One Component Membrane Reactor for Partial Oxidation of Methane Using Asymmetric Membranes

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Oxygen permeable asymmetric membranes of $Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\delta}$ were applied to a one-component membrane reactor (OCMR) for the partial oxidation of methane. CH_4 conversion and oxygen flux of OCMR with a 43-μm dense layer at 1173 K reached 71% and 1.7 mL min^{-1} cm^{-2}, respectively. These values are 2.5 times greater than that of a 500-μm self-supported membrane.

GTL (Gas to liquid) technology has attracted attention because the fuels produced by this process, such as methanol and DME, are promising alternatives to replace petroleum. The production of synthesis gas requires oxygen separation equipment and a catalytic reactor. Because a membrane reactor combines the separation and reaction processes, it is expected to cost less, be more compact, use less energy, and be a simpler process. Mixed ionic–electronic conductors such as perovskite-type oxides and ceramic composite materials were developed as oxygen permeable membranes.[1–3] In addition, membrane reactors with high chemical stability and high performance have been reported.[4–6] In previous studies, the catalyst and membrane materials were not identical components. Therefore, it is possible to damage the membrane by the reaction between the catalyst and the membrane. Our groups found that a $Ni/Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\delta}$ catalyst prepared by a solid-phase crystallization showed excellent activity of methane conversion into synthesis gas with negligible coke formation.[7] As $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\delta}$ of catalytic substrates indicated mixed ionic–electronic conductivity, our group proposed to apply this oxide to the catalytic substrate and membrane material as a OCMR.[8] The OCMR is expected to have a high chemical stability without any reaction between the catalyst and the membrane. In addition, we reported an asymmetric $Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\delta}$ membrane in which a thin dense layer was formed on a porous substrate with an identical chemical component.[9] In our study, we demonstrated that OCMR using an asymmetric membrane increased the CH_4 conversion and oxygen permeation flux.

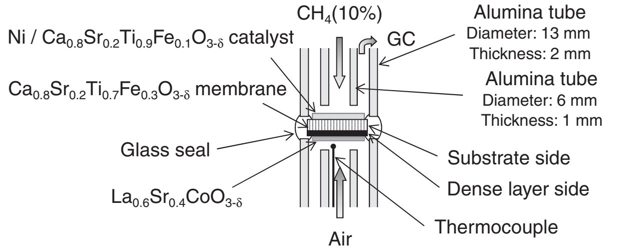

Figure 1. Schematic diagram of the asymmetric membrane assembly for OCMR.

A $Ni/Ca_{0.8}Sr_{0.2}Ti_{0.9}Fe_{0.1}O_{3-\delta}$ catalyst for the partial oxidation of methane was prepared by the citrate method.[7] A porous substrate material was prepared by a solid-state reaction in which a mixture of alkaline earth metal carbonate, titanium oxide, and iron oxide was treated in ambient air at 1523 K for 4 h. This material and 20 wt % of carbon black were ultrasonically agitated in isopropanol. This slurry was dried in air at about 387 K and was compacted uniaxially into a disk 13 mm in diameter at ca. 0.2 MPa. This disk was treated at 1423 K in ambient air to remove the carbon black. Subsequently, the disk was ground down to 0.5-mm thickness using waterproof sandpaper. A material of dense layer was prepared using the citrate method. This material of dense layer (8 wt %) was dispersed in isopropanol, and 0.3 mL of this mixture was delivered by drops on a porous substrate rotated at 800 rpm. After spin coating, the sample was dried at room temperature for 1 h, then presintered in ambient air at 1173 K for 1 h. The coating–drying cycles were repeated several times to vary the film thickness. The composite consisting of the film and substrate was calcined in ambient air at 1723 K for 15 h. Before OCMR experiments, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ was painted on the dense layer surface of the asymmetric membrane to enhance the dissociation of the molecular oxygen to ionic oxygen species and to prevent the dissociation process from the rate-determining process. And the $Ni/Ca_{0.8}Sr_{0.2}Ti_{0.9}Fe_{0.1}O_{3-\delta}$ catalyst was painted on the substrate side. OCMR experiments were carried out using the apparatus shown in Figure 1 at 1073–1223 K. The membrane was sealed with Pyrex glass at both ends of the outside dense alumina tubes. To check the physical leakage, air was fed to the film side at 50 mL min^{-1}, and helium as the sweep gas was fed to the substrate side at 30 mL min^{-1}. Next, to measure the performance of OCMR, air was fed into the dense layer side at 50 mL min^{-1}, and a gas mixture of 10% methane, 5% nitrogen, and 85% He was fed at 30 mL min^{-1}. Nitrogen was used as the reference gas. Analysis of the effluent gas was carried out by flow meters and gas chromatographs equipped with a thermal conductivity detector. After the experiments were over, the film thickness of the membrane was measured by SEM.

The asymmetric membranes prepared by 4 and 8 spin coating cycles were applied to OCMR using $Ni/Ca_{0.8}Sr_{0.2}Ti_{0.9}Fe_{0.1}O_{3-\delta}$ catalyst. The film thicknesses of these membranes prepared by 4 and 8 cycles were 43 and 68 μm, respectively. These values were reproducible.[9] The CH_4 conversion, CO selectivity, and oxygen permeation flux at 1173 K are listed in Table 1. The CH_4 conversions of asymmetric membranes increased when compared to that of the self-supported membranes of 500 μm. It is consider that this result is caused by an increase in oxygen permeation flux. CO selectivity of the self-supported membrane remained at a high, improved by over 99.8%. In addition, oxygen permeation fluxes of asymmetric membranes were two times higher than that of the self-supported membrane.

