

Communications

Bimodal Mesoporous Carbons for CO₂ Sorption Application

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We recently reported a series of new bimodal mesoporous silicas (BMSs) and their carbon replicas, bimodal mesoporous carbons (BMCs). The BMS-1 was prepared by a slow condensation process using an aqueous solution of cetyltrimethylammonium hydroxide (CTAOH) template in the absence of any extra base catalysts.¹ An addition of neutral auxiliary templates such as 1.0 g of Brij76 (1.41 mmol, HO(CH₂CH₂O)₁₀C₁₈H₃₅), 1.0 g of Pluronic P123 (0.182 mmol, HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H), and 0.5 g of P123 (0.09 mmol) gave BMS-2, BMS-3, and BMS-4, respectively. The corresponding BMC materials were obtained by hard templating of BMSs using furfuryl alcohol as a carbon source followed by carbonization and the dissolution of BMS templates by HF solution. These materials possess two different length scales of disordered pores, a smaller primary pore ranged from < 2 to 9.4 nm and a larger secondary mesopore from 18.5 to 28.1 nm. The BMC materials exhibited high surface area and large pore volume. Low pressure hydrogen uptake up to 1.33 wt % has been observed at 77 K. We envisioned that they might also be suited for CO₂ sorption application. Several reports demonstrated that nanoporous carbon materials showed promise in CO₂ adsorption for the storage or separation of gas phase CO₂.² The preparation of good CO₂ sorbing materials is of significant importance because an intense effort is being made to reduce the major green house gas. Despite the intensive current study of CO₂ sorption by metal-organic frameworks (MOFs)³ and amine-functionalized mesoporous silicas,⁴ the CO₂ uptake by mesoporous carbon materials has been less explored to date.

Here we report low pressure CO₂ uptake by the BMC materials at varied temperatures. We used a standard volumetric method using high purity CO₂ at 196 K, 273 K, and 298 K. We chose our BMC materials to elucidate the detailed correlations between the surface area, pore volume, and pore size and the CO₂ uptake amount. Low surface coverage adsorption enthalpy values were also obtained. Four BMCs were prepared according to the literature method.¹ Scanning and transmission electron microscopy images are shown in Figures S1 and S2, respectively. The BMC materials exhibited different textural properties as depicted in Table S1. The CO₂ sorption ability was also summarized in Table S1. Provided that the interaction between the carbonaceous wall and CO₂ gas is physisorption, high surface area and pore volume would be important factors for the

enhanced uptake of CO₂. In fact, the low temperature CO₂ adsorption measured at 196 K (dry ice/2-propanol bath) indicated that the CO₂ uptake amount is directly proportional to both the surface area and pore volume (Figure 1): BMC-1 ($S_{\text{BET}} = 961 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.92 \text{ cm}^3 \text{ g}^{-1}$), CO₂ 345.5 cm³ g⁻¹ (15.4 mmol g⁻¹); BMC-2 ($S_{\text{BET}} = 1,328 \text{ m}^2 \text{ g}^{-1}$, $V_p = 2.08 \text{ cm}^3 \text{ g}^{-1}$), CO₂ 453.8 cm³ g⁻¹ (20.3 mmol g⁻¹); BMC-3 ($S_{\text{BET}} = 1,069 \text{ m}^2 \text{ g}^{-1}$, $V_p = 1.39 \text{ cm}^3 \text{ g}^{-1}$), CO₂ 416.7 cm³ g⁻¹ (18.6 mmol g⁻¹); BMC-4 ($S_{\text{BET}} = 970 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.85 \text{ cm}^3 \text{ g}^{-1}$), CO₂ 333.6 cm³ g⁻¹ (14.9 mmol g⁻¹), where S_{BET} is a Brunauer-Emmett-Teller surface area and V_p is a single-point pore volume. The CO₂ sorption isotherms at 196 K indicated no significant hysteric behavior between adsorption and desorption branches, suggesting that the adsorption is pure physisorption. All of the isotherms showed a similar shape of isotherms that have been observed for the siliceous mesoporous material, MCM-41.⁵

Figure S3 indicated that the CO₂ uptake amounts significantly decreased at 273 K and 298 K with respect to those measured at 196 K: BMC-1, 63.5 cm³ g⁻¹ (2.8 mmol g⁻¹); BMC-2, 55.4

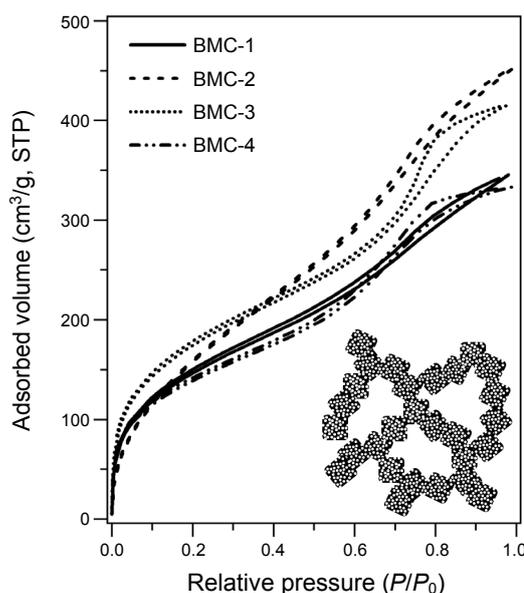


Figure 1. CO₂ sorption isotherms by BMC materials at 196 K. The schematic of the bimodal pore structure is shown together.

