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Improving low-pressure CO_2 capture performance of N-doped active carbons by adjusting flow rate of protective gas during alkali activation

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ABSTRACT

Alkali-activated N-doped active carbon (AC) is a promising material for capturing CO_2, but the possible role of flow rate of protective gas during alkali activation in adjusting CO_2 capture performance of AC is unknown. In this study, N-doped ACs for low-pressure CO_2 capture were prepared from chitosan char by KOH activation under flowing N_2 to study the effects of protective-gas flow rate on ultramicropore volume, chemical composition, and CO_2 capture performance of ACs. The results showed that increasing the flow rate changed the low-pressure CO_2 uptake and CO_2/N_2 selectivity by varying the ultramicropore volume and/or surface N/C ratio of ACs. Adopting a moderate flow rate during AC preparation was most favorable for enhancing low-pressure CO_2 capture performance. The sample prepared at this flow rate displayed high CO_2/N_2 selectivity, excellent recyclability, and moreover, a CO_2 uptake of 1.86 mmol/g (0.15 bar, 25 °C) which ranked among the highest values ever reported for N-doped ACs. This research revealed that controlling gas flow rate was an effective strategy to improve the CO_2 capture performance of ACs and should be taken seriously during preparation of ACs for CO_2 capture.

1. Introduction

The persistent increase in CO_2 concentration in the atmosphere has been considered as the major reason for global climate warming and ocean acidification. Approximately 44% of CO_2 emission is attributable to fossil fuel-fired power plants [1], which discharge flue gas typically consisting of 70% N_2 and 15% CO_2 [1]. Thus, it is necessary to develop technologies for low-pressure CO_2 capture. Among the developed technologies, adsorption of CO_2 using active carbons (ACs) is rather promising, due to their easy handling, tunable pore structure, adjustable surface chemistry property, and low cost [2].

Active carbons (ACs) for CO_2 capture can be prepared by physical or chemical activation [3–5]. The latter has advantages over the former in increasing surface area and pores, particularly when alkalis like KOH and K_2CO_3 are used as activators. During chemical activation, the carbon precursors and activators are heated to desired temperatures in inert gas flow to yield ACs. The CO_2 capture performances of the obtained ACs are significantly affected by process factors such as activation temperature, alkali/precursor ratio, and activation time [6,7]. The flow rate of protective gas used during activation has been found to impact specific surface area and total pore volume of ACs [8], but its effects on ultramicropore (<0.7 nm), chemical composition, or CO_2 capture performance of ACs are unknown.

Thus, this research aims to investigate the effects of protective-gas flow rate on properties and CO_2 capture performance of KOH-activated ACs. The feasibility of improving CO_2 capture performance of active carbons by adjusting protective-gas flow rate may allow preparation of high-performance active carbons for CO_2 capture at reduced alkali consumption and activation temperature, which was rather advantageous to decreasing preparation costs.

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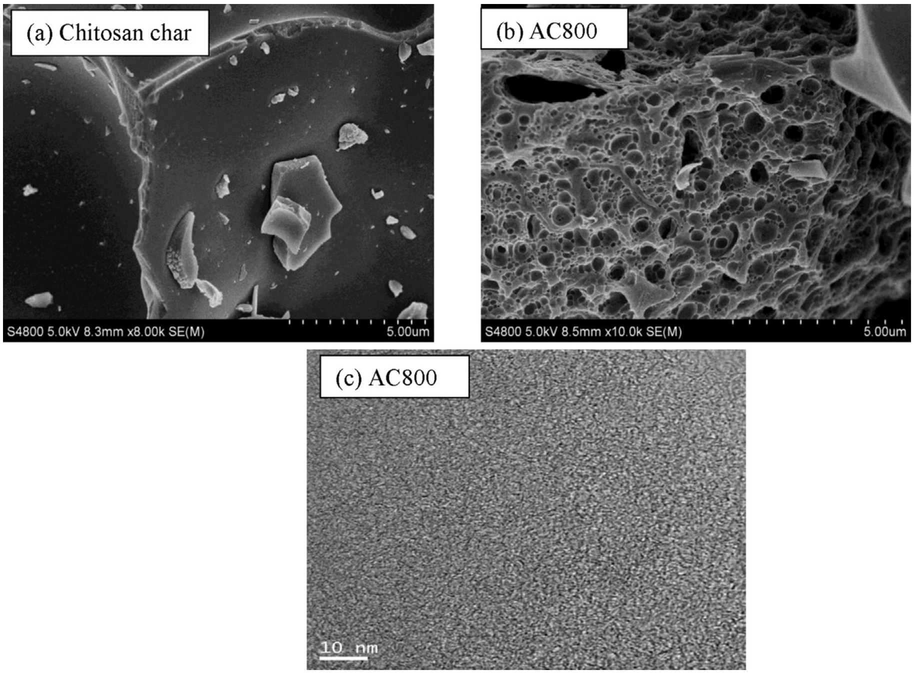

Fig. 1. SEM images of (a) chitosan char obtained by carbonization at 550 °C for 30 min and (b) AC800, and (c) TEM image of AC800.

