Significantly increasing porosity of mesoporous carbon by NaNH$_2$ activation for enhanced CO$_2$ adsorption

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ABSTRACT

Sodium amide (NaNH$_2$), a readily available strong base, was investigated as an efficient reagent for chemical activation of mesoporous carbon (MC) in the temperature range of 400–900 °C, aiming to enhance the CO$_2$ adsorption performance. Total surface area and pore volume of the activated MC increase greatly with the activation temperature up to 700 °C and then tend to level off. Small micropores with a diameter <1 nm are developed mainly at low temperatures (400–550 °C) and decrease continuously in volume as the activation temperature increases. Nitrogen species are incorporated onto the carbon activated at 400 °C but completely disappear at higher activation temperatures due to poor thermal stability. CO$_2$ adsorption experiments illustrated a substantial improvement in capacities at 0 °C for the NaNH$_2$-activated carbons (6.31 mmol/g at 1 bar and 2.06 mmol/g at 0.15 bar) in comparison to pristine MC (2.01 mmol/g at 1 bar and 1.00 mmol/g at 0.15 bar). The low-pressure CO$_2$ capacities are well correlated with the volume of small micropores rather than the total micropore volume and surface area. The activation ability of NaNH$_2$ was compared with those of KOH and NaOH, verifying the superiority of NaNH$_2$ in the MC activation under relatively moderate conditions, i.e., activation reagent/MC weight ratio of two and activation temperature of 550 °C.

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1. Introduction

The emission of CO$_2$, which is mostly produced from the combustion of fossil fuels, has attracted extensive attention across academic and industrial communities because of its potentially destructive impact on the environment. Carbon dioxide is a well-known greenhouse gas and its accumulation in the atmosphere is believed to be a major contribution to the continuous global warming over the past century. In the near future, fossil fuels will still be the major source of energy for human activities; therefore, the capture of CO$_2$ has been proposed as an essential solution to limit or slow climate change. A method commonly used in industry for the reduction of CO$_2$ emissions is absorption in aqueous amine solutions [1]. However, organic amines are highly volatile and

corrosive, and the regeneration of these absorbents is an energy-intensive process. These factors depict the inherently unfavorable nature of aqueous amines, and the exploration of new materials for CO$_2$ capture has thus been widely demanded.

Porous solid adsorbents such as metal-organic frameworks (MOFs) [2], porous polymer networks (PPNs) [3], covalent organic frameworks (COFs) [4], porous carbons (PCs) [5], and supported amines [6] are potential alternatives that have been widely investigated. Among them, porous carbons feature many inherent advantages, including potentially low cost, high stability, large surface areas, tunable pore structures, high thermal conductivity, and ease of surface functionalization [7]. Carbons have been demonstrated to have potential applications in many fields such as electrochemistry [8], catalysis [9], and gas separations [10]. Porous carbons with well-developed microporosity, especially small micropores with size below 1 nm, are particularly attractive for application in CO$_2$ adsorption, as described in several previous works [11–14]. To create abundant micropores, pristine carbons are usually subjected to post-synthesis activation. KOH [15–18] is the

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most frequently used activation agent, while K_2CO_3 [19], H_3PO_4 [20], $ZnCl_2$ [21], NH_3 [22,23], CO_2 [24,25], and H_2O [26,27] have been less frequently employed. Jaroniec et al. [28] compared the ability of different agents for the activation of a commercial carbon and found KOH-activated carbon had the most developed microporosity and enhanced adsorption capacity for CO_2.

However, the KOH-activation method usually requires high activation temperatures (>600 °C) to obtain porous carbons with optimized CO_2 adsorption performance. For example, Machnikowski et al. [29] synthesized granular activated carbons that could adsorb 6.2 mmol/g of CO_2 at 0 °C and 1 bar by activating coal-based cokes with KOH at 800 °C. Jaroniec et al. [11] reported the activation of phenolic resin-based mesoporous carbons by KOH at 700 °C to result in products showing a CO_2 adsorption capacity of 4.37 mmol/g at 25 °C and 1 bar. Park et al. [30] investigated the effect of KOH-activation temperature on CO_2 adsorption of carbon aerogels and found the sample activated at 900 °C exhibited the highest CO_2 adsorption capacity of 2.48 mmol/g at 25 °C and 1 bar. Suarez-Garcia et al. [31] activated carbon xerogels with KOH at 800 °C to result in products displaying CO_2 adsorption capacity of 4.9 mmol/g at 0 °C and 1 bar.

It is of significance to develop a new method for the efficient activation of carbon materials under relatively mild conditions. In our recent work [32], we introduced a low-temperature (230—380 °C) route to N-doped mesoporous carbons using a strong base — sodium amide ($NaNH_2$) as the N-doping agent. It was interesting to find that the incorporation of nitrogen species to the framework of mesoporous carbons was accompanied with the development of microporosity. This result demonstrated the potential utility of $NaNH_2$ for the activation of carbon materials. In this work, we have further explored $NaNH_2$ as an activation agent for the preparation of porous carbons with ultrahigh specific surface areas as well as large micropore volumes. A phenolic resin-based mesoporous carbon synthesized by a previously established soft-templating method [33—35] was used as the pristine carbon for activation, and prepared activated mesoporous carbons were found to display significantly enhanced CO_2 adsorption.

