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Design of one-component ceramic membrane-reactor for natural gas conversion

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Abstract

One-component ceramic membrane-reactor, constituting of the same type of $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ perovskite-type oxide for the catalyst involving support oxides, i.e., $Ni/Ca_{0.8}Sr_{0.2}Ti_{0.9}Fe_{0.1}O_{3-\alpha}$, and the oxide ionic and electronic mixed conductor, i.e., $Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\alpha}$, has been investigated for the partial oxidation of methane into synthesis gas in natural gas conversion process. Unique point of the membrane reactor is that the products formed between catalyst and membrane material should have no influence as a blocking layer against the oxygen pumping since catalyst and membrane material are consisted of same component, leading long time operation at the process of natural gas.

$Ni/Ca_{0.8}Sr_{0.2}Ti_{0.9}Fe_{0.1}O_{3-\alpha}$ used as a catalyst for partial oxidation of methane into synthesis gas shows the excellent activity for the anti-coking performance by the insertion of mixed conduction into the perovskite support. From the relationship between the amount of carbon deposited on the catalyst and the mixed conduction property in the support, it is suggested that a self-migration of lattice oxygen inside the support regulated the balance of the conductivities of oxide ion and electron plays an important role to prevent accumulation of carbon deposition.

$Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ performed as an oxygen separator from air chamber to reaction chamber, and its oxygen pumping property enhanced with increase in the Fe partial substitution. In addition, we demonstrated the one-component ceramic membrane-reactor for the methane conversion into synthesis gas at 1173 K. Methane conversion was drastically accelerated by the electrochemical oxygen pumping with one component membrane reactor. An addition of cathodic catalyst brought about further acceleration of methane conversion, and highly level of methane conversion (50%) and CO selectivity (95%) was reached. It is suggested that oxygen permeation was dependent on the cathodic process when the $Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\alpha}$ was used as a mixed conducting oxide in the membrane system.

Keywords: One-component ceramic membrane-reactor; Methane conversion; Self anti-coking performance

1. Introduction

GTL technology, namely natural gas conversion to liquid fuels, is a promising candidate to produce the fuels such as methanol, DME, and gasoline instead of the oil [1]. As for the capital cost down in the GTL process, shift toward the simple and less energy process at the synthesis gas preparation step provides a promising approach to promote the GTL technology, because this step account for 60% of all capital cost from the natural gas to the marketable products and thus its capital cost reduction brings greatest benefit [2]. A membrane reactor carrying out both the reaction and separation at the same time is expected as to promote the simple process. Especially, a ceramic membrane reactor using an oxide ionic and electronic mixed conductor has been focused as a key technology to be simpler and to supply less energy for methane conversion into synthesis gas, since oxygen generator from air is not neccessary to use and since both methane conversion and oxygen separation are carried out at the same time [3,4]. The technical innovation in this research field is strongly dependent on the development of the mixed conductors, having the potential for high oxygen permeability and stability under methane atomsphere, and a new type of catalyst, having for high conversion activity and suppresion of carbon deposition. In past few years, a new age in ceramic membrane reactors has opened up, and a group of new materials such as $LaGaO_3$-typed oxide [5] and Sr–Fe–Co typed perovsikite oxide [6] have been successively developed for the membrane materials. Significant advances in ceramics membrane reactors have been brought forth by the development of new mixed conductors having high oxygen permeability [7,8], but chemical stability remains unattractive for reaction between membrane and catalyst under methane

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reforming conditions. The product formed at the boundary as result of reaction between the catalyst and mixed conductor leads to block the oxygen permeation with mixed conduction from the membrane to gas phase. The phenomenon may cause several serious problems for long life operation in the GTL process, e.g., lower function of oxygen pumping, acceleration of carbon depositon, and consequently stop of the running methane conversion process. The catalyst applying for the ceramic mebrane reactor, threrefore, is required the chemical stability against the ceramic mebrane material. No such attempt to explore the catalyst having both high activity and chemical stability with membrane has been made so far.

