1. Introduction

Reforming of hydrocarbons is widely employed as a production process of hydrogen and synthesis gas. Synthesis gas, which mainly consists of hydrogen and carbon monoxide, is used as a feedstock for the manufacture of valuable chemicals and fuels. Recently, hydrogen production has become more important in Japan due to the commercialization of fuel cells, and presently relies heavily on the reforming of hydrocarbons, although much effort has been devoted to the development of new technologies using renewable energies for the hydrogen production.

Methane reforming has attracted much attention as an important chemical process and is mainly categorized into three types of reactions; steam reforming, dry reforming, and partial oxidation. In the steam reforming, methane endothermically reacts with steam to form hydrogen and carbon monoxide. In contrast, the partial oxidation, in which methane is combusted to form hydrogen and carbon monoxide, is an exothermic reaction. Thus, a combination of these reforming reactions, autothermal methane reforming, has been also applied to enhance the overall efficiency of the reactor. These processes are preferable for industrial application because water and oxygen are abundant and available. Moreover, methane can be also endothermically reformed by the reaction with carbon dioxide, which is called dry reforming. Recently, this dry reforming reaction has drawn increasing attention due to the rise in the concentration of carbon dioxide in the atmosphere. All these reforming reactions are catalyzed by noble and base metals. Consequently, many researches have focused on the development of highly-active catalysts and the clarification of the reaction mechanisms.

Efficient production of hydrogen via the various methane reforming processes requires monitoring of the catalyst performance by a simple method. Gas chromatography is widely accepted due to its high accuracy and reliability, but is unsuitable for real-time monitoring at multiple points inside the catalyst layer because a few minutes are required to obtain the results.

Oxygen sensor monitoring has been practically used for the control of gasoline combustion in automobiles, measurement of oxygen activity in molten metal, and so on. In a potentiometric sensor based on solid oxide-ion conducting electrolyte, the electromotive
force corresponds to the chemical potential gradient of oxygen species across the electrolyte. Such a sensor achieves fast response time, and enables real-time and continuous analyses at multiple points. In our previous study, the oxygen sensor was inserted into a catalyst bed of Ni/Al₂O₃ in a fixed bed reactor, and the effectiveness for the analysis of methane steam reforming was evaluated. The oxygen sensor achieved high accuracy and a good response under various conditions. Moreover, the deterioration behavior of catalytic activity was confirmed to depend on the position inside the catalyst bed.

In the present study, therefore, the oxygen sensor was introduced to the analyses of dry reforming and partial oxidation of methane over the Ni/Al₂O₃ catalyst. The catalyst performance was evaluated against temperature and time in these two reactions. The reaction process in the catalyst layer was also presumed based on the results.

2. Experimental

A series of experiments was conducted based on the method previously described. The oxygen sensor consisted of a tube closed at one end made of 8 mol% Y₂O₃-ZrO₂ (YSZ, Nikkato Corp., outer diameter: 8 mm, inner diameter: 5 mm, length: 300 mm) (Fig. 1). Five platinum wires were attached to the outer surface of the tube with platinum paste at an interval of 5 mm in the longitudinal direction. These five electrodes were named as “Terminal x” (x = 1-5); Terminals 1 and 5 correspond to the upstream and downstream parts, respectively, along the gas flow direction. A platinum wire was also fixed inside the closed end of the YSZ tube as a reference electrode. The fabricated sensor was then heat-treated at 900 °C for 5 h in air.

In this sensing system, the electromotive force (EMF, E) was measured as the chemical potential gradient of oxygen species across the YSZ electrolyte. The oxygen partial pressure in the reactor (p) was estimated from the Nernst equation.

\[ E = \frac{RT}{4F} \ln \frac{p_{\text{ref}}}{p} \]  

where R, T, F, and \( p_{\text{ref}} \) are the gas constant, absolute temperature around the electrodes, Faraday constant, and oxygen partial pressure of air in the YSZ tube (0.21 atm), respectively. Temperature was measured by placing three thermocouples in the vicinity of Terminals 1, 3, and 5. Temperature at Terminals 2 and 4 was taken as the average of the temperature for the terminals on both sides. The EMF and temperature were monitored with a data logger (GL220A, Graphtec).

The 1 wt% Ni/Al₂O₃ catalyst was synthesized by the impregnation method. Nickel nitrate hydrate, Ni(NO₃)₂·6H₂O (Wako Pure Chemical Industries, Ltd.), was dissolved in pure water at room temperature. The support material of γ-Al₂O₃ (Sumitomo Chemical Co., Ltd.) was added to the aqueous solution. The mixture was kept on a steam bath at 80 °C until the solution was evaporated. The resulting powder was calcined at 850 °C for 5 h in air.

