Oxide Ion Transport for Selective Oxidative Coupling of Methane with New Membrane Reactor

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Oxidative coupling of methane was conducted by using membrane reactors. The nonporous membrane film that consisted of PbO modified by alkaline or alkaline earth compound was supported on porous SiO_2-Al_2O_3 tube. Higher hydrocarbons were successfully synthesized with high selectivity (about 90%). A kinetic analysis was conducted to clarify whether oxide ion transportation through PbO film participated in the oxidative coupling of methane. The evaluated value of the diffusion coefficient of oxide ion transport based on the methane oxidation agreed well with that of published data. The simulated gradient of the oxide ion concentration through the PbO membrane agreed well with that measured by electron probe X-ray microanalyzer. A transient response simulated by using kinetic parameters evaluated from steady-state analysis also agreed well with the experiment. These results prove the validity of the reaction model that consists of surface reactions of methane with oxide ion which is transferred from inside to outside of the membrane reactor. Alkali modifiers on the PbO membrane surface exhibited a promotional effect on the surface reaction of methane coupling. Another membrane reactor containing Bi_2O_3 showed higher activity than the PbO membrane.

Introduction

Many catalysts for the oxidative coupling of methane have been reported (Keller and Bhasin, 1982; Otsuka et al., 1985a; Ito et al., 1985; Roos et al., 1987; Asami et al., 1987a). However, the selectivity level for C_2^+ hydrocarbons was not high enough because of the nonselective gas-phase reactions induced by catalyst surface. Therefore, new reaction systems, which differ from the conventional catalytic system, should be introduced for realizing high selectivity.

Recently, membrane reactor systems have been claimed as an advanced reaction method (Hsieh, 1991). Otsuka et al. (1985b), Eng and Stoukides (1991), and Nagamoto et al. (1990) conducted oxidative coupling of methane over yttria-stabilized zirconia membranes coated with catalyst electrode. In this system, oxygen was supplied from air side to methane side through a solid electrolyte in which oxide ion transport was controlled by electromotive force. The oxygen pumping systems resulted in higher selectivity than the conventional catalytic system. The selectivity, however, was still low, because, even in this system, gaseous oxygen supplied through the membrane caused CO_x formation.

Asami et al. (1987b) found that lattice oxygen of lead oxide on MgO carrier converted methane to C_2 hydrocarbons with high activity and selectivity, while other kinds of oxygen species caused by coexistence of O_2 gave CO_x formation. Therefore, the authors proposed a membrane reaction system (Omata et al., 1989; Fujimoto et al., 1991). In this system, methane and oxygen are separated by a nonporous PbO film, and methane is selectively converted to C_2 hydrocarbons by the lattice oxygen of lead oxide that is considered to transport through the membrane by the concentration gradient of lattice oxygen in the membrane between methane side and oxygen side.

This method, however, has a serious problem in that it is very difficult to make a pinhole-free PbO film on the porous support materials. The authors introduced molten alkali compounds as a modifier to make a nonporous membrane film which was much easier to prepare (Nozaki et al., 1992a). The authors introduced membrane reactors consisting of a PbO layer and nonporous support of perovskite-type mixed oxide conductor (Nozaki et al., 1992b). In this membrane system, there still remains a question whether oxide ion transport participates in the oxidative coupling of methane or not.

In this study, a kinetic analysis was conducted to discuss the

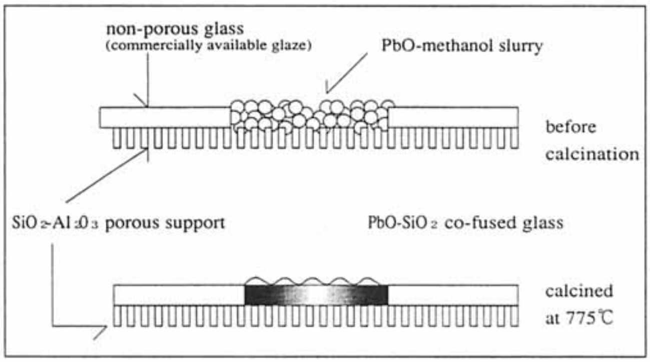

Figure 1. Preparation of nonporous membrane.

validity of the reaction model that consists of the balance among the rates of the surface reactions (oxidation of lead on the air side and methane oxidation on the methane side) and oxide ion transport through the membrane reactor. Furthermore, a possibility of realizing a more excellent membrane reactor is discussed.

Experiment

Preparation of PbO membrane reactors

Porous tubes (SiO_2-Al_2O_3) were employed as the supporting materials of PbO film membranes. Silica alumina tubes (10 mm OD, 5 mm ID, 300 mm long) were produced by pressing particles (0.1 mm) and calcining at 1,320°C. The porosity of the tubes was 0.3 and consisted of SiO_2, Al_2O_3 (1:2) and 3 wt. % metal oxide (iron oxide, CaO, and MgO).

