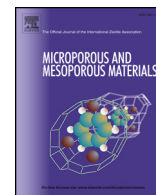




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Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromesoN-doping and ultramicroporosity-controlled crab shell derived carbons for enhanced CO₂ and CH₄ sorptionHee Soo Kim^a, Min Seok Kang^a, Seunghun Lee^a, Yong-Woo Lee^{a,b,*}, Won Cheol Yoo^{a,b,**}^a Department of Applied Chemistry, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Gyeonggi-do, 15588, Republic of Korea^b 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 CO₂ and CH₄ 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 CO₂ treatment, the CSCN obtained from 600 °C with the most developed ultramicroporosity showed higher CO₂ 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 CH₄ sorption capacities were identified for these samples. In addition, very efficient and selective separation of CO₂/N₂ was achieved from CSCN carbonized at 600 °C with maximum ultramicroporosity; meanwhile, similar selective separations of CH₄/N₂ were observed for both of the most activated CSCNs. As a result, the relationship between the ultramicroporosity and CO₂ and CH₄ 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, CO₂ is one of the dominant greenhouse gas mainly emitted from burning fossil fuels; thus it is urgent to store and capture CO₂ effectively [1–3]. In addition, the low-carbon energy source of CH₄, which is a main component of natural gas, is considered an alternative energy resource owing to less CO₂ emission [4,5]. Therefore, it is necessary to develop technologies that can aid in the efficient storage and selective capture of CO₂ and CH₄ 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 CO₂ and CH₄ capture, because of their controllable physical and chemical properties and relatively low cost and light weight [6–8]. As a CO₂ sorbent, highly enhanced CO₂ 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 CO₂ 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 CO₂ and electron-enriched nitrogen sites, which results in high selectivity for CO₂ over N₂, 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 CO₂ 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% CH₄), and therefore, it is inevitable to effectively separate CH₄ over impurities such as N₂ and CO₂ [14–17]. The development of ultramicroporosity of adsorbents is imperative to achieve enhanced CH₄ uptake capacity as well as effective adsorption-based separation of CH₄ over N₂ [12,14,18]. Owing to the nonpolar nature of CH₄ and N₂, the polarizability difference between CH₄ (2.59 Å) and N₂ (1.74 Å) is the key for effectively separating CH₄ over N₂ using highly developed ultramicroporosity of carbonaceous materials [12,14,18,19].

In attempts to simultaneously accomplish highly enhanced CO₂ and CH₄ adsorption and effective adsorption-based separation of CO₂/N₂ and CH₄/N₂, 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

* Corresponding author. Department of Applied Chemistry, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Gyeonggi-do, 15588, Republic of Korea.

** Corresponding author. Department of Applied Chemistry, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Gyeonggi-do, 15588, Republic of Korea.

E-mail addresses: yongwoolee@hanyang.ac.kr (Y.-W. Lee), wcyoo@hanyang.ac.kr (W.C. Yoo).