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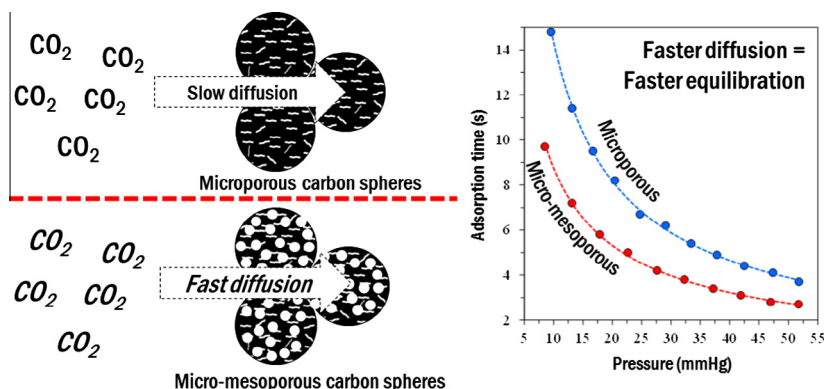
Tailoring porosity in carbon spheres for fast carbon dioxide adsorption



Jowita Marszewska, Mietek Jaroniec*

Department of Chemistry and Biochemistry, Kent State University, Kent, OH 44242, USA

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 September 2016

Revised 13 October 2016

Accepted 14 October 2016

Available online 15 October 2016

Keywords:

Carbon spheres

Microporosity

Mesoporosity

Nitrogen adsorption

CO₂ adsorption

ABSTRACT

Highly-porous carbon spheres were prepared by modified Stöber method combined with silica templating and CO₂ activation. Silica was delivered in the form of either colloids or tetraethyl orthosilicate and used to create porosity. Subsequently, CO₂ activation was used to develop microporosity. CO₂ activation was done either: (1) on carbon spheres, following silica etching or (2) on silica-carbon composites, before silica removal. Both methods delivered carbon materials with well-developed structures and, importantly, preserved spherical morphology. Still, activation of the silica-carbon composites with subsequent silica etching afforded carbons with better structural properties and CO₂ adsorption. Between materials prepared with silica colloids and TEOS-generated silica, the former showed more developed structures. The best material had specific surface area reaching 1500 m² g⁻¹ and total pore volume exceeding 1.2 cm³ g⁻¹ and showed CO₂ uptakes as high as 7.8 mmol g⁻¹ (0 °C, 1 bar) and 4.0 mmol g⁻¹ (23 °C, 1 bar). Mesoporosity improved mass transfer, which directly translated to faster CO₂ equilibration (30–40% on average). The proposed synthesis afforded carbons with high and fast CO₂ adsorption, which makes them good candidates for CO₂ sorption applications. Moreover, it was shown that both, microporosity and mesoporosity, are important in development of prospective CO₂ sorbents.

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1. Introduction

Nanoporous carbon materials are used in applications ranging from gas capture and storage, separation, to energy storage and con-

version [1–3]. Capture and storage of carbon dioxide (CO₂) is one of the areas where carbon sorbents are the primary candidates. Prospective CO₂ sorbents should have high thermal stability, recyclability, and a well-developed structure with large surface area and large volume of pores < 1 nm [4–7]. These structural features of carbon materials can be developed and controlled through different methods such as: hard-templating, soft-templating, and post-synthesis activation [8]. Unfortunately, none of these methods

* Corresponding author.

E-mail address: jaroniec@kent.edu (M. Jaroniec).

provide good control over the size of micropores, which is important from a viewpoint of CO₂ adsorption. For this reason, researchers have tried to optimize conditions of syntheses and activation processes to obtain small micropores with sizes < 1 nm required for efficient CO₂ adsorption at ambient conditions. So far, KOH and CO₂ activations have generated large volumes of small micropores resulting in high CO₂ uptakes [9–11]. The best reported carbons can adsorb more than 4 mmol g⁻¹ of CO₂ (25 °C, 1 bar) and more than 8 mmol g⁻¹ (0 °C, 1 bar) [10,12,13]. Notably, when the material is highly microporous, it may result in long equilibration times for CO₂ adsorption, which may impact practical application of such a material. One solution to improve gas diffusion within the material is by introduction of larger pores, such as mesopores [14,15]. Large mesopores enable faster transfer of gas from the bulk phase to micropores, and thus, result in faster equilibration. One way to introduce mesopores in carbon spheres is through using soft templating [16], but such mesopores usually have sizes only up to few nanometers. Because of this, these pores only slightly improve the diffusion process. Templating with silica colloids can afford much larger pore sizes and gives an option to easily control the pore size by selecting silica colloids with desired diameters. Overall, quick and effective CO₂ adsorption requires both large volume of small micropores and the presence of large mesopores forming a well-interconnected micro-mesoporous carbon structure.

