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Short communication

NaA zeolite/carbon nanocomposite thin films with high permeance for CO_2/N_2 separation

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Abstract

Novel NaA zeolite/carbon nanocomposite thin films were successfully prepared on a porous α-Al_2O_3 substrate by dip-coating method. The prepared films were characterized by XRD, SEM and single gas permeation tests. NaA zeolite/carbon nanocomposite thin films exhibited the ideal separation factor of CO_2/N_2 of 6.04 with the carbon dioxide permeance of 3.39×10^{-7} mol Pa^{-1} m^{-2} s^{-1} at room temperature and 100 kPa, which was two orders of magnitude higher than that of pure carbon membrane reported by previous literature. The observed adsorption isotherms indicated that the incorporation of zeolite NaA crystal improved the CO_2 adsorption ability of carbon materials, and decreased its N_2 adsorption ability. The ideal permselectivity of CO_2/N_2 of carbon/NaA composite films was 6.04, higher than the ideal adsorption selectivity, probably because the small molecule of CO_2 diffused faster than N_2. From the SEM images, the thickness of nanocomposite films was 1–2 μm, which was helpful to decrease the resistance and increase the flux of gas permeance.

Keywords: NaA zeolite; Carbon materials; Nanocomposite; Thin films; High permeance

1. Introduction

Both carbon and zeolites are very potential membrane materials because of their resulting pore sizes, which are near to molecule diameters of low molecular weight compounds and are expected for separating those mixtures. In the past decade, much effort has been made to develop nanoporous carbon membranes and zeolite membranes for gas separation [1–12], especially, the separation of carbon dioxide and nitrogen, because the greenhouse effect created by the accumulation of carbon dioxide in the atmosphere is threatening to human life. Carbon membranes are effective materials to the CO_2/N_2 separation. However, the carbon dioxide permeance of membranes, which is still so far below 10^{-9} mol m^{-2} Pa^{-1} s^{-1}, is too low to industrial use. To tackle this challenging issue, some strategies such as the synthesis of composite membranes by incorporation of zeolite into polymer have been reported [13–15], but it is still far from satisfactory.

To solve the challenging task mentioned above, herein NaA zeolite/carbon nanocomposite thin films were prepared by incorporating nanosized NaA zeolite into the polymeric precursor with the expectation to significantly improve the gas flux without losing the permselectivity of films. To the best of our knowledge, this is the first report on the NaA zeolite/carbon nanocomposite films used in CO_2/N_2 separation.

2. Experimental

Below is the detailed description about the process for making NaA zeolite/carbon nanocomposite thin films with continuous carbon matrix and dispersed NaA zeolite. In our paper, NaA zeolite nanocrystals were synthesized by hydrothermal method from a clear solution with a molar composition of 1.00 Al_2O_3:3.40 SiO_2:4.20 $(TMA)_2O$:0.30 Na_2O:237 H_2O. The starting solution was placed in a Teflon-lined stainless steel autoclave and the crystal synthesis was performed at 100 °C for 24 h. The nanosized zeolites formed were collected and washed by centrifugation to a pH of 8, and then the nanosized zeolites were calcined (heating/cooling rate 1 K/min) at 723 K in air for 4 h to burn off organic templates of tetramethylammonium hydroxide before the casting step. The nanosized zeolites above were added

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to the novolak-type phenolic resin dissolved into ethanol and dispersed by the ultrasonic for 2 h, and the water in ultrasonic pool was maintained at 298 K. The weight ratio was 40:1:59 for phenolic resin:NaA zeolite:ethanol, respectively. Tubular α-Al_2O_3 substrate with o.d. of 12.0 mm, length of 8.0 mm, and mean pore diameter of 0.5 μm was dip-coated with the polymer-zeolite precursor and dried in air at 298 K for 24 h then calcined (heating rate 0.5 K/min and cooling rate 1 K/min) at 873 K for 2 h in a stainless tube. During the entire pyrolysis process, the reaction stainless tube was purged with nitrogen at a flow rate of 50 ml/min. Finally, the nanocomposite films were prepared by only one dip-coating step.

The nanocomposite films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and single-component gas permeation experiments. The films were calcined (heating/cooling rate 1 K/min) at 423 K for 4 h in order to remove the remained gas when permeating gas specie was switched to another. The permeation tests were done at room temperature by a soap-films flow meter with a pressure difference of 0.10 MPa.

