

Influence of Nitrogen moieties on CO₂ capture of Carbon Aerogel

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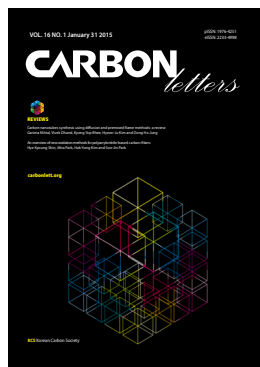
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Abstract

Carbon aerogel is a porous carbon material possessing high porosity and high specific surface area. Nitrogen doping reduced the specific surface area and micropores, but it furnished basic sites to improve the CO₂ selectivity. In this work, N-doped carbon aerogels were prepared with different ratios of resorcinol/melamine by using the sol-gel method. The morphological properties were characterized by scanning electron microscopy (SEM). Nitrogen content was studied by X-ray photoelectron spectroscopy (XPS) and the specific surface area and micropore volume were analyzed by N₂ adsorption-desorption isotherms at 77 K. The CO₂ adsorption capacity was investigated by CO₂ adsorption-desorption isotherms at 298 K and 1 bar. Melamine containing N-doped CAs showed a high nitrogen content (5.54 wt.%). The prepared N-doped CAs exhibited a high CO₂ capture capacity of 118.77 mg/g (at resorcinol/melamine = 1:0.3). Therefore, we confirmed that the CO₂ adsorption capacity was strongly affected by the nitrogen moieties.

Key words: carbon aerogel, CO₂ capture, CO₂ adsorption, N-doping, N-doped carbon aerogel

1. Introduction

Recently, many studies have focused on carbon dioxide (CO₂) because it is a primary cause of global warming and adverse effects of climate change are expected to increase in the future [1,2]. Also, new environmental problems related to indoor air quality in urban areas, as well as climate change, are being emphasized [3]. The IEA (International Energy Agency, IEA) has reported that industrial facilities such as fossil fuel fired power plants will increase the world CO₂ concentration drastically [4].

CO₂ capture has been widely studied in order to facilitate its effective and economical separation. Research on CO₂ adsorption technology has mainly been performed using the membrane separation method, the absorption method, and the adsorption method [5-7].

The membrane separation process is a simple process used for the separation and purification of a particular component. However, it is expensive and consumes a large amount of energy. An important disadvantage of the absorption method is the generation of waste [8, 9]. The adsorption method is considered to be an economical method because it involves minimum energy, its products can be recycled, and it can be applied at low concentrations and low temperature. Adsorption method has favorable terms with the adsorption method of low-level CO₂ [10].

Solid adsorbents such as porous carbons, macroporous silica (SBA-15, MCM-41), zeolites, and metal-organic frameworks (MOFs) are widely studied [11-21]. Porous carbons have attracted considerable interest owing to their outstanding properties such as high porosity, high specific surface area, chemical and mechanical stability, tunable pore size, high hydrophobicity, and low cost [22-26]. Carbon aerogel (CA) is a light 3D-bonded network that contains nanosized micro-

pores; it has high porosity in the range of 80–90%, stable mesopores with sizes ranging from 2–50 nm, and a large specific surface area [27–32]. Two different approaches have been adopted to improve the CO₂ adsorption capacities of porous carbons. Both physical adsorption and chemical adsorption with surface modification have been widely studied. The usage of nitrogen, sulfur, metal oxides, and boron can improve their physicochemical properties [33–37]. Nitrogen doping has been found to reduce the specific surface area and number of micropores; however, it furnished basic sites that improved the CO₂ selectivity [38–41].

In this study, using the sol-gel method, we present the preparation and characterization of N-doped CAs; resorcinol and melamine are the carbon and nitrogen precursors, respectively. The CO₂ capture capacities of the prepared N-doped CAs vary with the nitrogen moieties [42].

2. Experimental

2.1. Materials and preparation

For the N-doped CA synthesis, we used formaldehyde (Duk-san Pure Chemicals, Korea) as the initiator, resorcinol as the carbon precursor, and sodium carbonate (Sigma-Aldrich, USA) as the catalyst.

