantial portion of micropores (see Fig. 4.9) to significantly reduce q .

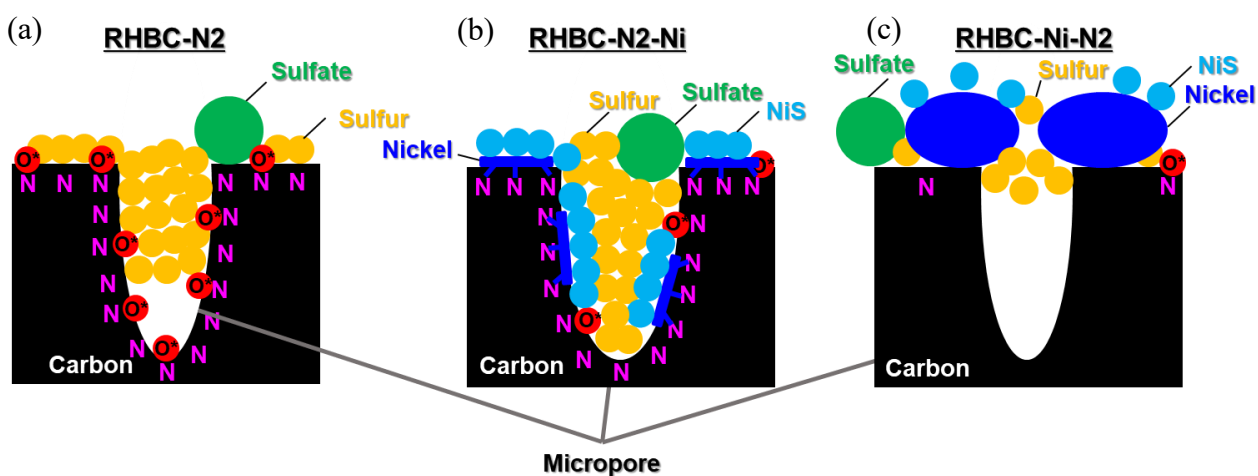


Figure 4.10: Schematic illustration explaining the differences in H_2S adsorption behavior between (a) RHBC-N2, (b) RHBC-N2-Ni, and (c) RHBC-Ni-N2.

4.4.3. H_2S adsorption capacity of paper-structured biochar

H_2S adsorption curve of the paper-structured sample (PS[RHBC-N2-Ni]) is compared with the powered sample (RHBC-N2-Ni) in Fig. 4.11. PS[RHBC-N2-Ni] had q_0 of $16.6 \text{ mg H}_2\text{S g-BC}^{-1}$, about 2-fold of RHBC-N2-Ni (see Table 4.4), because of the enhanced diffusivity of H_2S and longer contact time with the biochar surface. However, q was lowered from $75.4 \text{ mg H}_2\text{S g-BC}^{-1}$ (RHBC-N2-Ni) to $47.9 \text{ mg H}_2\text{S g-BC}^{-1}$ (PS[RHBC-N2-Ni]).

When Ni metal particle reacts with H_2S , it tends to swell and agglomerate as a result of the formation of NiS [27]. TEM-EDX images of the Ni particles loaded on the powered sample (RHBC-N2-Ni) before and after the H_2S adsorption test shown in Figs. 4.12a and b, respectively, clearly shows the swelling of Ni by the H_2S adsorption. This

swelling is considered to be faster for the paper-structured sample (PS[RHBC-N2-Ni]) due to the enhanced accessibility of H₂S to Ni. As illustrated in Fig. 4.13, the swelled Ni (NiS) can block the micropores to reduce the chance of sulfur to diffuse into the micropores.

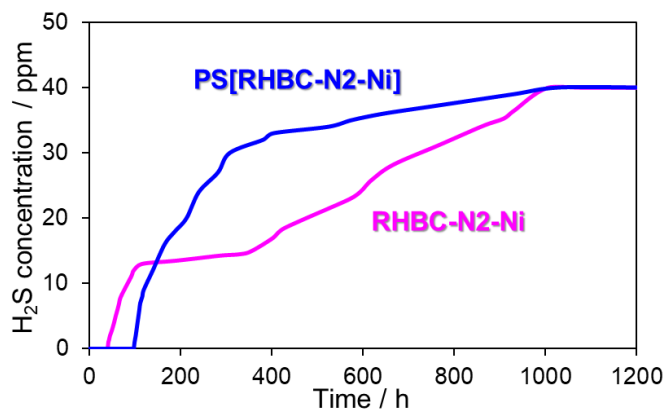


Figure 4.11: Results of the H₂S adsorption tests for the powdered sample (RHBC-N2-Ni) and the paper-structured sample (PS[RHBC-N2-Ni]).

Table 4.4: H₂S adsorption capacities of the powdered and the paper-structured samples of Ni-loaded biochars.

Sample	q_0 / mg H ₂ S g-BC ⁻¹	q / mg H ₂ S g-BC ⁻¹
RHBC-N2-Ni	6.95	75.4
PS[RHBC-N2-Ni]	16.6	47.9

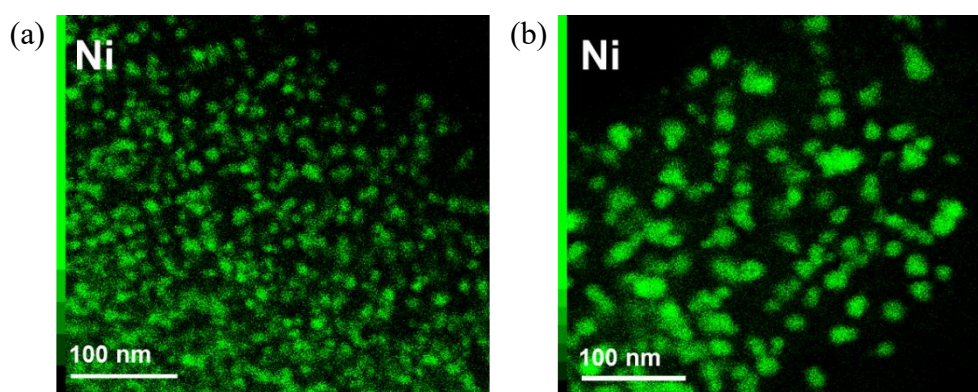


Figure 4.12: High-resolution TEM-EDX image of Ni particles loaded on RHBC-N2-Ni (a) before and (b) after the H₂S adsorption test.

