Carbon 122 (2017) 258–265

Contents lists available at ScienceDirect

Carbon

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

Ultramicroporous carbon with extremely narrow pore distribution and very high nitrogen doping for efficient methane mixture gases upgrading

Ke Xin Yao [b, 1], Yanli Chen [a, 1], Yue Lu [a], Yunfeng Zhao [a, *], Yi Ding [a]

[a] *Tianjin Key Laboratory of Advanced Functional Porous Materials, Institute for New Energy Materials and Low-Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China*

[b] *Advanced Membranes and Porous Materials Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia*

ARTICLE INFO

Article history:
Received 13 April 2017
Received in revised form
15 June 2017
Accepted 22 June 2017
Available online 24 June 2017

ABSTRACT

It is notably challenging to fabricate heavily heteroatom-doped porous carbonaceous materials with narrow ultramicropore size distributions for highly effective mixed-gas separation. In this study, new carbon-based materials with narrow ultramicropore size (<7 Å) distributions (>95%) and high N doping contents (>10 at%) are fabricated through the pyrolysis of a perchloro-substituted porous covalent triazine-based framework (ClCTF). In particular, the sample prepared at 650 °C (ClCTF-1-650) possesses the highest ultramicropores content (98%) and large N content (12 at%) and demonstrates a very high CH_4 and CO_2 capacity, as well as a low N_2 uptake under ambient conditions. The extraordinarily high CH_4/N_2 and CO_2/N_2 selectivities correlate with both the ideal adsorption solution theory (IAST) method and performed dynamic separation experiments (breakthrough experiments). The results reported in this study far exceed the CH_4/N_2 and CO_2/N_2 selectivities of previously reported carbon-based adsorbents including various nitrogen-doped ones. These results are believed to be associated with the unusually high N content, as well as the suitably narrow ultramicropore size distribution. This report introduces a new pathway to design porous absorbents with precisely controlled ultramicropores for gas separation.

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1. Introduction

The purification of gas mixtures is of critical importance in the fields related to chemical engineering and energy [1]. The separation of gas mixtures containing gases of similar physical properties continues to be challenging. Traditional thermal-driven separation technologies, such as distillation, evaporation, and drying, are all high energy consumption processes. The separation of various mixed gases by selective physical absorption has been developed and employs porous materials, which are considered to be the most promising technology for this application due to their inherent advantages, which include low energy consumption, environmental friendliness, and easy regeneration [2–12]. Particular requirements need to be met in order to realize a high separation efficiency for a gas mixture with gases of similar physical properties during the design and preparation of the porous materials, e.g., narrowly distributed pores sizes with feature dimensions equivalent to that of a gas's molecular diameter and polarized frameworks [13]. From the kinetic perspective, an adsorbent with a well-defined pore size between the kinetic diameters of the gas molecules would provide an infinitely high selectivity. Additionally, the polarity of the framework can enable weak interactions between the porous materials and the guest molecules, which may further help to separate the mixture [14,15].

By optimizing the pore size of a zeolite to be centered between the molecular sizes of CO_2 and N_2 and introducing K^+ to enhance the interaction between CO_2 and the molecular framework, Hedin and Akhtar et al. separated the CO_2 and N_2 mixture with high efficiency [16,17]. By controlling the pore chemistry and size with SiF_6^{2-} groups, Cu-based metal-organic frameworks (MOFs) effectively captured acetylene from ethylene [18]. Cadiau et al. showed that a $NbOF_5^{2-}$ loaded MOF (NbOFFIVE-1-Ni) had a high adsorption capacity and selectivity for propane/propylene separation [19]. In

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[*] Corresponding author.
E-mail address: yfzhao@tjut.edu.cn (Y. Zhao).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.carbon.2017.06.073
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contrast, although various carbonaceous porous materials, such as activated carbon, possess many advantages for a wide range of industrial application and energy storage devices, their wide pore size distribution and weakly polar surface make them less suitable for highly efficient gas mixture separation. Nitrogen (N)-doping can increase the polarity of a carbon framework and has been determined to be useful for CO_2 capture and separation from flue gas [20–22]. Various chemical and physical activation strategies have been employed to increase the surface area and generate micropores in carbon materials, but the lack of a high-degree of control over the micropores distribution is still the critical factor limiting their performance for gas separation.

In this work, we report a strategy to obtain N-doped porous carbon materials with extremely narrow pore size distributions in the ultramicropore range (pore width < 7 Å). Tetrachloroterephthalonitrile was selected as the precursor to the perchloro-substituted covalent-triazine framework (ClCTF). Upon thermal treatment, the ultramicropores are generated by the elimination of the chlorine atoms. The resulting ultramicropores possess a high degree of N-doping. Thus, prepared N-doped ultramicroporous carbon materials display ultrahigh CH_4 capacities and low N_2 capacities; therefore, high CH_4/N_2 separation factors (23 at 0 bar or 8.6 at 1 bar in IAST method) are obtained. Moreover, the coalbed gas ($CH_4/N_2 = 1/1$) can be successfully separated with a factor of 6 under ambient conditions, which is almost double the reported values of previous porous materials. At the same time, the CO_2/CH_4 and CO_2/N_2 separations are also evaluated by means of IAST and dynamic separation. IAST factors of 8 (CO_2/CH_4) and 140 (CO_2/N_2) are achieved for ClCTF-1-650.

