Synthesis gas production in methane conversion using the Pd|yttria-stabilized zirconia|Ag electrochemical membrane system

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The electrochemical membrane reactor of YSZ (yttria-stabilized zirconia) solid electrolyte coated with Pd and Ag as anode and cathode, respectively, has been applied to the partial oxidation of methane to synthesis gas ($CO + H_2$). The Pd|YSZ|Ag catalytic system has shown a remarkable activity for CO production at 773 K, and the selectivity to CO was quite high (96.3%) under oxygen pumping condition at 5 mA. The H_2 production strongly depended on the oxidation state of the Pd anode surface. Namely, the H_2 treatment of the Pd anode at 773 K for 1 h drastically reduced the rate of H_2 production, while air treatment enhanced the H_2 production rate. From the results of the partial oxidation of CH_4 with molecular oxygen, it is considered that the reaction site of the electrochemical oxidation of CH_4 to synthesis gas was the Pd–YSZ–gas-phase boundary (triple-phase boundary). In addition, it is found that the oxygen species pumped electrochemically over the Pd surface demonstrated similar activity to adsorbed oxygen over Pd, PdO_{ad}, for the selective oxidation of CH_4 to CO, when the Pd supported on YSZ was used as a fixed-bed catalyst for CH_4 oxidation with the adsorbed oxygen. The difference with respect to the H_2 formation between the electrochemical membrane system and the fixed-bed catalyst reactor results from differences in the average particle size of Pd and the way of the oxygen supply to the Pd surface.

Keywords: synthesis gas, methane conversion, electrochemical membrane system, yttria-stabilized zirconia

1. Introduction

Recently, partial oxidation of CH_4 to CO and H_2, namely synthesis gas, has been studied as a promising method for CH_4 conversion [1–5]. Metals in group VIII such as Rh, Ni, Ru, Pt and Pd are active catalysts for reaction (1):

$$CH_4 + (1/2)O_2 \rightarrow CO + H_2 \tag{1}$$

This reaction is basically composed of reactions including complete oxidation of CH_4, reforming of CH_4 by H_2O and CO_2, and the water gas shift reaction. The partial oxidation of CH_4 to synthesis gas is normally performed at high temperatures such as 800–1000 K, because the reforming reactions are highly endothermic. At 900 K, the equilibrium conversion of CH_4 to synthesis gas is approximately 90% at 0.01–1 atm.

Schmidt et al. [6] have suggested the possibility of the direct oxidation of CH_4 to synthesis gas using an Rh- or Pt-coated monolith catalyst during a short residence time. Rh was found to be a superior catalyst, compared with Pt, for the selective production of H_2 because of the higher activation energy for OH formation from adsorbed hydrogen and oxygen on Rh (20 kcal/mol) than on Pt (2.5 kcal/mol). We have also reported that synthesis gas is obtained by the reaction of CH_4 with adsorbed oxygen, O_{ad}, on an Rh/SiO_2 catalyst at a relatively low temperature of 773 K [7]. These studies suggest that the direct conversion of CH_4 to synthesis gas can be carried out continuously by supplying oxygen species such as adsorbed oxygen, O_{ad}, over the Rh.

Recently, an electrochemical membrane system, constructed from an oxide ionic conductor, has been demonstrated to be useful for the partial oxidation of hydrocarbons [8–13]. Most commonly, the electrochemical cell is constructed with yttria-stabilized zirconia (YSZ) as the oxide ionic conductor. In these studies, we have focused on the features of the catalytic activity and the nature of the oxygen species produced electrochemically [11–13]. As a result, it was found that the electrochemically pumped oxygen species have unique catalytic activities for the selective oxidation of the hydrocarbons to oxygenated compounds, where the hydrocarbons reacted with the oxygen species at the gas–electrode–solid electrolyte boundary, that is, a triple-phase boundary. Furthermore, we have reported that the synthesis gas was obtained continuously by the direct conversion of CH_4 at 773 K, when an YSZ-based electrochemical cell with a rhodium anode served as an oxygen pump to the rhodium surface [14]. In this work, it is likely that oxygen species appearing at the triple-phase boundary migrate onto the Rh surface and there play an important role for producing the synthesis gas, indicating that the membrane system can be applied for the continuous supply of the active oxygen species over the catalyst. In addition, it was also found that the oxidation state of Rh controlled by the electrochemical oxygen pumping has

