

Synthesis of B-Doped Porous Carbons via Sodium Metaborate Tetrahydrate Activating Agent: A Novel Approach for CO₂ Adsorption

(Supplementary materials)

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Carbonization

Water chestnut shell to be used as a precursor have been cleaned, crushed, and sieved into the particles in the size range of 100–140 mesh (105–150 μm). Carbonization was performed in a horizontal quartz tubular reactor under a nitrogen flow (using a flow rate of 200 mL/min). The samples were heated from room temperature to 500 °C with a heat rate of 5 °C/min. The samples were maintained at

the final temperature for 2 h and then cooled in the nitrogen atmosphere. To simplify, carbonized water chestnut shell was denoted as WSC.

NaBO₂·4H₂O activation

For a typical reaction, 2 g WSC was combined with a solution that contained 2g NaBO₂·4H₂O. After stirring vigorously for 6 h, the mixture was left overnight to dry at 120 °C in an oven. Afterwards, the sample was activated to 750 °C for 2 h. During the activation process, the heating rate is 5 °C/min and nitrogen flow rate is 400 mL/min. Following activation, the sorbent was rinsed with distilled water until the pH value of the filtrate was roughly 7. The wet sample was then dried at 150 °C under vacuum for 24 h. The obtained sample was denoted as WSCSM-750-2.

Characterization

Powdered X-ray diffraction (XRD) patterns were carried out on a PHILIPS PW3040/60 powder diffractometer using CuK α radiation ($\lambda = 0.15406\text{nm}$). Scanning electron microscopy (SEM Hitachi S-4800) was used to observe the morphology of the samples of carbon materials. Further details of the pore structure were determined by transmission electron microscopy (TEM, JEOL-2100F) operated at 200 kV. Nitrogen adsorption and desorption isotherms were measured on a Beishide 3H-2000PS2 sorption analyzer at -196°C. Ultrahigh-purity N₂ (99.999%, Shanghai Pujiang Gas Co., Ltd) was used for measurement. Before measurement, the samples were degassed in a vacuum at 200°C for at least 12h. The specific surface area (S_{BET}) was calculated according to the multipoint Brunauer-Emmett-Teller (BET) method from the adsorption data in the relative pressure range between 0.001 and 0.01. The total micropore volume (V_t) was deduced from the N₂ adsorption data by the t-plot method, and the total pore volume (V_0) was estimated from the adsorbed amount of liquid nitrogen at a relative pressure of 0.99. The error of porosity measurement is

within 3%. The pore size distribution was calculated using the density functional theory (DFT) method. In addition, X-ray photoelectron (XPS) measurements were performed using an AXIS Nova spectrometer (Kratos Inc., NY, USA) equipped with a monochromatic Al K α X-ray source (1486.6 eV). XPS survey spectra were recorded with a pass energy of 160 eV, and high-resolution spectra with a pass energy of 40 eV.

The CO₂ adsorption isotherms were measured using the Beshide 3H-2000PS2 sorption analyzer at 0°C and 25°C, respectively. Pure CO₂ (99.99%, Shanghai Pujiang Gas Co., Ltd) was used for adsorption. Prior to each adsorption experiment, the sample was degassed for 12 h at 200°C to remove the guest molecules from the pores. The volume of narrow micropores (with sizes <1 nm), V_n , was calculated from CO₂ adsorption at 0°C using the Dubinin–Radushkevich (D-R) equation. The measurements were repeated for each sample, until the values fell within $\pm 2\%$ of each other.

Measurement of dynamic CO₂ uptake of the sorbents

The dynamic CO₂ uptake of the sorbents was tested on a fixed-bed reactor schematically illustrated in Scheme S1 at 1 bar and 25 °C. First, sample was heated at 100°C for 1 h under N₂ at a flow rate of 20 mL/min. The gas flow was shifted from nitrogen to a 10% mixture of CO₂ in N₂ at a flow rate of 10 mL/min, when the sample temperature was lowered to 25°C. The effluent gases were monitored online using an Agilent 7820A gas chromatograph with a thermal conductivity detector (TCD) to obtain the breakthrough curve.

The dynamic CO₂ uptake of the sorbent (q_d) was calculated from the breakthrough curves using the following equation:

$$q_d = \frac{Q_F C_0 t_s}{w} \quad (1)$$

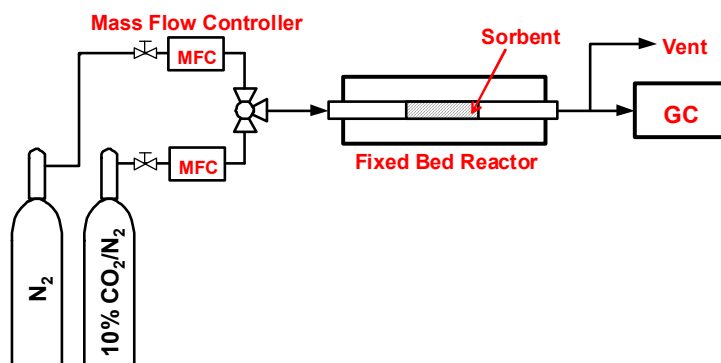
In the above equation, Q_F is the feed molar flow rate, C_0 is the concentration of the adsorbate in the feed stream, w is the weight of the adsorbent materials loaded in the column and t_s is the stoichiometric time, which can be estimated from breakthrough curves using the equation below:

$$t_s = \int_0^\infty \left(1 - \frac{C_A}{C_0} \right) dt \quad (2)$$

Where C_A is the adsorbate concentration at the column outlet.

Measurement of CO₂ adsorption kinetics

The adsorption kinetics of CO₂ was measured in a thermogravimetric analyzer (NETZSCH STA 449C). In the kinetic analysis, the sample (~5 mg) was degassed under a He stream at 200°C for 1 h. Next, the temperature was cooled to the experimental temperature of 25°C. Then the CO₂ gas was fed into the test chamber with a flow rate of 50 mL/min and the weight variation with time was recorded. The measurement's error is within 2%.



Scheme S1. Schematic of the fixed-bed reactor system.



Figure S1: Material Safety Data Sheet (MSDS) of KOH and NaBO₂·4H₂O, Sources:

<https://studylib.net/> and <https://datasheets.scbt.com/>

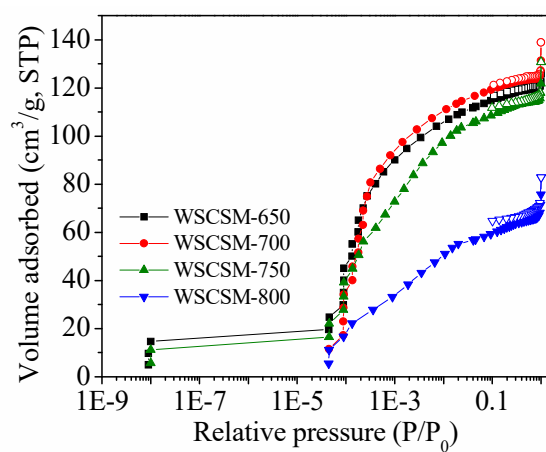


Figure S2. Semi-plot of the N₂ isotherm for WSCSM-T samples. Filled symbols denote the adsorption branches, whereas empty symbols indicate the desorption branches.