2. Experimental

2.1. Materials

ClCTF-1-400 was synthesized according to the method described in the literature [23–25] with several modifications as follows. In a typical synthesis, 2.5 g of tetrachloroterephthalonitrile and 2.5 g of $ZnCl_2$ were thoroughly mixed by grinding and the mixture was transferred into a beaker that was then well-sealed by Al foil. The mixture was subsequently heated at 400 °C for 40 h. The product was washed thoroughly with diluted HCl (1 M) and DI water overnight to remove the residual salt. Finally, the resulting black powder was dried in a vacuum oven at 70 °C for 12 h before further treatment. The yield of ClCTF-1-400 is approximately 40%. The ClCTF-1-400 was heated to 550, 650 and 750 °C at a rate of 5 °C min^{-1} and held for 5 h to prepare the samples denoted as ClCTF-1-550/650/750, respectively.

2.2. Characterization and gas adsorption measurements

Scanning electron microscopy (SEM) was performed with an FEI Verios scanning electron microscope. Transmission electron microscopy (TEM) was performed with an FEI Talos. X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IV. The valence states of elements were measured by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). Fourier transform infrared spectroscopy (FTIR) was performed with a PerkinElmer (FrontierMid-IRFTIR) spectrometer. Raman spectra were obtained from a HORIBA EVOLVTION spectrometer. The thermogravimetric analysis (TGA) curves were evaluated using a TG 209 F3 analyzer. Textural properties of various adsorbents were measured by Ar adsorption isotherms at 87 K using a Micromeritics ASAP 2420 surface area and porosimetry analyzer. The samples were degassed at 473 K overnight before the measurements. The pore size distributions and microporous surface areas were determined using the non-local density function theory (NLDFT) method. The CO_2, CH_4 and N_2 adsorption isotherms at two different temperatures (273 K and 298 K) were collected from a Micromeritics ASAP 2050 Xtend pressure sorption analyzer. The temperatures were controlled by means of a circulating bath. The gas purity was 99.9999% for N_2, 99.995% for CH_4 and 99.9995% for CO_2. The breakthrough curves were recorded with a homemade setup (see supporting information) with a real-time mass analyzer (Hidden, HPR-20) as a gas detector.

3. Results and discussion

The chemical structure and synthesis route of perchlorate covalent triazine-based framework (ClCTF-1-400) is shown in Fig. 1. The tetrachloroterephthalonitrile was chosen as the monomer to expand the family of covalent triazine-based frameworks. The chemical structure of ClCTF-1-400 can be regarded as simply chlorine substituted benzene and triazine, which are typically used as the building blocks to design flame-resistant polymers [26]. In comparison to the completely fluorine atom substituted FCTF-1-400 [23] and the non-substituted CTF-1 [24,25], the fully chlorine substituted polymer (ClCTF-1-400) has a better thermal stability (Fig. S1) below synthesis temperature (400 °C) in an N_2 atmosphere. This approach enables the controlled pyrolyzation of the ClCTF-1-400 and therefore for the optimization of the textural structures and chemical compositions. In the traditional synthesis route, the nitrile (—CN) groups of the monomer polymerize into triazine-rings at 400 °C in a sealed ampule in the presence of $ZnCl_2$ [23–25,27–31]. Normally, a large amount of gas would be generated during the heating process because of the partial decomposition of the monomers. This increases the danger of the explosion of the ampule and limits the batch production of CTFs. In this study, substituted CTFs were successfully synthesized in an open container. Up to 3 g of ClCTF-1-400 were prepared in a 200 ml beaker. By heating ClCTF-1-400 to higher temperatures, a series of porous carbonaceous materials ClCTF-1-Ts (ClCTF-1-550, ClCTF-1-650 and ClCTF-1-750) were obtained, in which the suffix “T” represents the synthesis temperature.

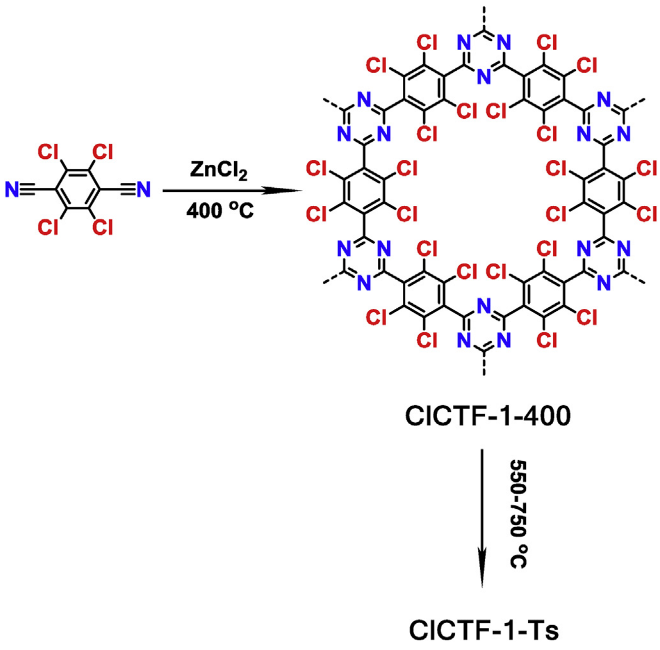

Fig. 1. Synthesis of ClCTF-1-Ts.

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