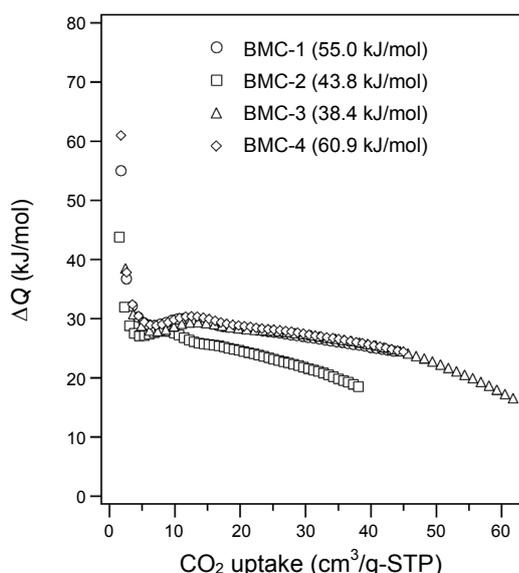


Figure 2. Isosteric heats of CO₂ adsorption by BMC materials. Low surface coverage values are also indicated.

cm³ g⁻¹ (2.5 mmol g⁻¹); BMC-3, 79.5 cm³ g⁻¹ (3.5 mmol g⁻¹); BMC-4, 64.1 cm³ g⁻¹ (2.9 mmol g⁻¹) at 273 K and BMC-1, 43.5 cm³ g⁻¹ (1.9 mmol g⁻¹); BMC-2, 38.1 cm³ g⁻¹ (1.7 mmol g⁻¹); BMC-3, 61.8 cm³ g⁻¹ (2.8 mmol g⁻¹); BMC-4, 45.0 cm³ g⁻¹ (2.0 mmol g⁻¹) at 298 K. The values at 298 K, 1.7 ~ 2.8 mmol g⁻¹, are comparable to the reported data of commercially available microporous activated carbon Norit RB2 which exhibited 2.0 mmol g⁻¹ CO₂ uptake under the same condition.⁶ Interestingly, BMC-3 outperformed Norit RB2 at 298 K. The Norit RB2 has a BET surface area of 1,012 m² g⁻¹ and a pore volume of 0.34 cm³ g⁻¹.⁷ It is noteworthy to mention that the BET surface area of BMC-3, 1,069 m² g⁻¹, is quite similar to that of Norit RB2 but BMC-3 has a much larger pore volume, 1.39 cm³ g⁻¹. Despite the lower surface area of BMC-3, it showed higher CO₂ uptake compared with BMC-2 at 273 K and 298 K. Therefore, the unique bimodal mesoporosity with a large pore volume of the BMC materials as well as high surface area is important for the efficient CO₂ adsorption.

To probe the physisorption strength, the isosteric heats of CO₂ adsorption, ΔQ , were estimated from the adsorption data measured at 273 K and 298 K by using the subroutine implemented in the BEL Master software of the Belsorp-miniII equipment. The subroutine uses the Clausius-Clapeyron equation to estimate the adsorption enthalpies. The observed ΔQ values at low surface coverage are: BMC-1, 55.0 kJ mol⁻¹; BMC-2,

43.8 kJ mol⁻¹; BMC-3, 38.4 kJ mol⁻¹; BMC-4, 60.9 kJ mol⁻¹ as shown in Figure 2. Despite the lowest level of CO₂ uptake at 196 K, the BMC-4 exhibited the highest enthalpy. BMC-1 also showed a larger value compared with those of BMC-2 and BMC-3. The opposite trend of adsorption enthalpies relative to the surface area and pore volume may be attributed to the different pore sizes and microporosity of the walls. In fact, BMC-4 possesses a much smaller primary pore than other materials (Table S1). Therefore, the surface area and pore volume should be the primary importance to design high CO₂ uptake materials.

In summary, our investigations of the CO₂ sorption abilities by various BMC materials indicate that the mesoporous carbon materials are also good CO₂ sorbents. The uptake abilities of BMC materials are comparable to the known activated carbons. For example, the BMC-3 outperformed the commercial activated carbon Norit RB2 at 298 K. We also estimated the CO₂ adsorption enthalpies for the four BMC materials. There is an interesting correlation between the pore size and adsorption enthalpy of the materials. These results suggest that bimodal mesoporous carbon materials would be promising sorbents for CO₂ adsorption.

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