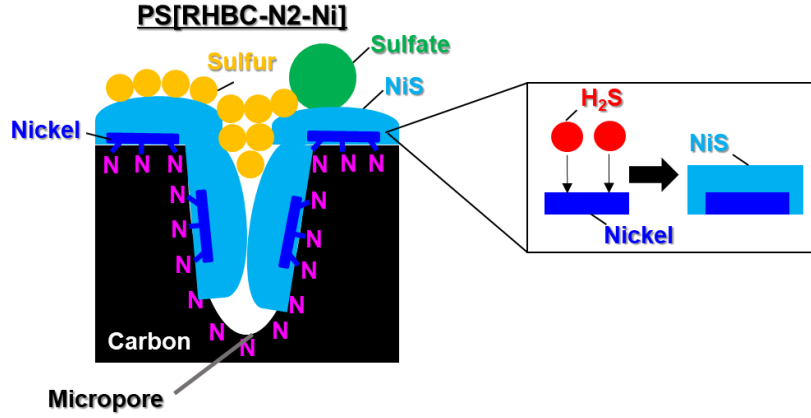


Figure 4.13: Schematic illustration explaining the reduction of H₂S adsorption capacity of Ni-loaded biochar attributed to Ni swelling and agglomeration caused by the reaction with H₂S.

If PS[RHBC-N2-Ni] is applied for the real system described in Chapter 3, its necessary amount to obtain H₂S free biogas for 100,000 h is estimated at 10.8 kg, corresponding to 50% weight reduction compared to PS[RHBC-N2].

4.4.4. Kinetic study

H₂S adsorption on the biochar samples was kinetically discussed. Considering the reactions (1.8) and (2.1) as the major processes of H₂S adsorption, reaction rate ($-r_{\text{H}_2\text{S}} = v$) can be expressed as;

$$-r_{\text{H}_2\text{S}} = v = k[\text{HS}^-]^x[\text{O}^*]^y \quad (4.6)$$

,where k is the rate constant and $[\text{HS}^-]$ and $[\text{O}^*]$ are the concentrations of HS^- and O^* on the surface. In the present study, continuously supplying H₂S at the constant concentration, $[\text{HS}^-]$ can be regarded as constant, under which if the pseudo-first-order reaction is assumed, reaction rate can be expressed as;

$$v = k'[\text{O}^*] \quad (4.7)$$

When the $[\text{O}^*]$ is equated with $\text{SO}_4^{2-}/\text{C-S}$,

$$v = k''\text{SO}_4^{2-}/\text{C-S} \quad (4.8)$$

The results of the H₂S adsorption test for the biochar samples are again shown in Fig. 4.14 focusing on the stage just after the change in H₂S concentration at the outlet is visible. RHBC was excluded due to its small q_0 and q which makes the kinetic estimation difficult. For all samples, the adsorption curves could be divided into two stages with different gradients of k_1 and k_2 .

For the kinetic study, H₂S adsorption curves of Fig. 4.14 were converted into the H₂S conversion curves using equation (4.9), that are shown in Fig. 4.15.

$$\text{H}_2\text{S conversion} = \frac{C_0 - C}{C_0} \quad (4.9)$$

,where C_0 is the H₂S concentration at the inlet and C is the H₂S concentration at the outlet at a certain time.

The gradients v_1 and v_2 of the curves of Fig. 4.15 corresponding to k_1 and k_2 , respectively. As can be seen in Fig. 3.6, higher content of pyridinic-N on the surface to produce more O* results in the promotion of sulfate formation and its accumulation. Because the concentration of O* cannot be measured directly, the level of surface O* was estimated through the ratio of sulfate to sulfur ($\text{SO}_4^{2-}/\text{C-S}$) evaluated by XPS.

