

N₂-O₂ Separation Properties of SrY-type Zeolite Membranes

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Y-type zeolite membranes containing Na⁺ ions were synthesized on the outer surface of a porous α -alumina support tube by means of a hydrothermal reaction. The Na⁺ ions of the membranes were ion-exchanged with Sr²⁺ ions, and the separation properties of the membranes were investigated at 313 K for mixtures of N₂ and O₂. Although the exchange of Na⁺ ions with Sr²⁺ ions greatly increased the N₂ adsorption capacity, the SrY-type zeolite membranes had oxygen over nitrogen selectivities (up to 2.1) and O₂ permeances of the order of 10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹. Those findings suggest that N₂ permeability was hindered by the Sr cations present that would interact strongly with N₂, resulting in an increased O₂ permeability, compared to N₂.

Key words: Y-type zeolite membrane, gas separation, ion-exchange, nitrogen, oxygen

1. INTRODUCTION

Gas separation processes using zeolite membranes [1-9] are based on an affinity between pore walls and gas molecules, as well as the size of the molecules permeating through the membrane. Van den Broeke et al. [10] studied the permeation of binary mixtures of gases including N₂-O₂, CO₂-N₂, CO₂-CH₄, C₂H₆-CH₄ and *n*-C₄H₁₀-H₂, through a silicalite-type zeolite membrane. These authors showed that the permeation of the more strongly adsorbed component in the mixture was affected by the presence of a more weakly adsorbed component to a negligible extent. Kusakabe et al. [11,12] investigated the gas permeation properties of ion-exchanged FAU-type (Y-type) zeolite membranes and proposed a sorption-diffusion model to explain the permeation of CO₂ and N₂. The high separation factors of CO₂ to N₂ for the binary mixed feed were caused by an increase in the selective sorption of CO₂. Hasegawa et al. [13,14] synthesized FAU-type (Y-type) zeolite membranes which were then ion-exchanged with K, Rb and Cs and reported that the CO₂/N₂ separation factor was dependent on the cation species present on the membrane. The contributions of surface structure to the CO₂/N₂ selectivities of NaY- and NaA-type zeolite membranes were reported by Mizukami et al. [15].

It is also known that the FAU-type zeolites possess the unique ability to adsorb N₂ more strongly than O₂, due to the interaction between the quadrupole moment of N₂ and cations such as Li⁺ or Ca²⁺ when they are attached to the zeolite framework. As a result, these zeolites have been examined for use in air separation. Hutson et al. [16] synthesized Li_xAg_yX-type zeolites, which have a high capacity for N₂, and evaluated their performance for air separation by pressure swing adsorption. Rege and Yang [17] examined the limits for air separation using LiX-type zeolite particles. Guan et

al. [18] investigated N₂/O₂ separations using Y-type zeolite membranes and proposed a permeation mechanism for the N₂-O₂ system. The resulting membranes were found to be N₂-selective largely due to high affinity between the zeolitic pores and N₂ molecules.

The present paper employed SrY-type zeolite membranes, which can adsorb N₂ strongly, in an investigation of N₂ separation from N₂/O₂ mixture systems. The original NaY-type zeolite membranes prepared on a porous α -alumina support tube by hydrothermal synthesis were ion-exchanged with Sr cations, and N₂-O₂ separation properties of the membranes were evaluated.

2. EXPERIMENTAL

A porous α -alumina tube (NOK Corporation, Japan, outer diameter = 2.3mm, inner diameter = 1.8mm, length = 30 mm, void fraction = 0.39, average pore size = 150-170 nm) was used as the support for the zeolite membrane. An aqueous solution of water glass, sodium aluminate and sodium hydroxide was homogenized by stirring for several hours at room temperature. The SiO₂/Al₂O₃ ratio in the initial solution was 6.4 or 12.8 on a molar basis. The outer surface of the support tube was rubbed with a standard NaX-type zeolite powder (Tosoh Corporation, Japan, #F-9; Si/Al = 1.25, 200 mesh under) to implant nucleation seeds. After the rubbing treatment, the four support tubes were fixed vertically in a Teflon holder in a Teflon-lined autoclave containing 80 cm³ of the initial solution. The hydrothermal reaction was carried out at 363 K for 6-20 h. After the synthesis, the tubes were thoroughly washed with deionized water and dried in air at 323 K. The zeolite membrane formed was then subjected to ion-exchange treatment and to permeation tests. Cation

