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Membrane Reactor for Oxidative Coupling of CH_4 with an Oxide Ion–Electron Hole Mixed Conductor

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A membrane reactor for the oxidative coupling of CH_4 has been constructed with an oxide ion–electron hole mixed conductor, $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$. 10% CH_4 diluted with Ar and an O_2–Ar mixture at a given ratio were fed into opposite sides of the membrane at 1173 K. The formation rate of C_2–hydrocarbons (ethane and especially ethene) in the CH_4 compartment increased with P_{O_2} in the O_2–Ar compartment. This enhancement was due to electrochemical oxygen permeation, causing the conductor to short-circuit itself, resulting from the mixed conduction. For comparison, 10% CH_4 and a small amount of O_2 were co-fed into one side of the membrane. The membrane operation gave a C_2 selectivity two times that of the co-feed operation for all CH_4 conversions. From a catalytic study using $BaCe_{1-x}Gd_xO_{3-\alpha}$ powders as catalyst, it was found that increasing both the oxide-ion and electron-hole conductivities enhanced the formation of C_2 hydrocarbons, but reduced that of CO_2. On the basis of these results, a mechanism for the oxidative coupling of CH_4 of the mixed-conductor membrane was proposed.

The oxidative coupling of CH_4 is of interest, because it constitutes a one-step process from CH_4 to C_2 hydrocarbons:

$$2CH_4 + 1/2O_2 \rightarrow C_2H_6 + H_2O \quad (1)$$

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \quad (2)$$

Typical catalysts for this reaction are combinations of basic oxides and refractory oxides, *e.g.* Li/MgO,[1] Sr/La_2O_3,[2] Ba/La_2O_3.[3] There is general agreement that adsorbed and non-fully reduced oxygen species (*e.g.* O^-, O_2^- or O_2^{2-}) are active sites for the formation of C_2 hydrocarbons.[4–9] This reaction has also been studied using pure oxide ionic conductors, such as CSZ and YSZ as solid-oxide membranes.[10–14] One side is exposed to CH_4 and serves as the catalysis electrode (anode), while O_2 is present on the other side, which serves as the counter-electrode (cathode). By applying a dc voltage between the two electrodes, C_2 hydrocarbons are formed *via* the oxidation of CH_4 by oxygen species transferred through the membrane. This offers a few advantages. The undesirable gas-phase combustion of CH_4 by gaseous O_2 can be depressed, because oxygen first reaches the catalyst through the membrane. Also, the flux of O^{2-} through the membrane can give rise to the partially reduced oxygen species more easily than gaseous O_2.

Oxide ion–electron mixed conductors, in contrast to pure oxide ionic conductors, allow the transfer of O^{2-} through the membrane even at open circuit under the gradient of an oxygen chemical potential, because the O^{2-} flux is counterbalanced by an equivalent electron flux in the opposite direction (*i.e.* by a self-discharge of the conductor).[15] If such a mixed conductor is used as the solid-oxide membrane, there arise additional advantages. The external electric source, the electrode material, the current connector and output terminal are eliminated from the reactor, leading to a reduction in the cost required to design the reactor or to operate it. Moreover, some of the mixed conductors themselves have been found to be good catalysts for the oxidative coupling of CH_4.[16] Using such a mixed conductor, the formation of C_2 hydrocarbons can be promoted without special catalysts.

In order to exploit the mixed conductor to full advantage, it is necessary to optimize the O^{2-} flux through the membrane. Although it is generally agreed that both the oxide ionic and electronic conductivities in the mixed conductor need to be as high as possible, it is not yet known whether n- or p-type electron conduction should be employed. Hazbun[17] has proposed a membrane reactor for the oxidative coupling of CH_4 using the mixed conductor YSZ–TiO_2, where n-type electrons serve as the current carrier. However, it would be expected that the supply of O_2 to one side of the membrane would favour p-type electron conduction (electron holes), because the concentration of electron holes in the mixed conductor increases with $P_{O_2}{}^{1/4}$ in the atmosphere.[15] Also, it is known that selective catalysts show p-type electronic conduction.[16]