The methane reforming reactions over Ni/Al₂O₃ were performed in a fixed-bed reactor under atmospheric pressure. The synthesized catalyst powder was pelletized and pulverized to 10-18 mesh. A 4.8 g of catalyst was placed into the reactor. The oxygen sensor was inserted into the center of the catalyst bed as shown in Fig. 2. The length of the catalyst bed was 25 mm and Terminals x (x = 1-5) were located at the relative positions of 0.2, 0.4, 0.6, 0.8, and 1, respectively, from the upstream part. Prior to the catalytic reaction test, the catalyst was reduced at 800 °C for 2 h in H₂. Reaction conditions are summarized in Table 1.

Dry reforming of methane (reaction (2)) and partial oxidation of methane (reaction (3)) mainly proceed as follows.

\[ \text{CH}_4 (g) + \text{CO}_2 (g) \rightleftharpoons 2\text{CO} (g) + 2\text{H}_2 (g) \]  

K₁ = \( \frac{p_{\text{CO}}^2 \cdot p_{\text{H}_2}^2}{p_{\text{CH}_4} \cdot p_{\text{CO}_2}} \)  

(2)

\[ \text{CH}_4 (g) + \frac{1}{2}\text{O}_2 (g) \rightleftharpoons \text{CO} (g) + 2\text{H}_2 (g) \]  

K₂ = \( \frac{p_{\text{CO}} \cdot p_{\text{H}_2}^2}{p_{\text{CH}_4} \cdot p_{\text{O}_2}^{1/2}} \)  

(3)

where K₁ and K₂ are the equilibrium constants of the reaction and the partial pressure of A in the reactor, respectively. The chemical compositions in the cate-
lyst layer were determined with the following procedure. First, only the gas species of CH$_4$, H$_2$, CO, CO$_2$, H$_2$O, and O$_2$ were considered. The following reactions were assumed to reach equilibrium during the methane reforming reactions of (2) and (3).

$$\text{H}_2 (g) + 1/2 \text{O}_2 (g) \leftrightarrow \text{H}_2\text{O} (g)$$

$$K_1 = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{O}_2}^{1/2}}$$

$$K_4 = \frac{p_{\text{CO}_2}}{p_{\text{CO}} p_{\text{O}_2}^{1/2}}$$

The mass balances of hydrogen, carbon, and oxygen elements were expressed as three equations. However, oxygen molecule in the catalyst layer was not considered because its amount was negligibly small. Moreover, the unreacted CH$_4$ was presumed to have no effect on the output value from the sensor. Then, based on the mass balances and the equilibrium reactions, the flow rates of each gas species in the catalyst layer could be calculated. Next, the compositions were estimated including carbon deposition because all the conditions applied in this study were in the thermodynamic region of carbon deposition. Carbon was assumed to be produced via the Boudourd reaction.

$$2 \text{CO} (g) \leftrightarrow \text{CO}_2 (g) + \text{C}(s)$$

$$K_3 = \frac{p_{\text{CO}_2}}{p_{\text{CO}} p_{\text{O}_2}^{1/2}}$$

Equation (6) was applied to evaluate the chemical compositions instead of the mass balance of carbon.

Methane conversion was defined as follows.

Methane conversion% = $1 - \frac{F_{\text{CH}_4}}{F_{\text{CH}_4}^0} \times 100$ (7)

where $F_{\text{CH}_4}^0$ and $F_{\text{CH}_4}$ are the flow rates of methane in the inlet and outlet gases, respectively. Then, the methane conversions in the absence and presence of deposited carbon could be calculated using the partial pressure of oxygen obtained from the oxygen sensor (Eqs. (8)-(11)).

(i) Dry reforming

(a) Absence of deposited carbon

$$\text{Methane conversion%} = \frac{F_{\text{CO}_2}^0 (K_3^{1/2} + 1)}{F_{\text{CH}_4}^0 \left( 2K_4 \sqrt{p} (2K_4^{1/2} + 1) + 3K_3^{1/2} p + 1 \right)} \times 100$$ (8)

(b) Presence of deposited carbon

$$\text{Methane conversion%} = \frac{\left( K_3^{1/2} + 1 \right) \left( F_{\text{CO}_2}^0 - F_{\text{CO}_2} \sqrt{p} \left( 2K_4^{1/2} + 1 \right) \right)}{F_{\text{CH}_4}^0 (2K_4^{1/2} K_3^{1/2} p + 2K_4^{1/2} p + K_3)} \times 100$$ (9)

