$Ba_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ Dense Ceramic as an Oxygen Permeable Membrane for Partial Oxidation of Methane to Synthesis Gas

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Oxygen permeable membranes of perovskite crystals with $Ba_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFN) composition coated with a noble metal catalysts supported by a layered Mg–Al compound ($MgAlO_x$) are demonstrated to provide very high and stable oxygen permeation fluxes. In reactions 300 h in duration, the oxygen permeation flux of this membrane remains greater than 20 mL/(cm^2 min). This is the first report of such performance over reactions in 300 consecutive hours.

Oxygen permeable membranes of perovskite crystals exhibit mixed oxygen ionic and electronic conductivity.[1] This property can be exploited in oxygen permeable membrane reactors to produce synthetic gas by introducing methane on one side of the membrane and air on the other.[2] In such reactors, oxygen separation from air and partial oxidation of methane proceed simultaneously in a single reactor system, making it possible to reduce the cost of such systems to 30% of that required for conventional gas-to-liquid (GTL) plants.[3] Many perovskite compounds[4] have been investigated as oxygen permeable membrane material. Shao et al. reported $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ as an oxygen permeable membrane that achieves an oxygen permeation flux of 11.5 mL/(cm^2 min) over 500 h using the partial oxidation reaction.[5] For practical use, however, permeation fluxes greater than 20 mL/(cm^2 min) are required.[6] The present authors have shown that $Ba_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFN) also provides very high oxygen permeation flux[7] and have determined that to increase the membrane permeation flux it is necessary to improve not only the membrane performance but also the performance of the partial oxidation catalysts. Partial oxidation catalysts degrade over time accompanied by a corresponding decrease in methane conversion rate. BCFN membranes coated with noble metal catalysts supported by a layered Mg–Al compound ($MgAlO_x$) are shown in the present study to achieve high oxygen permeability with much lower degradation in the activity of the partial oxidation reaction over time. The partial oxidation catalysts used in the present study were prepared by intercalation as follows. Hydrotalcite, a layered Mg–Al compound, was prepared by dropping a solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ into a solution of 0.5 M $Na_2CO_3 \cdot 10H_2O$ and aging the precipitate.[8] The resultant compound was then dropped into a solution of complex anions of a noble metal (Pt, Rh, Ru, Ir, or Pd) and stirred until the top layer of the solution became clear, indicating complete intercalation of the noble metal into the hydrotalcite compound. After filtering, washing, and then drying at 353 K for 24 h, the precipitate was heated at 773 K for 16 h and then 1173 K for 5 h. Oxygen permeable BCFN membranes were prepared by the wet blending method. The reagents ($BaCO_3$, Co_3O_4, Fe_2O_3, and Nb_2O_5) were first weighed out so as to obtain mole ratios of Ba:Co:Fe:Nb = 1.0:0.7:0.2:0.1. The powder components were mixed thoroughly and then calcined at 1073 K for 20 h, ground, and then formed into a disk under pressure of 2 ton/cm^2. The disk was sintered at 1373 K for 20 h, then, dressed to 13 mm in diameter and 1 mm in thickness. The permeation membrane was coated with the partial oxidation catalyst by fixing a silver ring around the membrane, placing the $Ba_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ dense ceramic as an oxygen permeable membrane for partial oxidation of methane to synthesis gas. Pressing the specimen under a hydrostatic pressure of 2 ton/cm^2 to bond the catalyst to the membrane. Oxygen permeation reactions were carried out using the reactor system shown in Figure 1. The catalyst-coated membrane was placed between two alumina reaction tubes of 13-mm outer diameter and 9-mm inner diameter. The temperature of the reactor was maintained at 1173 K by an external electrical heater, and the entire cell was held in a helium atmosphere. The reaction was started by the introduction of methane and air at rates of 30 and 300 mL/min, respectively. No oxygen was detected at methane side during the methane partial oxidation reaction examinations. The reacted gas was analyzed by thermal conductivity (TCD) gas chromatography, and the oxygen permeability of the disk sample was determined from the content of CO and CO_2 in the reacted gas and the yield of H_2O evaluated from the balance of hydrogen before and after the reaction. The quantity of oxygen permeated through the membrane was also confirmed from the content of oxygen in the air after the reaction. H_2/CO was about 2 from the analytical result. Preliminary oxygen permeation experiments indicated that Pt, Rh, and Ru were the most promising of the nobel metals considered as a catalyst. Co of BCFN acted as an oxygen dissociation catalyst. The methane conversion and oxygen permeability of the three types of cata-

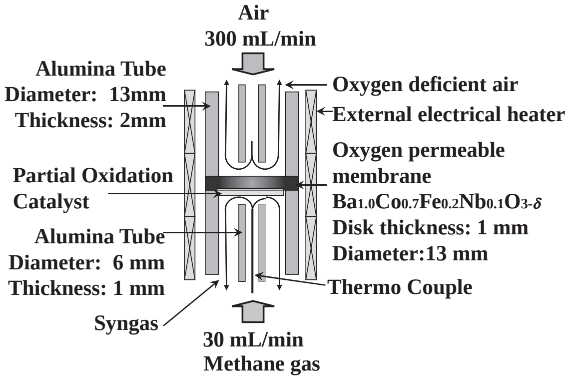

Figure 1. Schematic diagram of the membrane reactor and gas flow direction.