Recently, Bonanos *et al.* have reported that the electric conduction of $BaCeO_3$ oxide is dramatically changed upon partial substitution of Gd^{3+} for Ce^{4+} in the oxide.[18,19] The dopant cations, Gd^{3+}, are compensated by oxide-ion vacancies and electron holes, and mixed conduction thus appears in the oxide. The total conductivity reaches 10 mS cm^{-1} at 873 K, which is higher than that of YSZ at the same temperature. The object of this study is to test the Gd^{3+}-doped $BaCeO_3$ ($BaCe_{1-x}Gd_xO_{3-\alpha}$) oxide as a solid-oxide membrane for the oxidative coupling of CH_4. A mechanism for the enhanced formation of C_2 hydrocarbons will be discussed.

Experimental

The $BaCe_{1-x}Gd_xO_{3-\alpha}$($0 \leqslant x \leqslant 0.3$) powders and their sintered compacts were prepared as follows. The desired amounts of starting materials [$Ba(MeCO_2)_2$, CeO_2 and Gd_2O_3] were mixed with ethanol and calcined at 1623 K for 10 h in air. The $BaCe_{1-x}Gd_xO_{3-\alpha}$ powders were obtained by grinding the calcined oxide in a ball mill at a rotation rate of 112 rpm for 1 h. The crystalline structure and surface area of the powders were examined by XRD analysis and the BET method, respectively. In the latter, Kr gas was used as an adsorbate at 77 K. The sintered $BaCe_{1-x}Gd_xO_{3-\alpha}$ compact was obtained by pressing the powders into a pellet at 2×10^3 kg cm^{-2}. The pellet was sintered at 1923 K for 10 h in air. The density of the sintered compact was >95% of its theoretical value and its total conductivity was measured at 1173 K by a complex impedence method. Two porous Pt films were used as electrode materials. The measurements were carried out in a gas flow at various P_{O_2}.

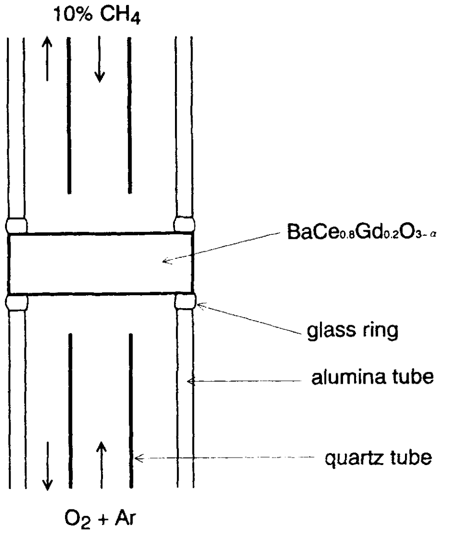

Fig. 1 Schematic illustration of a membrane reactor for oxidative coupling of CH_4

The sintered compact was cut into a disk (diameter 12 mm and thickness 0.35 mm). Two gas compartments were constructed by interposing the disk between two alumina tubes, as shown in Fig. 1. Each compartment was sealed by melting a glass ring round the joins at 1173 K. 10% CH_4 diluted with Ar was fed into one compartment at 1173 K, and an O_2–Ar mixture at a given ratio was fed into the other compartment at the same temperature. In the CH_4 compartment, the flow rate of the inlet gas was 20 ml min^{-1}, and the composition of the outlet gas was analysed by gas chromatography with Porapack Q and molecular sieve 5A column packings. In the O_2–Ar compartment, P_{O_2} of the outlet gas was monitored using a YSZ oxygen sensor (sample gas, Pt | YSZ | Pt, air), which was heated at 1173 K.

In order to compare the effects of the oxygen species transferred through the membrane with those of gaseous O_2, 10% CH_4 and a small amount of O_2 were co-fed into one compartment at 1173 K. Then, an H_2–Ar mixture with $P_{O_2} = 4 \times 10^{-14}$ atm was fed into the other compartment in order to block the O^{2-} flux through the membrane. The reaction conditions were the same as described above.