(ii) Partial oxidation

(a) Absence of deposited carbon

$$\text{Methane conversion%} = \frac{2F_{\text{O}_2}^0 (K_3^{1/2} + 1)}{F_{\text{CH}_4}^0 \left( 2K_4 \sqrt{p} (2K_4^{1/2} + 1) + 3K_3^{1/2} p + 1 \right)} \times 100$$ (10)

(b) Presence of deposited carbon

$$\text{Methane conversion%} = \frac{\left( K_3^{1/2} + 1 \right) \left( F_{\text{O}_2}^0 - F_{\text{O}_2} \sqrt{p} \left( 2K_4^{1/2} + 1 \right) \right)}{F_{\text{CH}_4}^0 (2K_4^{1/2} K_3^{1/2} p + 2K_4^{1/2} p + K_3)} \times 100$$ (11)

where $F_{\text{CO}_2}^0$, $F_{\text{O}_2}^0$, $F_{\text{CO}_2}$ are the flow rates of carbon dioxide and oxygen, and total flow rate in the inlet gas, respectively.

The outlet gas from the reactor was simultaneously analyzed with an on-line gas chromatograph equipped with a thermal conductive detector (CP-4900, Valian). The concentrations of the gas species in the outlet gas were measured. The methane conversion was also calculated from Eq. (7) assuming that the flow rate of inert gas was constant during the reactions. The equilibrium methane conversion was calculated thermodynamically using software (HSC Chemistry 5.11, Outokumpu).

3. Results and Discussion

3.1. Dry Reforming of Methane

Gas composition in the 1 wt% Ni/Al$_2$O$_3$ catalyst bed was analyzed during the dry reforming of methane. Furnace temperature was set at 500-700 °C. CO$_2$/CH$_4$ ratios were fixed at 1.0 and 0.4. Thermodynamic carbon deposition occurs under these conditions. Methane conversion was calculated from the obtained EMF with Eqs. (8) and (9). Values estimated from Eq.

Table 1 Reaction Conditions for Dry Reforming and Partial Oxidation of Methane

| Reaction                  | Furnace temperature [°C] | Reactant gas                  | Space velocity (S.V.) [L kg$^{-1}$ h$^{-1}$] |
|--------------------------|-------------------------|--------------------------------|---------------------------------------------|
| Dry reforming            | 500-700                 | 25 % CH$_4$-25 % CO$_2$-50 % He | 2500                                        |
| Dry reforming            | 500-700                 | 25 % CH$_4$-10 % CO$_2$-65 % N$_2$ | 5000                                        |
| Partial oxidation        | 700                     | 25 % CH$_4$-10 % O$_2$-65 % N$_2$ | 3000-6000                                   |

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were outside the range of 0-100 % assuming carbon deposition, whereas plausible values were obtained in the absence of carbon deposition. Therefore, it could be concluded that carbon was not kinetically deposited under these conditions, and the conversion was evaluated using Eq. (8).

**Figure 3** shows the conversion for the dry reforming of methane obtained from Eq. (8) as a function of relative position in the catalyst layer. The equilibrium conversions and the results analyzed by the gas chromatograph (GC) at each temperature are also displayed at the right side of the figures. The horizontal axis indicates the normalized position in the catalyst bed. The relative positions of 0.2 and 1 correspond to the front and end parts of the catalyst bed (Terminals 1 and 5), respectively. Methane conversion reached 61.9 % and 44.2 % at Terminal 1, followed by a gradual increase to 80.8 % and 65.1 % at the end of catalyst bed at 700 °C and 650 °C, respectively, at CO2/CH4 = 1.0 and S.V. = 2500 L kg⁻¹ h⁻¹. These findings indicated that the catalyst located between the inlet part and Terminal 1 was mainly responsible for the reforming reaction. Similarly, methane was converted over the catalyst between the inlet position and Terminal 1, and then methane conversion scarcely increased from Terminal 1 to Terminal 5 at CO2/CH4 = 0.4 and S.V. = 5000 L kg⁻¹ h⁻¹. Under both conditions, methane conversions at Terminal 5 were relatively close to the results from GC analysis at all the temperatures investigated. Accordingly, monitoring of methane conversion under these conditions was successfully achieved as in the previous study\(^{15}\). The obtained methane conversion at the end part was comparable to the equilibrium value at each temperature under CO2/CH4 = 1.0 and S.V. = 2500 L kg⁻¹ h⁻¹. On the other hand, the corresponding methane conversion did not reach the equilibrium value, and the difference increased with lowering furnace temperature at CO2/CH4 = 0.4 and S.V. = 5000 L kg⁻¹ h⁻¹. This phenomenon was probably due to the insufficient reaction rate under this condition.