3. Results and discussions

3.1. The characterization of NaA zeolite/carbon nanocomposite

The SEM image of as-synthesized zeolite NaA nanocrystals was shown in Fig. 1. The average particle size was 250 nm by SEM image (Fig. 1) and DLS image (Fig. 2). The X-ray diffraction patterns shown in Fig. 3 confirmed that both samples of CA-1 powders which were the composite NaA/carbon (unsupported on the substrate), prepared and calcined with the same procedures and conditions as those of composite thin films, and CA-2 powders which were the synthesized NaA nanocrystals were of zeolite NaA structure. However, the peak intensity of the pure zeolite (CA-2) was higher than that of the composite films (CA-1). The main reason was that the amorphous carbon materials were a barrier to X-rays and the peak intensity could be weakened, and a broad peak attributed to amorphous solids of carbon materials, at approximately 24° 2θ. It also indicated that the zeolite was combined with carbon materials by pyrolysis process.

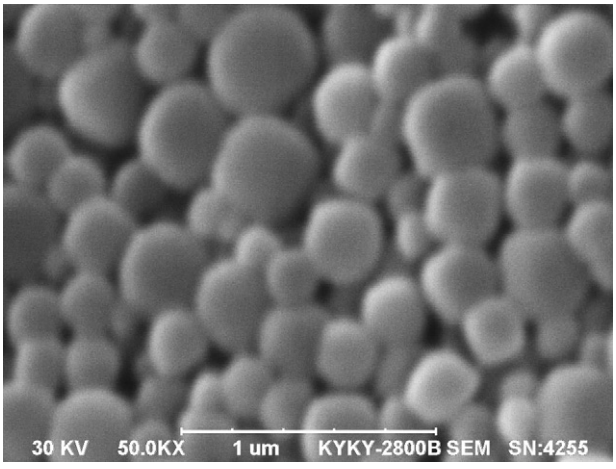

Fig. 1. SEM image of the NaA zeolite nanocrystals, here the scale bar is 1 μm.

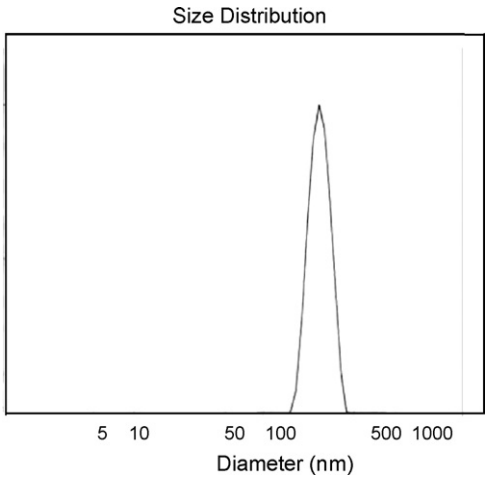

Fig. 2. DLS image of the NaA zeolite nanocrystals.

3.2. Adsorption isotherms of CO_2 and N_2

Adsorption isotherms of single-component CO_2 and N_2 for the NaA zeolites, the NaA/carbon composites, and carbon materials at room temperature were shown in Fig. 4. The adsorption selectivity of CO_2/N_2 (the ratios of adsorbed amount at 100 kPa) for all above powders was in the order: NaA zeolites > NaA/carbon composites > carbon materials, indicating that the incorporation of zeolite NaA crystals enhanced the CO_2 adsorption ability of carbon materials, and simultaneously decreased its N_2 adsorption ability, it was favorable for CO_2 to preferentially diffuse through films, potentially giving a good permselectivity of CO_2/N_2 for the resulting films.

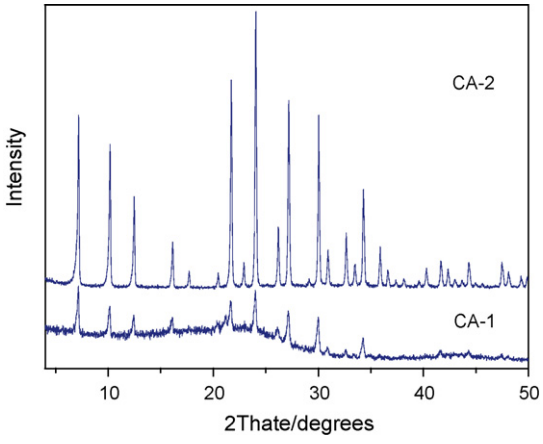

Fig. 3. XRD patterns of zeolite A nanocrystals. Sample CA-1 is the composite carbon/NaA powder, prepared and calcined with the same procedures and conditions as those of composite films; sample CA-2 is synthesized NaA nanocrystals.