At the previous investigation of the methane conversion catalysts, Ni-based materials [9–11] have been widely regarded as efficient one for synthesis gas production, but the susceptibility to carbon deposition leading to deactivation of the catalysts prevents their industrial application for natural gas [12]. Many attempts to suppress the carbon deposition have been made so far by controlling (1) dispersion of Ni particles [13], (2) metal-support interaction including the formation of solid solutions [14–16], and (3) basicity of the catalysts [17]. The Ni-based catalysts having high ability of anti-coking performance, however, have not been still investigated. On the other hand, we previously reported that Ni catalysts supported on the perovskite type oxide, i.e., Ni/$Ca_{0.8}Sr_{0.2}TiO_3$ and Ni/$BaTiO_3$ prepared by a solid-phase crystallization (spc) [18,19] method, show both excellent activity of methane conversion into synthesis gas and negligible coke formation. Here, it should be noted that Fe doped $CaTiO_3$, denoted as $CaTi_{1-x}Fe_xO_{3-\alpha}$, exhibited the oxide ionic and elctronic mixed conduction [20]. When Fe doped $Ca_{0.8}Sr_{0.2}TiO_3$ denoted as $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$, can be applied to both catalyst support and membrane, one component ceramic membrane reactor would be constructed to solve the intrinsic probleme of ceramic membrane reactor. Furthermore, it is expected that amount of carbon deposition may decrease by the lattice oxygen migration in $Ca_{0.8}Sr_{0.2}TiO_3$ support since the lattice oxygen is well known to migrate easily in the perovskite oxide.

In this paper, we would report mainly the development of the one-component ceramic membrane-reactor, OCMR, which may be the trigger for a step change in the natural gas conversion to synthesis gas (Fig. 1). Firstly, we have attempted to elucidate the influence of lattice oxygen migration on the carbon deposition by intentionally assembling the oxide ionic and electronic mixed conducting perovskite oxides as supports [21]. In addition, we show the newly conceptual approach of the investigation for the ceramic membrane reactors for the natural gas conversion, which is consisting of the same component as catalyst support and ceramic membrane based on $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$.

2. Experimental

2.1. Preparation of the nickel catalyst and the mixed conducting oxide

Nickel supported on the $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ ($0 \leqq x \leqq 0.3$), namely $Ni_{1.0}/Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ was prepared by the citrate method as previously reported [18,19]. The catalyst samples were characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

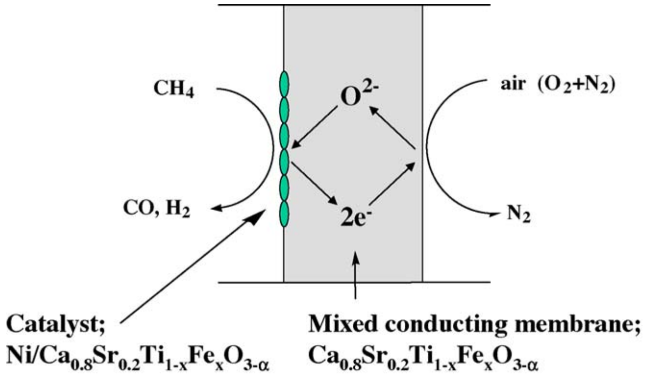

Fig. 1. Principle of the methane conversion with air using one component ceramic membrane reactor.

Mixed conducting oxide specimens used as oxygen transporting membranes, $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ ($0 \leqq x \leqq 0.3$), were prepared by calcining a mixture of the components; the mixtures of $CaCO_3$ (99.9%), $SrCO_3$ (99.9%), TiO_2 (99.9%) and Fe_2O_3 (99.9%) were ball-milled for 24 h and then calcined at 1523 K for 10 h in air. The powders obtained were pulverized and subsequently pressed into a disk at 2.0 tonnes/cm^2. The pressed disk was sintered at 1873 K in air. The density of the sintered pellet was more than 95% of its theoretical value. From X-ray diffraction measurements, the diffraction patterns of the $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ ($0 \leqq x \leqq 0.3$) were attributed to a perovskite type structure.

