

## Oxidative Coupling Reaction of CH<sub>4</sub> Using Oxide Ion and Electron Hole Mixed Conductive BaCe<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3-α</sub> Ceramic as a Membrane Reactor

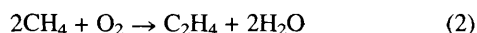
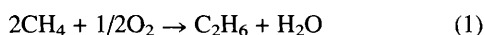
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When CH<sub>4</sub> and O<sub>2</sub> are fed into opposite sides of an electrochemical reactor using BaCe<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3-α</sub> ceramic as a solid oxide membrane, the formation of C<sub>2</sub> hydrocarbons is enhanced by self-short circuiting the reactor owing to oxide ion and electron hole mixed conduction in the ceramic.

Mixed conductors are materials which exhibit both ionic and electronic conductivities. These materials have been studied for gas separation, hydrogen storage, electrodes for batteries, photographic processes, electrochromic display, *etc.* Recently, Bonanos *et al.* have reported that the electric conduction of BaCeO<sub>3</sub> ceramic is dramatically changed by partial substitution of Gd<sup>3+</sup> for Ce<sup>4+</sup> in the ceramic.<sup>1</sup> The dopant ions, Gd<sup>3+</sup>, are compensated by oxide ion vacancies and electron holes, and oxide ion and electron hole mixed conduction thus appears in the ceramic.

The oxidative coupling reaction of CH<sub>4</sub> is of interest because of the advantage of having a one-step process from CH<sub>4</sub> to C<sub>2</sub> hydrocarbons:



In addition to heterogeneous catalytic research, this reaction has been studied using pure oxide ion conductors such as CSZ and YSZ ceramics as solid oxide membranes.<sup>2</sup> One side is exposed to CH<sub>4</sub> and serves as the catalysis electrode (anode), while the other side is exposed to O<sub>2</sub> and serves as the counter electrode (cathode). By supplying a direct current between the two electrodes, C<sub>2</sub> hydrocarbons are formed *via* the oxidative coupling reaction of CH<sub>4</sub>. This offers the advantage of eliminating the undesirable gas-phase combustion of CH<sub>4</sub> by gaseous O<sub>2</sub>. However, if the above-mentioned BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-α</sub> ceramics are used as the solid oxide membrane, there

arises another advantage. The external electric source, the electrode materials, the current collectors and the output terminals are not necessary for transporting oxide ions through the membrane, because of a self-discharge of the reactor owing to the mixed conduction in the ceramic. We report here such an occurrence when a BaCe<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3-α</sub> ceramic, which shows the highest conductivity among BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-α</sub> ceramics, is used as the solid oxide membrane.

The BaCe<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3-α</sub> ceramic was prepared by solid-state reaction followed by sintering. The desired amounts of starting materials [Ba(MeCO<sub>2</sub>)<sub>2</sub>, CeO<sub>2</sub> and Gd<sub>2</sub>O<sub>3</sub>] were mixed with ethanol and calcined at 1623 K for 10 h in air. The oxide was ground in a ball mill at a rotation rate of 112 rpm for 1 h and pressed into a pellet at  $2 \times 10^3$  kg cm<sup>-2</sup>. The pellet was sintered at 1923 K for 10 h in air and cut into a disk (thickness 0.35 mm, diameter 12 mm). Since the density of the ceramic was >95% of its theoretical value, the mechanical leakage of gas through the disk was negligible.

Two gas compartments were constructed by interposing the disk between two alumina tubes. Each compartment was sealed by a glass ring gasket. Methane (10%, diluted with Ar) was fed into one compartment at 1173 K, and an O<sub>2</sub>-Ar mixture at a given ratio was fed into the other compartment at the same temperature. In the CH<sub>4</sub> compartment, the flow rate was 20 ml min<sup>-1</sup>. In the O<sub>2</sub>-Ar mixture compartment, *p*<sub>O<sub>2</sub></sub> was monitored using an YSZ oxygen sensor. The outlet gas from the CH<sub>4</sub> compartment was analysed by gas chromatography.