For the synthesis of N-doped CAs, sodium carbonate and formaldehyde were added to a solution of resorcinol and melamine. The resorcinol/formaldehyde and resorcinol/sodium carbonate ratios were chosen to be 0.5 and 200, respectively. Melamine was dispersed by stirring the solution for 3 h at room temperature (298 K). The resulting solution was solidified by stirring at 80°C for 24 h and subsequently heated in an oven at 80°C for 48 h to induce gelation. The wet gels were soaked in an acetone bath at 50°C for 24 h to replace the water in the gel with acetone. Subsequently, the sample was dried in an oven for 24 h to remove the residual water. Finally, the carbonization process was performed in a tube furnace under flowing nitrogen by heating the sample at the rate of 2°C/min up to 900°C and maintaining this temperature for 60 min. Fig. 1 provides a schematic diagram of the formation of N-doped CAs using the sol-gel method.

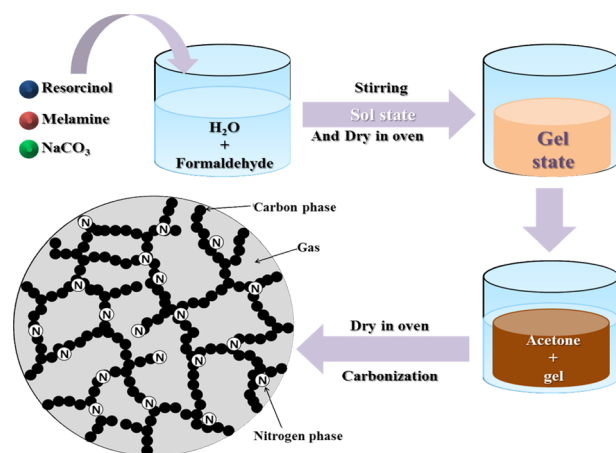


Fig. 1. Schematic diagram of the preparation of N-doped carbon aerogel.

2.2 Characterization

The surface characteristics and morphologies of the prepared N-doped CA samples were studied by field emission scanning electron microscopy (FE-SEM, Hitach S-4300, Japan). Elemental analysis of the sample was conducted using X-ray photoelectron spectroscopy (XPS, ESCALAB220i-XL VG Scientific, UK) to determine the elemental composition of the N-doped carbon aerogel. The specific surface area and pore structure were determined from the nitrogen adsorption-desorption isotherms at 77 K using a surface area and pore size analyzer (BELSORP Inc., Japan). Prior to the measurements, the dried samples were outgassed at 200°C for 12 h under vacuum in the degas port of the adsorption instruments. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area, and the total pore volume (V_t) was obtained from the nitrogen adsorption volume at $P/P_0 = 0.990$. The mesopore volume (V_m) was measured using the Barrett-Joyner-Halenda (BJH) model.

The samples were evaluated for CO₂ capture capacity by BELSORP. The samples were degassed at 200°C for 12 h before cooling down to the required adsorption temperature (25°C). Then, we measured the CO₂ adsorption volume with relative pressure (P/P_0) at 298 K.

3. Results and Discussion

3.1. SEM analyses

The morphology and microstructure of the samples were studied using SEM; the results are shown in Fig. 2. The CAs show typical aerogel structures with sizes ranging from 20–30 nm, as was reported previously. In Figs. 2 (b)–(d), the N-doped CAs show nanometer sized spherical structures without smooth

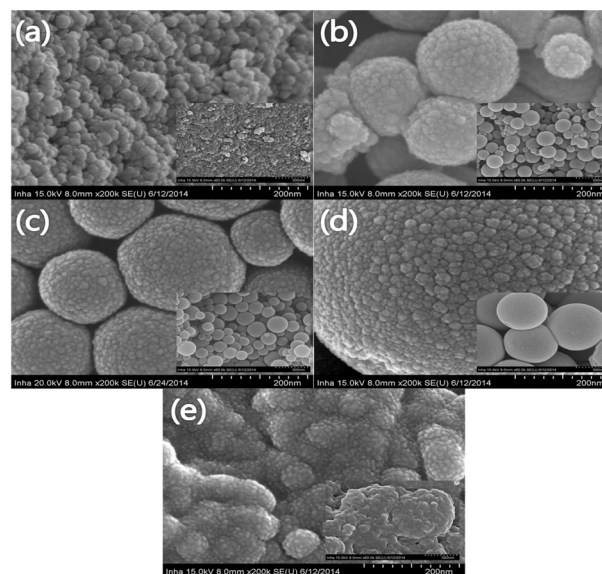


Fig. 2. Scanning electron microscopy images of the N-doped carbon aerogels; (a) RM1:0-CA, (b) RM1:0.1-CA, (c) RM1:0.3-CA, (d) RM1:0.5-CA, and (e) RM1:0.8-CA