2.2. Characterization of the mixed conduction oxides

In order to elucidate the effect of partial substitution by Fe ions on the lattice oxygen migration with the oxide ionic and electronic mixed conduction in the $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$, ionic transport number was measured by the electrochemical oxygen pumping technique with a dense ceramics disk (1.0 mm thickness and 12.0 mm diameter) of $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ ($0 \leqq x \leqq 0.3$) sintered at 1873 K for 15 h in air. A value of ionic transport number at 1173 K was estimated by the comparison between the actual rates of steam evolved at anode by applying the direct current to the oxygen concentration cell, as described in Eq. (1), and the theoretical value calculated from Faraday's law.

$$(\text{anode})\,2\%\,H_2,\quad Pt|Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}\,(0 \leqq x \leqq 0.3)|Pt,\; 100\%\,O_2\,(\text{cathode}). \tag{1}$$

Here, 2% H_2 diluted with He was used as a reductive anode gas instead of methane because the carbon deposition from methane influences the transport number measured under the reductive conditions. Basically, the ionic transport number of the oxide ionic and electronic mixed conducting oxide is dependent on the equivalent oxygen partial pressure around the oxide. Therefore, the ionic transport number under the condition of the partial oxidation of methane with air (PO) and with carbon dioxide (DR) are identical to that under the condition corresponding to an equivalent oxygen partial pressure of $1.0\,x\,10^{-15}$ and $1.0\,x\,10^{-17}$ atm, respectively. The equivalent oxygen partial pressure of 2% H_2 used as the anode gas in this study is $1.4\,x\,10^{-17}$ atm, and this value was almost the same extent as that in DR. Here, steam evolution rate at the anode was monitored by a dew point meter (MBW ELECTRONIC CH-5430 WETTINGEN, DP-14).

2.3. Catalytic activity of Ni/$Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ for CH_4 conversion to synthesis gas

A gaseous mixture of methane (1.0 l/h) and air (2.4 l/h) was passed over the Ni-catalyst (300 mg) at 1173 K for 1 h in order to figure out the catalytic activity for the partial oxidation of methane. As for the methane dry reforming, the catalyst (150 mg) was tested at 1173 K for 1 h. Methane (1.0 l/h), carbon dioxide (1.0 l/h) and nitrogen (1.4 l/h) was passed as the reagent gas mixture. The reaction products were monitored using an on-line gas chromatography apparatus. Separation of all gases was obtained using helium or argon carrier gas through Porapak Q and molecular sieve 5A packed column, and detected using a thermal conductivity detector. The amount of carbon deposited on the catalysts under PO or DR conditions was estimated by the temperature program oxidation (TPO); the catalyst after the reaction was heated in air (1.0 l/h) from 723 to 1173 K at 2.5 K/min, while the formation of carbon dioxide by the oxidation of carbon was measured by GC.

2.4. Partial oxidation of methane with a ceramic membrane reactor

The ceramics diaphragm in membrane reactor was constructed from a $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ ($0 \leqq x \leqq 0.3$) disk (diameter: 13 mm, thickness: 0.5 mm). Ni metal supported on $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ was used as an anodic catalyst for the methane conversion. As for the catalyst to enhance the dissociation of the molecular oxygen to ionic oxygen species in air, $La_{0.6}Sr_{0.4}MnO_3$ (LSM) such as a typical cathode catalyst for solid oxide fuel cell (SOFC) was used. LSM was prepared by the citrate method as previously reported [18,19]. Both catalysts for the methane conversion and oxygen dissociation were respectively painted on each side of the disk, and then was fired at 1173 K in air for 1 h. The ceramics membrane attached with catalysts was mounted between two alumina tubes and sealed by low melting point glass. As the gas inlet, a quartz tube was placed inside the alumina tube, where the end of the quartz tube was close to the disk, thus allowing good contact between the CH_4 gas and the Ni-based catalyst. Finally, the reactor was placed in a vertical electric furnace, controlled by a temperature controller, and the temperature of the reactor was monitored by a thermocouple positioned next to the ceramics membrane.

Ten percentage methane and 5% nitrogen diluted with He (1.2 l/h) as a reaction gas was introduced into the anode chamber at 1173 K for testing the catalytic activity of the membrane reactor. Here, it is noted that nitrogen in methane mixture gas was used as a standard gas. Air was passed (18 l/h) through the cathode chamber. Analysis of the effluent gas was carried out by the TCD gas chromatography. Prapak Q and molecular sieve 5A were used for the analysis of the hydrocarbons and inorganic gases, respectively.