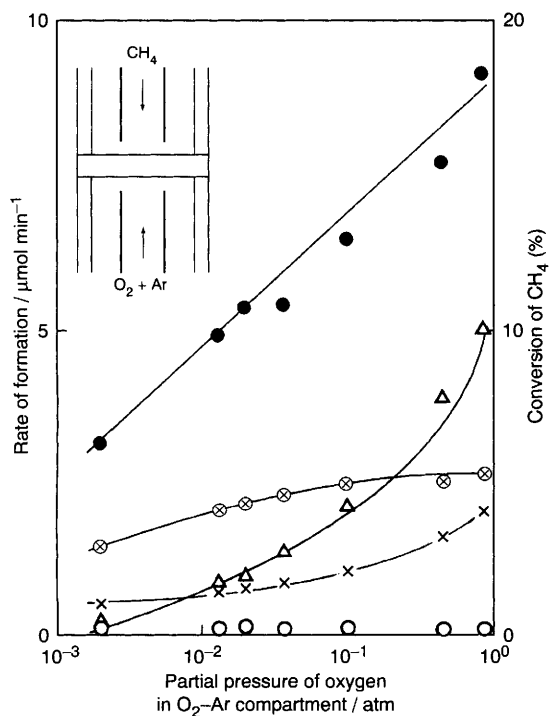


Fig. 1 Effect of *p*<sub>O<sub>2</sub></sub> in the O<sub>2</sub>-Ar compartment on formation rates of products and conversion of CH<sub>4</sub>. ⊗ = C<sub>2</sub>H<sub>4</sub>; ○ = C<sub>2</sub>H<sub>6</sub>; △ = CO; × = CO<sub>2</sub>; ● = CH<sub>4</sub> conversion.

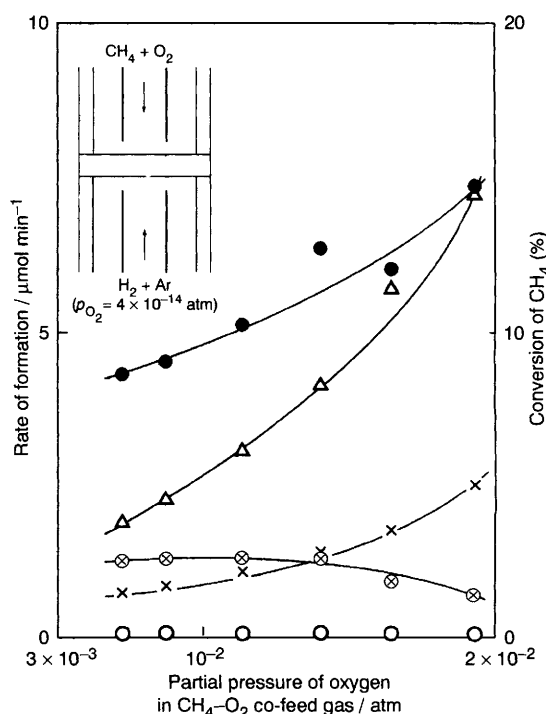


Fig. 2 Effect of *p*<sub>O<sub>2</sub></sub> in the CH<sub>4</sub>-O<sub>2</sub> co-feed gas on formation rates of products and conversion of CH<sub>4</sub>. The symbols correspond to those shown in Fig. 1.

To compare the oxygen species transported through the membrane with gaseous  $O_2$  in the gas phase, 10%  $CH_4$  and a small amount of  $O_2$  were co-fed into one compartment at 1173 K. In this case, a  $H_2$ -Ar mixture with  $p_{O_2} = 4 \times 10^{-14}$  atm was fed into the other compartment in order to block the oxygen species through the membrane.

