Preparation of a porous magnetic filter for O₂ gas concentration

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We produced porous ceramics for gas separation using membrane formation of Nd₂Fe₁₄B powders on alumina (Al₂O₃) support. The average pore size and porosity of the alumina support were, respectively about 67 nm and 34–40%. Selectivity of this support was about 1.07, which well agreed with Knudsen diffusion. The coated Nd₂Fe₁₄B membrane thickness was about 166 μm. The sample selectivity after membrane formation was 1.07. Gas selectivity properties were not developed. When magnetized on the same sample, gas selectivity appeared at low differential pressure at gas permeation. Samples with a lower gas flow rate of the alumina support exhibited higher selectivity. The maximum was 1.22.

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1. Introduction

In recent years, the simultaneous pursuit of measures for alleviating global warming and securing energy resources presents urgent issues. Particularly, the situation of nuclear power generation has been reconsidered dramatically and studies of clean energy such as solar cells,¹⁾ fuel cells,²⁾ and an integrated gasification combined cycle³⁾ have been promoted to an increasing degree.

Improving the efficiency of existing thermal power plants is an important energy measure. Among the many methods which have been investigated, oxygen combustion for efficient power generation using limited fuels has been gaining much attention. With oxygen combustion, air with rich oxygen concentration (oxygen-enriched air) is used as combustion assistance gas for burners and boilers. Nishimura et al. reported that if oxygen concentration in the atmosphere (21%) were enriched to 30–40%, then 20–30% of fuel could be conserved and energy saving effects of greater than 46–48% could be expected together with heat recovery from exhaust gases.^{4),5)}

Oxygen-enriched air is produced by removing nitrogen selectively from air. To date, Pressure Swing Adsorption (PSA),^{6),7)} by which oxygen and nitrogen are separated such that air and zeolite having nitrogen adsorptive capacity are placed in a cylinder, and pressurization and depressurization are repeated. The oxygen enrichment membrane method^{8),9)} has been used practically. It uses polymer membranes as gas separation membranes for the selective dissolution of oxygen gas. Although these methods develop high-concentration performance, the gas treatment capability per unit time is low and costs are high. Therefore, their applications to medical and health appliances remain. Although oxygen separation materials making use of solid electrolyte have been proposed recently,^{10),11)} they have not been materialized yet because of the disadvantage that their operation is possible in high-temperature atmospheres only.

Moreover, the proposed use of gas separation membrane has recently been given some attention because of the fact that N₂ is a diamagnetic particle and O₂ is a paramagnetic particle. Rybak et al. produced an ethyl cellulose membrane with which

Nd₂Fe₁₄B powders are dispersed. They examined a possible relation between magnetic flux density and gas permeability characteristic of the membrane.¹²⁾ Results showed that a membrane having maximum magnetic flux density (1.25 mT) exhibited selectivity of 2.8, as calculated using O₂ gas permeability coefficient/N₂ gas permeability coefficient. Results revealed that with polymer gas separation membrane, O₂ gas permeation is made easy and gas separation capability is developed by imparting magnetism. However, the gas permeability coefficient of an organic membrane is a function of solubility to gas membrane and the diffusion rate of a gas in the membrane. This causes such a problem that the gas treatment amount per unit of time is less. Furthermore, high costs and lack of durability have been pointed out.

Advantages of porous ceramic filters are their greater gas processing amount per unit time and low running costs attributable to maintenance-free features. Therefore, application to gas separation technology is expected. Porous ceramic filters separate gases based on their diffusion properties such as molecular sieving, surface diffusion, and Knudsen diffusion. However, when the molecular weight and molecular size are comparable, as are N₂ and O₂, diffusion properties of gas in the pore are similar and separation is difficult. Accordingly, for N₂ gas and O₂ gas separation by porous ceramics, it is said that gas separation methods other than those related to molecular weight and molecular size must be used.

Then, the objective of this study is to produce novel porous ceramics for N₂/O₂ gas separation that satisfies both higher gas permeability coefficient and gas selectivity through composition of porous ceramics and magnetic materials, devoting attention to the magnetic characteristics of O₂.

2. Experimental procedure

2.1 Filter preparation

First, 30 vol.% high purity α-Al₂O₃ (TM-DAR; Taimei Chemicals Co. Ltd., Nagano, Japan) was mixed with 70 vol.% distilled water and 0.62 mass % poly(ammonium acrylate) (PAA) (Ceruna D-305; Chukyo Yushi Co. Ltd., Aichi, Japan) as a dispersant. Mixing was done using a planetary-type mixer¹³⁾ without stainless steel mesh for 1 min, rotated at 800 rpm and revolved at 2000 rpm for 1 min. Then the mixtures were treated

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for 10 min using a mixer with the mesh to disperse the α -Al₂O₃ particles in the slurry. After mesh treatment, the suspensions were re-mixed without mesh for 1 min to remove bubbles. The respective rotation and revolution rates were 60 and 2000 rpm. The resulting slurries were slip-casted into a 16 mm ϕ gypsum mold for 5 min. They were dried at room temperature for 24 h and were subsequently heated at 1073 K for 2 h to burn out the dispersant. Samples were sintered at 1273–1373 K for 2 h. The present samples were cut into 1 mm in thickness by diamond wheel.

