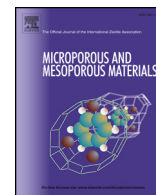




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## Microporous and Mesoporous Materials

journal homepage: [www.elsevier.com/locate/micromeso](http://www.elsevier.com/locate/micromeso)N-doping and ultramicroporosity-controlled crab shell derived carbons for enhanced CO<sub>2</sub> and CH<sub>4</sub> sorptionHee Soo Kim<sup>a</sup>, Min Seok Kang<sup>a</sup>, Seunghun Lee<sup>a</sup>, Yong-Woo Lee<sup>a,b,\*</sup>, Won Cheol Yoo<sup>a,b,\*\*</sup><sup>a</sup> Department of Applied Chemistry, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Gyeonggi-do, 15588, Republic of Korea<sup>b</sup> Department of Chemical and Molecular Engineering, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Gyeonggi-do, 15588, Republic of Korea

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## ABSTRACT

Highly N-doped crab shell-derived carbon nanofibers (CSCNs) with enhanced sorption capacity for CO<sub>2</sub> and CH<sub>4</sub> are presented. Two different carbonization temperatures, 600 °C and 900 °C were utilized to control the N-doping level of the CSCNs; the N-content of CSCN processed at 600 °C is higher than that processed at 900 °C. After judicious activation process to fine-tune ultramicroporosity (< 1 nm) by hot CO<sub>2</sub> treatment, the CSCN obtained from 600 °C with the most developed ultramicroporosity showed higher CO<sub>2</sub> uptake capacity compared to that of CSCN carbonized at 900 °C due to higher N-doping level, although the ultramicroporosity of the two samples is similar. In contrast, similar CH<sub>4</sub> sorption capacities were identified for these samples. In addition, very efficient and selective separation of CO<sub>2</sub>/N<sub>2</sub> was achieved from CSCN carbonized at 600 °C with maximum ultramicroporosity; meanwhile, similar selective separations of CH<sub>4</sub>/N<sub>2</sub> were observed for both of the most activated CSCNs. As a result, the relationship between the ultramicroporosity and CO<sub>2</sub> and CH<sub>4</sub> uptake capacities, and N-doping effect are clearly elucidated.

## 1. Introduction

The global warming and climate change mainly caused by the greenhouse effect and the shortage of energy reserves owing to rapid industrialization are some of the major challenges to be addressed urgently. For example, CO<sub>2</sub> is one of the dominant greenhouse gas mainly emitted from burning fossil fuels; thus it is urgent to store and capture CO<sub>2</sub> effectively [1–3]. In addition, the low-carbon energy source of CH<sub>4</sub>, which is a main component of natural gas, is considered an alternative energy resource owing to less CO<sub>2</sub> emission [4,5]. Therefore, it is necessary to develop technologies that can aid in the efficient storage and selective capture of CO<sub>2</sub> and CH<sub>4</sub> gases.

Among various porous materials such as zeolites, metal-organic frameworks (MOFs), mesoporous silica, and microporous polymers, carbonaceous materials are considered to be promising sorbents for CO<sub>2</sub> and CH<sub>4</sub> capture, because of their controllable physical and chemical properties and relatively low cost and light weight [6–8]. As a CO<sub>2</sub> sorbent, highly enhanced CO<sub>2</sub> adsorption capacity can be achieved via the development of ultramicropores (< 1 nm) by judicious activation processes and heteroatom doping (e.g., nitrogen) through careful choice of precursors or post-treatment processes that facilitate acid-base interaction between acidic CO<sub>2</sub> and basic N-doped carbons [8–13].

Increased chemisorption ability addressed as the isosteric heats of adsorption ( $Q_{st}$ ) of N-doped porous carbons via quadrupole-dipole interactions between CO<sub>2</sub> and electron-enriched nitrogen sites, which results in high selectivity for CO<sub>2</sub> over N<sub>2</sub>, has been reported [8–13]. Therefore, the capability to fine-tune the pore size distribution (PSD) and to incorporate basic moieties into a carbon framework by heteroatom doping is important for highly enhanced CO<sub>2</sub> uptake.

In addition, unconventional natural gases (UCNs) such as land fill gas and shale gas need to be upgraded to achieve the pipeline quality (> 90% CH<sub>4</sub>), and therefore, it is inevitable to effectively separate CH<sub>4</sub> over impurities such as N<sub>2</sub> and CO<sub>2</sub> [14–17]. The development of ultramicroporosity of adsorbents is imperative to achieve enhanced CH<sub>4</sub> uptake capacity as well as effective adsorption-based separation of CH<sub>4</sub> over N<sub>2</sub> [12,14,18]. Owing to the nonpolar nature of CH<sub>4</sub> and N<sub>2</sub>, the polarizability difference between CH<sub>4</sub> (2.59 Å) and N<sub>2</sub> (1.74 Å) is the key for effectively separating CH<sub>4</sub> over N<sub>2</sub> using highly developed ultramicroporosity of carbonaceous materials [12,14,18,19].

In attempts to simultaneously accomplish highly enhanced CO<sub>2</sub> and CH<sub>4</sub> adsorption and effective adsorption-based separation of CO<sub>2</sub>/N<sub>2</sub> and CH<sub>4</sub>/N<sub>2</sub>, the development of ultramicroporosity and N-doping of carbonaceous materials to a high level are indispensable. In addition, it is essential to develop sustainable and cost-effective means to produce

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