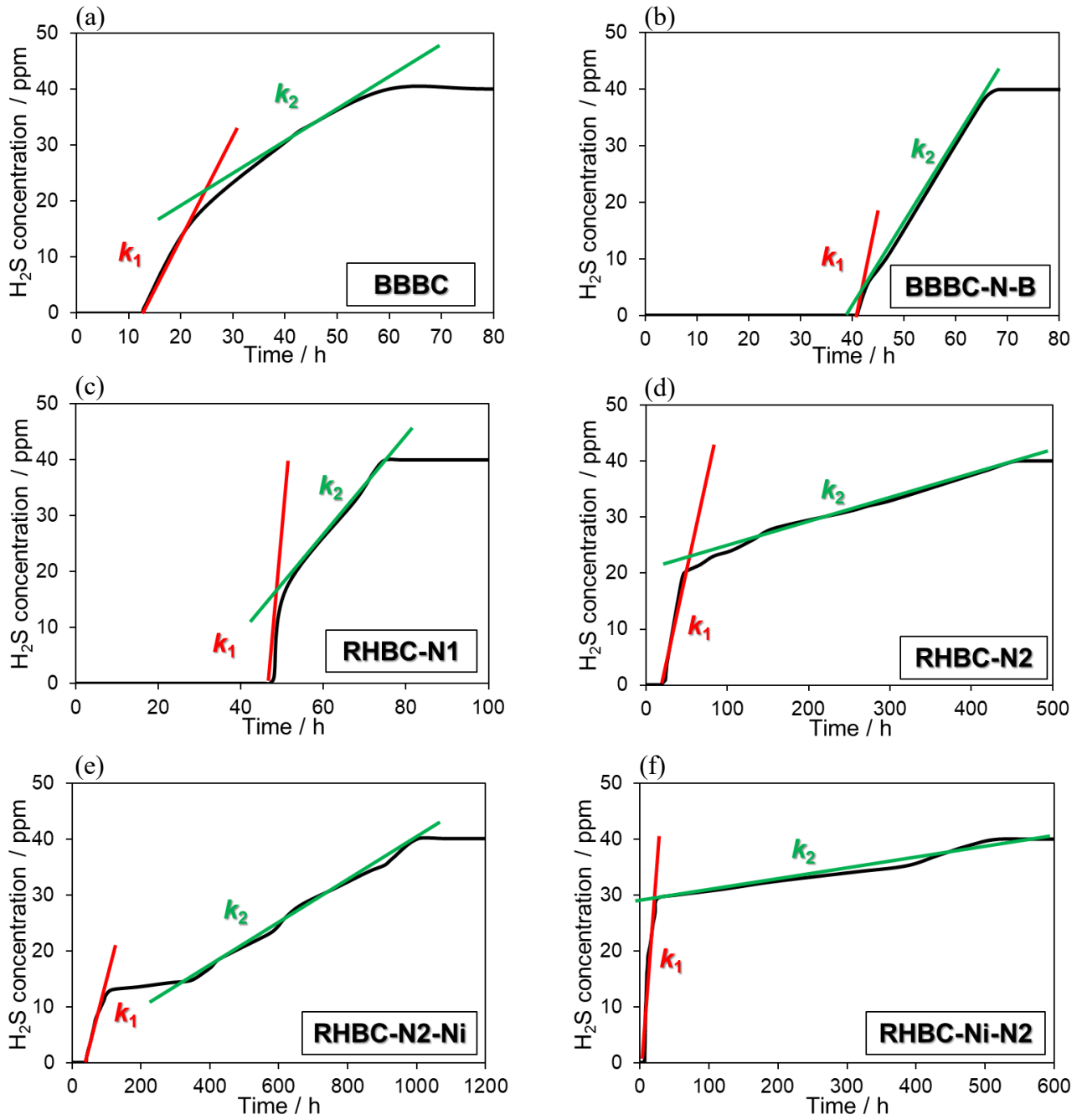


Figure 4.14: Results of the H₂S adsorption tests for: (a) BBBC, (b) BBBC-N-B, (c) RHBC-N1, (d) RHBC-N2, (e) RHBC-N2-Ni and (f) RHBC-Ni-N2, showing the gradients k_1 and k_2 .

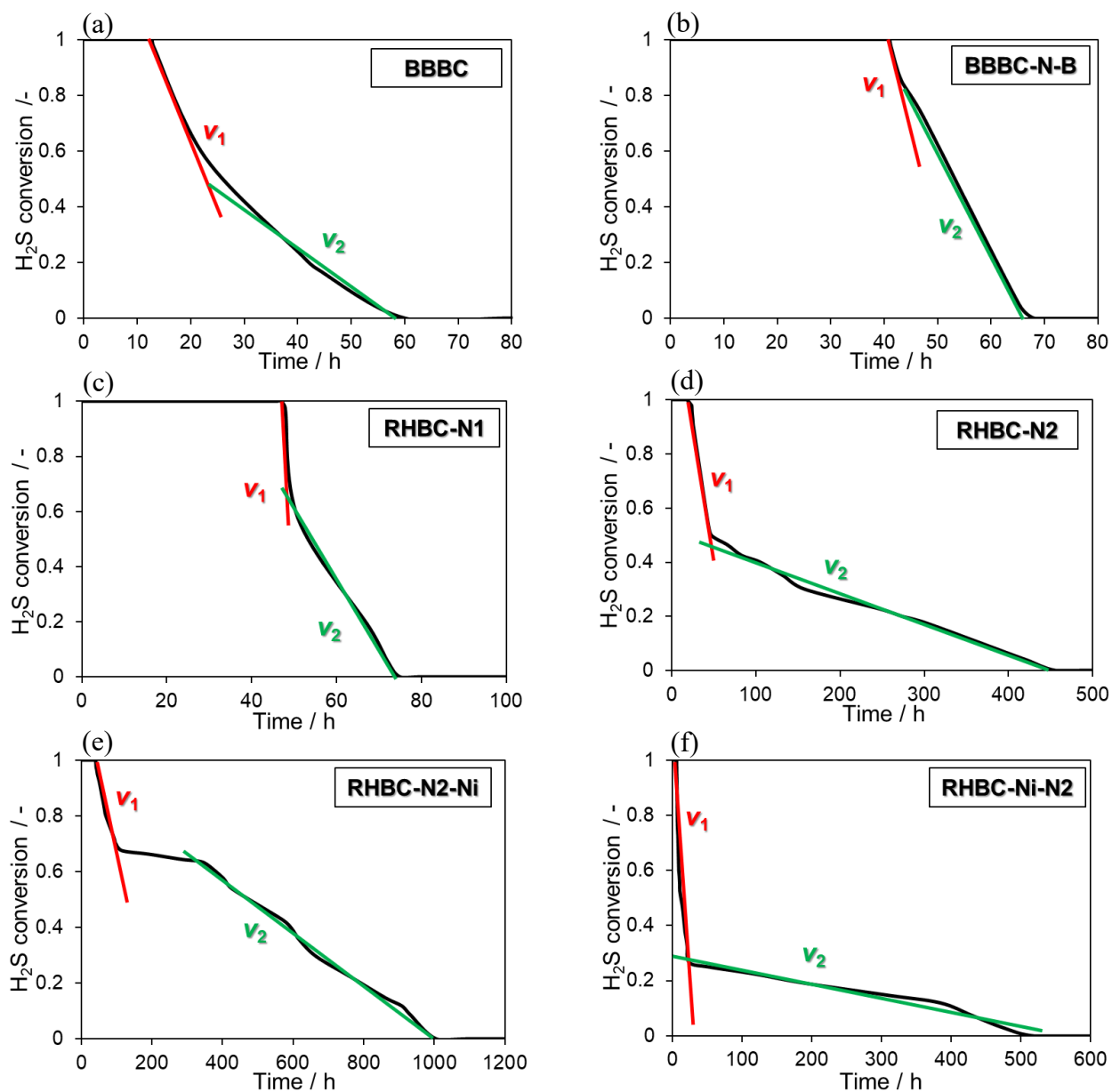


Figure 4.15: H₂S conversion curves for: (a) BBBC, (b) BBBC-N-B, (c) RHBC-N1, (d) RHBC-N2, (e) RHBC-N2-Ni and (f) RHBC-Ni-N2, showing the gradients v_1 and v_2 .