Lead oxide film was coated on the supporting materials by coating slurry (lead oxide and methanol) and calcining at 750–800°C. The coating zone was 50 mm in length, and the rest of the porous tube was sealed by fused silica fired at 1,300°C (commercially available glaze, which did not have an activity for methane conversion). Figure 1 shows the procedure of producing a leak-free membrane film. Lead oxide was physically mixed with silica melts at 750–800°C (Levin and McMurdie, 1964), though the melting point of PbO is 900°C and that of SiO_2 is above 1,500°C. Therefore, a glassy and nonporous liquid membrane was established. The thickness measured by a scanning electron microscope (SEM) was about 0.1 mm, in Figure 2, which was almost equal to the calculated thickness from the weight of PbO and alkali compounds divided by their density and coating area.

Apparatus

Figure 3 summarizes the membrane reaction system. The membrane support tube (10 mm OD) coated with lead oxide layer (50 mm long) was inserted in an alumina tube (13 mm ID). Methane was supplied into the annular space between the outer tube and inner tube at 90 mL/min, while air was supplied to the inside of the inner tube at 60 mL/min. While the reactor was heated to reaction temperature (700–800°C), helium was fed between the outer and inner tube, instead of methane. When the temperature reached the reaction temperature, helium was replaced by methane to start the reaction. Temperature was measured by thermocouple that was inserted in the inner tube and located at the center of the membrane.

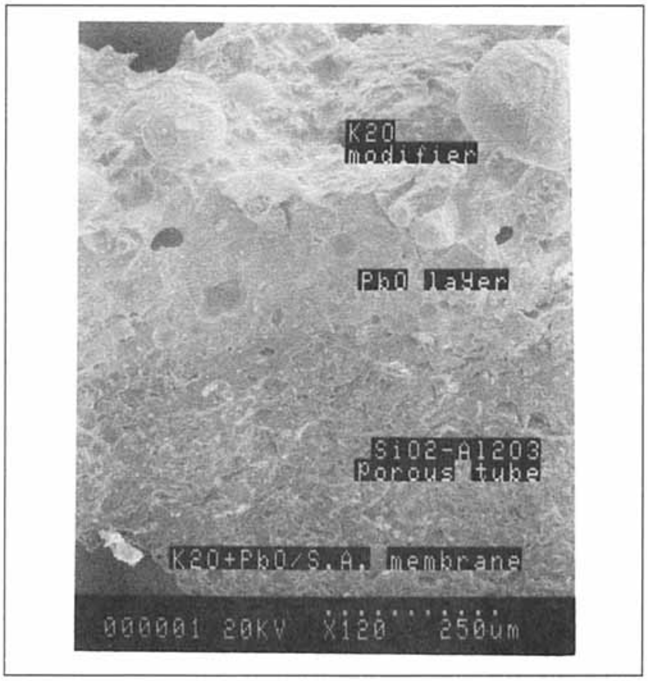

Figure 2. SEM photograph of the K_2O modified PbO/SiO_2 membrane.

The product gas was analyzed by gas chromatography. Carbon oxides and C_2 hydrocarbons were measured by the FID detector with a methanator and Porapack-N column. Water concentration was measured by TCD detector with Porapack-Q column. Nitrogen and oxygen concentration in the methane side of the membrane reactor were monitored by TCD detector with MS-13X column. However, neither nitrogen nor oxygen was detected in the methane stream. It means that methane was converted only by lattice oxygen of the membrane.

Results and Discussion

A kinetic study

Effect of Reaction Conditions. Figure 4 shows the activity change as a function of process time. Though the rate of CH_4 conversion on the membrane was very high at the beginning of the reaction, the level decreased to reach a steady level in

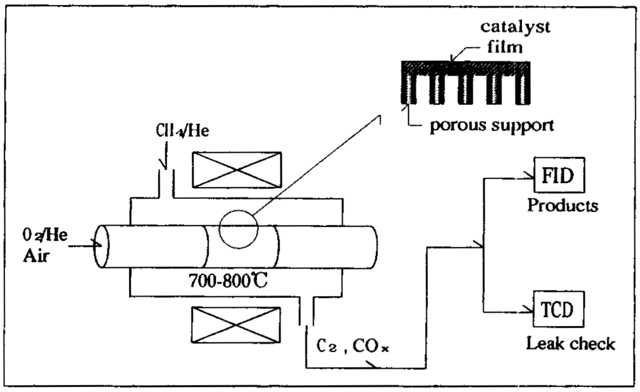

Figure 3. Membrane reactor system.

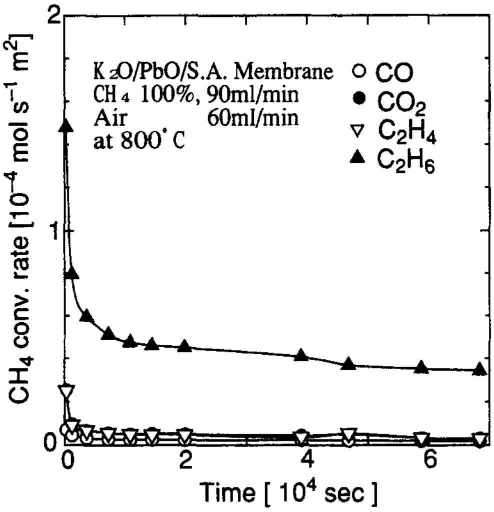

Figure 4. Activity change of the membrane reactor as a function of the process time.