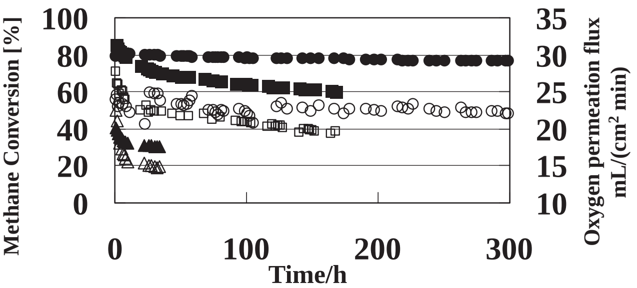

Figure 2. Methane conversion (closed symbol) and oxygen permeable flux (open symbol): ▲, Pt$_{2wt\%}$/MgAlO$_x$; △, Pt$_{2wt\%}$/MgAlO$_x$; ■, Rh$_{2wt\%}$/MgAlO$_x$; □, Rh$_{2wt\%}$/MgAlO$_x$; ●, Ru$_{2wt\%}$/MgAlO$_x$; ○, Ru$_{2wt\%}$/MgAlO$_x$.

Table 1. Physical properties of the BCFN membrane and catalysts before and after the reaction

	Pt$_{2wt\%}$ /MgAlO$_x$ for 34 h[a] /m^2 g^{-1}	Rh$_{2wt\%}$ /MgAlO$_x$ for 160 h[a] /m^2 g^{-1}	Ru$_{2wt\%}$ /MgAlO$_x$ for 300 h[a] /m^2 g^{-1}
Oxygen permeable membrane			
Specific surface area fresh	6.0	5.9	6.0
after examination	5.8	5.8	5.7
Partial oxidation Catalyst			
Specific surface area fresh	44.8	43.1	46.4
after examination	39.8	35.4	34.2
Metal surface area fresh	2.1	2.3	2.2
after examination	1.7	1.6	1.7

[a]Reaction time.

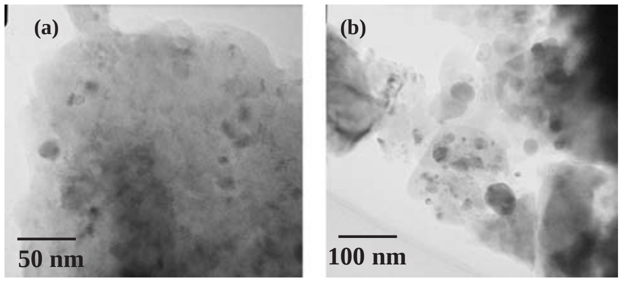

Figure 3. TEM micrograph images of Ru$_{2wt\%}$/MgAlO$_x$ catalyst: (a) Fresh catalyst, (b) After examination. The diameter of the catalysts particle before an examination was less than 20 nm. The catalyst particle after an examination became large. The diameter of a catalyst particle grew up into 20–50 nm.

lyst-loaded membrane were compared in Figure 2. The Pt catalyst exhibited relatively low methane conversion (<40%). The oxygen permeation flux of the Pt-loaded membrane started at 25 mL/(cm^2 min) but decreased rapidly with time to 15 mL/(cm^2 min) after 34 h. The Ru-loaded membrane exhibited high initial methane conversion (ca. 85%), but decreased to 60% after 160 h. The oxygen permeability also decreased with time, although less rapidly than the decrease in methane conversion, from 28 mL/(cm^2 min) at the onset of the reaction to less than 20 mL/(cm^2 min) after 140 h, beyond which the conversion rate remained unchanged to the end of the reaction (160 h). The Ru-loaded membrane exhibited an initial methane conversion rate of 80% or more, and the rate decreased only slowly to better than 75% after 300 h, at which time the reaction was halted. The oxygen permeation flux was also very stable in this case, decreasing from 25 mL/(cm^2 min) to 20 mL/(cm^2 min) at the end of the reaction. The physical properties of the membrane and catalyst before and after the reaction changed. The specific surface area of the membrane decreased slightly by the reaction, whereas the decrease in the specific surface areas of the catalysts (10–30%) and metal surface (20–30%) was more pronounced. These results were shown in Table 1. These results indicate that the membrane is thermally stable, attributable to prior sintering at 1373 K for 20 h. The catalysts, which were calcined at 1273 K for just 5 h, are less thermally stable in the reaction. Nevertheless, in all of the present experiments, the oxygen permeation flux and methane conversion exhibit similar tendencies of variation over the course of the reaction. A decrease in catalytic activity due to sintering in the reaction is inevitable, because the partial oxidation reaction is performed at 1173 K. Transmission electron microscopy observation of the catalyst particles suggests that a sinter ring is formed around the particles during the reaction (Figure 3). The combination of Ru$_{2wt\%}$/MgAlO$_x$ catalyst and BCFN membrane afforded the best oxygen permeation performance. This is the first report of such high flux performance for a reaction in 300 h.

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