3. Results and discussions

3.1. Effect of partial substitution of Fe into catalyst supports on the methane conversion

We have already reported that Ni/$Ca_{0.8}Sr_{0.2}TiO_3$ shows not only the high catalytic activity in the partial oxidation of methane to synthesis gas but also the negligible small carbon deposition rather than that of Ni/Al_2O_3.[18,19]. Here, we explored the partial substitution of Fe into Ti site of perovskite support in the Ni based catalysts in order to clarify the effect of the Fe doping into support oxide on the catalytic activity for synthesis gas formation. The catalytic activity of the $Ni_{1.0}$/$Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ ($0 \leqq x \leqq 0.3$), for methane conversion is shown in Table 1. For all of the catalysts with various Fe contents, the conversions by PO, partial oxidation of methane with air, and DR, dry reforming of methane with carbon dioxide, were close to 100% with selectivities for synthesis gas of ~95%, respectively. The partial substitution by Fe thus did not affect the catalytic activity for both PO and DR. On the other hand, the amount of the deposited carbon on the catalysts drastically varied depending on the Fe content in the perovskite support. Fig. 2 shows the effect of the Fe content on the amount of the deposited carbon on the catalysts under the PO and DR conditions, respectively. The values during PO decreased up to $x = 0.1$ and then increased with increasing the Fe content as shown in Fig. 2 (a). The trend in carbon deposition relating to Fe content in DR was quite similar to those seen for PO as shown in Fig. 2 (b) although the amount of carbon deposition in DR was about 10 times more than that in PO. These results indicate that the partial substitution of Ti by Fe is closely related to the anti-coking performance over the Ni-based catalysts,

Table 1
Catalytic activity of Ni/$Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ for the methane conversion at 1173 K

Fe content (x)	CH_4 conversion (%)	CO selectivity (%)	H_2/CO
(a) Partial oxidation of methane			
$x = 0$	99.8	96.0	1.72
$x = 0.01$	99.9	97.0	1.62
$x = 0.05$	99.9	96.3	1.69
$x = 0.10$	99.9	96.0	1.75
$x = 0.15$	99.4	96.4	1.89
$x = 0.20$	99.5	95.8	1.86
$x = 0.30$	98.3	95.3	1.89
(b) Dry reforming of methane			
$x = 0$	98.8	97.2	1.04
$x = 0.01$	98.6	95.0	1.06
$x = 0.05$	98.9	90.3	1.14
$x = 0.10$	98.8	97.5	1.05
$x = 0.15$	98.7	98.2	1.03
$x = 0.20$	98.6	98.9	1.03
$x = 0.30$	95.4	90.2	1.13

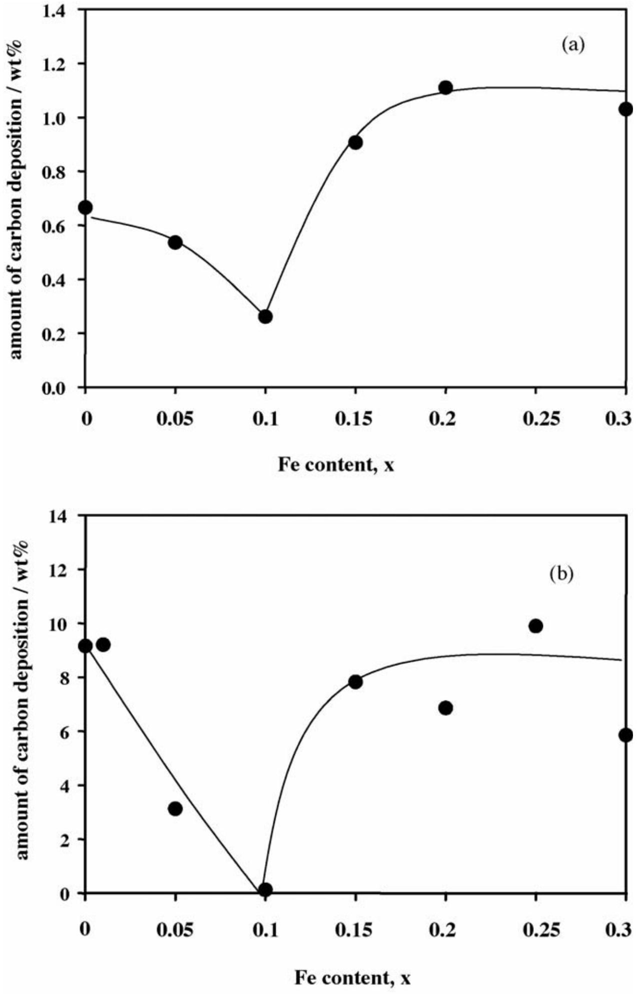

Fig. 2. Dependence of carbon deposition on the Fe content. Amounts of carbon deposition under the partial oxidation (a) and dry reforming (b) of methane were estimated by the TPO (temperature program oxidation) from 523 to 1173 K at the rate of 2.5 K/min under flowing air (2.4 l/h), as reported previously [18].