The catalytic activities and selectivities for the oxidative coupling of CH_4 were studied for the $BaCe_{1-x}Gd_xO_{3-\alpha}$ powders with a conventional gas-flow system. The reaction conditions were as follows: 0.1 g catalyst; 1173 K; reactant, 8.3% CH_4–1.7% O_2 mixture in Ar; flow rate, 24 ml min^{-1}.

Results and Discussion

Fig. 2 shows the total conductivities of the sintered compacts of $BaCe_{1-x}Gd_xO_{3-\alpha}$ with $0 \leqslant x \leqslant 0.3$ at 1173 K as a function of P_{O_2} in the gas flow. The conductivities of $BaCe_{1-x}Gd_xO_{3-\alpha}$ showed a maximum at $x = 0.2$. From X-ray spectroscopy of the $BaCe_{1-x}Gd_xO_{3-\alpha}$ powders, it was found that $BaCe_{1-x}Gd_xO_{3-\alpha}$ with $x \leqslant 0.2$ consisted of a single phase of orthorhombic perovskite-type structure, but with $x = 0.3$ a small amount of Gd_2O_3 as a secondary phase was present. Therefore, these two results indicate that the substitutable limit for Gd^{3+} is $x = 0.2$. The conductivity of the non-doped $BaCeO_3$ was roughly proportional to $P_{O_2}^{-1/6}$ over the entire P_{O_2} range. According to the general theory of defect equilibria in semiconductors, this means that $BaCeO_3$ has an n-type electron conduction over all P_{O_2}. On the other hand, the conductivities of the Gd^{3+}-doped $BaCeO_3$ samples were roughly proportional to $P_{O_2}^{1/4}$ at high P_{O_2}, but independent of P_{O_2} at low P_{O_2}. The defect equilibria in the oxide ion–electron hole mixed conductors are as follows:[15]

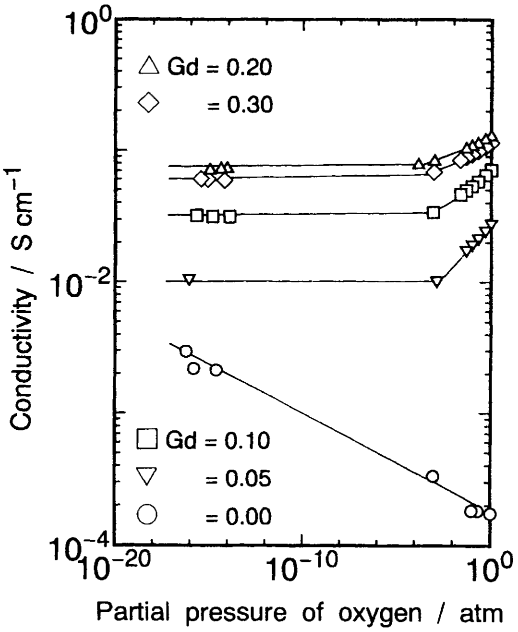

Fig. 2 Total conductivity of a sintered compact of $BaCe_{1-x}Gd_xO_{3-\alpha}$ at 1173 K in a gas stream with various P_{O_2}

$$O_{latt} + 2h^{\bullet} \rightarrow 1/2O_2 + V_O^{\bullet\bullet} \qquad (3)$$

$$K_1 = [V_O^{\bullet\bullet}]P_{O_2}^{1/2}p^{-2} \qquad (I)$$

where O_{latt}, $h^{\bullet}$ and $V_O^{\bullet\bullet}$ denote the oxide ions on the normal lattice sites in the conductor, the electron holes and the oxide-ion vacancies, respectively. K_1 and p are the equilibrium constant at a given temperature and the electron holes concentration, respectively. If $[V_O^{\bullet\bullet}]$ is large and essentially constant, then eqn. (I) reduces to

$$p = KP_{O_2}^{1/4} \qquad (II)$$

where K is a constant. Therefore, the conductivities of the oxide ion–electron hole mixed conductors should be proportional to $P_{O_2}^{1/4}$. The agreement between the theoretical and observed P_{O_2} dependences means that the $BaCe_{1-x}Gd_xO_{3-\alpha}$ samples exhibit oxide ion–electron hole mixed conduction. Unless stated otherwise, $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$, which showed the highest conductivity among the $BaCe_{1-x}Gd_xO_{3-\alpha}$ samples, was used as the solid-oxide membrane in the subsequent experiments.

