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Comparative study of activation methods to design nitrogen-doped ultra-microporous carbons as efficient contenders for CO_2 capture

Adeela Rehman, Soo-Jin Park*

Department of Chemistry, Inha University, 100 Inharo, Incheon 22212, South Korea

HIGHLIGHTS

- One-step polymerization and activation method is used for designing nitrogen-enriched carbons.
- MCKC-3 possesses high surface area (2060 m^2/g), ultramicropores (< 0.7 nm) and high nitrogen content (2.3 wt%).
- Excellent CO_2 uptake performance of 354 mg/g (8.03 mmol/g) at 273 K and 1 bar was observed.

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ABSTRACT

Microporous carbon materials are envisaged as efficient contenders for mitigating CO_2 levels by virtue of their favorable surface chemistry, high specific surface area, tunable pore structures, moderate heat of adsorption, and facile regeneration. This study presents a solvent-free one-step polymerization and activation method for designing a series of nitrogen-enriched carbons to delineate the role played by nitrogen moieties and ultra-micropores on CO_2 capture. Two activating agents were used at high temperature to fabricate microporous carbons with tunable pore structure and variable nitrogen content. The optimized material, MCKC-3, possesses high surface area (2060 m^2/g) comprising of ultramicropores (< 0.7 nm) and high nitrogen content (2.3 wt%). This material exhibit an outstanding CO_2 uptake performance of 354 mg/g (8.03 mmol/g) at 273 K and 1 bar, comparable to the highest adsorption reported so far for carbon-based materials. In conclusion presence of both the ultra-micropores and nitrogen functionalities contribute a major role in CO_2 adsorption, the former being predominant.

1. Introduction

Carbon dioxide emissions largely contribute towards climate change and environmental pollution [1–4]. As a greenhouse gas, CO_2 is emitted on a large scale from fossil fuel combustion. With the growing population, energy demands are continuously increasing, and the lack of sufficient clean and renewable sources; wind, solar, and hydrogen, necessitates the use of fossil fuels as the primary energy source. To mitigate global warming and climate change, effective strategies are needed to capture CO_2 from large point-sources [5]. Current CO_2 capture methods include membrane separation, amine scrubbing, and ionic liquid absorption. However, solid adsorbents are promising alternatives by virtue of their economical production, wide availability, large surface area, tunable textural properties, rich surface chemistry, physicochemical stability, low energy requirements, and clean processing [6]. Among solid adsorbent carbons, zeolites [7], metal-organic frameworks (MOFs) [8], and porous organic polymers [9] are widely used in gas and energy storage. Particularly, carbon-based materials have gained significant consideration owing to their inexpensive and easy preparation, ease of regeneration, and relative lack of sensitivity towards moisture in comparison with other CO_2-philic materials.

Recently, various techniques have been developed to design porous carbons. In the last few years, one-step polymerization and activation has been regarded as a facile green method to fabricate porous carbon materials without the use of toxic solvents. It is preferable to conventional liquid phase synthesis, hard and soft templating methods, and physical activation methods. Compared to physical activation, lower temperature and usually less activation time is required for chemical activation. Additionally, the resultant activated carbons possess high surface area and narrow pore size distributions with excellent carbon yields. This is primarily due to the dehydrogenation characteristics of the chemical activating agents, which prevent the production of tar and decrease the generation of other volatile substances. However, the detailed mechanism of chemical activation is poorly understood. Some

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* Corresponding author.
E-mail address: sjpark@inha.ac.kr (S.-J. Park).

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other drawbacks of the chemical activation method include the washing steps required to remove impurities left from the activating agent, and the corrosiveness of the chemicals used.

From the literature, various chemicals have been reported as activators including KOH, $ZnCl_2$ [10,11], H_3PO_4 [12], and NaOH [13]. Among these activating agents, KOH is the most commonly used with the ability to induce high porosity in the resulting materials [14]. However, toxicity and environmental effects should be taken under consideration while selecting the activating agent. KOH activation has two intrinsic disadvantages that retard its commercial application. The first is the corrosion of the equipment at high temperatures during activation. Secondly, KOH can cause pollution during residue removal from the products and is considered to be a serious environmental hazard. During activation, KOH readily impregnated in the carbon material and as a high boiling salt (1327 °C), the vaporization is usually incomplete. Thus, a significant fraction of KOH is expected to be released into the environment during washing. Due to strong basic nature of KOH, it is highly toxic to human health [15]. Additionally, KOH promotes eco-toxicity in water body. Hence, to circumvent these difficulties, researchers are trying to develop a mild activator that is environmentally benign. Among the potential candidates, K_2CO_3 is an excellent choice as it is commonly used in food additives. Moreover, K_2CO_3 possess similar activation performance as KOH for preparing porous carbons [16]. Furthermore, K_2CO_3-activated materials can be used as CO_2 adsorbents, with examples including the carbon material CN-600-3 with an uptake of 5.12 mmol/g of CO_2 [17] and PANI-C400-KC650 with 7.6 mmol/g of adsorbed CO_2 at 273 K and 1 bar [18]. Similarly, KOH-activated KLB2 exhibited an uptake of 6.3 mmol/g [19] and A-WN700 showed 7.2 mmol/g uptake of CO_2 at 273 K and 1 bar [20]. However, it remains challenging to design microporous carbons, with the optimum surface area by a single step strategy in an environmental friendly manner, possessing excellent CO_2 adsorption performance to be used in commercial applications.