irrespective of the methane conversion with air or carbon dioxide. It has been reported [13–17] that the carbon deposition behavior over the Ni-based catalyst depends on the dispersion of Ni particles, basicity of the catalyst support and the Ni-support interaction. However, no effect of the Ni dispersion was observed in this study because the BET surface area of all the catalysts tested was almost the same (about 5 m^2/g) and because the TEM images of $Ni_{1.0}/Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ ($0 \leqq x \leqq 0.3$) showed that the Ni metal particles were highly dispersed over each perovskite support with a size of about 30 nm. The basicity of the support materials should not influence the suppression of carbon deposition, because the amounts of Ca and Sr, affecting the basicity of the support strongly, were constant for all the perovskite supports. In addition, XRD spectra showed no formation of a solid solution between the Ni metal and the perovskite support oxide for all the samples studied. The relationship between the carbon deposition and the partial substitution by Fe ions shown in Fig. 2 is thus not attributed to the effect of the Ni particle size, the Ni-support interaction and the basicity of catalyst supports. Therefore, it is likely that carbon deposition was suppressed by the different mechanism reported so far. In order to figure out the mechanism, the mixed conduction leading to the lattice oxygen migration was elucidated.

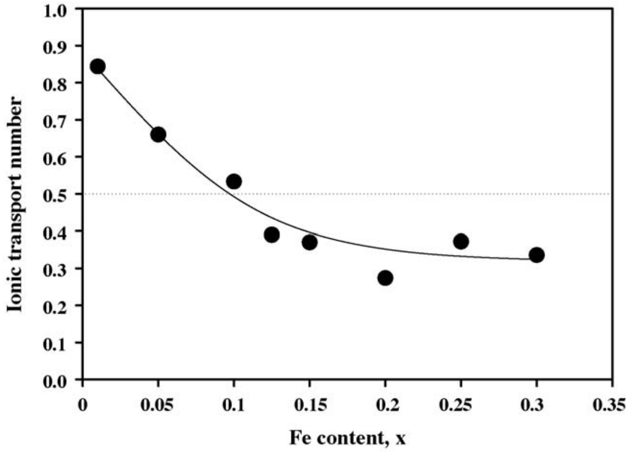

Fig. 3. Relationship between the oxide ionic transport number and Fe content, x, in $Ni/Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$.

3.2. Mixed conduction properties of $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$

We measured the ionic transport number, t_{ion}, for the $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ ($0 \leqq x \leqq 0.3$) at 1173 K by the electrochemical oxygen pumping technique in order to clarify the ratio of the oxide ionic conduction and electronic mixed conduction. Fig. 3 shows the relationship between the oxide ionic transport number and the Fe content in the $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$. It was found that the oxide ionic transport number gradually decreased with increasing Fe content. This indicates that electronic conduction became predominately by the partial substitution of Fe into Ti site.

From the previous studies about the oxygen permeation property in the oxide ionic and electronic mixed conduction [24], oxygen permeation was regulated by the balance of the oxide ionic conductivity, σ_{ion} (S/cm), and electronic conductivity, σ_e (S/cm). Furthermore, it is figured out that the highest permeability of oxygen is expected when σ_{ion} is equal to σ_e, that is, t_{ion} is 0.5. Here, it should be emphasized that ionic transport number at $x = 0.1$, where the best anti-coking performance was achieved, was 0.53. That is, the carbon deposition level was lowest when the migration rate of the lattice oxygen, J_{ion}, is maximized at $t_{ion} = 0.5$ as expected from Eq. (5). It is, therefore, concluded that the deposited carbon is burned off by the migrated lattice oxygen through the $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ support, where the kinetics of the carbon deposition is controlled by the balance of oxide ionic and electronic mixed conduction, which is further controlled by the doping of Fe into the $Ca_{0.8}Sr_{0.2}TiO_3$ perovskite. We thus propose the model for the self anti-coking catalyst [21], as shown in Fig. 4. The lattice oxygen migrating through the perovskite support appears at the Ni metal-perovskite support boundary, where the carbon deposited by the dissociation of

