Oxygen-permeable Membranes of $Ba_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ for Preparation of Synthesis Gas from Methane by Partial Oxidation

Makoto Harada,*[1] Kazunari Domen,[2] Michikazu Hara,[3] and Takashi Tatsumi[3]
[1]*Teikoku Oil Co., Ltd., 9-23-30 Kitakarasuyama, Setagaya-ku, Tokyo 157-0061*
[2]*Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656*
[3]*Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuda, Midori-ku, Yokohama 226-8503*

(Received May 9, 2006; CL-060550; E-mail: m_harada@teikokuoil.co.jp)

Oxygen-permeable membranes of $Ba_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFN) coated with $Ru_{2.0\,wt\%}Rh_{0.2\,wt\%}/Co_{0.3}Mg_{0.7}O$ catalyst have high oxygen permeability and can be used for the production of synthesis gas from methane by partial oxidation. Tests over 160 h show that the oxygen permeation flux is greater than 18 mL(STP)/(cm^2 min), substantially exceeding the oxygen permeability of existing perovskite crystal systems.

Perovskite-based oxygen-permeable membranes exhibit oxygen ionic and electronic mixed conductivity, and are thus suitable for synthesis gas production.[1,2] The use of these membranes makes it possible to reduce the size and cost of reactors.[3] However, perovskite crystals undergo a phase transition at high temperature under the reducing atmosphere required for synthesis gas preparation, resulting in a gradual degradation of the efficiency of mixed conduction.[4] Balachandran and co-workers reported a permeation flux of approximately 3 mL/(cm^2 min) at 1173 K using an $SrFeCo_{0.5}O_{3.25}$ membrane.[5,6] Shao and co-workers[7,8] reported a higher oxygen-permeation flux of 12 mL/(cm^2 min) over 500 h using a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) membrane. The present authors have discovered $Ba_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFN) as a new oxygen-permeable membrane capable of an oxygen-permeation flux of 18 mL/(cm^2 min) at 1173 K. This is the first report of an oxygen-permeable membrane with this composition. In the investigation of membranes with various compositions, membranes were prepared by a wet mixing process combining oxides and carbonates of metals; $BaCO_3$, $SrCO_3$, Co_3O_4, Fe_2O_3, and Nb_2O_5. The desired amounts of the reagents were dissolved in methanol solution and mixed thoroughly in a mortar. After evaporation of methanol, the mixture was pressed under 1 ton/cm^2 to form a disk of 15 mm in diameter, which was then calcined at 1073 K for 20 h as primary calcination. The disk was cooled and then ground into small particles of 300–500 μm and dispersed again in methanol solution. After evaporating the methanol, the mixture was formed into a disk of 15 mm in diameter under pressure of 2 ton/cm^2. The disk was calcined again at 1373 K for 20 h (secondary calcination). After cooling, the disk was polished to a thickness of 1 mm and subjected to permeability testing. All membranes examined in the present report were prepared by this method. The prepared membranes were checked by powder X-ray diffraction (XRD) to confirm the cubic perovskite structure. The phase transition under a reducing atmosphere was investigated by exposing the sample membrane to an atmosphere of He containing 5% H_2 at 1173 K for 60 min and then checking the crystal structure. BSCF membranes, despite having high oxygen permeability, exhibit changes in the XRD pattern upon use in the reduction reaction, indicating that a phase transition takes place. The effect of substituting Nb at the B site of BSCF was examined by preparing a perovskite crystal of $Ba_{0.5}Sr_{0.5}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$. This Nb-doped sample exhibited little change in the XRD patterns upon reduction treatment. This result suggests that the substitution of Nb helps to preserve the cubic structure, making the crystal resistant to reduction. As a next step, a $Sr_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ crystal was prepared in which the A sites of the perovskite structure are singly occupied by Sr. A considerable change in the XRD pattern occurred upon reduction of this sample, demonstrating that this composition is susceptible to phase transition during the reduction reaction. Finally, a $Ba_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ crystal was prepared, in which Sr in the A sites is substituted by Ba. As shown by the XRD patterns in Figure 1, this crystal underwent almost no structural change during the reduction process, indicating that the perovskite structure of the sample is preserved under typical conditions of synthesis gas production. This tendency was the same as that of a BSCF membrane.[9] In catalytic methane partial oxidation, the catalyst is coated directly onto the oxygen-permeable membrane. It is thus important that the catalyst employed for the reaction is chemically stable in contact with the membrane in order to prevent the formation of a new crystalline layer that may reduce the oxygen permeability. The catalyst must therefore be chemically stable at temperatures above 1173 K, and must have sufficiently high catalytic activity to reduce the oxygen partial pressure on the methane side of the membrane to obtain high oxygen-permeation flux. A range of catalysts have been surveyed with respect to compatibility with the BCFN membrane, and tests of catalytic performance have been conducted for the most suitable catalysts. Al_2O_3, MgO, ZrO_2, Y_2O_3, YSZ, TiO_2, and CeO_2 were examined as candidates for catalyst supports. In the tests, powders of the catalyst support and BCFN were mixed in equal weights and sintered in air at 1327 K for 5 h. XRD analysis of the crystal structure revealed that all catalysts

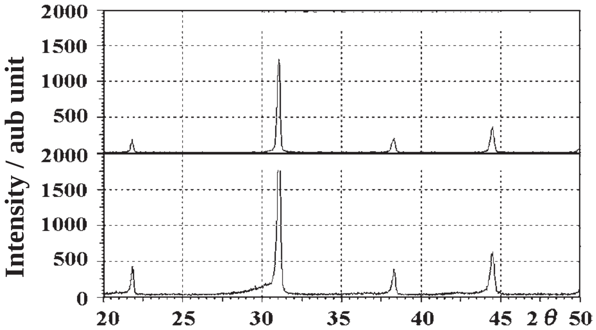

Figure 1. X-ray diffraction patterns of reduction-proof nature examination to $Ba_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$.