Herein, we studied the CO_2 adsorption behavior of microporous carbons synthesized by a single-step solvent-free synthesis. A comparative study was performed regarding the development of microporous structures by physical and chemical activation methods. Furthermore, upon comparison of KOH and K_2CO_3 activation, it was revealed that the K_2CO_3-activated sample outperformed all other samples with an uptake capacity of 354 mg/g (8.03 mmol/g) of CO_2 at 273 K and 1 bar.

2. Experimental

2.1. Materials

Melamine (99%), 4,4′-Biphenyldicarbaldehyde (99%), potassium hydroxide (95%), and potassium carbonate (95%) were used in this study. All the materials were obtained from Sigma-Aldrich and used without further purification.

2.2. Synthetic protocol

Microporous carbons were prepared by a facile single-step strategy involving simultaneous polymerization and carbonization followed by the in situ activation of two aromatic organic precursors, melamine and 4,4′-Biphenyldicarbaldehyde. The 1:1 reaction mixture was prepared by grinding the precursors together for 30 min. Subsequently, KOH/K_2CO_3 was added in mass ratios of activating agent to organic precursors of 3/1 and 4/1. The reaction mixture was ground in an agate mortar until a homogeneous powder was formed. It was then heated in a tubular furnace at the ramp rate of 3 °C/min to 800 °C for 100 min under inert gas. The resultant black powder was cooled to room temperature and washed several times with HCl solution and distilled water sequentially to remove impurities. The obtained samples were then dried at 120 °C overnight in an oven. Final carbonized samples were labeled as MCK-X, MCKC-X, and MC, where MCK denotes the microporous carbons prepared by KOH activation, MCKC represents the K_2CO_3 activated samples, MC corresponds to the samples prepared without any chemical agent and X represents the mass ratio. However the non-carbonized grounded mixture was labeled as NCMC, NCMCK and NCMCKC where NC represents non-carbonized samples.

2.3. Materials characterization

The synthesized carbon materials were characterized by various analytical techniques. Fourier transform infrared (FTIR) spectra of the fabricated samples were attained using a FTIR vacuum VERTEX 80 V spectrometer. A thermal gravimetric analyzer (TGA; TG209F3) was used to determine the thermal stability of the materials to be carbonized under a nitrogen atmosphere. X-ray diffraction (XRD) patterns were recorded using a D2 PHASER, BRUKER, X-ray diffractometer. To examine the morphological structures of the samples, field emission scanning electron microscope (FE-SEM; Model SU8010, Hitachi Co., Ltd.) and Field emission transmission electron microscope (FE-TEM; JEM-2100F) were used. The elemental composition was determined by elemental analysis performed with an EA1112 element analyzer. Further surface characterization was performed by X-ray photoelectron spectroscopy (XPS, VG Scientific Co., ESCA LAB MK-II).

2.4. Gas adsorption measurements

Nitrogen adsorption-desorption measurements were performed using a Model Belsorp Max instrument (BEL Japan, Inc.) to explore the textural properties. The adsorption capacity for CO_2 was determined at 273, 283, and 298 K at 1 bar. The adsorption isotherms were recorded by the Model Belsorp Max instrument (BEL Japan, Inc.). To investigate the selective adsorption behavior of the prepared samples, nitrogen adsorption isotherms were recorded at 273 K using a Model Belsorp Max instrument (BEL Japan, Inc.). Prior to all the measurements, the prepared samples were degassed at 120 °C for 6 h under vacuum to remove any moisture and CO_2 molecules adsorbed in the pores.

3. Results and discussions

3.1. Morphological and structural analyses

This study relied on the Schiff base condensation of the melamine and 4,4′-Biphenyldicarbaldehyde with subsequent carbonization and activation (Scheme 1). The surface functionalities of grounded mixture (NCMC) and activated carbons were examined using FTIR spectroscopy and the results are presented in Fig. 1. The successful condensation of mixture of 4,4′-Biphenyldicarbaldehyde and melamine is evident by the imine stretch (C=N) at 1626 cm^{-1} (Fig. 1, inset). Moreover, the unreacted part of the aldehyde appeared as a sharp band at approximately 1687 cm^{-1}. The effect of carbonization and chemical activation were studied by comparison of the FTIR spectra of all prepared materials. The MCK and MCKC samples exhibited similar absorbance bands. However, by analyzing the FTIR spectra presented here and in the literature [21], it is suggested that MC had surface functional groups with C—O and C=C linkages, as indicated by a very intense band at approximately 1400 cm^{-1}. This can be attributed to the higher degree of carbonization shown by MC, as evident in the XRD pattern (Fig. S1). The peak at 3500 cm^{-1} is attributed to the N—H stretching vibrations of amine groups. The peaks at approximately 1000 cm^{-1} is assigned as C—O stretching modes of oxygenated functionalities appeared on the surface of the activated carbons. It is likely that during carbonization and activation at high temperatures many weak bonds disappeared. Similarly, absence of sharp peaks of the characteristic imine functionality indicates the effective carbonization of the polymer structure at the targeted temperature. However, the results indicate the presence of leftover nitrogen functionalities which play a vital role in enhancing