In this work, the porous carbon spheres were synthesized to achieve high CO₂ adsorption capacity and fast equilibration. The porosity was tailored by using two methods: (1) CO₂ activation, to develop microporosity for high CO₂ uptake and (2) silica templating, to develop micro- and mesoporosity for fast CO₂ equilibration. The resulting materials had small micropores and large mesopores resulting in superior CO₂ sorption properties. In addition, the study compares the effect of CO₂ activation on the microporous structure before and after silica etching and between materials with incorporated silica colloids and TEOS-generated silica. Finally, we demonstrate the benefits of microporosity and mesoporosity in CO₂ adsorption on carbon spheres.

2. Experimental

2.1. Chemicals

Resorcinol (98%), formaldehyde (37%), and tetraethyl orthosilicate (TEOS) were acquired from Acros Organics (Fair Lawn, NJ,

USA). Ludox AS-40 colloidal silica (d = 12 nm) was acquired from Aldrich Chemical Company (Milwaukee, WI, USA). Ammonia (29%) was acquired from Fischer Scientific (Fair Lawn, NJ, USA). Technical grade ethanol (98%) and deionized water were used in all experiments.

2.2. Materials

Microporous and micro-mesoporous carbon spheres were prepared using the modified Stöber method [17] combined with either colloidal silica templating [18] or TEOS introduction [19]. In each series, samples with 2.5 and 3 wt ratios of silica to carbon were prepared. The resulting silica-carbon composites were either: (1) first activated with CO₂ and then etched with NaOH solution or (2) first etched and then activated.

Briefly, resorcinol (0.60 g) and formaldehyde (0.84 mL) were mixed in a water-ethanol solution (60 mL of water and 24 mL of ethanol) in the presence of ammonia (0.3 mL) and colloidal silica nanoparticles or TEOS. The mixture was stirred at 30 °C for 24 h and then subjected to hydrothermal treatment in an autoclave at 100 °C for another 24 h. Then, the solution was transferred to a Petri dish and dried at 100 °C for 24 h. The dried materials were transferred to quartz boats and carbonized in a tube furnace under nitrogen atmosphere at 350 °C for 2 h (1 °C min⁻¹ ramping rate); after temperature reached 600 °C (1 °C min⁻¹ ramping rate) the materials were kept at that temperature for 4 h. Silica etching was performed by immersing the composites in 3 M NaOH aqueous solution at 60 °C overnight; afterwards, the materials were filtered, washed with deionized water, and dried. CO₂ activation was performed by heating the materials to 850 °C under nitrogen atmosphere (10 °C min⁻¹ ramping rate) in a tube furnace. After temperature reached 850 °C, gas was switched to CO₂ for 4 h, and switched back to nitrogen afterwards, for the cooling period. This technique was used to avoid uncontrolled activation with CO₂ during heating and cooling stages. Table 1 lists all prepared samples and explains the labeling scheme. Figs. 1 and 2 show schematic of the synthesis using colloidal silica and TEOS as the silica source, respectively.

2.3. Measurements

Nitrogen adsorption-desorption isotherms were measured at -196 °C, carbon dioxide adsorption isotherms were measured at

Table 1
Labeling scheme for all prepared samples.

Sample	Silica precursor	Silica to carbon ratio	Etched	Activated	Order of etching and activation
C-Si-2.5	Colloidal silica	2.5	No	No	-
C-Si*-2.5	Colloidal silica	2.5	Yes	No	-
C-Si-2.5-A	Colloidal silica	2.5	No	Yes	-
C-Si-2.5-A*	Colloidal silica	2.5	Yes	Yes	Activated first
C-Si*-2.5-A	Colloidal silica	2.5	Yes	Yes	Etched first
C-Si-3	Colloidal silica	3	No	No	-
C-Si*-3	Colloidal silica	3	Yes	No	-
C-Si-3-A	Colloidal silica	3	No	Yes	-
C-Si-3-A*	Colloidal silica	3	Yes	Yes	Activated first
C-Si*-3-A	Colloidal silica	3	Yes	Yes	Etched first
C-T-2.5	TEOS	2.5	No	No	-
C-T*-2.5	TEOS	2.5	Yes	No	-
C-T-2.5-A	TEOS	2.5	No	Yes	-
C-T-2.5-A*	TEOS	2.5	Yes	Yes	Activated first
C-T*-2.5-A	TEOS	2.5	Yes	Yes	Etched first
C-T-3	TEOS	3	No	No	-
C-T*-3	TEOS	3	Yes	No	-
C-T-3-A	TEOS	3	No	Yes	-
C-T-3-A*	TEOS	3	Yes	Yes	Activated first
C-T*-3-A	TEOS	3	Yes	Yes	Etched first

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