Nd₂Fe₁₄B was planetary ball milled at 300 rpm for 24 h. The obtained powder with an average particle size of 1 μ m was mixed with 2 mass % methylcellulose and 14 mass % distilled water. The present paste was drop-cast onto the Al₂O₃ support and dried at 313 K for 12 h. The obtained filter was magnetized in about 105 mT for 5 min.

2.2 Characterization

The density and porosity of the Al₂O₃ supports were measured using the Archimedes technique with water. The average pore size of the samples was measured using mercury intrusion porosimetry (Pascal 140 and Pascal 240; CE Instruments Ltd., Italy). Their microstructures were observed using a scanning electron microscope (SEM, JSM-5310; JEOL Ltd., Tokyo, Japan).

Oxygen (μ_{O_2}) and nitrogen (μ_{N_2}) permeability coefficient were measured at 25°C in a controlled-temperature room using Eq. (1) and gas permeametry equipment, as described in previous reports.¹⁴⁾

$$\mu = \frac{Q}{\Delta P} \cdot \frac{L}{A} \quad (1)$$

Therein, ΔP is a differential pressure from the entrance to the exit of the filter, Q is the flow rate (mol/s), and A and L respectively denote the cross sectional area and the filter thickness (1 mm). In addition, ΔP and Q were measured using this equipment.

The N₂/O₂ selectivity, α_{N_2/O_2} , was calculated using Eq. (2)

$$\alpha_{N_2/O_2} = \frac{\mu_{O_2}}{\mu_{N_2}} \quad (2)$$

3. Results and discussion

3.1 Assessment of alumina support

For assessment of gas permeability coefficient of Al₂O₃/Nd₂Fe₁₄B composite as attempted in this study, it is considered that effects of the membrane-formed magnetic material can be identified by a detailed survey of alumina support before composition. Properties of the alumina support we produced are presented in **Table 1**. The average pore size and porosity of a sample being calcinated at 1073 K were, respectively 74 nm and 41%. The average pore size of samples being baked at 1273–1373 K was about 67 nm and nearly constant. The porosity decreased from 40 to 34% as the baking temperature increased, which is regarded as reduction accompanied by contraction

because of baking. To date, the authors have baked green bodies produced by casting molding at various temperature conditions and have reported the relations between baking conditions and porosity, and average pore size.¹⁵⁾ Results revealed that a slight difference exists between the temperature from which porosity starts to decrease and the temperature from which pore size starts to decrease. Results obtained in this study agree well with this finding. The baking temperature of the present experiment is expected to correspond to the temperature at which pore size does not change markedly and porosity decreases.

Furthermore, the N₂ gas permeability coefficient decreased from 6.5×10^{-10} to 3.9×10^{-10} m $\cdot$ mol $\cdot$ m⁻² $\cdot$ s⁻¹ $\cdot$ Pa⁻¹ as the baking temperature increased, which is regarded as attributable to reduction in the porosity. The gas permeability coefficient was measured in a range where the differential pressure was 0.02–0.2 MPa and a lack of pressure dependence was confirmed. The selectivity was calculated from the permeability coefficient of N₂ gas and O₂ gas. Selectivity of the sample baked at 1073 K was 0.98 (close to 1). Results showed that no selectivity exists, which is attributable to the fact that the average pore size was greater and that the gas passed through the pore in the form of viscous flow. The average pore size of the sample baked at 1273–1373 K was about 67 nm, which was slightly smaller than that of the sample baked at 1073 K. The permeability coefficients of N₂ gas and O₂ gas were measured for these samples. The gas selectivity was calculated as 1.07.

In general, Knudsen diffusion coefficient, D_k , is given by:

$$D_k = \frac{2}{3} r \left(\frac{8RT}{\pi M} \right)^{1/2} \quad (3)$$

where, r , R , T and M are, respectively, pore radius, gas constant, absolute temperature and molecular weight. Thus, theoretical values of the gas selectivity of Knudsen diffusion were calculated as follows using the respective molecular weights of oxygen (M_{O_2}) and nitrogen (M_{N_2}).¹⁶⁾

$$\alpha_{N_2/O_2} = \sqrt{\frac{M_{O_2}}{M_{N_2}}} \quad (4)$$

The theoretical value of Knudsen diffusion calculated using this equation is 1.07, which well agrees with the selectivity of the filter produced in this study. Based on the results presented above, we produced alumina supports of three types, each having a different gas permeability coefficient from those baked at 1273–1373 K, although the selectivity was unchanged by Knudsen diffusion.

3.2 Assessment of membrane formation of Nd₂Fe₁₄B and its characteristics

Figure 1 shows microstructure of a section being cut by a diamond cutter while the sample obtained is fixed using epoxy resin. The thickness of Nd₂Fe₁₄B membrane was about 166 μ m. Results showed that Nd₂Fe₁₄B membrane and alumina support were closely adhered. In the membrane, Nd₂Fe₁₄B were packed closely. No pinhole was noticed. From the observations described above, results showed that the structure, which was sought in this study, was obtained.