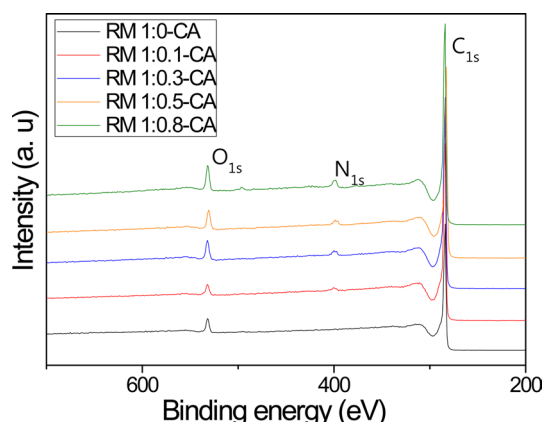


Fig. 3. X-ray photoelectron spectroscopy spectra for the N-doped carbon aerogels

Table 1. Composition of N-doped carbon aerogels (wt.%)

samples	C	N	O
RM1:0-CA	93.9	0	6.1
RM1:0.1-CA	94.9	1.9	3.2
RM1:0.3-CA	92.4	2.5	5.1
RM1:0.5-CA	90.7	3.1	6.2
RM1:0.8-CA	89.4	5.5	5.1

surfaces. The spherical structures are derived from the N-doped CAs formed from the interconnected sphere-like nanoparticles. In addition, the size of the samples tends to increase with increasing melamine content. In the case of RM1:0.8-CA, the decomposition of the spherical structure was observed. Therefore, we concluded that the structure resulted from excess melamine content.

3.2. XPS analyses

The nitrogen functional groups in the modified samples were also confirmed by XPS measurement. The XPS results of the N-doped CAs are shown in Fig. 3. As can be seen in Fig. 3, three elements, C, N, and O, can be identified, with peaks at ~285 eV (C_{1s}), ~400 eV (N_{1s}), and ~532 eV (O_{1s}), respectively. The peak at 400 eV is attributed to the presence of nitrogen atoms from molecularly adsorbed nitrogen-containing compounds on the surface of the samples. The surface nitrogen content increased with the increase of the amount of melamine from 5.54 wt.% to 0. Noticeably, the RM1:0.8-CA sample contained a very large amount of nitrogen (5.54 wt.%) (Table 1).

3.3. N₂ adsorption-desorption isotherms

N₂ adsorption/desorption isotherms and pore size distribution at 77 K on N-doped CAs are presented in Fig. 4. The adsorption/desorption isotherms of CAs and N-doped CAs appear as

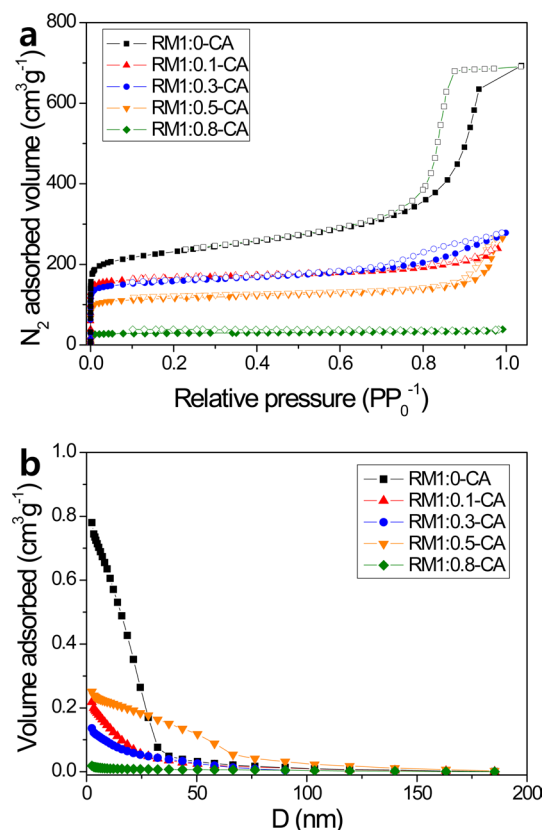


Fig. 4. (a) N₂ full isotherms and (b) pore size distribution of the N-doped carbon aerogels