Table 1. Partial oxidation of OCMR[a]

	Film thickness /µm	CH_4 conversion /%	CO selectivity /%	H_2/CO	O_2 flux /mL min^{-1} cm^{-2}
Asymmetric membrane	43	71.1	99.8	2.19	1.73
	68	38.0	100.0	2.31	0.89
Self-supported membrane	500	27.8	98.6	2.02	0.59

[a]Reaction condition: 10% CH_4, 1173 K.

Oxygen flux with the partial oxidation reaction is higher than that without reaction because the oxygen-permeated membrane is immediately consumed by reaction with methane. The oxygen permeation flux of the self-supported membrane without reaction was 0.18 mL min^{-1} cm^{-2} with Pt as the recombination catalyst from ionic oxygen to molecular oxygen, on the substrate side.[9] Thus, oxygen flux estimated at OCMR increased to 3.3 times of that without reaction. In contrast, the values of 1.2 and 0.74 mL min^{-1} cm^{-2} were obtained as the oxygen fluxes for the asymmetric membrane with dense layers of 43 and 68 µm estimated by film thickness, respectively.[9] A 1.3–1.5-fold improvement of the oxygen flux was observed by application of OCMR using these membranes. Therefore, the degree of improvement of the asymmetric membrane was lower than that of the self-supported membrane. In the case where the asymmetric membrane was applied to OCMR, most of the partial oxidation catalyst existed just upper part of the substrate. Hence, there seem to be two types of permeable oxygen using partial oxidation of methane. One is oxygen permeated in the molecular state through the pores of the substrate because of the distance between the catalyst and dense layer. The other is oxygen reacted on the catalyst in the ionic state through the bulk of the substrate. There is a possibility that the improvement of oxygen flux of a membrane reactor using asymmetric membranes is lower than that of the self-support membrane because the majority of oxygen passes through the pores of the substrate. Further studies are needed to improve the installation of the partial oxidation catalyst on the substrate side of the asymmetric membrane.

We verified the performance of OCMR using a 43-µm asymmetric membrane and tested the durability at brief time periods over several temperatures. CH_4 conversion, oxygen permeation flux, CO selectivity, and formation rates of H_2, CO, and CO_2 are shown in Figure 2. CH_4 conversion and oxygen permeation flux were about 88% and 2.5 mL min^{-1} cm^{-2}, respectively. Moreover, 0.2 mL min^{-1} cm^{-2} of the CO_2 formation was observed at 1223 K, therefore, showing a CO selectivity of 94.6%. It is considered that the oxidation from CO to CO_2 is caused by high oxygen permeation. In addition, this catalyst might be insufficient for use in high oxygen permeation. Oxygen flux decreased with decreasing temperature. As a result, CH_4 conversion and formation rates of H_2 and CO also decreased. CO selectivity increased to about 100% below 1173 K because the oxidation of CO was uppressed by the decreasing oxygen flux. The ratio of H_2/CO was about 2.2 at all studied temperatures. This value was higher than the theoretical value of partial oxidation of methane. It is thought that this result indicated carbon deposition on the catalyst. This result might be caused by the fact that the majority of oxygen passes through the pores of the substrate. Even though the reaction time at respective temperatures was a short period of about 100 min, stable performance is obtained without significant deterioration. However, there is the possibility of the reaction between $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and $Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\delta}$ and of the deterioration of catalyst due to carbon deposition in long term durability.

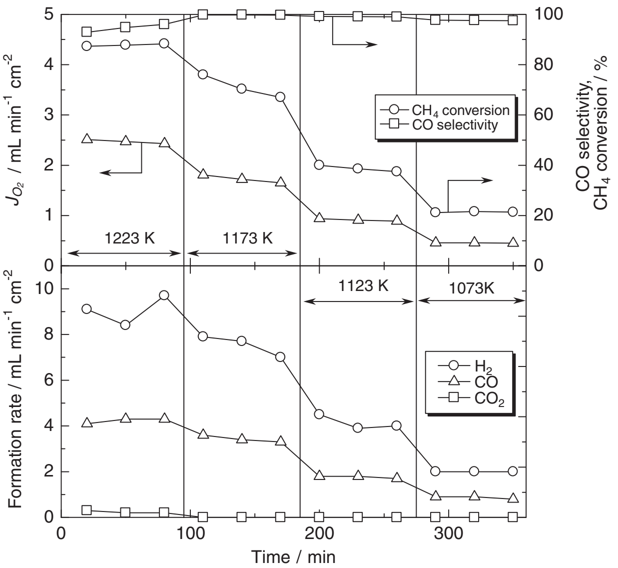

Figure 2. Effect of time on J_{O_2}, CH_4 conversion, CO selectivity, and the formation rate for OCMR. Film thickness: 43 µm, 10% CH_4.

In conclusion, the performance of OCMR was improved by using an asymmetric membrane. The primary cause is the increase of oxygen permeation through the membrane. We will discuss the chemical and catalytic stability by studying long-term durability and development of catalysts constructed from $CaTiO_3$ to enhance the dissociation of molecular oxygen in the future.

The work was partially supported by the Industrial Technology Research Grant Program in 2005 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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Published on the web (Advance View) April 4, 2009; doi:10.1246/cl.2009.452