Typical results for the oxidative coupling of CH_4 by feeding CH_4 and an O_2–Ar mixture into opposite sides of the membrane are shown in Fig. 3. C_2H_4, C_2H_6, H_2, CO and CO_2 were formed in the CH_4 compartment. The formation rate of the products in the CH_4 compartment depended strongly on the P_{O_2} in the O_2–Ar mixture compartment: all formation rates, as well as the CH_4 conversion, increased with P_{O_2}. In order to understand this result better, the experiment was repeated with Ar only in the CH_4 compartment; the result is shown in Fig. 4. The permeation of O_2 from the O_2–Ar mixture compartment to the CH_4 compartment through the membrane was observed even at $P_{O_2} = 4 \times 10^{-3}$ atm in the O_2–Ar mixture compartment, and the permeation rate became progressively larger as P_{O_2} in the O_2–Ar mixture compartment increased. From permeation tests on other gases, it was found that mechanical leakage of gas through the membrane was negligible. These results indicate that O_2 is transferred from the O_2–Ar mixture compartment to the

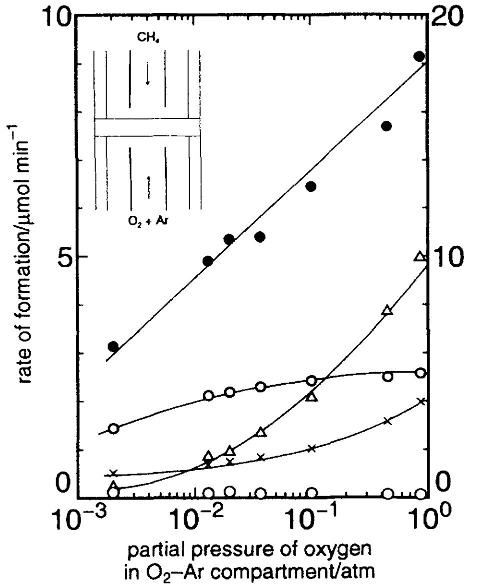

Fig. 3 Effect of P_{O_2} in the O_2–Ar mixture compartment on the formation rate of products and conversion of CH_4 at 1173 K. ○, C_2H_4; ○, C_2H_6; △, CO; ×, CO_2; ●, CH_4 conversion.

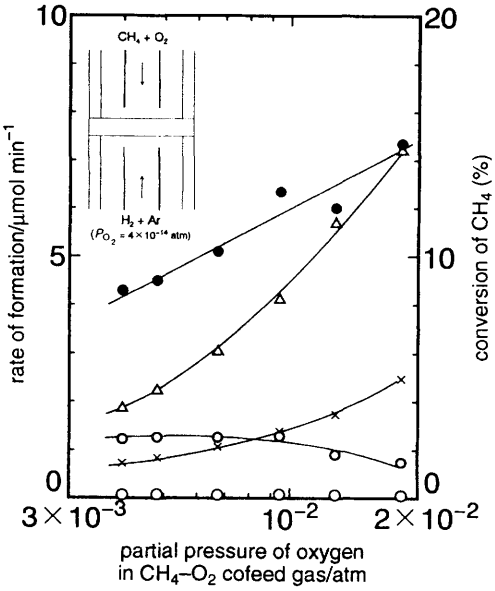

Fig. 5 Effect of P_{O_2} in the CH_4–O_2 co-feed gas on formation rate of products and conversion of CH_4 at 1173 K. The symbols correspond to those shown in Fig. 3.

CH_4 compartment by a self-discharge phenomenon resulting from the presence of mixed conduction in the membrane. Furthermore, CH_4 fed into the CH_4 compartment reacts with the oxygen species transferred through the membrane to form C_2 hydrocarbons, CO and CO_2.