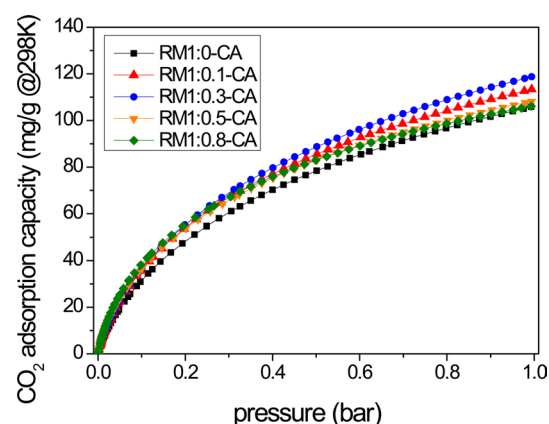
Type IV, showing a hysteresis loop at relative pressures above 0.4, which indicates the existence of mesopores. The isotherms of all the samples show a steep increase in nitrogen adsorption below $P/P_0 = 0.1$. This reflects the broad pore size distribution of RM1:0.3-CA, RM1:0.5-CA, and RM1:0.8-CA. However, in the cases of RM1:0-CA and RM1:0.1-CA, most of the sample pore volume is filled below a relative pressure of about 0.1. As can be seen in Table 2, the BET surface area of the RM1:0-CA sample was 853 m²/g, with a BJH pore volume of 0.80 cm³/g. The specific surface area of all the samples decreased to RM1:0.8-CA. The micropore volume, mesopore volume, and total volume decreased from RM1:0-CA to RM1:0.3-CA. However, the micropore volume, mesopore volume, and total volume again increased at RM1:0.5-CA and decreased to RM1:0.8-CA. When melamine was introduced, the surface area and the pore volume decreased with increasing nitrogen content because nitrogen occupied the pore spaces of the aerogel.

3.4. CO₂ capture capacity

Fig. 5 shows the CO₂ capture capacities of all the samples at 298 K and 1 bar. For CO₂ adsorption, the pore size plays an important role in developing a high capacity porous carbon adsorbent. Also, the presence of nitrogen causes an increase in the CO₂ capture capacity of RM1:0-CA. Owing to its basic characteristics, nitrogen plays a momentous role in the formation of

Table 2 Textural properties of the N-doped carbon aerogels

Samples	S_{BET}^a ($\text{m}^2 \text{g}^{-1}$)	V_{total}^b ($\text{cm}^3 \text{g}^{-1}$)	V_{meso}^c ($\text{cm}^3 \text{g}^{-1}$)	V_{micro}^d ($\text{cm}^3 \text{g}^{-1}$)	D^e (nm)
RM1:0-CA	853	1.031	0.780	0.251	4.799
RM1:0.1-CA	656	0.423	0.219	0.204	2.776
RM1:0.3-CA	609	0.370	0.136	0.234	2.253
RM1:0.5-CA	451	0.407	0.251	0.156	3.570
RM1:0.8-CA	116	0.059	0.018	0.041	2.032

^a Specific surface area (m^2/g): BET equation ($P/P_0 = 0.05-0.1$)^b Total pore volume (cm^3/g): V_{ads} ($P/P_0 = 0.990$)^c Micropore volume (cm^3/g): Dubinin-Radushkevich equation^d Mesopore volume (cm^3/g): BJH equation^e Mean pore diameter (nm)**Fig. 5.** CO_2 adsorption isotherms of the N-doped carbon aerogels.

CO_2 -friendly sites. The RM1:0.3-CA exhibits the highest CO_2 capture capacity of 118.77 mg/g. In the low relative pressure range, the adsorbed weights of all the CAs are in the following order: RM1:0.3-CA > RM1:0.1-CA > RM1:0.5-CA > RM1:0.8-CA > RM1:0-CA. In spite of a decrease in the specific surface area and micropore volume of RM1:0.3-CA, the enhancement of CO_2 capture capacity is due to the effect of the CO_2 -friendly sites. However, in the cases of RM1:0.5-CA and RM1:0.8-CA, the pore structure is destroyed and CO_2 capture capacity is reduced. The amount of melamine plays a crucial role in determining the CO_2 capture capacity.

4. Conclusions

In this work, the sol-gel method was implemented for the preparation of N-doped CAs for CO_2 capture, using resorcinol and melamine as the carbon and nitrogen precursors, respectively. The melamine containing N-doped CAs showed a high nitrogen content (5.54 wt.%). The prepared N-doped CAs exhibited a high CO_2 capture capacity of 118.77 mg/g (at resorcinol/melamine = 1:0.3). The excellent CO_2 capture capacity was attributed to the presence of nitrogen basic groups as CO_2 -friendly sites.

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