Preparation of a porous magnetic filter for O₂ gas concentration

Toshihiro ISOBE,¹ Kosuke YANAGISAWA, Sachiko MATSUSHITA and Akira NAKAJIMA

Graduate School of Science and Engineering, Tokyo Institute of Technology, 2–12–1 Ookayama, Meguro-ku, Tokyo 152–8550, Japan

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 cycle 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-enriched air, 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.³,⁴,⁵

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 method⁸ 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. Accordingly, for N₂ 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 the composition of magnetic characteristics of O₂.

2. Experimental procedure

2.1 Filter preparation

Nd₂Fe₁₄B powders dispersed. They examined a possible relation between magnetic flux density and gas permeability characteristic of the membrane. 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 that satisfy both higher gas permeability coefficient and gas selectivity through composition of porous ceramics and magnetic materials, devoting attention to the magnetic characteristics of O₂.

¹ Corresponding author: T. Isobe; E-mail: isobe.t.ad@m.titech.ac.jp

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for 10 min using a mixer with the mesh to disperse the $\alpha$-Al$_2$O$_3$ 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 mmØ 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.

Nd$_2$Fe$_{14}$B was planetary ball milled at 300 rpm for 24 h. The obtained powder with an average particle size of 1 µm was mixed with 2 mass% methylcellulose and 14 mass% distilled water. The present paste was drop-cast onto the Al$_2$O$_3$ 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 Al$_2$O$_3$ 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.15

\[
\mu = \frac{Q}{\Delta P} \cdot \frac{L}{A}
\]  

(1)

Therein, $\Delta P$ 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, $\Delta P$ and $Q$ were measured using this equipment.

The $N_2/O_2$ selectivity, $\alpha_{N_2/O_2}$, was calculated using Eq. (2)

\[
\alpha_{N_2/O_2} = \frac{\mu_{N_2}}{\mu_{O_2}}
\]  

(2)

## 3. Results and discussion

### 3.1 Assessment of alumina support

For assessment of gas permeability coefficient of Al$_2$O$_3$/Nd$_2$Fe$_{14}$B 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 calcined 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 $N_2$ gas permeability coefficient decreased from $6.5 \times 10^{-10}$ to $3.9 \times 10^{-10}$ m·mol·m$^{-2}$·s$^{-1}$·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 $N_2$ gas and $O_2$ 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 $N_2$ gas and $O_2$ gas were measured for these samples. The gas selectivity was calculated as 1.07.

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

\[
D_k = \frac{2}{3} \rho \left( \frac{8RT}{\pi M} \right)^{1/2}
\]  

(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$_{N_2}$):10

\[
\alpha_{N_2/O_2} = \frac{M_{O_2}}{\sqrt{M_{N_2}}}
\]  

(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 Nd$_2$Fe$_{14}$B 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 Nd$_2$Fe$_{14}$B membrane was about 166 µm. Results showed that Nd$_2$Fe$_{14}$B membrane and alumina support were closely adhered. In the membrane, Nd$_2$Fe$_{14}$B were packed 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.

**Figure 2** shows the permeability coefficient of $N_2$ gas and $O_2$ gas and selectivity of the sample, where a Nd$_2$Fe$_{14}$B membrane was formed on the alumina support baked at 1373 K. The permeability coefficient of $N_2$ gas was only slightly dependent on the pressure. It was nearly constant at $3.9 \times 10^{-10}$ m·mol·m$^{-2}$·s$^{-1}$·Pa$^{-1}$. The Nd$_2$Fe$_{14}$B membrane coated in the

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**Table 1.** Properties of the obtained Al$_2$O$_3$ support

<table>
<thead>
<tr>
<th>Sintering temperature [K]</th>
<th>1073</th>
<th>1273</th>
<th>1323</th>
<th>1373</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average pore size [nm]</td>
<td>74</td>
<td>67</td>
<td>67</td>
<td>66</td>
</tr>
<tr>
<td>Porosity [%]</td>
<td>41</td>
<td>40</td>
<td>38</td>
<td>34</td>
</tr>
<tr>
<td>$N_2$ gas permeability $\times 10^{-10}$ [kmol·m·m$^{-2}$·s$^{-1}$·Pa$^{-1}$]</td>
<td>6.5</td>
<td>5.9</td>
<td>5.7</td>
<td>3.9</td>
</tr>
<tr>
<td>$\alpha_{N_2/O_2}$</td>
<td>0.98</td>
<td>1.07</td>
<td>1.07</td>
<td>1.07</td>
</tr>
</tbody>
</table>

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The present experiment comprises Nd$_2$Fe$_{14}$B particles of about 1\,\mu m. Its membrane thickness is sufficiently less than that of the alumina support (1.2 mm). Therefore, it is considered that the permeability coefficient of the gas would change only slightly by mere coating. The selectivity \( N_2/\text{O}_2 \) 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$_2$Fe$_{14}$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 \( \text{O}_2 \) gas was influenced by the magnet. Its permeability was restricted.

To verify the discussions described above, gas permeability experiments were performed by coating Nd$_2$Fe$_{14}$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$_2$Fe$_{14}$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$_2$Fe$_{14}$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, \( \text{O}_2 \) gas molecules having magnetism are affected easily by the magnetic action of the Nd$_2$Fe$_{14}$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 \( \text{O}_2, \text{N}_2 \) or air mixture. And the gas permeability of pure \( \text{O}_2 \) gas is higher than that of pure \( \text{N}_2 \) gas. Moreover, they explained the enhancement of gas permeability for air mixture by the aggregation between \( \text{O}_2 \) and \( \text{N}_2 \) 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$_2$Fe$_{14}$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$_2$Fe$_{14}$B membrane was about 166\,\mu m. No debonding was noticed between Nd$_2$Fe$_{14}$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).

References
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