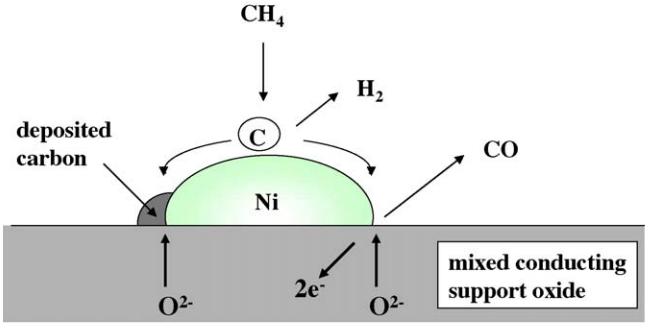

Fig. 4. Proposed scheme for the self anti-coking performance of catalyst by lattice oxygen migration.

methane is burned off, resulting in a decrease in the amount of deposited carbon. At this moment, it is considered that the lattice oxygen to burn off the deposited carbon might be continuously supplied from the gas phase into the perovskite oxide under the reaction by the mixed conduction. Here, the observation of carbon deposition at $x = 0.1$ as an optimum Fe substitution (Fig. 2) might be due to the coke formation onto the Ni metal surface, namely encapsulating carbon [12]. The unique points of the proposed mechanism are that (i) the carbon deposition level strongly depends on the oxygen migration through the lattice oxygen in the support material; (ii) the surface reaction of carbon deposition at the Ni metal-perovskite support boundary is regulated by changing the bulk characteristic of the supports with respect to mixed conduction property. In other words, the effect described above may be applied to the development of the self anti-coking catalysts for the oxidation of other gaseous hydrocarbons. This concept is thus expected to provide useful information for developing new industrial catalysts without carbon deposition during hydrocarbon oxidation.

3.3. One-component ceramic membrane-reactor, OCMR, for methane conversion

Recently, a ceramic membrane reactor using an electronic and oxide ionic mixed conductor has been expected to construct a simply and compact process for the natural gas conversion, since methane conversion and oxygen separation can be carried out at the same time on each surface of the ceramic reactor, as shown in Fig. 1. The technical innovation in this research field is strongly depended on the development of the new type ceramics having a potential of high oxygen permeability and stability under methane atmosphere and new type methane conversion catalysts. Significant advances in ceramics membrane reactors have been brought forth by the development of new mixed conductors having high oxygen permeability [5–8], but chemical stability remains unattractive for reaction between membrane and catalyst under methane conditions. The one-component ceramic membrane-reactor, namely OCMR, consisting of the same component between the catalyst involving support oxides and the mixed conductor has attracted considerable attention to achieve the chemical stability, because the reaction among the same components should have no influence on the permeation of the oxide ion. So, we have attempted the development of the ceramic membrane reactor consisting of Fe doped $Ca_{0.8}Sr_{0.2}TiO_3$ used as not only support material but also mixed conducting material for the natural gas conversion into synthesis gas.

Firstly, we examined an oxygen permeation property with mixed conduction of $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$, $(0 \leqq x \leqq 0.3)$ using an oxygen concentration cell, described as $N_2|Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ membrane |air. Fig. 5 shows the oxygen permeation with mixed conduction in $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ $(0 \leqq x \leqq 0.3)$. It was found that oxygen permeation with electrochemical mixed conduction was carried out when $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$ was used as a separation membrane. Oxygen permeation rates obtained in this study increased with increasing the operating temperature from 1073 to 1273 K and enhanced with increasing amount of Fe content, resulting from the enhancement of the mixed conduction with increasing the operating temperature and partial substitution of Fe contents. Oxygen permeation rates through $Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\alpha}$ membrane under the oxygen concentration cell at 1173 K were as high as about four times larger than that of $Ca_{0.8}Sr_{0.2}Ti_{0.9}Fe_{0.1}O_{3-\alpha}$ membrane and reached values of 0.3 mmol/h/cm^2 at 1173 K for $Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\alpha}$ membrane, as shown in Fig. 5. Here, it is noted that the oxygen permeation flux obtained at $x = 0.3$ was higher than that obtained at $x = 0.1$, although the balance between the ionic and electronic conductivity was observed at $x = 0.1$, as described above. We consider at this moment that the discrepancy observed here was attributed to the difference with respect to the oxide ion in the surface reaction of catalyst and in the bulk diffusion in mixed conducting material, as described below; The oxygen permeation flux, as shown in Fig. 5, is regulated by both the bulk diffusion and surface reaction of oxide ion. Especially, the flux is strongly controlled by bulk diffusion process when the dense disk (membrane thickness; 1.0 mm) is used as a mixed conducting membrane. On the other