Typical results of the oxidation reactions of  $CH_4$  by the oxygen species transported through the membrane are summarized in Fig. 1. The products  $C_2H_4$ ,  $C_2H_6$ ,  $H_2$ , CO and  $CO_2$  were formed in the  $CH_4$  compartment, but  $O_2$  was not observed in its outlet gas, indicating that all oxygen species transported are consumed in the oxidation of  $CH_4$  without the formation of

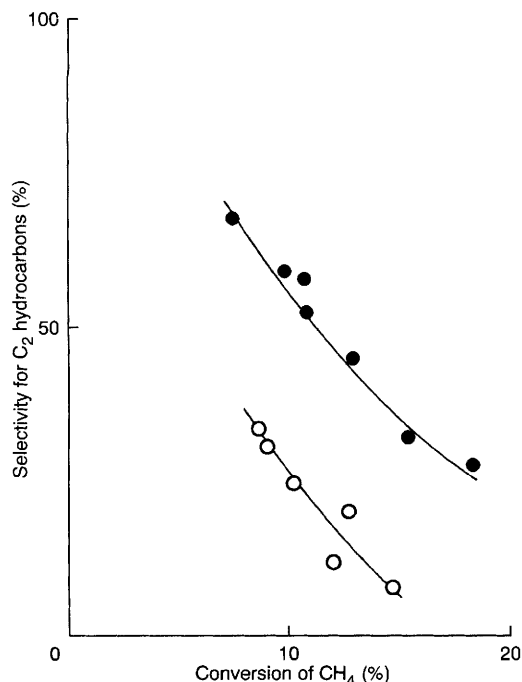


Fig. 3 Difference in  $C_2$  selectivity between membrane and co-feed operations. ● = membrane operation; ○ = co-feed operation.

gaseous  $O_2$ . The formation rates of the products in the  $CH_4$  compartment were strongly dependent on  $p_{O_2}$  in the  $O_2$ -Ar mixture compartment: all formation rates as well as the  $CH_4$  conversion increased with  $p_{O_2}$ .

Typical results of the oxidation reaction of  $CH_4$  by gaseous  $O_2$  in the gas phase are summarized in Fig. 2. Compared with the membrane operation shown in Fig. 1, the formation of  $CO_2$  and CO was enhanced, and that of  $C_2$  hydrocarbons was reduced. The difference between the two operations is quantitatively represented in Fig. 3. The membrane operation gave higher selectivity for  $C_2$  hydrocarbons than the co-feed operation for all  $CH_4$  conversions. The reason for this difference can be considered as follows: (i)  $C_2$  hydrocarbons are formed by reacting  $CH_4$  with the lattice oxide ion on the surface of  $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$  ceramic; (ii)  $CO_2$  is formed by reacting  $CH_4$  with gaseous  $O_2$ ; (iii) the oxygen species transported from the  $O_2$ -Ar compartment are consumed by reoxidizing the reduced surface in the  $CH_4$  compartment. More recently, we have studied the powders of  $BaCe_{1-x}Gd_xO_{3-\alpha}$  as a heterogeneous catalyst for the oxidative coupling reaction of  $CH_4$ . Increasing both the oxide ion and electron hole conductivities in the powders enhanced the formation of  $C_2$  hydrocarbons, but reduced that of  $CO_2$ . This result supports the above-mentioned considerations.

In summary, the membrane reactor using the oxide ion and electron hole mixed conductive  $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$  ceramic has effectively formed  $C_2$  hydrocarbons via the oxidative coupling reaction of  $CH_4$ . This reactor can be characterized by the fact that the driving force for the oxygen species transport is not the external electric source but the oxygen concentration gradient across the membrane.

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## References

- 1 N. Bonanos, B. Ellis and M. N. Mahmood, *Solid State Ionics*, 1991, **44**, 305.
- 2 For example, J. S. Lee and S. T. Oyama, *Catal. Rev. Sci. Eng.*, 1988, **30**, 249; D. Eng and M. Stoukides, *Catal. Rev. Sci. Eng.*, 1991, **33**, 375.