Typical results for the oxidative coupling of CH_4 by co-feeding CH_4 and a small amount of gaseous O_2 in the CH_4 compartment are shown in Fig. 5. Compared with the result shown in Fig. 3, the formation of CO_2 and CO was enhanced, and that of C_2 hydrocarbons was reduced. The difference between these two operations is quantitatively represented in Fig. 6. The membrane operation exhibited a higher selectivity to C_2 hydrocarbons than the co-feed operation for all CH_4 conversions, indicating that the oxygen species passing through the membrane is more active for C_2 formation than gaseous O_2. Many research groups have observed similar differences with pure oxide ionic conductors.[10–14] The conclusion, *i.e.* that the oxygen species partially reduced on the electrode surface could lead to activation of CH_4, appears to be consistent with studies involving pure oxide ionic conductors. However, this conclusion cannot be applied fully to this case, because there is no electrode in this reactor. It is probable that an oxygen species is present either on the $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$ surface or on the lattice site in the oxide.

In order to ascertain whether $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$ itself is a good catalyst for the oxidative coupling of CH_4, the catalytic activity and selectivity of the $BaCe_{1-x}Gd_xO_{3-\alpha}$ powders were studied at 1173 K as a function of Gd^{3+} content. The results are summarized in Fig. 7. H_2, CO, C_2H_4 and C_2H_6 and CO_2 were observed as products. The formation rates of the products, especially C_2H_4 and CO_2, were strongly dependent on the Gd^{3+} content. At $x \leqslant 0.2$, the formation rate of C_2H_4 increased from 2.6 to 4.5 µmol min^{-1}, and that of CO_2

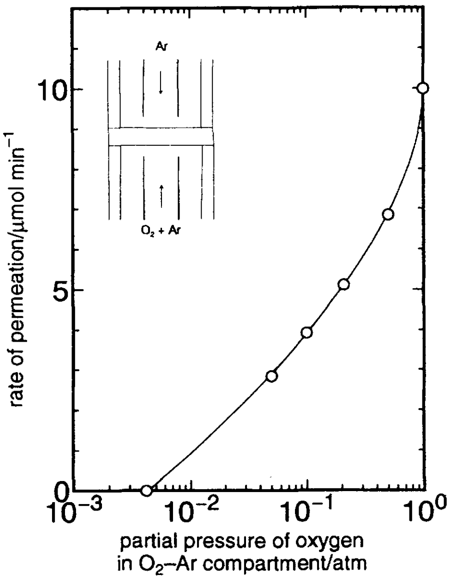

Fig. 4 Effect of P_{O_2} in the O_2–Ar mixture compartment on permeation rate of O_2 at 1173 K

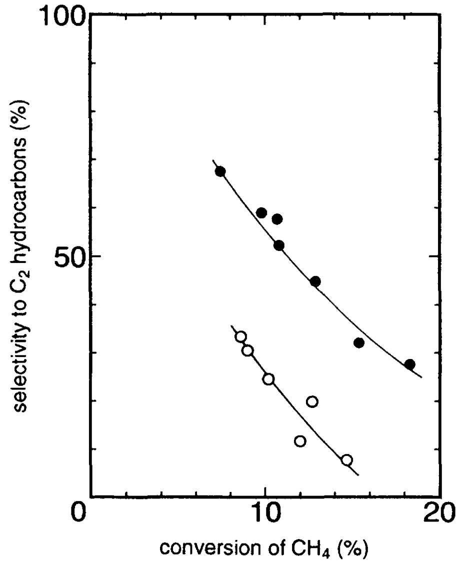

Fig. 6 Difference in C_2-selectivity between membrane and co-feed operations. ●, Membrane operation; ○, co-feed operation.