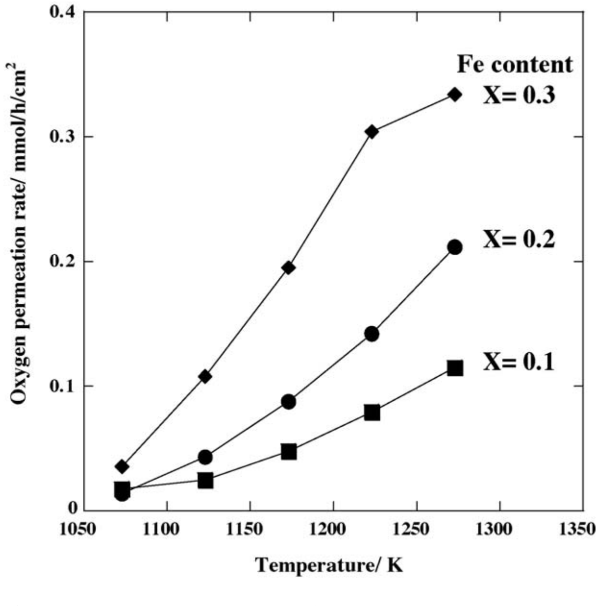

Fig. 5. Oxygen permeation property of $Ca_{0.8}Sr_{0.2}Ti_{1-x}Fe_xO_{3-\alpha}$. Membrane thickness: 1.0 mm.

hand, the oxygen extraction to suppress the coke accumulation was only carried out onto the catalyst surface, indicating that only lattice oxygen extracted from surface of oxide was used for the self anti-coking performance. Therefore, it is likely that the oxygen pump phenomena from the catalytic surface discussed in this study are only characterized by the balance the between ionic and electronic conductivity described as a theoretical equation because it is not necessary to consider the long bulk diffusion. The reason for the difference observed in this study remains unclear at this time, so further studies are needed to clarify this point.

In order to study the catalytic activity and electrochemical cell performance of OCMR, we constructed the membrane reactor at 1173 K as described below;

$$\text{(anode) } 10\%\,\mathrm{CH_4},\quad \mathrm{Ni/Ca_{0.8}Sr_{0.2}Ti_{0.9}Fe_{0.1}O_{3-\alpha}}$$
$$|\mathrm{Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\alpha}}|\text{ air (cathode).}$$

When 10% methane and 100% helium were introduced into anode and cathode chamber, respectively, carbon monoxide and hydrogen were slightly observed in the anode, and then no oxidative products were observed after 20 min later. It is likely that the partial oxidation of methane was carried out by using the oxygen from nickel oxide. On replacing air from the He in cathode chamber, the formation rates of carbon monoxide and hydrogen drastically increased while no carbon dioxide formation was observed. The conversion of methane and selectivity to CO were 6.6% and 100%, respectively. Oxygen permeation rate estimated by the amount of oxidative products was 0.19 mmol/h/cm^2. These results indicate that we have demonstrated acceleration of the partial oxidation of methane with oxygen permeation by using OCMR. Several studies [22,23] of the SOFC research and development indicated that the catalysts such as (La, Sr)$\mathrm{CoO_3}$ (LSC) and (La, Sr)$\mathrm{MnO_3}$ (LSM), to accelerate the cathodic reaction, namely, the insertion of oxide ion from molecular oxygen in the gas phase, acts to enhance the electrochemical oxygen pumping property, leading to the higher performance of the fuel cell. We explored to attach the cathodic catalyst onto the OCMR purposed in this study to accelerate the methane conversion. Here, it should be noted that a ceramic membrane reactor attaching the cathodic catalyst is also involved in the conceptual approach to establish the OCMR, because the serious problem at the present stage for the ceramic membrane reactor is the chemical stability between the mixed conductor and anodic catalyst at the methane conversion conditions.