As plotted in Fig. 4.16a, strong correlation between v_1 and $\text{SO}_4^{2-}/\text{C-S}$ can be observed. This suggests that the v_1 represents the surface reaction in the H₂S adsorption. On the other hand, no correlation between v_2 and $\text{SO}_4^{2-}/\text{C-S}$ was confirmed as shown in Fig 4.16b. The v_2 probably reflects the diffusion of sulfur species into the micropores, although further studies are necessary to clarify the mechanism.

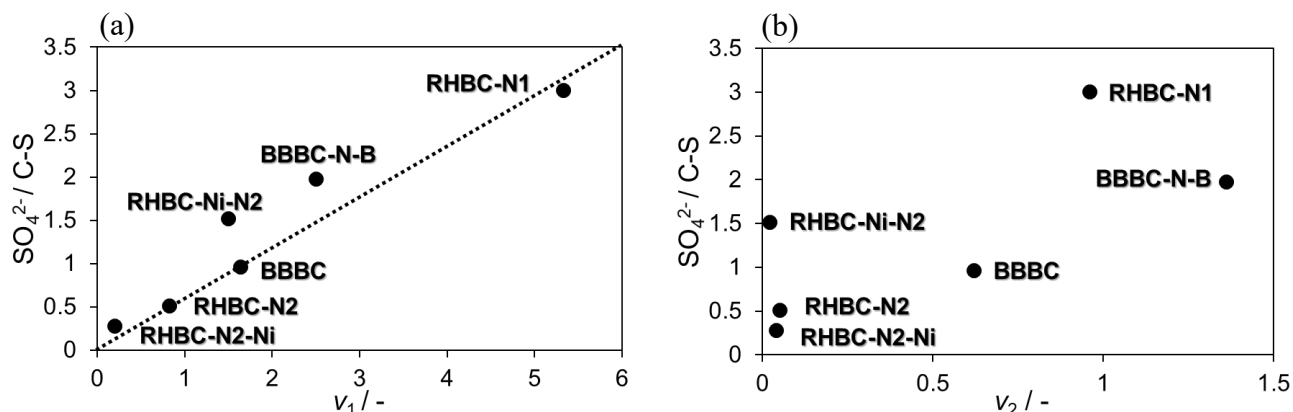


Figure 4.16: Correlations (a) between v_1 and $\text{SO}_4^{2-}/\text{C-S}$ and (b) between v_2 and $\text{SO}_4^{2-}/\text{C-S}$.

The linear correlation between v_1 and $\text{SO}_4^{2-}/\text{C-S}$ shown in Fig.4.16a supports that the rate of H_2S adsorption can be expressed by (4.8), which proves that the H_2S adsorption is dominated by the content of O^* , in other words, the content of pyridinic-N on the surface.

4.4.5. Comparison with commercial desulfurizers

Performance of the Ni-loaded biochars in the present study as desulfurizer is compared with the commercial desulfurizers in Table 4.5. The Ni-loaded biochars exhibited the performance comparable to the commercial and the reported ones. For instance, IRMOF-3, a metal organic framework of N-doped carbon impregnated with Zn, captures H_2S inside its framework, during which the framework is seriously destroyed by the swelling caused by the chemical reaction of Zn with H_2S , resulting in low q [31,32]. Although q_0 of RHBC-N2-Ni was lower than IRMOF-3, q of RHBC-N2-Ni was 5-fold of IRMOF-3. The larger q of RHBC-N2-Ni compared to IRMOF-3 may come from its stable structure not strongly affected by H_2S adsorption. By employing the paper-structured type, q_0 of RHBC-N2-Ni surpassed IRMOF-3.

Table 4.5: H₂S adsorption capacities of the biochars of this chapter together with the commercial and the reported desulfurizers.

Product name	SSA / m ² g ⁻¹	V_{mic} / 10 ⁻⁷ m ³ g ⁻¹	q_0 / mg H ₂ S g-BC ⁻¹	q / mg H ₂ S g-BC ⁻¹	Ref.
RHBC-N2-Ni	260	0.99	6.95	75.4	This study
PS[RHBC-N2-Ni]	-	-	16.6	47.9	This study
Chemviron Carbon ¹⁾	930	3.8	1.3	8	[28]
CECA 13X ²⁾	700	2.6	46	177	[29]
SBA-15 ³⁾	950	13.1	0.54	1.09	[30]
IRMOF-3 ⁴⁾	2200	-	10.6	15.4	[31,32]

1) Coconut-based activated carbon manufactured by Chemviron Ltd. (Commercial)

2) 13X zeolite manufactured by Arkema S.A. (Commercial)

3) Molecular sieve made from Pluronic P123 and TEOS in HCl

4) Zinc-based metal-organic framework, a Zn impregnated N-doped carbon made by dissolving NH₂-BDC (carbon precursor) and Zn(NO₃)₂ in DMF

All desulfurizers were tested in dry condition at ambient temperature. Chemviron carbon and CECA13x were tested using 80 ppm H₂S at 4000 mL min⁻¹ for 10 g adsorbent. SBA-15 was tested using 4000 ppm H₂S at 100 mL min⁻¹ for 1.0 g adsorbent. IRMOF-3 was tested using 0.1 ppm H₂S at 100 mL min⁻¹ for 0.25 g adsorbent.

4.5. Conclusions

Aiming at the enhancement of H_2S adsorption capacity, the effect of Ni-loading on RHBC was studied, and the synergetic effect of N-doping and Ni-loading was discussed.