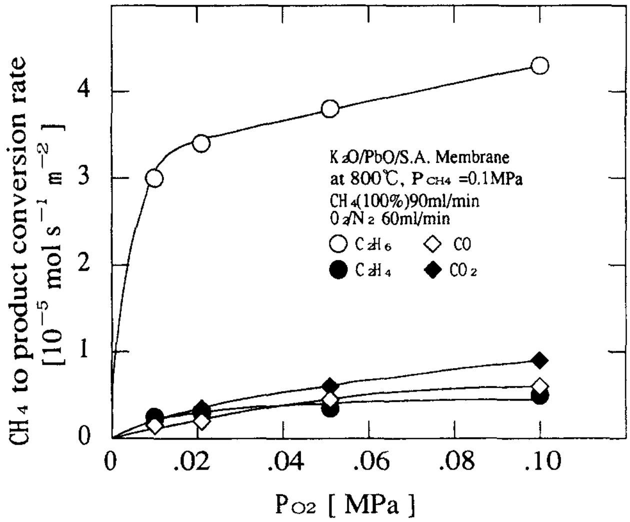

Figure 6. Effect of the partial pressure of oxygen on the products distribution.

several hours. The initial rate is assumed to be caused by the reduction of lead oxide on the membrane surface, and then its level reached the rate which is equal to the rate of oxygen transport. The driving force of oxygen transport might be the gradient of the concentration of oxide ion through PbO membrane. The kinetic model will be discussed later.

The effects of partial pressure of methane and oxygen on the formation rate of products are shown in Figures 5 and 6. In these experiments, ethane was the main product (sel. 65–85%). The higher partial pressure of methane or the lower partial pressure of oxygen gave higher C_2^+ selectivity.

The effect of temperature on C_2^+ formation rate as a function of P_{CH4} is shown in Figure 7. The rate is 0.5–1st order with respect to P_{CH4} at 725–825°C. The result that the order is higher at higher temperature can be attributed to the effect of the temperature on the rate of oxide ion transport. The details will be discussed later. The apparent reaction order with respect to P_{O2} is around 0.2 over 725–825°C in Figure 8, due possibly to the reaction rate of reoxidation of reduced lead oxide, which may be quite larger than the rate of methane oxidation and that of O^{2-} diffusion (Asami et al., 1987b). This result indicates that air can be used instead of pure oxygen, because the difference between the rates at $P_{O2}=0.02$ and at $P_{O2}=0.1$ MPa is not so large. This is one of the most marked characteristics of the membrane reaction system. When air is used as the oxidant in the traditional catalytic reaction system, a large quantity of nitrogen, which is not easy to separate from methane or product hydrocarbons, is introduced into the reaction mixture. Although the utilization of pure oxygen can overcome this problem, it is costly. In the membrane reactor system,

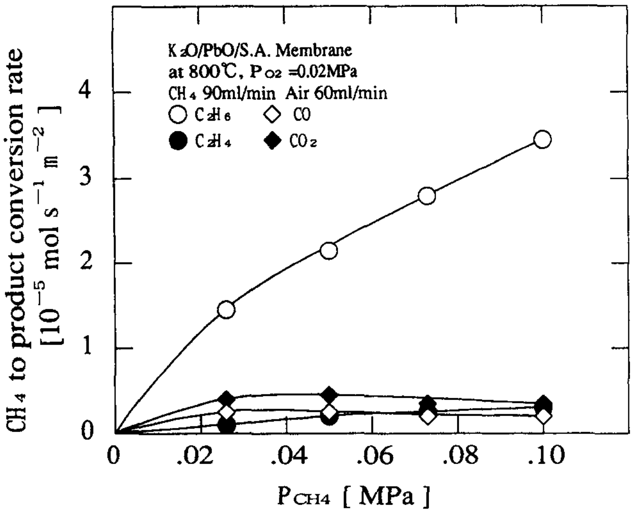

Figure 5. Effect of the partial pressure of methane on the products distribution.

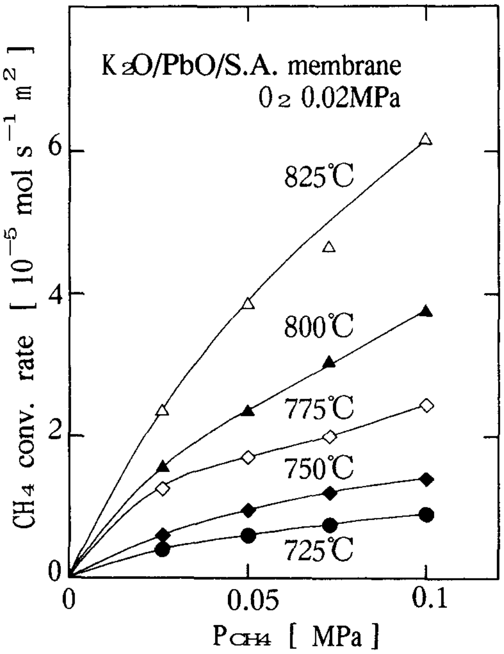

Figure 7. Effect of the partial pressure of methane on C_2 formation activity: CH_4/He, 90 mL/min; air, 60 mL/min.