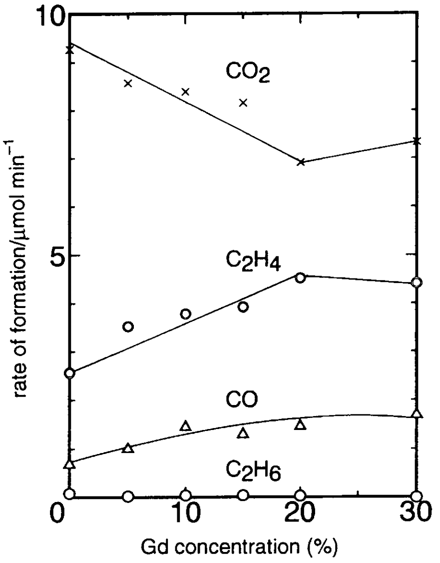

Fig. 7 Formation rates of products over $BaCe_{1-x}Gd_xO_{3-\alpha}$ powders at 1173 K as a function of Gd^{3+} content

decreased from 9.3 to 6.9 μmol min^{-1}. At $x = 0.3$, however, the formation rate of C_2H_4 decreased to 4.4 μmol min^{-1}, and that of CO_2 increased to 7.3 μmol min^{-1}. For CO and C_2H_6, the formation rates increased slightly with Gd content. As a result, the conversion of CH_4 increased from 21 to 36%, and the selectivity to C_2 hydrocarbons increased from 21 to 35%. At all Gd^{3+} contents, the conversions of O_2 were 100%. The surface areas of the $BaCe_{1-x}Gd_xO_{3-\alpha}$ powders were 0.7–1.0 m^2 g^{-1} (by BET) with a maximum at $x = 0.3$. Consequently, the difference in catalytic activity among the $BaCe_{1-x}Gd_xO_{3-\alpha}$ powders is attributed not to differences in surface area, but rather to those in conductivity. Based on the self-discharge phenomenon occurring *via* mixed conduction in $BaCe_{1-x}Gd_xO_{3-\alpha}$ powders, the gaseous O_2 species are freely able to pass into and out of the oxides (the exchange rate is determined by both the oxide-ion and electron-hole conductivities). Here, assuming that the oxidative coupling of CH_4 is carried out by reacting CH_4 with the oxygen species on the lattice site in the $BaCe_{1-x}Gd_xO_{3-\alpha}$ oxides and that the reduced $BaCe_{1-x}Gd_xO_{3-\alpha}$ surfaces are reoxidized by gaseous O_2, the formation rate of C_2 hydrocarbons increases with the conductivity of $BaCe_{1-x}Gd_xO_{3-\alpha}$. A similar effect has been reported using a number of metal oxides as catalysts: for example, in the cases of Group 3–5 metal oxides, the oxygen species incorporated into the oxide lattice is the oxidant, rather than the gaseous O_2 outside the membrane;[4] in the cases of metal oxides where the metals have two accessible positive oxidation states, the oxygen reactant is the oxide ion on the oxide lattice site rather than the gaseous O_2.[20]

From the above reasoning, the following mechanism has been proposed for the solid-oxide membrane consisting of the mixed conductor, $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$. The CH_4 fed into the CH_4 compartment is oxidized by the oxygen species on the $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$ surface lattice site to form C_2 hydrocarbons, while the gaseous O_2 fed into the O_2–Ar mixture compartment permeates to the CH_4 compartment through the bulk oxide to reoxidize the reduced $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$ surface in the CH_4 compartment. Unfortunately, the non-fully reduced oxide ions pointed out by many research groups[4–9]) have not been identified in this study. However, since the oxide-ion vacancies and electron holes, which are thought to be required for the formation of non-fully reduced oxide ions,[16] are present in abundance in $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$, one would expect such an oxide ion to be formed on $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$ surface lattice site. Further studies are needed to clarify this point.

Conclusion

Oxidative coupling of CH_4 was carried out using the oxide ion–electron hole mixed conductor $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$ as the solid-oxide membrane. Mixed conduction allowed the transfer of oxygen through the membrane at open circuit when CH_4 and O_2 were fed into opposite sides of the membrane. The oxygen species transferred through the membrane were more selective for the formation of C_2 hydrocarbons than gaseous O_2. The oxide ion on the lattice site of the $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$ surface is considered to be such an active oxygen species.

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