When the N-doped RHBC studied in Chapter 3 is loaded with Ni (RHBC-N2-Ni), atomic level incorporation of Ni at the pyridinic-N site of the carbon structure can take place during heat-treatment, resulting in well-dispersion of Ni particles. If Ni is loaded on the RHBC prior to the NH_3 treatment (RHBC-Ni-N2), the Ni particles can catalyze the decomposition of NH_3 in the subsequent NH_3 treatment to significantly suppress the N-doping on the biochar surface, resulting in coarsening and agglomeration of Ni particles that have no strong interaction with the surface.

H_2S adsorption on N-doped biochar is dominated by the surface O^* induced by pyridinic-N to produce sulfur as adsorbate which can enter the micropore. When Ni is loaded on the N-doped surface, the strong interaction between pyridinic-N and Ni makes Ni particles finer. The finely distributed Ni on both outer and inner surfaces of the carbon may promote the diffusion of sulfur deep into the micropore to considerably increase q .

The kinetic study confirmed that the concentration of O^* on the surface is crucial for determining the rate of H_2S adsorption.

The N-doped biochar loaded with Ni developed in this study exhibited the excellent adsorption capacity surpassing most of commercial desulfurizers when it dispersed in the ceramic fiber network.

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CHAPTER V

Conclusion

5.1. General outline

Production of biogas (the mixture of CH_4 and CO_2) from local biomass wastes and its utilization should be more promoted especially in rural areas or in agricultural sector to practice local energy and material circulations for SDGs. Highly efficient biogas power generation with solid oxide fuel cell (SOFC) is expected to become a core technology for making this circulation concept possible, in which biogas purification, especially the removal of trace H_2S , will be the key factor. Generally, zeolite and activated carbon are used for the fine desulfurization [1,2], however these adsorbents are not easily available in a rural area. For wider dissemination of SOFC, a process to obtain an excellent desulfurizer made from locally available material is required. In this point of view, this study focused on the biochar (BC), a carbon-based material obtained by heat treatment of biomass in the O_2 -free condition (pyrolysis).

BCs were produced from bamboo (BB) and rice husk (RH), labeled BBBC and RHBC, respectively. These BCs subjected to the steam or ammonia (NH_3 gas) treatment, H_2S adsorption tests were performed, and breakthrough capacity (q_0) and total H_2S adsorption capacity (q) were evaluated. Steam and NH_3 treatments effectively increased q_0 and q of the BBBC and RHBC. As for the RHBC, intense steam treatment must be avoided so as not to expose silica on the surface which negatively affects the H_2S absorption ability.

NH_3 treatment changes the surface chemistry of the biochar by N-doping to form nitrogen functional groups such as pyridinic-, pyrrolic- and graphitic-N. The presence of pyridinic-N promoting the formation of oxygen radicals (O^*) on the surface has been proven to be crucial to increase q_0 and q . By the NH_3 treatment of RHBC at 900°C , q_0 and q increased from 0.27 to 8.02 $\text{mgH}_2\text{S g-BC}^{-1}$ (30-fold) and from 2.54 to 9.58 $\text{mgH}_2\text{S g-BC}^{-1}$ (4-fold), respectively, whereas these increases for BBBC were only from 2.18 to 6.90 $\text{mgH}_2\text{S g-BC}^{-1}$ (3-fold) and from 4.83 to 8.91 $\text{mgH}_2\text{S g-BC}^{-1}$ (2-fold), respectively. Compared to BBBC, carbon structure of RHBC was more receptive to N-doping, due to less basic surface, without formation of nitrate, and the sulfate formation during H_2S adsorption, which can negatively affect the adsorption capacity, was more mitigated. Although the NH_3 treatment of BC resulted in the remarkable improvement of the desulfurizing ability, unavailability of NH_3 gas must be taken into consideration especially in a rural area. Moreover, for further enhancement of q , the interaction between

H₂S and N-doped surface must be moderately weakened to increase the utilization rate of mass transfer zone in the micropores. Considering these aspects, one of the promising approaches is the treatment of RHBC with NH₃ evaporated from digestate liquid discharged from a methane fermentation tank to realize the mild N-doping on the biochar surface.

N-doping of RHBC was performed using two different methods. In the first method (N1 treatment), RHBC was heat-treated for 120 min at 900°C in flowing NH₃ gas (NH₃: 25vol%, N₂: 75vol%). This sample was labelled RHBC-N1. In the second method (N2 treatment), 10wt% NH₄⁺ aqueous solution was prepared to simulate the concentrated digestate liquid. Nitrogen carrier gas was bubbled through this solution at 30°C, and in the resulting gas flow with 15.7vol% NH₃ and 3.8vol% steam, RHBC was heat-treated at 850°C for 270 min. This sample was labelled RHBC-N2. N contents doped on the surface of RHBC-N1 and -N2 were 3.69 and 2.52wt%, respectively, and the corresponding pyridinic-N contents were 2.29 and 1.31wt%, respectively. O* is essential for promoting chemical adsorption of H₂S on the surface of RHBC. DFT calculation proved that among the N-doped sites on the biochar surface the pyridinic-N plays a crucial role to promote the formation of O* by donating electron from its lone pair to oxygen molecule to break the O-O bond. That is the reason why q_0 and q increased from 0.27 to 8.02 mgH₂S g-BC⁻¹ and from 2.54 to 9.58 mgH₂S g-BC⁻¹, respectively, by N1 treatment. Considerably larger q of RHBC-N2 (23.0 mgH₂S g-BC⁻¹) compared to RHBC-N1 (9.58 mgH₂S g-BC⁻¹) was due to less formation of sulfate on the surface during H₂S adsorption. Sulfate accumulation on the RHBC-N1 caused by the excess formation of oxygen radicals as a result of strong N-doping covered the micropore openings, leading to the lower q .

For further improvement of the q_0 and q of RHBC-N2, facilitating the diffusion of H₂S onto the biochar surface is indispensable. From this point of view, the powdered RHBC-N2 sample was formed into a sheet state by the paper-making process using ceramic fibers [3]. The paper-structured biochar denoted as PS[RHBC-N2] exhibited q_0 and q of 8.71 and 96.1 mgH₂S g-BC⁻¹, respectively. When a 4 ppm H₂S containing biogas is considered, only 20.5 kg of RHBC-N2 is needed to obtain H₂S-free biogas continuously for 100,000 h. The developed paper-structured biochar, which is mechanically flexible and easily mounted into an adsorbent vessel, will be practically applicable for fine desulfurization of biogas containing several ppm H₂S.