Fig. 6 shows the methane conversion with OCMR attached with LSM as the cathodic catalyst. The reaction cell was described below;

$$\text{(anode) } 10\%\,\mathrm{CH_4},\ \mathrm{Ni/Ca_{0.8}Sr_{0.2}Ti_{0.9}Fe_{0.1}O_{3\text{-}\alpha}}$$
$$|\mathrm{Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3\text{-}\alpha}}|\text{LSM, air (cathode).}$$

As air was introduced into cathode chamber, partial oxidation of methane carried out at 1173 K, and the selectivity to carbon monoxide was 95%. Here, it should be emphasized that methane conversion increased to 50% from 6.6% by applying LSM, and that its value was 5.6 times higher than that of OCMR having no cathodic catalysts. This result indicates that acceleration of methane conversion was attributed to the application of the cathodic catalyst, suggesting that attachment of LSM leaded to enhance the oxygen permeation property effectively.

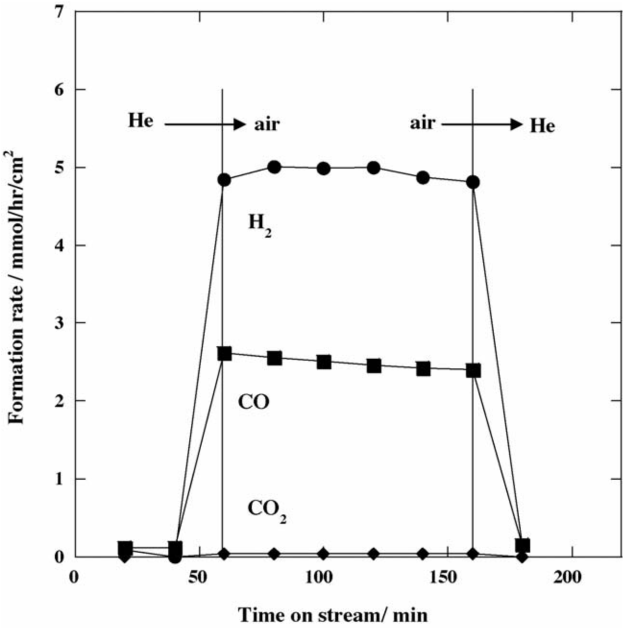

Fig. 6. Methane conversion with one component ceramic membrane reactor. Conditions; membrane: $\mathrm{Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\alpha}}$ (0.5 mm), anode gas: 10% $\mathrm{CH_4}$, anode catalyst $\mathrm{Ni/Ca_{0.8}Sr_{0.2}Ti_{0.9}Fe_{0.1}O_{3-\alpha}}$, cathode gas: air, cathode catalyst: $\mathrm{La_{0.6}Sr_{0.4}MnO_3}$, reaction temperature: 1173 K.

From the viewpoint of practical use of ceramic membrane system into natural gas conversion, we will attempt to investigate the way to obtain higher oxygen permeability, e.g., by fabricating thinner membranes of mixed conducting materials or by developing new mixed conducting materials. In addition, a suitable cathodic catalyst would be required to improve the system performance.

4. Conclusions

OCMR was proposed to improve the ceramic membrane reactor for the natural gas conversion. Fe doped $\mathrm{Ca_{0.8}Sr_{0.2}TiO_3}$ was examined to clarify the activity not only as for the support materials in the Ni based catalyst but also as for the mixed conducting oxide membrane.

Fe doped $\mathrm{Ca_{0.8}Sr_{0.2}TiO_3}$ used as a support material in the Ni based catalyst affected the suppression of the carbon deposition over the catalyst in the partial oxidation of methane at 1173 K. Especially, 10 mol% Fe doped one, $\mathrm{Ca_{0.8}Sr_{0.2}Ti_{0.9}Fe_{0.1}O_{3-\alpha}}$, as a support showed the highest catalytic activity including the suppression of carbon deposition on the catalyst. From the fact that lattice oxygen in the support oxide migrates spontaneously by the oxide ionic and electronic mixed conduction, the Ni-based catalyst composed of a mixed conducting support oxide had the function of self anti-coking phenomenon in the methane conversion.

Fe doped $\mathrm{Ca_{0.8}Sr_{0.2}TiO_3}$ exhibited the oxide ionic and electronic mixed conduction, and its membrane had the potential to be applied for the oxygen separator. The OCMR demonstrated the acceleration of the methane conversion at 1173 K by the electrochemical oxygen pumping. This type of reactor was one of promising candidates of the mixed conducting ceramics membrane reactor for natural gas conversion.

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