Time course of conversion for the methane dry reforming at CO2/CH4 = 0.4 and S.V. = 5000 L kg⁻¹ h⁻¹ was examined as shown in **Fig. 4(a)**. Regardless of the terminal position, relatively stable conversion was observed although the conversion slightly dropped during the initial three hours. Note that the findings of GC measurement were fairly close to those monitored at Terminal 5. The gas compositions were evaluated at each relative position in the catalyst layer at 5 h after the beginning of reaction (see **Fig. 4(b)**). The concentrations of methane and carbon dioxide decreased drastically accompanied by the formation of hydrogen and carbon monoxide at the upstream part. These chemical species exhibited monotonous change in concentration along the gas flow direction, whereas the steam concentration reached a local maximum at Terminal 1. The supplied carbon dioxide and the generated hydrogen should produce steam via the reverse water gas shift reaction (CO2 (g) + H2 (g) ⇌ CO (g) + H2O (g)) at the upstream part. The steam would then be consumed by methane steam reforming (CH4 (g) + H2O (g) ⇌ CO (g) + 3H2 (g)) toward the downstream part in addition to the water gas shift reaction.

### 3.2. Partial Oxidation of Methane

Partial oxidation of methane was examined at the O2/CH4 ratio of 0.4 and the methane conversions were evaluated by Eqs. (10) and (11). As in the case of dry reforming, plausible values were obtained by assuming no carbon deposition. **Figure 5** shows the methane conversion and temperature as a function of relative position in the 1 wt% Ni/Al2O3 catalyst layer. Space velocity was set at 3000-6000 L kg⁻¹ h⁻¹ and furnace temperature was fixed at 700 °C. Temperatures in the catalyst bed were measured with three thermocouples.
in the vicinity of Terminals 1, 3, and 5, as shown in Fig. 1. Equilibrium methane conversion at 700 °C is 74.8%. The conversions obtained at Terminal 5 and by GC analysis were comparable, as in the case of dry reforming. Therefore, monitoring with the sensor is suitable for the evaluation of gas composition in the catalyst bed during the partial oxidation of methane. Furthermore, methane conversion varied with relative position as for dry reforming conditions (Fig. 3). Methane conversion showed a steep increase at the upstream part, suggesting that the catalyst located at the upstream part largely contributed to the promotion of reforming reaction. The effect of space velocity on the conversion appeared at the relative positions of 0.2 and 0.4. Note that methane conversion gradually approached the equilibrium value (74.8%) at the downstream part under every space velocity condition. In Fig. 5(b), the influence of space velocity was also confirmed for the temperature distribution. The temperature at Terminal 1 was much higher than those at Terminals 3 and 5 at any space velocity, indicating that the exothermic reaction proceeded at the upstream part of the catalyst layer. Interestingly, the temperature achieved a local minimum at Terminal 3. This means that endothermic processes were involved in this reforming reaction because methane conversion continuously increased along the gas flow direction. The temperature rose with an increase in space velocity at Terminal 1, whereas the opposite tendency was observed at the other terminals. The temperature distribution in the catalyst layer for methane reforming have been already investigated in detail. Tomishige et al. reported that maximum temperature was recorded near the inlet part for methane reforming involving methane oxidation\(^{21-23}\). Thus, in this study, the temperature at the inlet part should be much higher than that measured at

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Reaction conditions: 25 % CH\(_4\)-10 % CO\(_2\)-65 % N\(_2\) (CO\(_2/\)CH\(_4\) = 0.4), S.V. = 5000 L kg\(^{-1}\) h\(^{-1}\); furnace temperature: 700 °C.

Fig. 4 (a) Time Course of CH\(_4\) Conversion for Dry Reforming of Methane over 1 wt% Ni/Al\(_2\)O\(_3\) and (b) Gas Composition as a Function of Relative Position in the Catalyst Layer at 5 h after the Beginning of the Reaction

Reaction conditions: 25 % CH\(_4\)-10 % O\(_2\)-65 % N\(_2\) (O\(_2/\)CH\(_4\) = 0.4), S.V. = 3000-6000 L kg\(^{-1}\) h\(^{-1}\); furnace temperature: 700 °C.