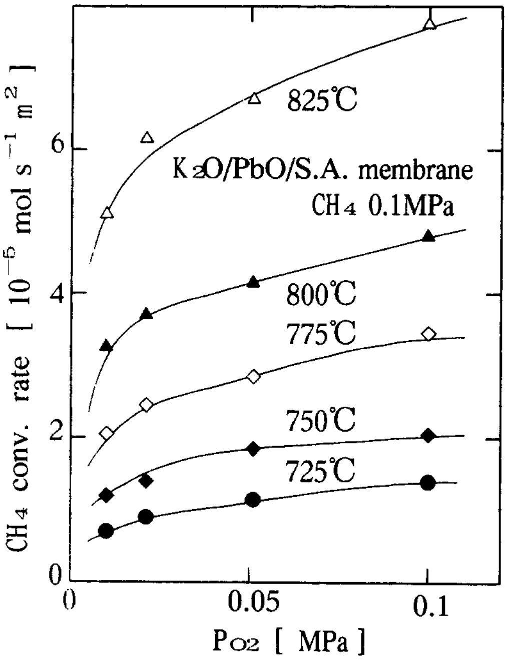

Figure 8. Effect of the partial pressure of oxygen on C_2 formation activity: CH_4 (100%), 90 mL/min; O_2/He, 60 mL/min.

however, ethane and ethylene are produced with high selectivity (90%) by extracting oxygen selectively from air, while preventing the mixing of nitrogen into hydrocarbon stream.

Kinetic Analysis of the Steady-State Reaction. The steady-state reaction rate in the membrane reactor system can be attributed to the dynamic balance among the rate of methane oxidation by PbO, the reoxidation rate of reduced PbO, and the transport rate of O^{2-}:

$$R = k_O f(P_{O2})(C_t - C_O) = -D(dC/dr) = k_C g(P_{CH4}) C_C \quad (1)$$

Here, the surface reaction rates are approximated as 1st order [$f(P_{O2}) = P_{O2}$, $g(P_{CH4}) = P_{CH4}$]. The thickness of the film, 0.1 mm, is considered to be small compared with the diameter of the supporting tube, 10 mm. Therefore, the O^{2-} distribution through the membrane can be approximated as $D(dC/dr) = D(C_C - C_O)/d$. Equation 1 can be solved as expressed by Eq. 2, which is similar to a Langmuir-type equation:

$$R = \frac{k_O C_t P_{O2}}{1 + [1/(k_C P_{CH4}) + d/D] k_O P_{O2}} \quad (2)$$

Hence, the rate constants k_C, k_O and diffusion coefficient D can be evaluated by using a langmuir plot, as shown in Figure 9.

Figure 10 shows the rate constants k_C, k_O, and O^{2-} diffusion coefficient as a function of reaction temperature. The activation energy of the rate constant k_C is 160 kJ/mol and that of k_O is 220 kJ/mol. The activation energy 160 kcal/mol of k_C is a little lower than the case of catalytic reaction on PbO/MgO catalyst (210 kJ/mol, Asami, 1987b). In this reaction, there are two important reaction steps: the activation of methane, $CH_4 + (O) \rightarrow CH_3 + (OH)$; regeneration of the catalyst, $(OH) + 1/4\ O_2 \rightarrow (O) + 1/2\ H_2O$. In the case of the catalytic reaction system, due to the coexistence of oxygen with methane, regeneration of the catalyst may be fast enough to determine the total reaction rate by the methane activation step. In the case of the membrane reaction system, however, activation energy is influenced by regeneration of oxide species on the surface of the membrane. Therefore, the activation

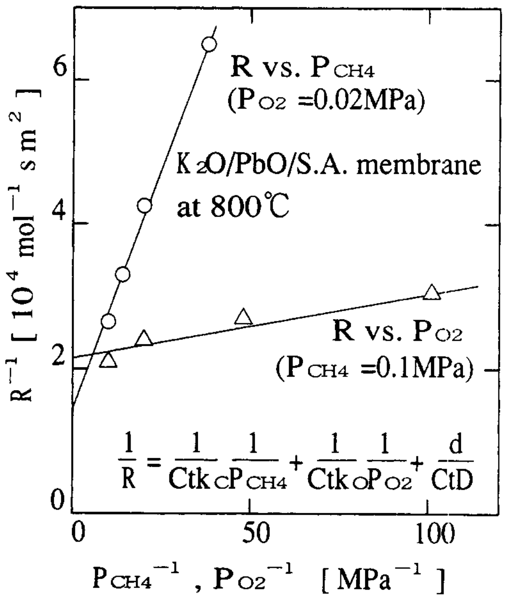

Figure 9. Relations between R^{-1} and P_{CH4} or P_{O2}.