exchange of the zeolite membrane was carried out in a 0.5 mol dm⁻³ solution of SrCl₂ for 4 h at 353 K. After the ion-exchange treatment, the membranes were thoroughly washed with deionized water and then air dried at 323 K. Zeolite powders were also prepared under the same conditions as were used for the synthesis of the membranes. Details of the preparation procedures have been described elsewhere [11]. The morphology of the membranes was observed by scanning electron microscopy (SEM).

Gas permeation tests using a coaxial cylindrical permeation cell were carried out as described elsewhere [19]. The both ends of the membrane (30 mm length) were connected to a stainless-steel tube with epoxy resin, and the membranes were then fixed in a permeation cell which was maintained at 313 K by an electric furnace. The permeation portion of the membrane was about 10 mm in length. A binary mixture of N₂ and O₂ was fed on the outside of the membrane, and the gas that permeated through the membrane was swept by He carrier gas. The total pressure on both sides of the membrane was maintained at 101.3 kPa. The concentrations of permeants were measured with a gas chromatograph equipped with a thermal conductivity detector. The total flow rates on the feed and permeate sides were determined with soap-film flow meters. Permeance was defined as moles of gas permeated per unit time per unit membrane area, divided by the difference in partial pressure between the feed and permeate sides. The separation factor, α , was defined by the ratio of the permeances.

3. RESULTS AND DISCUSSIONS

Fig.1 shows the top surface and fractured section of a NaY-type zeolite membrane formed at SiO₂/Al₂O₃ = 6.4 in the initial solution using a 20-h reaction time. A continuous polycrystalline film was formed on the α -alumina support after a 6 h synthesis, and small zeolite crystals were also deposited in the α -alumina macropores underneath the top polycrystalline layer, as reported previously by Kusakabe et al. [11,12]. The overall thickness of the zeolite layer formed in a 20 h synthesis was ca. 10 μ m. The morphology of the NaY-type zeolite membranes was not affected by the initial SiO₂/Al₂O₃ ratio.

To examine the performance of the prepared zeolite membranes, gas permeation tests using equimolar mixtures of CO₂ and N₂ were performed. It is known that Y-type zeolite membranes with minimal defects are capable of separating CO₂ from CO₂-N₂ mixtures with high selectivities. The CO₂/N₂ separation factors of the NaY- and SrY-type membranes used in this study were in the range of 28-60 and 22-60, respectively, and the CO₂ permeances of the membranes were of the order of 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹. These results are in relatively good agreement with those reported by Kusakabe et al. [11].

Fig.2 shows the adsorption isotherms for single-components of N₂ and O₂ for the Y-type zeolite powders at 313 K and 0-100 kPa using a gravimetric adsorption unit (BEL Japan FMS-BI-H). The samples were outgassed under vacuum at 673 K for several hours prior to the actual adsorption measurements. The exchange of Na⁺ ions for Sr²⁺ ions greatly increased the N₂ adsorption. The adsorption capacity of N₂ for the

SrY-type zeolite was approximately three times as high as that of O₂ at 100 kPa. Guan et al. [18] reported that N₂/O₂ separation through Y-type zeolite membranes is largely dependent on the differences in the adsorptivity of N₂ and O₂ on the micropore walls. They revealed that zeolite membranes which can adsorb N₂ in preference to O₂ were promising N₂-selective membranes.