Figure 2 shows the permeability coefficient of N₂ gas and O₂ gas and selectivity of the sample, where a Nd₂Fe₁₄B membrane was formed on the alumina support baked at 1373 K. The permeability coefficient of N₂ gas was only slightly dependent on the pressure. It was nearly constant at 3.9×10^{-10} m $\cdot$ mol $\cdot$ m⁻² $\cdot$ s⁻¹ $\cdot$ Pa⁻¹. The Nd₂Fe₁₄B membrane coated in the

Table 1. Properties of the obtained Al₂O₃ support

Sintering temperature [K]	1073	1273	1323	1373
Average pore size [nm]	74	67	67	66
Porosity [%]	41	40	38	34
N ₂ gas permeability $\times 10^{-10}$ [kmol $\cdot$ m $\cdot$ m ⁻² $\cdot$ s ⁻¹ $\cdot$ kPa ⁻¹]	6.5	5.9	5.7	3.9
α_{N_2/O_2}	0.98	1.07	1.07	1.07

Fig. 1. Cross section of the filter observed using SEM micrograph.

Fig. 2. (Color online) Gas permeability coefficient and N_2/O_2 selectivity of the filter before magnetization.

present experiment comprises $Nd_2Fe_{14}B$ particles of about $1\mu m$. Its membrane thickness is sufficiently less than that of the alumina support ($1.2mm$). Therefore, it is considered that the permeability coefficient of the gas would change only slightly by mere coating. The selectivity α_{N_2/O_2} at that time was about 1.07, which agrees with the selectivity of alumina support alone. Therefore, this selectivity is regarded as attributable to Knudsen diffusion that occurred when the gas passed through the alumina support. Consequently, gas selectivity is known not to be developed by mere coating of the $Nd_2Fe_{14}B$ membrane.

Figure 3 shows the gas permeability coefficient in a sample magnetized by 105 mT. The selectivity is 1.07, whereas the differential pressure is greater than 0.1 MPa. No difference exists compared with that before magnetization. When the differential pressure is less than 0.1 MPa, the selectivity increases as the pressure decreases. It reached 1.22 (maximum) with differential pressure of 0.02 MPa, which is regarded as attributable to the fact that the detention time of gas in the filter was lengthened and influenced by magnetism for long time. As shown by Eq. (1), the gas flow rate is proportional to the gas pressure. Accordingly, if the differential pressure is low, then the permeability rate becomes sluggish and the gas is retained within the filter for a long time. During this period, paramagnetic O_2 gas was influenced by the magnet. Its permeability was restricted.

Fig. 3. (Color online) N_2/O_2 selectivity of the filter after magnetization.

Table 2. Gas selectivity of the obtained filter at 0.02 MPa of differential pressure

Sintering temperature [K]	1273	1323	1373
N_2 gas permeability $\times 10^{-10}$ [$kmol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot kPa^{-1}$]	5.9	5.7	3.9
α_{N_2/O_2}	1.07	1.07	1.22

To verify the discussions described above, gas permeability experiments were performed by coating $Nd_2Fe_{14}B$ membrane to three alumina supports, each having different permeability coefficient produced in 3.1. The obtained results are shown in **Table 2**. The filter selectivity for $Nd_2Fe_{14}B$ membranes formed onto the alumina support baked at 1273 and 1323 K, was 1.07, which is lower than that of the filter, where $Nd_2Fe_{14}B$ was membrane-formed onto the alumina support baked at 1373 K.

The discussions presented above also suggest that by lowering the gas permeability coefficient, i.e., by lengthening gas detention time in the filter, O_2 gas molecules having magnetism are affected easily by the magnetic action of the $Nd_2Fe_{14}B$ membrane, thereby developing the selectivity.

The separation and gas permeation mechanism of ethyl cellulose/magnetic powder were introduced.^(12),17) They measured the permeability of the pure O_2 , N_2 or air mixture. And the gas permeability of pure O_2 gas is higher than that of pure N_2 gas. Moreover, they explained the enhancement of gas permeability for air mixture by the aggregation between O_2 and N_2 in the pore channel. Since this discussion might be related to our results, we will discuss the matter in detail after further results were given.

4. Summary

In this study, we produced porous ceramics for gas separation using membrane formation of $Nd_2Fe_{14}B$ powders on an alumina support. The obtained results can be summarized as follows:

1. The average pore size and porosity of the alumina support were, respectively, 67 nm and 34–40%. The selectivity of this support was about 1.07, which well agreed with Knudsen diffusion.
2. Thickness of $Nd_2Fe_{14}B$ membrane was about 166 μm . No debonding was noticed between $Nd_2Fe_{14}B$ membrane and alumina support. No pinhole was detected.

3. Selectivity of the sample after membrane formation was 1.07. Gas selectivity was not developed.
4. If the same sample was magnetized, then gas selectivity was developed while differential pressure at gas permeation is low. The lower the gas flow rate, the more the selectivity increased, eventually reaching 1.22 (maximum).

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