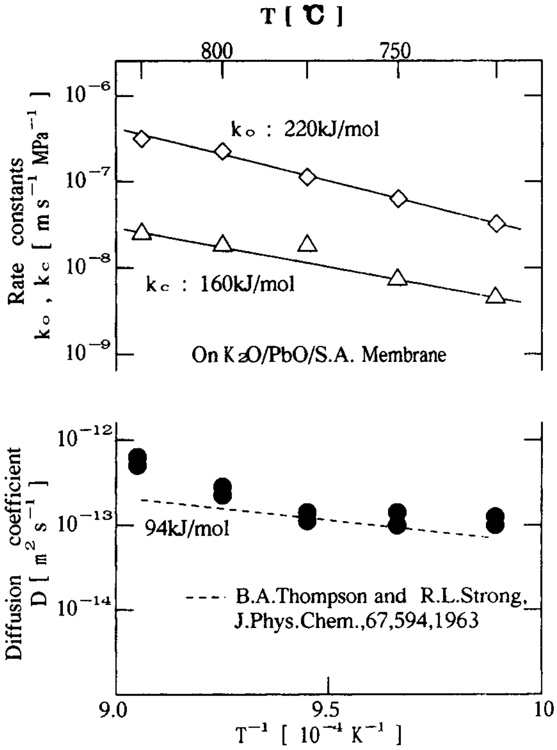

Figure 10. Arrhenius plots of the rate constants k_C, k_O and the diffusion coefficient of oxide ion.

energy of the methane coupling in the membrane system may differ from that of the catalytic system.

The diffusion coefficient of oxide ion in the Pb/PbO is evaluated from the data in Figures 5 and 6 by using Eq. 2, as shown in Figure 10. The results of Thompson and Strong (1963), which is the diffusion coefficient of O^{2-} in PbO in Figure 10, agree well with our result. This indicates that the titled reaction proceeds with oxide ion transport through the oxide membrane film. In the case of some other membrane materials such as stabilized zirconia, O^{2-} conductivity is controlled by its countercurrent of electron (Nozaki et al., 1993). However, the membrane material used in this study may have enough electron conductivity, because it also contains metallic Pb as the case of Thompson and Strong (1963). The activation energy of the diffusion coefficient is changed at 775°C, which is the melting point of the PbO/SiO_2 membrane film. This change may be attributed to the change of the phase of the membrane film.

In Figure 11, the PbO concentration in the membrane film simulated by using the parameters in Figure 10 and Eq. 1 is compared with the value of lattice oxygen measured by electron probe X-ray microanalyzer (EPMA). They show a good agreement, indicating that oxide ion transport by the gradient of the concentration participates in the membrane reaction system.

Simulation of Transient Response. By using the parameters obtained from the steady-state analysis, the transient response immediately after the start of the reaction was simulated. Since the thickness of the membrane film is relatively smaller than the diameter of the supporting tube, the model can be approximated as the one-dimensional model. The change in PbO concentration can be described by Fick's second equation (Crank, 1956):

$$\frac{\partial C(t, X)}{\partial t} = D\frac{\partial^2 C(t, X)}{\partial X^2} \tag{3}$$

Here, initial and final conditions are:

$$C = C_t \quad (t=0) \tag{4}$$

$$C = C_O + \frac{(C_C - C_O)}{d}X \quad (t=\infty) \tag{5}$$

The change in O^{2-} concentration in the membrane should be attributed to the difference between the O^{2-} flux of oxidation side and that of methane side. Therefore, the material balance of oxide ion should be expressed as:

$$\frac{\partial}{\partial t}\int_0^d C(t, X)dX = k_O P_{O2}[C_t - C(t, 0)] - k_C P_{CH4} C(t, d) \tag{6}$$

These equations are solved as:

$$C = C_O + \frac{C_C - C_O}{d}X + \frac{4\alpha(C_t - C_C)}{\pi}\Sigma\frac{(-1)^{n+1}}{n} \times \exp\left\{-\frac{Dn^2\pi^2 t}{\alpha^2(d+X_1)^2}\right\}\sin\left\{\frac{n\pi(X+X_1)}{\alpha(d+X_1)}\right\} \tag{7}$$

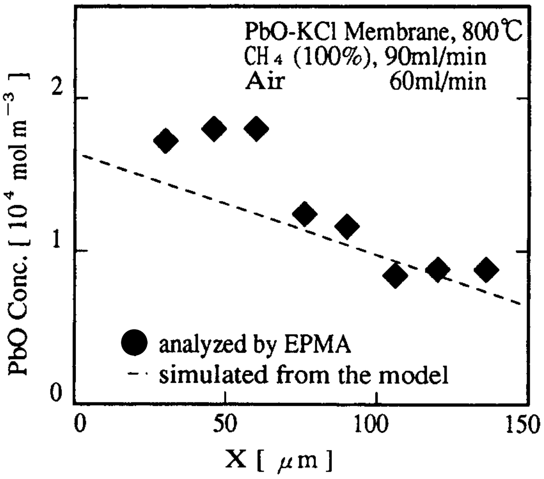

Figure 11. Concentration of oxide ion in the membrane film.

