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Vacuum seeding and secondary growth route to sodalite membrane

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Abstract

Sodalite membrane has been successfully fabricated on tubular porous α-Al_2O_3 supports by secondary growth method with vacuum seeding. In the seeding process, the colloidal seeding particles were agglutinated not only onto the surface of alumina support but also within the pores by vacuum sucking method. To obtain defect-free sodalite membrane, the sodalite crystals were grown directly on the alumina support in a mixture solution containing alumina and silica species under the hydrothermal reaction condition. The as-synthesized sodalite membranes were characterized by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The thickness and the quality of sodalite membrane could be controlled by the hydrothermal reaction time (12∼24 h) and temperature (100∼150 °C) under the mother solution of $5Na_2O:2SiO_2:Al_2O_3:1000H_2O$.

Keywords: Sodalite; Membrane; Vacuum seeding; Secondary growth; Hydrothermal reaction

1. Introduction

Zeolite membranes can be used as catalysis in reactors, as sensors for detection and/or controlling, and as devices for the separation of gas and/or liquid separations [1]. These properties have been attracting the interest of researchers for several years. Especially, many attempts have been made to develop zeolite membranes for separation of gas [2]. Several preparation methods have been developed, such as in situ hydrothermal synthesis, vapor phase transport, or embedding microcrystals of the zeolite into a matrix. Although zeolite membranes prepared by these methods usually have a very good separation factor, the permeation is too low for practical applications and it has been difficult to control the membrane thickness and uniformity. Thus the most challenging work in the field of zeolite membranes is to prepare membranes with high permeation, while keeping the high separation factor.

In an attempt to overcome this problem, recently, secondary growth methods have been developed [3]. However, there are two challenging issues related to the synthesis of membrane by secondary growth method. One is how to prepare colloidal solution of zeolite particles [4], and the other is how to coat the seeds onto the support [5]. Herein, we report a simple and effective method to synthesize sodalite membrane using colloidal sodalite solution obtained by a new process. The colloidal sodalite solution could be prepared by ultrasonication from a discrete nanocrytalline sodalite with the average particle size of ∼40 nm obtained by a solid−solid transformation of the Al pillared clay. The synthetic method of zeolite is a quite original idea that has been not reported so far [6]. Compared with conventional hydrothermal synthesis, the solid−solid transformation of Al pillared clay into sodalite has the advantage of very short time, nanometer sodalite particle size, discrete sodalite particle size distribution, and high purity. The colloidal sodalite particles are then agglutinated at the surface and within the pores of a porous ceramic alumina membrane by suction method using vacuum. And then the membrane agglutinated by nanocrystalline sodalite is then subjected to a further hydrothermal treatment in a mixture solution containing alumina and silica species. In this process the colloidal particles act as seeds for secondary growth, thus producing a uniform membrane layer. Therefore, this study is focused on a new seeding method by

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vacuum suction, the mother solution for hydrothermal reaction, and the reaction period.

2. Experimental section

2.1. Preparation

The α-Al_2O_3 membrane tube (inner diameter : outer diameter = 7 : 10, made by Exekia-France) with mean pore sizes of 10 μm (external layer), 0.8 μm (intermediate layer), and 0.2 μm (internal layer) was used as a support. Before synthesis, the inner surface of support was coated with nanocrystalline sodalites as nucleation seeds by suction using vacuum pump [7]. The nanocrystalline sodalite (30∼50 nm) was synthesized from Al-pillared clay through the solid–solid transformation [6]. The colloidal sodalite solution was prepared to be 1 wt.% suspension using ultrasonication. The sodalite membrane is then synthesized by a hydrothermal reaction in a mixture solution containing alumina and silica species. The molar ratio of the mixture solution was $5Na_2O : 2SiO_2 : Al_2O_3 : 1000H_2O$. The prepared pre-seeding sodalite membrane tube was immersed into the resulting solution, and then hydrothermal reaction was carried out at 150 °C for 12 and 24 h, respectively. After synthesis, resulting sodalite membrane was washed by distilled water, and then dried at 150 °C for 4 h by oven. If a defect-free sodalite membrane would not be formed, the hydrothermal reaction for sodalite membrane is carried out again as the above synthetic method.

2.2. Characterization

Powder X-ray diffraction patterns of the samples were recorded on a Philips PW1830 automated powder X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å). The morphology and particle size for the products were investigated by HITACHI S-4500 scanning electron microscopy (SEM) after the samples were coated with Pt/Pd alloy for 180 s with E-1030 ion sputter.

2.3. Gas permeation measurements

Gas permeation measurements. Membrane permeation of He and N_2 (single gases) was measured with IEM (Institut Eurpéen Des Membranes) group-made apparatus at different temperatures between 20 and 130 °C as a function of the transmembrane pressure ΔP ($\Delta P = P_{\mathrm{int}} - P_{\mathrm{ext}}$). The permeate flux for a given temperature was measured with a volumetric method through bubble soap flowmeters, after stabilization of the flow rate. For each gas the permeation at the steady state was calculated as follows [8]:

$$\prod = D/S\Delta P$$

S	permeable area of membrane (2.199×10^{-3} m^2)
ΔP	transmembrane pressure (Pa)
D	moles of transported gas per time (mol s^{-1})

$$D = (V/V_m) \times 1/t$$

V	volume of transported gas (ml)
V_{m}	volume per the 1 mole of gas
t	permeation time at volume of transported gas (s)

The ratio of the pemeations of two pure gas measured at the same temperature is the ideal selectivity or permselectivity (α):

$$\alpha\left(\frac{i}{j}\right) = \frac{\text{permeation}_i}{\text{permeation}_j}$$

$$\lambda = \frac{1}{\sqrt{2}\,\overline{\sigma}^2}\,\frac{\mathrm{RT}}{P}.$$

Knudsen value is defined by $Kn = \lambda/d_{\mathrm{p}}$ with λ being the average free path length of the gas molecules and d_{p} the characteristic pore diameter, with the average collision diameter of gases, σ.

Permselectivity values are compared with the Knudsen diffusion limit $\alpha_{Kn}(i/j)$; when this mechanism is predominant light gases permeate faster heavier gases. The selectivity in the case of Knudsen diffusion is independent from the pressure and is proportional to the inverse square root of the molecular weight:

$$\alpha_{Kn}\left(\frac{i}{j}\right) = \sqrt{\frac{M_j}{M_i}}$$

An experimental selectivity higher than the Knudsen limit may indicate that the mean pore size of the membrane is comparable to the molecular dimensions of the largest species [8,9].

3. Results and discussion

Fig. 1 represents the X-ray diffraction patterns for alumina tube support and the sodalite membranes prepared after the different secondary growth at 150 °C. After the hydrothermal reaction for 12 h, the XRD patterns are represented by the sum of the peaks of alumina membrane and the sodalite, confirming that the sodalite membrane forms on the alumina membrane. After 24 h, the intensity of diffraction peaks for alumina decrease and the sodalite phase becomes dominant, which implies that the more sodalite crystals by secondary growth form on the alumina support. This is apparent evidence for the more crystal growth of sodalite on the alumina membrane, which leads to the increase in the thickness of sodalite layer on the alumina membrane. Therefore, theses results show that the crystallinity of sodalite on the alumina support could be controlled by the hydrothermal reaction time.

Fig. 2 shows the SEM images for the side view and the top view of the membrane support and the sodalite