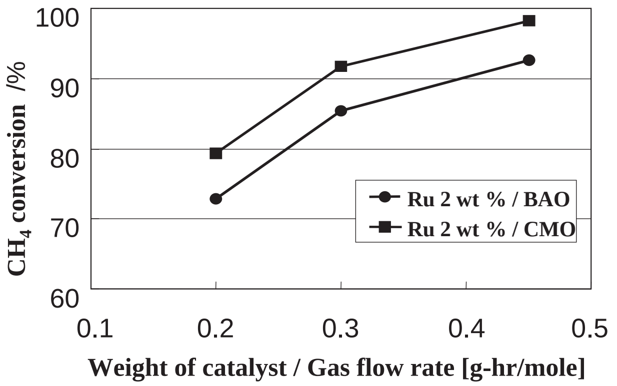

Figure 2. Partial oxidation catalyst examination results of BAO and CMO.

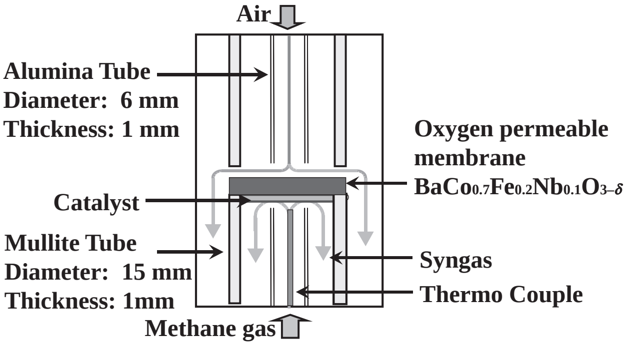

Figure 3. Schematic diagram of the membrane reactor and gas flow direction.

were reactive to BCFN, although the XRD changes for Al_2O_3 and MgO were relatively small. A $BaAl_2O_4$ spinel structure was formed in the former case by reaction with Ba, while a solid solution of Co in MgO was produced in the latter. To suppress these reactions, two new candidates of catalyst supports were prepared; $BaAl_2O_4$ (BAO), obtained by solid-phase reaction between Al_2O_3 and Ba, and $Co_{0.3}Mg_{0.7}O$ (CMO), obtained by formation of the solid solution of Co in MgO. The catalytic activity of these two supports was examined using a fixed-bed flow reactor. To the catalyst powder was added 2 wt % Ru as an active metal by impregnation. An 80 mg sample of each catalyst powder classified using a 300–500 μm was then placed in the reactor for partial oxidation reaction at 1173 K in atmospheric air.

The methane conversion rates are shown in Figure 2. The $Ru_{2\,wt\%}$/CMO catalyst exhibits the highest activity of the two candidates. Partial oxidation using the BCFN membrane with each of the catalysts was then performed using a membrane reactor at atmospheric pressure according to the test setup shown in Figure 3. The membrane was formed into a disk of 15 mm in diameter and 1 mm in thickness and placed between two mullite tubes. The temperature was maintained at 1173 K by an external electric heater. Methane was introduced on one side of the membrane at a flow rate of 40 mL/min, and air on the opposite side was extracted at a flow rate of 200 mL/min. Co of BCFN acted as an oxygen-dissociation catalyst. The methane-conversion catalyst was applied on the methane side of the membrane so as to bring methane immediately into reaction with the permeated oxygen. 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. Oxygen was not detected at methane side during the methane partial oxidation reaction examinations. As shown in Figure 4, the highest oxygen-permeation flux in the methane partial oxidation reaction was obtained by the combination of the BCFN membrane and $Ru_{2\,wt\%}Rh_{0.2\,wt\%}$/CMO catalyst. This system achieved an oxygen-permeation flux of 18 mL/(cm^2 min) in a continuous test over 160 h.

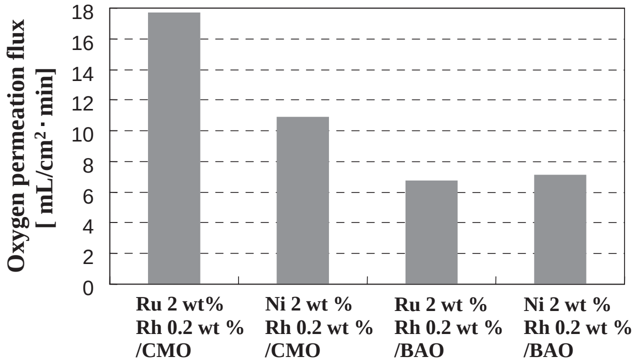

Figure 4. Oxygen-permeation flux by the difference in a partial oxidization catalyst.

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Published on the web (Advance View) August 5, 2006; doi:10.1246/cl.2006.968