$$C_C = \frac{k_O P_{O2} C_t}{k_C k_O P_{O2} P_{CH4} d/D + k_O P_{O2} + k_C P_{CH4}} \tag{8}$$

$$C_O = \frac{(1 + K_C P_{CH4} d/D) k_O P_{O2} C_t}{k_C k_O P_{O2} P_{CH4} d/D + k_O P_{O2} + k_C P_{CH4}} \tag{9}$$

$$X_1 = \frac{C_t - C_O}{C_O - C_C}d \tag{10}$$

Here, $\alpha = 1.36$ is determined by Eq. 6. Figure 12 shows O^{2-} concentration in the membrane as a function of time and depth (the oxidation side is $X=0$, the coupling side is $X=100$ μm). By using O^{2-} concentration of the coupling side and Eq. 2, the transient response after beginning the reaction can be simulated as shown in Figure 13. The simulated value shows good agreement with the experimental results except only the initial point. Lead oxide is known to be oxidized into Pb_2O_3 by air at 400-500°C, which decomposes slowly to form PbO over 600°C. At the beginning of the reaction, lead oxide might be oxidized into $PbO_{1+\delta}$, which gave higher activity (Kubaschewski and Hopkins, 1962). The model used in this study is simplified enough to explain the observed results. For applying extended condition, therefore, the model should be improved

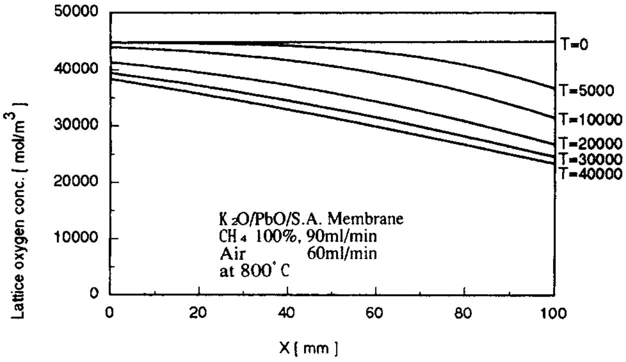

Figure 12. Simulated concentration of oxide ion in the membrane film.

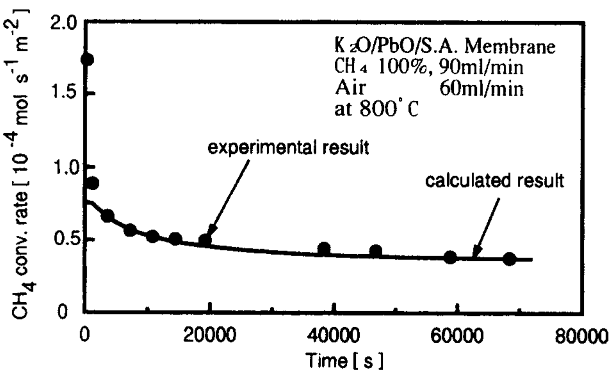

Figure 13. Transient response after initiating the membrane reaction.

considering the stoichiometry of Pb:O and the reaction orders of the surface reactions. However, almost all the results show good agreement, indicating that the kinetic model based on the O^{2-} transporting system is valid for explaining this membrane reaction.

Development of excellent membrane reactors

Limit of C_2 Product Yield. Product yield as a function of residence time of methane is shown in Figure 14. The yield of ethane, the main product of this reaction, seems to approach the saturated value with increasing residence time. This result can be explained by considering the reaction mechanism in Figure 15. According to the reaction mechanism of gas-phase oxidation of methane (Zhanthoff and Baerns, 1990; Chen et al., 1991), ethane is formed from methyl radical ($CH_3\cdot$) and is destroyed also by $CH_3\cdot(C_2H_6+CH_3\cdot\rightarrow C_2H_5\cdot+CH_4$, $C_2H_5\cdot\rightarrow C_2H_4+H\cdot)$. Then, assuming that the methane conversion level is so low that $[CH_4]$ is considered to be constant, and concentration of $[CH_3\cdot]$ reaches steady state more quickly than $[C_2H_6]$ and $[C_2H_4]$, $[CH_3\cdot]$ is approximated as:

$$[CH_3\cdot]=\sqrt{\frac{k_1[CH_4]}{4k_2}} \tag{11}$$

Then, C_2H_6 yield is expressed as:

$$\frac{[C_2H_6]}{[CH_4]}=\frac{k_2}{k_3}\sqrt{\frac{k_1}{4k_2[CH_4]}}\{1-\exp(-k_3\sqrt{k_1[CH_4]/4k_2}\,t)\} \tag{12}$$

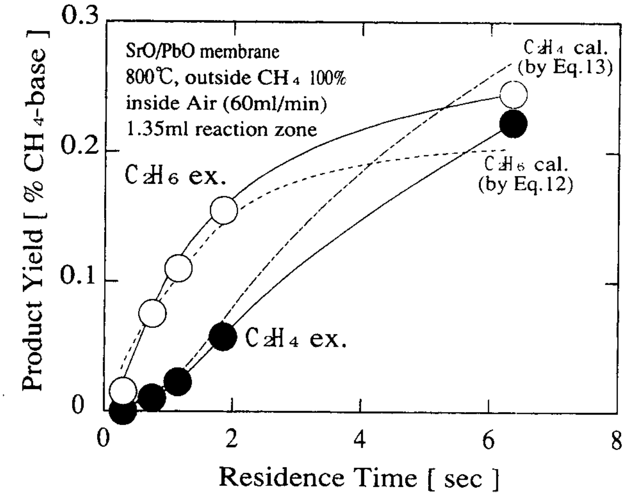

Figure 14. C_2 products yield as a function of residence time.