2. Experimental

2.1. Raw materials

Low-molecular-weight powdered chitosan with N content of 14.6 wt%, C content of 54.1 wt%, H content of 8.8 wt%, ash content of 0.21 wt%, particle size of >0.15 mm, and deacetylation degree of 91.0% was bought from Qingdao BZ Oligo Biotech Co. Ltd. KOH (AR) was provided by Shanghai Guoyao Co. Ltd. The water used for washing samples was self-made distilled water.

2.2. Preparation of ACs

To prepare ACs, 24.0 g of chitosan was carbonized in N_2 flow (450 mL/min, 99.9% purity) at 550 °C for 30 min. Then, 3.6 g of the as-obtained char with desired particle sizes (0.1–0.9 mm) was mixed with powdered KOH (<0.1 mm) at a char/KOH ratio of 1:1 under continuous stirring. Subsequently, the mixture was heated via following a two-step heating procedure which can allow yielding porous carbons with high low-pressure CO_2 uptake according to our previous research [6]. More specifically, the mixture was first heated at a heating rate of 8 °C/min to 400 °C with a retention time of 30 min under flowing N_2 of 450 mL/min, and then heated at 10 °C/min to 600 °C with a retention time of 90 min under flowing N_2 of different flow rates (100, 450, 800, or 1040 mL/min). The use of different N_2 flow rates is to study the effects of protective-gas flow rate on ultramiropore volume, surface chemical composition, and CO_2 capture performance of ACs; such effects hardly received any attention in previous research. The heated sample was cooled to room temperature under flowing N_2, washed with copious water until the elute pH was about 7.0, and finally dried at 120 °C for 10 h. The obtained active carbon (AC) was denoted as ACx, where x represented the N_2 flowing rate used during activation at 600 °C.

2.3. Characterization and adsorption performance measurement

Surface morphologies of samples were observed by using Scanning Electron Microscopy (SEM, S4800, Japan) and Transmission Electron Micrograph (TEM, EOL JEM-2100UHR, Japan), which operated at 5.0 kV and 200 kV, respectively. The SEM was coupled with an energy dispersive X-ray spectrometer (EDX, GENESIS XM2 SYSTEM 60x) which was employed to determine K/C atomic ratio. Elemental compositions of samples were determined by an elemental analyzer (Vario EL III, Elementar Corp., Germany). X-ray photoelectron spectroscopy (XPS) spectra were measured by an ESCALAB 250XL electron spectrometer (Thermo Fisher Scientific, USA) using Al-Ka radiation, with the binding energies for the XPS spectra calibrated by setting C 1s to 284.4 eV. Software package XPSpeak 4.1 was employed to fit the N1s core-level spectrum peaks. During fitting, Shirley-type background and Gauss-Lorentz curves were adopted. Relative contents of characteristic elements (C, N, and O) on sample surfaces were calculated by using peak areas in the XPS spectra and sensitivity factors provided by the instrument manufacturer.

Adsorption/desorption isotherms for N_2 and CO_2 at different temperatures (−196 or 25 °C) were measured by a volumetric adsorption analyzer (ASAP 2020, Micromeritics Corp., USA). Micropore volume (V_{micro}), total pore volume (V_t), BET specific area (S_{BET}), and distribution of pores larger than 1 nm were obtained by using t-plot method, liquid volume of N_2 adsorbed at relative pressure of 0.95, Brunauer-Emmett-Teller equation, and non-local density functional theory (NLDFT, slit-pore model), respectively, based on the N_2 adsorption isotherms at −196 °C. Narrow-micropore size distributions (<1 nm) and ultramicropore volumes ($V_{<0.7\ nm}$) of ACs were derived from their CO_2 adsorption isotherms at 0 °C by employing slit-pore model and NLDFT. The CO_2 adsorption isotherms at 0 °C were measured by an automated gas sorption analyzer (Autosorb, Quantachrome Corp., USA). The CO_2/N_2 selectivity of samples at 25 °C was calculated from $0.85Q_{CO2,0.15}/0.15Q_{N2,0.85}$, where $Q_{CO2,0.15}$ and $Q_{N2,0.85}$ represented the CO_2 uptake at 0.15 bar and N_2 uptake at 0.85 bar, respectively, according to the ideal adsorbed solution theory (IAST) [9]. Isosteric adsorption heats for samples were estimated by applying the Clausius-Clapeyron equation to the CO_2 adsorption isotherms at 0 °C and 25 °C, as described elsewhere [10,11]. Before adsorption tests, each sample