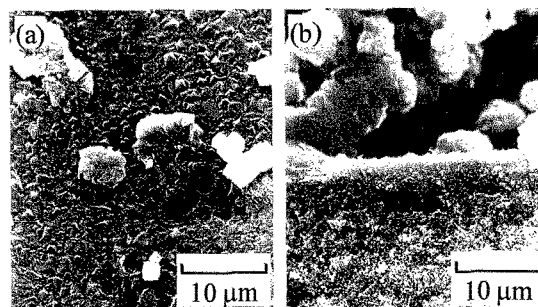


Fig.1 SEM images of a NaY-type zeolite membrane synthesized for 20 h. (a) Top view, and (b) fractured section.

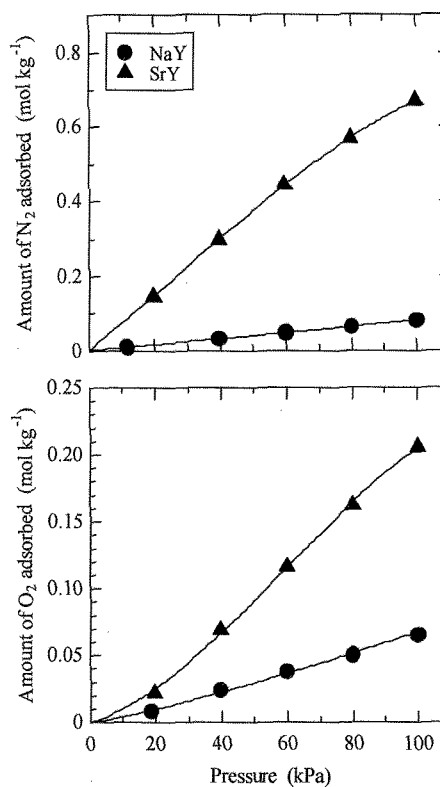


Fig.2 Adsorption isotherms of single-component N₂ and single-component O₂ at 313 K for Y-type zeolite powders synthesized for 20 h. Ratio of SiO₂/Al₂O₃ in the starting solution = 6.4.

Fig.3 shows the relationship between N₂ and O₂ permeance of the Y-type zeolite membranes for an equimolar N₂-O₂ mixture. The permeances to N₂ and O₂ were scattered over a range of 10⁻⁹-10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹, and tended to decrease after the ion-exchange treatment.

Fig.4 illustrates the effect of ion-exchange on O_2 permeance and O_2/N_2 selectivity for the Y-type zeolite membranes. Owing to the higher affinity of the SrY-type zeolite for N_2 as indicated in Fig.2, the Sr^{2+} -exchanged membranes would be expected to be N_2 -selective membranes. However, the SrY-type zeolite membranes gave higher selectivities for O_2 than the original membrane, as shown in Fig.4. The highest separation factor of 2.1 for O_2 was obtained using an SrY-type zeolite membrane formed with $SiO_2/Al_2O_3 = 12.8$ for 20 h.

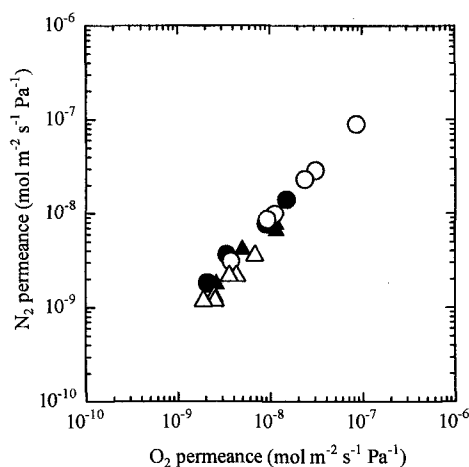


Fig.3 Relationship between N_2 and O_2 permeance of Y-type zeolite membranes. Feed – equimolar mixtures of N_2 and O_2 ; permeation temperature – 313 K. Ratios of SiO_2/Al_2O_3 in the starting solution – 6.4 (● NaY, ▲ SrY) and 12.8 (○ NaY, △ SrY).