Since ethylene is also known to be destroyed by $CH_3\cdot$ (Zhanthoff and Baerns, 1990; Chen et al., 1991), C_2H_4 yield can be approximated as:

$$\frac{[C_2H_4]}{[CH_4]}=\frac{k_2}{k_4}\sqrt{\frac{k_1}{4k_2[CH_4]}}\{1-\exp(-k_4\sqrt{k_1[CH_4]/4k_2}\,t)\}$$
$$+\frac{k_2}{k_4-k_3}\sqrt{\frac{k_1[CH_4]}{4k_2}}\{\exp(-k_4\sqrt{k_1[CH_4]/4k_2}\,t)$$
$$-\exp(-k_3\sqrt{k_1[CH_4]/4k_2}\,t)\} \tag{13}$$

Broken lines in Figure 14 were simulated by using Eqs. 12 and 13. Here, the value $k_1=1.1\times10^{-3}\,s^{-1}$ was determined from C_2H_6 yield at the residence time 0.3 s, while the values $k_2=1.0\times10^{13}$, $k_3=2.2\times10^{10}$ and $k_4=1.3\times10^{10}\,mol^{-1}\cdot cm^3\cdot s^{-1}$ were used (Zhanthoff and Baerns, 1990). Equations 12 and 13 indicate that C_2^+ yield should be saturated with sufficient reaction time. Therefore, C_2^+ yield cannot be enhanced markedly by the increased residence time. However, it can be enhanced by modifying the surface of the membrane, because the rate constant k_1 is influenced by the ability of the membrane, which is determined by the surface activity and the capacity of O^{2-} transportation.

Surface Modification. The surface of the PbO membrane was modified by adding basic compounds on PbO/SiO_2 membrane, as shown in Figure 16. The extent of surface modifi-

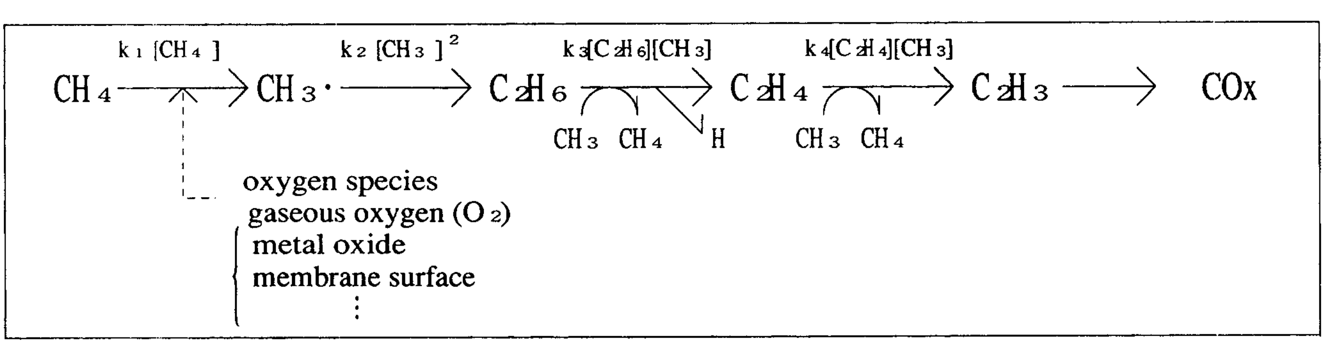

Figure 15. Radical reaction.

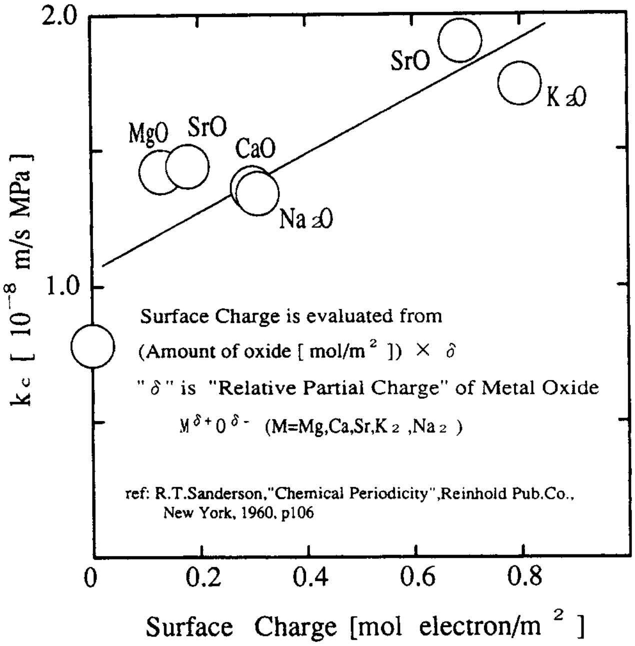

Figure 16. Effect of the surface modification by basic compounds.

cation was evaluated by using "relative partial charge" (Sanderson, 1960). As shown in Figure 16, the rate constant of the surface reaction between CH_4 and PbO is enhanced by adding basic modifiers. Asami (1987a) also reported that the oxidative coupling of methane on PbO catalyst could be enhanced when PbO was supported by basic carriers such as MgO and $\beta'' - Al_2O_3$. However, further study should be carried out to characterize the modification effect of basicity on PbO activity.