Fig. 5 (a) CH\(_4\) Conversion and (b) Temperature as a Function of Relative Position in the Catalyst Layer for Partial Oxidation of Methane over 1 wt% Ni/Al\(_2\)O\(_3\) (The results analyzed by the gas chromatograph are displayed at the right side of Fig. 5(a).)
Terminal 1 since this terminal was distant from the inlet part in the gas flow direction. Furthermore, Shishido et al. reported that the maximum temperature was strongly dependent on the space velocity and the catalyst24). The increased temperature in the Ni/CaTiO$_3$ catalyst layer was more than 150$^\circ$C in the partial oxidation of methane at a space velocity of 360,000 L kg$^{-1}$ h$^{-1}$, which was much higher than that in this study.

Two reaction mechanisms for partial oxidation have been already proposed, although the dominant mechanism is considered to depend on the metal catalysts and the support materials. In one possible mechanism, methane and oxygen adsorbed on the metal catalyst directly react to form hydrogen and carbon monoxide25),26). In another mechanism, methane is combusted to steam and carbon dioxide (complete oxidation of methane), followed by the conversion of unreacted methane by these products via the steam and dry reforming reactions14),27). Combining the obtained results with the suggested mechanisms, it could be concluded that the complete oxidation of methane to form steam and carbon dioxide mainly occurred at the upstream part. Then, the unreacted methane was subsequently reformed by the products along the flow direction, resulting in the remarkable drop of temperature from Terminal 1 to Terminal 3. Moreover, the oxygen partial pressure was extremely low, 10$^{-21}$-10$^{-23}$ atm, even at Terminal 1. This means that the supplied oxygen gas was consumed very fast by the complete oxidation of methane over the catalyst layer at relative position of 0-0.2. The complete oxidation of methane would be dominant at the inlet part of the layer, and then the main reaction should change to the steam and CO$_2$ reforming reactions at a certain position within 0-0.2. Furthermore, the decrease in space velocity should shift this position to the upstream side; the longer contact time between the catalyst and the reactant gases facilitated the complete oxidation of methane, followed by the subsequent reforming reaction of unreacted methane with steam and carbon dioxide.

The stability test for the partial oxidation under O$_2$/CH$_4$ = 0.4 was carried out at 700 $^\circ$C. Time course of methane conversion is shown in Fig. 7. Relatively stable conversion was confirmed at the end part of the catalyst within ca. 35 h. On the other hand, conversion at the upstream part continuously reduced throughout this stability test; the decrease rates for 35 h were ca. 2% and ca. 1% at Terminals 1 and 2, respectively. This result indicated that deactivation of the catalyst proceeded gradually from the upstream part to the
downstream part. This deactivation behavior would be attributed to the differences in the contributions to the reforming reaction and the catalyst temperatures depending on the position. It was reported that the major reasons for the deactivation of Ni/Al₂O₃ catalyst were the covering of active sites by deposited carbon, volatilization of Ni, and formation of NiAl₂O₄. Consequently, deactivation of the catalyst during the partial oxidation of methane could be successfully monitored.

4. Conclusions

The YSZ oxygen sensor was applied for analyzing dry reforming and partial oxidation of methane over Ni/Al₂O₃. The reactions could be continuously monitored at multiple points inside the catalyst bed. This monitoring method allowed us to analyze the distribution of gas species inside the catalyst bed, to clarify the deactivation behavior of catalyst, and to propose plausible reaction processes. In the previous and present studies, the main reforming reactions of methane were successfully analyzed using the oxygen sensor. Such relatively inexpensive components and simple technique will be useful for the on-site feedback control of reforming reactions and the prediction of catalyst lifetime in the future, although further investigations of the reaction under various conditions are required.

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要旨

メタンのCO₂改質および部分酸化反応における酸素センサを用いたガス組成分析

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現在、水素は主に炭化水素の改質反応から製造されている。水素製造時に生成ガス成分の変化や触媒の劣化状況をモニタリングすることは重要である。本研究では、Ni/Al₂O₃触媒を用いたメタンのCO₂改質および部分酸化反応の進行過程を解析した。触媒層内の酸素センサを挿入することにより、層内の酸素の測定において酸素分圧を求め、得られた値からメタン転化率や各ガス種の濃度を算出した。両改質反応において、酸素センサを用いた測定手法により得られたメタン転化率はガスクロマトグラフによる分析結果とよく一致し、本方法でメタン改質反応を正確に分析できることが確認された。陰極酸化時の転化率の経時変化より、触媒劣化の程度が層内の位置によって異なることが明らかとなった。また、部分酸化反応については、触媒層内のガス種とガスの分布から想定される反応機構を提案した。