Although the capacity of RHBC-N2 for H₂S adsorption could be increased by adopting the paper-structured geometry, the H₂S adsorption ability itself, directly related to q_0 , must be essentially enhanced. To increase the surface affinity with H₂S, loading of nickel (Ni), which is well known as a material susceptible to sulfur poisoning in the field

of catalyst chemistry, on the biochar surface was studied. Ni was loaded on the RHBC-N2 by wet impregnation method using 0.1 M NiNO₃ solution. The dried sample was then heat treated at 500°C for 2 h in N₂ flow. The resulting sample was denoted as RHBC-N2-Ni. In addition, to understand the effect of Ni loading, the RHBC was first impregnated with the NiNO₃ solution, and then subjected to the N₂ treatment. This sample was denoted as RHBC-Ni-N2. RHBC-N2-Ni had q_0 and q of 6.95 and 75.4 mgH₂S g-BC⁻¹, respectively, which were 1.8 and 3.3-fold of RHBC-N2 (q_0 : 3.96 mgH₂S g-BC⁻¹, q : 23.0 mgH₂S g-BC⁻¹), respectively. The enhanced adsorption capacity results from the moderation of the O* formation effect of pyridinic-N as a result of the settlement of Ni on the pyridinic-N site, the adsorption ability of Ni itself, and the enlargement of micropore openings during Ni loading process. If Ni is loaded on the RHBC prior to the N₂ treatment (RHBC-Ni-N2), q_0 and q were significantly lowered to 1.13 and 15.3 mgH₂S g-BC⁻¹, respectively, because the Ni particles can catalyze the decomposition of NH₃ in the subsequent N₂ treatment to significantly restrain the N-doping on the biochar surface. Furthermore, these Ni particles without N-Ni bonding are easily coarsened and agglomerated.

RHBC-N2-Ni was also made into a sheet state denoted as PS[RHBC-N2-Ni], which exhibited q_0 of 16.6 mgH₂S g-BC⁻¹ larger than those of PS[RHBC-N2] and RHBC-N2-Ni. This means only 10.8 kg of RHBC-N2-Ni is needed to obtain H₂S free biogas from a biogas with 4 ppm H₂S for 100,000 h. However, its q was smaller than the expectation, which would be attributed to the acceleration of Ni swelling and agglomeration caused by the improved accessibility of H₂S on the biochar surface in the paper-structured geometry.

5.2. Outcomes

H₂S adsorption capacities (q_0 and q) of the biochars of this study are summarized and compared with the commercial and the reported desulfurizers in Figure 5.1. Among the powdered rice husk biochars (RHBCs), RHBC-N2-Ni (RHBC treated with NH₃ evaporated from the NH₄⁺ aqueous solution (N2 treatment) followed by Ni loading) exhibited the largest q_0 and q of 6.95 and 75.4 mgH₂S g-BC⁻¹, respectively, that far surpassed the carbon-based commercial desulfurizer, Chemviron Carbon, with q_0 and q of 1.30 and 8.0 mgH₂S g-BC⁻¹, respectively [4]. However, its performance still lower than the silica-based desulfurizer (CECA 13X) with q_0 and q of 46 and 177 mgH₂S g-BC⁻¹, respectively [5]. While further optimization studies to adjust preparation conditions of biochar such as the carbonization temperature and time, the ammonia treatment temperature and time, the concentration of metal precursor solution for impregnation, etc. are required to maximize the H₂S adsorption capability of biochar, by dispersing the RHBC-N2 in the ceramic fiber network (PS[RHBC-N2]), q_0 and q were boosted from 3.96 and 23.0 mgH₂S g-BC⁻¹ to 8.71 and 96.1 mgH₂S g-BC⁻¹ respectively. By making the RHBC-N2-Ni into the sheet state (PS[RHBC-N2-Ni]), q_0 was further increased to 16.6 mgH₂S g-BC⁻¹, however q was reduced to 47.9 mgH₂S g-BC⁻¹.

In summary, this study found the process to obtain the biochar-based desulfurizer practically applicable for real fuel cell systems. Outcomes are summarized below.

- NH₃ treatment to dope nitrogen (N) on the biochar surface is effective for the enhancement of H₂S adsorption capacity, however the N-doping should be moderate.
- Utilization of pure NH₃ gas is not recommended for N-doping due to its toxicity and unavailability especially in rural areas. NH₄⁺ aqueous solution, for example digestate liquid, can be utilized as an alternative nitrogen source for obtaining an excellent desulfurizer based on biochar.
- Ni loading on biochar effectively improves the H₂S adsorption capacity by the combination with NH₃ treatment, provided that the proper treatment sequence (NH₃ treatment followed by Ni loading) is employed.
- By the simple paper-making process using ceramic fibers, industrially useful biochar-based desulfurizer can be efficiently produced.