Development of Other Membrane Materials. The capacity of oxide ion transportation is also important for determining the methane conversion level, because the reaction rate is determined by the balance between the rate of surface reaction and that of O^{2-} transportation. Other materials such as Bi_2O_3, which is a well-known oxide ion conductor, were employed (Figure 17). The activity of Bi_2O_3 was about three times greater than that of PbO membrane. The C_2^+ selectivity was influenced by various modifiers. Iron group modifier (known as reforming catalyst) gave higher selectivity for CO_2 formation. Cerium oxide gave higher selectivity for CO formation. SnO-Bi_2O_3 membrane gave the C2$^+$ selectivity as high as the PbO membrane. These results indicate the possibility that the enhanced capacity of O^{2-} transportation and of surface reaction by choosing new membrane materials gives a membrane reactor with higher activity and selectivity for the oxidative coupling of methane. In this article, methane conversion activity of the membrane reactor has been discussed. However, the stability of the membrane materials is also very important. In the case of PbO membrane, all amount of PbO loaded may be lost within two weeks because of its vapor pressure (7 Pa at 800°C). Therefore, new materials should be developed considering activity and stability.

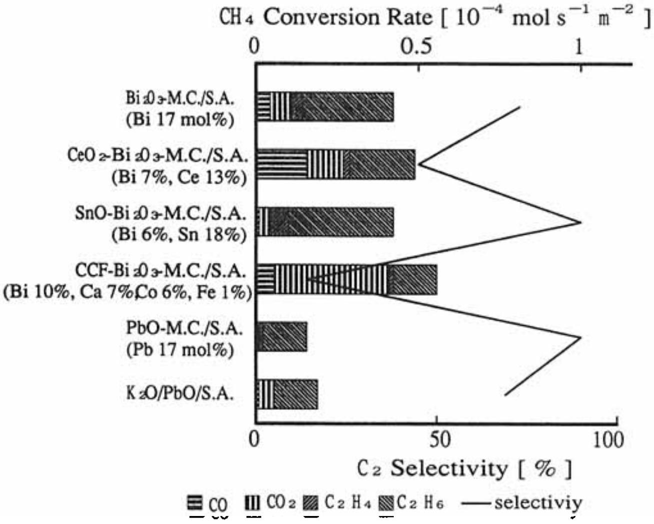

Figure 17. Methane conversion on membrane reactors.

Conclusion

Oxidative coupling of methane was conducted by using membrane reactors, which consisted of PbO modified by alkaline or alkaline earth compound supported on porous SiO_2-Al_2O_3 tube to give C_2 hydrocarbons with high selectivity (about 90%). A kinetic analysis shows that oxide ion transportation through PbO film participated in the oxidative coupling of methane. The evaluated value of the diffusion coefficient of oxide ion transport was valid for considering oxide ion participated in this reaction. The simulated gradient of the oxide ion concentration through the PbO membrane showed good agreement with the oxide ion concentration measured by EPMA. A transient response was simulated by using kinetic parameters evaluated from steady-state analysis to exhibit good agreement with the experimental results. These results indicate the validity of the reaction model that consists of the balance between the rates of surface reactions and oxide ion transportation. Furthermore, surface modification of PbO membrane and application of other materials were examined for promoting the membrane activity. Alkali modifiers exhibited some effect on the surface reaction of methane coupling. Another membrane reactor containing Bi_2O_3 showed higher activity compared with PbO membrane.

Acknowledgment

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Notation

C_l = stoichiometric concentration of PbO lattice oxygen, 4.5×10^4 mol·m^{-3}
C_C = concentration of PbO lattice oxygen of methane side, mol·m^{-3}
C_O = concentration of PbO lattice oxygen of air/O_2 side, mol·m^{-3}
d = thickness of the membrane, m
D = diffusion coefficient, m^2·s^{-1}
k_t = oxide ion transporting coefficient, m·s^{-1}
k_C = reaction rate constant for methane coupling, m·s^{-1}·MPa^{-1}
k_O = reaction rate constant for oxidation of lead, m·s^{-1}·MPa^{-1}
k_1 = initiating reaction rate constant, s^{-1}
k_{2-4} = gas-phase reaction rate constant, mol^{-1}·m^3·s^{-1}

R = reaction rate per unit surface area, $\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$
$[Y]$ = concentration of element Y, $\text{mol}\cdot\text{m}^{-3}$
α = (the length of the Fourier series)/(the thickness of the membrane)

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