2. Experimental section

2.1. Chemicals

CO_2 (99.99 mol%) and N_2 (99.99 mol%) were supplied by Airgas Co. Ltd.. Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer ($EO_{106}PO_{70}EO_{106}$, Pluronic F127), phloroglucinol (98 wt%), formaldehyde (37% in aqueous solution, stabilized with 10—15 wt% methanol), sodium amide (99 wt%), sodium hydroxide (99 wt%) and potassium hydroxide (99 wt%) were purchased from Sigma-Aldrich Chemicals Co. Ltd.. All the chemicals were used as received without further purification. Warning: sodium amide is highly hygroscopic and should be operated in a dry box!

2.2. Synthesis of materials

The pristine mesoporous carbon (MC) was synthesized by carbonization of a nanostructured polymeric composite at 600 °C, which was obtained by self-assembly of block copolymer (Pluronic F127) and phenolic resin (phloroglucinol-formaldehyde) under acidic condition via an established soft-templating route [33—35]. The activation of MC by $NaNH_2$ was performed as following: 1 g of MC and 2 g of $NaNH_2$ were mixed manually in a nickel crucible, and then heated in a tubular furnace under flowing N_2 (100 mL/min) to a target temperature (400—900 °C) at 10 °C/min and kept for 1 h. The activation of MC by NaOH or KOH was performed as following:

1 g of MC was mixed with 5 g of 40 wt% aqueous NaOH or KOH (containing 2 g of activators) in a nickel crucible and sonicated for 1 h, then heated in a tubular furnace under flowing N_2 (100 mL/min) to 120 °C at 10 °C/min and kept for 12 h to ensure the evaporation of water, and finally heated to a target temperature (550 or 700 °C) at 10 °C/min and kept for 1 h. After cooling down naturally to room temperature, the resultant powder was washed with deionized water to neutral pH, followed by being dried at 120 °C for 12 h. The obtained activated MCs were named as AMC-$NaNH_2$-T, AMC-NaOH-T or AMC-KOH-T, where T is the activation temperature.

2.3. Gas adsorption measurements

CO_2 adsorption at 0 and 25 °C, and N_2 adsorption at −196 °C and 25 °C were measured on a Micromeritics Gemini 2390a surface area analyser. Prior to the measurement, each sample was dried at 200 °C under flowing N_2 for 2 h.

2.4. Characterizations

N_2 adsorption isotherms at −196 °C and CO_2 adsorption isotherms at 0 °C were used to calculate the textural properties of porous carbons. Total surface area was calculated from N_2 adsorption isotherms using the BET equation in the relative pressure range of 0.02—0.15. Total pore volume was determined from the amount of N_2 adsorbed at the relative pressure of 0.97. Micropore surface area and micropore volume were calculated from N_2 adsorption isotherms using the Carbon Black STSA t-plot equation within the thickness range of 0.45—0.60 nm. Mesopore volume was calculated by subtracting the micropore volume from the total pore volume. The pore size distribution was derived from the N_2 adsorption isotherms using the BJH model. Moreover, the volume of small micropores (size < 1 nm) was calculated from CO_2 adsorption isotherms using NLDFT theory by assuming a slit-like geometry of the micropores.

X-ray photoelectron spectra (XPS) were acquired using a PHI 3056 spectrometer with an AI anode source operated at 15 kV and an applied power of 350 W to determine the surface elementary nature of porous carbons. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed on a Zeiss Auriga Crossbeam scanning electron microscope at an acceleration voltage of 5 kV to illustrate the morphology of porous carbons.

3. Results and discussion

3.1. Textural properties

We first investigated the activation of MC by $NaNH_2$ at different temperatures. Fig. 1 shows the N_2 adsorption isotherms at −196 °C and pore size distributions of the pristine MC and $NaNH_2$-activated MCs. The calculated textural properties are summarized in Table 1. MC displays a type IV N_2 adsorption isotherm with a steep capillary condensation step at the relative pressure of around 0.7—0.8, indicating the presence of mesopores. With the activation temperature increasing from 400 to 550 °C, the capillary condensation step in the N_2 adsorption isotherms of AMCs gradually vanishes, and the N_2 adsorption isotherms of AMC-$NaNH_2$-500 and AMC-$NaNH_2$-550 become more like type I isotherms (see Fig. 1A). This phenomenon indicates the mesoporous structure of MC collapses after activation by $NaNH_2$, which can be further observed from the pore size distributions illustrated in Fig. 1C. As presented in Table 1, the mesopore volumes of AMC-$NaNH_2$-500 and AMC-$NaNH_2$-550 are 0.24 and 0.34 cm^3/g respectively, lower than that of the pristine MC (0.43 cm^3/g). With the activation temperature further increasing from 550 to 900 °C, the capillary condensation step in