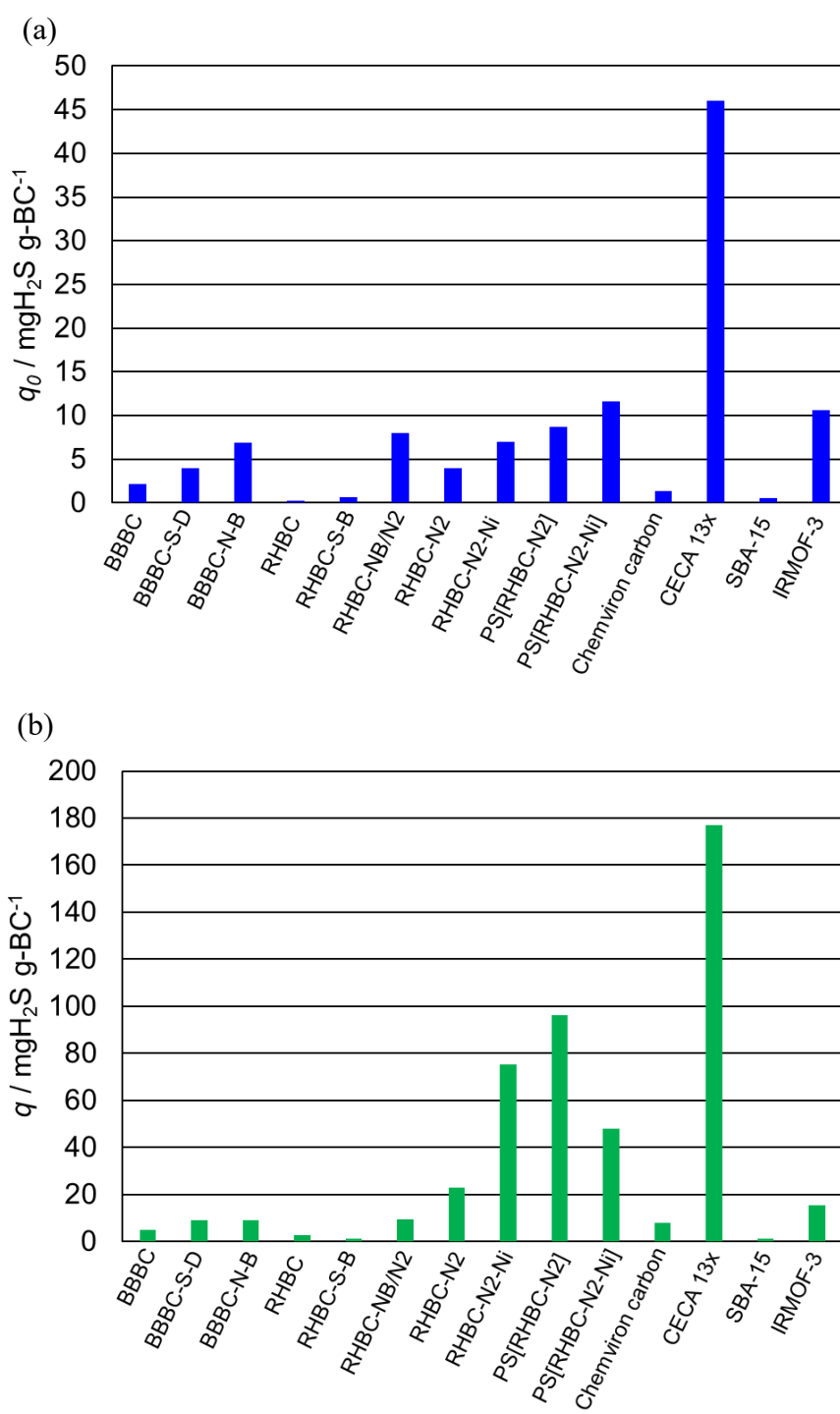


Figure 5.1: H₂S adsorption capacities (a) q_0 and (b) q of the biochars prepared in this study together with the commercial and the reported desulfurizers.

5.3. Future prospects

5.3.1. Application to the real system

Based on the biogas-fueled SOFC demonstration reported by Shiratori *et al.* [6], practical application of the PS[RHBC-N2-Ni] was considered as described in Figure 5.2. Raw biogas ($0.33 \text{ Nm}^3 \text{ h}^{-1}$) is passed through a desulfurizing tower packed with 40 kg of iron oxide pellets, resulting in a H_2S concentration of around 4 ppm. Then, this biogas is passed through the second desulfurizing unit packed with PS[RHBC-N2-Ni]. Finally, the H_2S -free biogas is supplied to the SOFC system to generate 1 kW electricity. Considering the breakthrough capacity (q_o) of $16.6 \text{ mgH}_2\text{S g-BC}^{-1}$, required amount of RHBC-N2-Ni for the continuous supply of H_2S -free biogas to SOFC is calculated at 10.8 kg. In future work, durability of the biochars developed in this study must be evaluated for practical application, especially focusing on the dispersion of metal particles loaded on the surface.

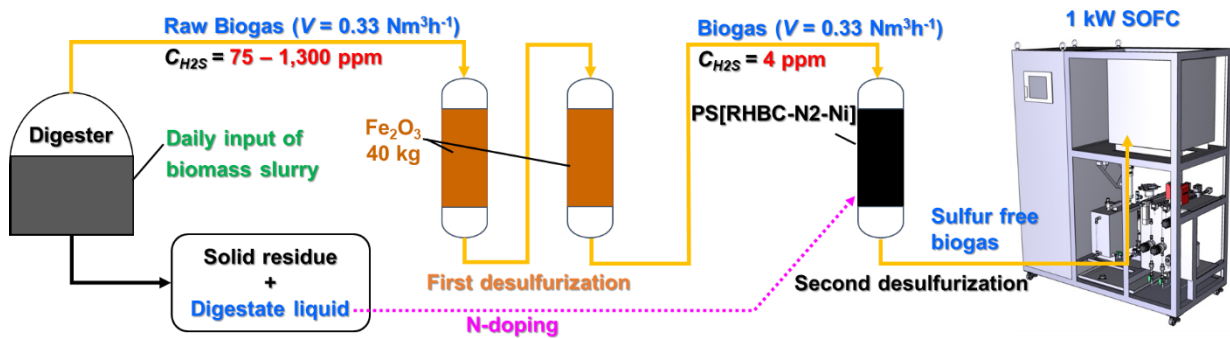


Figure 5.2: Schematic drawing of the biogas power generation test with SOFC installed in Mekong Delta, Vietnam [6] using the biochar adsorbent (PS[RHBC-N2-Ni]) developed in this study as desulfurizer.

