Microporous and Mesoporous Materials 272 (2018) 92–100

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

N-doping and ultramicroporosity-controlled crab shell derived carbons for enhanced CO_2 and CH_4 sorption

Hee 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

ARTICLE INFO

Keywords:
Crab shell-derived carbon
N-doped carbon
CO_2 adsorption
CH_4 adsorption
CO_2/N_2 and CH_4/N_2 separation

ABSTRACT

Highly N-doped crab shell-derived carbon nanofibers (CSCNs) with enhanced sorption capacity for CO_2 and CH_4 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_2 treatment, the CSCN obtained from 600 °C with the most developed ultramicroporosity showed higher CO_2 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_4 sorption capacities were identified for these samples. In addition, very efficient and selective separation of CO_2/N_2 was achieved from CSCN carbonized at 600 °C with maximum ultramicroporosity; meanwhile, similar selective separations of CH_4/N_2 were observed for both of the most activated CSCNs. As a result, the relationship between the ultramicroporosity and CO_2 and CH_4 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_2 is one of the dominant greenhouse gas mainly emitted from burning fossil fuels; thus it is urgent to store and capture CO_2 effectively [1–3]. In addition, the low-carbon energy source of CH_4, which is a main component of natural gas, is considered an alternative energy resource owing to less CO_2 emission [4,5]. Therefore, it is necessary to develop technologies that can aid in the efficient storage and selective capture of CO_2 and CH_4 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_2 and CH_4 capture, because of their controllable physical and chemical properties and relatively low cost and light weight [6–8]. As a CO_2 sorbent, highly enhanced CO_2 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_2 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* quadrapole-dipole interactions between CO_2 and electron-enriched nitrogen sites, which results in high selectivity for CO_2 over N_2, 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_2 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_4), and therefore, it is inevitable to effectively separate CH_4 over impurities such as N_2 and CO_2 [14–17]. The development of ultramicroporosity of adsorbents is imperative to achieve enhanced CH_4 uptake capacity as well as effective adsorption-based separation of CH_4 over N_2 [12,14,18]. Owing to the nonpolar nature of CH_4 and N_2, the polarizability difference between CH_4 (2.59 Å) and N_2 (1.74 Å) is the key for effectively separating CH_4 over N_2 using highly developed ultramicroporosity of carbonaceous materials [12,14,18,19].

In attempts to simultaneously accomplish highly enhanced CO_2 and CH_4 adsorption and effective adsorption-based separation of CO_2/N_2 and CH_4/N_2, 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).

https://doi.org/10.1016/j.micromeso.2018.06.021
Received 11 April 2018; Received in revised form 18 May 2018; Accepted 12 June 2018
Available online 15 June 2018
1387-1811/