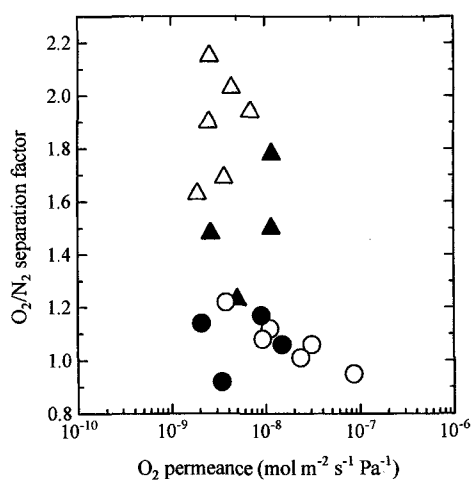


Fig.4 Effect of ion-exchange on the O_2/N_2 separation factor for Y-type zeolite membranes. Feed – equimolar mixtures of N_2 and O_2 ; permeation temperature – 313 K. Ratios of SiO_2/Al_2O_3 in the starting solution – 6.4 (● NaY, ▲ SrY) and 12.8 (○ NaY, △ SrY).

Fig.5 shows the permeation properties of the SrY-type membrane for single-component N_2 and O_2 , in comparison with the binary system for N_2 and O_2 . The membrane showed lower permeation rates and a higher

O_2/N_2 separation factor (α) for the binary system than those for the single-component system. This indicates that the two gases in the mixture did not behave independently. Since the micropores of a Y-type zeolite membrane are much larger than the sizes of small molecules such as N_2 and O_2 , the adsorptivities and diffusivities of the permeants are key factors for achieving high permselectivities [18,20]. The above results suggest that the mobility of the N_2 molecules adsorbed was decreased as the result of strong interactions between N_2 molecules and the Sr cations present in the ion-exchanged zeolite membrane, thus increasing the relative permeability of O_2 . The mechanism by which Sr cations retard N_2 permeance is not clear at the present stage of the investigation, and further study will be required to understand this.

Fig.6 shows the O_2/N_2 selectivity of the SrY-type membrane as a function of the mole fraction of O_2 in feed gas. The O_2/N_2 separation factor remains relatively unchanged in an O_2 fraction range of 0.2-0.8.

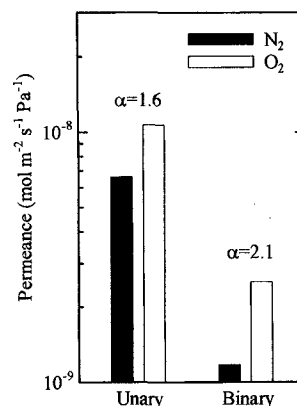


Fig.5 N_2 and O_2 permeances of SrY-type zeolite membrane for unary and binary systems at 313 K. Ratio of SiO_2/Al_2O_3 in the starting solution – 12.8.

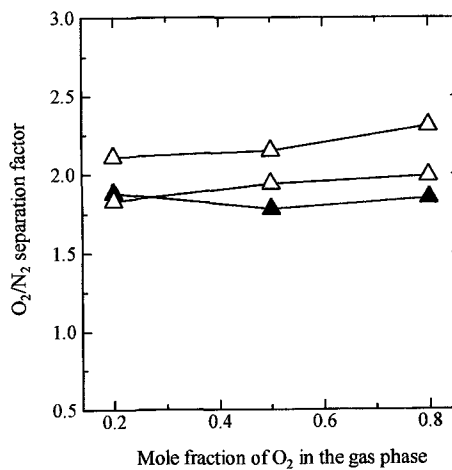


Fig.6 O_2/N_2 separation factor of SrY-type zeolite membranes for mixtures of O_2 and N_2 at 313 K. Ratio of SiO_2/Al_2O_3 in the starting solution – 6.4 (▲) and 12.8 (△).

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