Other than H_2S , biogas includes H_2O and NH_3 which can also adsorb on the biochar surface [7,8]. Although H_2O can help the adsorption of H_2S by providing oxygen needed for the oxidation and ionization of H_2S , too high level of H_2O can show adverse effect by blocking the pores of the carbon [9,10]. To maximize the selectivity for the H_2S adsorption, the biochar adsorbent developed in this study must be further modified either by metal loading (other than Ni) or other methods such as the addition of a basic precursor (KOH, MgOH, etc.) followed by heat treatment [11,12]. It has been reported that H_2S adsorption capacity of RHBC made from maple wood was increased from $q = 6.1$ to $23.9 \text{ mgH}_2\text{S g-BC}^{-1}$ by Fe-loading [13]. On the other hand, q increased from $6.8 \text{ mgH}_2\text{S g-BC}^{-1}$ to 33.0 and $46.2 \text{ mgH}_2\text{S g-BC}^{-1}$ by the Zn and Cu-loadings on commercial

activated carbon (Darco G40, Norit), respectively. Effectiveness of co-loading was also reported. For example, co-loading of Zn and Cu on the activated carbon showed further enhancement of q to 49.6 mgH₂S g-BC⁻¹ which is 1.5-fold compared to the single loading of Zn and 1.1-fold compared to the single loading of Cu [14]. Dependence on the type of precursor also should be explored. For example, in the Ni-loading, the type of precursor was proved to influence on the Ni particle size [15]. By choosing a precursor without oxygen such as NiCl₂, oxygen content on the surface, which is a predominant factor for H₂S adsorption, can be controlled.

As mentioned before, the kind of biomass feedstock used for the production of biochar affects the contents of organic and inorganic components in biochar. Dependences of the adsorption ability on these contents should be explored using various types of biomass feedstock [16]. For building a local resource circulation system, it is highly recommended that the solid residue of the methane fermentation is utilized as a raw material to produce biochar.

Removal of siloxane, one of the major impurities of digestion gas, by biochar should also be studied [17], even though its poisoning effect on the reforming catalyst and the SOFC anode is weaker than that of H₂S [18].

5.3.2. Further studies

The kinetic study in Chapter IV (Sec. 4.4.4) was for the phenomenon just after the breakthrough corresponding to the first gradient (k_1). To fully understand the mechanism of H₂S adsorption on the biochar, further studies are needed for the process before the breakthrough. For this purpose, the temperature programmed desorption (TPD) technique is powerful tool which can estimate the contents of acidic and basic functional groups on the biochar surface. As for the basic functional groups, by evaluating the amounts of CO and CO₂ released at an elevated temperature from the surface of a sample exposed in a CO₂ flow, the existences of carbonyl, quinone, phenol and ether groups and carboxyl and lactone groups, respectively, can be evaluated [19]. On the other hand, the TPD measurement at an elevated temperature after exposing a biochar in a NH₃ flow, for example, carboxylic amides and nitriles will be detected to show the existence of carboxylic group [20].

Regeneration of a spent biochar is worth investigating. Fig. 5.3 shows a result of the H₂S adsorption test during which blackout happened at 406 h, then at 497 h H₂S supply was restarted. The result indicates that the regeneration of adsorption capacity proceeded by just stopping the supply of a H₂S-containing gas without heating and purging.

However, for the Ni-loaded biochar, with stronger chemical interaction with H₂S, heating must be necessary for the recovery of the adsorption capacity.

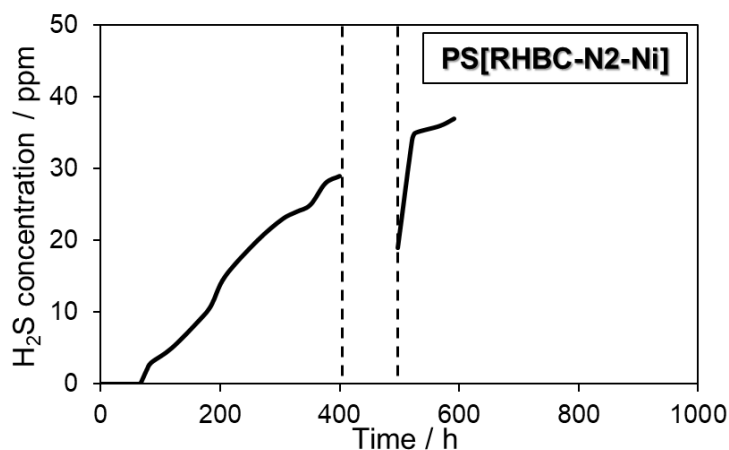


Figure 5.3: Results of the H₂S adsorption tests for PS[RHBC-N2-Ni]. At 406 h, 40 ppm H₂S supply was stopped due to blackout, then at 497 h H₂S supply was restarted.

5.3.3. Application of the spent biochar as fertilizer

Biochar, which contains essential nutrients for plants such as nitrogen (N), phosphorous (P), potassium (K), silica (Si), and other minerals, is widely applied as a soil amendment or a slow-release fertilizer. These contents in the commercial fertilizer (Sulfachar) and the biochars spent for the desulfurization tests in this study are listed in Table 5.1. N content in the spent RHBC-N2 was very high due to the ammonia treatment, and its S content was comparable to N and K because of the H₂S adsorption. N can increase the productions of amino acid and chlorophyll in plants, P can boost energy storage and transfer, K can serve as an enzyme activator, and Si can increase the plant's tolerance to drought and pathogens [21]. Moreover, S is one of the essential nutrients required for protein synthesis [22,23]. In the case of chemical fertilizer, only one third of N can transfer into the soil, on the other hand, by using biochar as an alternative fertilizer, N uptake into the soil is increased [24]. In this point, the N-doped biochar developed in this study is promising material as an organic fertilizer as well as a desulfurizer [25].

Table 5.1: Content of nutrients in the commercial fertilizer (Sulfachar) and the biochars spent for the H₂S adsorption in this study.

Sample	Content* / mg g ⁻¹			
	N ¹⁾	P ²⁾	K ²⁾	S ³⁾
Sulfachar [22]	12	34	38	365
RHBC spent for desulfurization	4.2	2.1	52	2.6
RHBC-N2 spent for desulfurization	22	2.1	49	23

1) measured by CHN corder

2) measured by XRF

3) determined by q value

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