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great influence on the activity of synthesis gas formation. Among extensive studies dealing with metal catalysts composed of group VIII metals [15–17], it has been pointed out that the activity of Pd metal for the partial oxidation of CH_4 is lower compared with the other metals, Rh, Ru and Ni. On the other hand, Matsumoto et al. [18,19] have recently suggested an important role of the oxidation state of Pd in the partial oxidation of CH_4 to synthesis gas over Pd/Y-zeolite catalyst. They have reported that small clusters of Pd and PdO coexist in the zeolite crystals, and that they can work as catalytic sites via a reversible redox mechanism. Accordingly, supplying the active oxygen species continuously to the Pd surface under the controlled oxidation state of Pd is expected to allow the selective production of synthesis gas from the CH_4 oxidation. In this paper, we report the partial oxidation of CH_4 using an electrochemical membrane system, namely Pd|YSZ|Ag, and compare the results with those of the Rh|YSZ|Ag reactor.

2. Experimental

2.1. Reactor construction

A schematic diagram of the Pd|YSZ|Ag electrochemical reactor is shown in figure 1. The electrochemical reactor was constructed from an 8 mol% yttria-stabilized zirconia (YSZ) disk (32 mm in diameter × 1 mm in thickness: density 5.4 g/cm^3; Nippon Kagaku Togyo Co.). Thin compact films of Pd (0.8 μm) and Ag (2.0–4.0 μm) were used as the anode and the cathode, respectively, on each face of the disk. On one side, a thin film of Pd was prepared by the electroless plating method using a formaldehyde-based bath (N.E. Chemcat. Co.). On the opposite side, an Ag cathode was prepared from Ag paste (Fujikura Kasei), because the Ag is active for the dissociation of molecular oxygen.

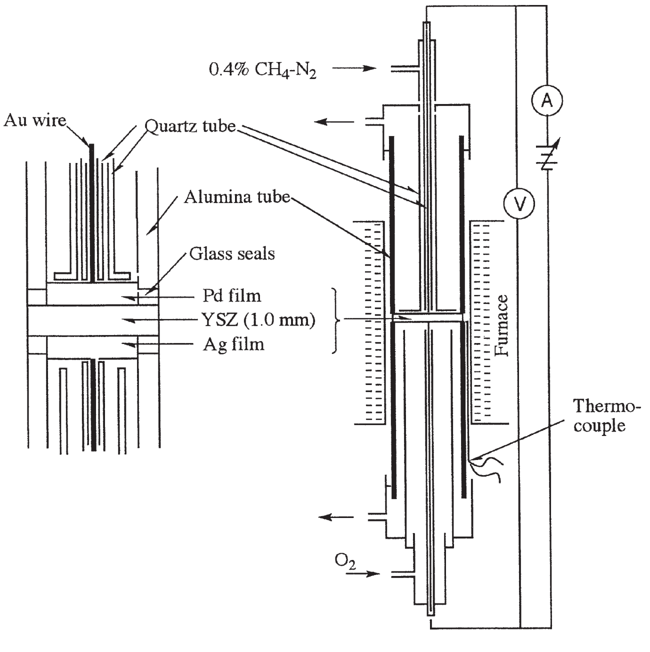

Figure 1. A schematic diagram of the Pd|YSZ|Ag electrochemical reactor.

Au wire (1 mm diam., anode) and Pt wire (1 mm diam., cathode) were used to connect the center of the electrodes to an electrical circuit for controlling the oxygen flux across the YSZ electrolyte. The Pd|YSZ|Ag disk was mounted between two vertical 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 reactant hydrocarbon and the Pd anode. 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 Pd|YSZ|Ag disk.

2.2. Partial oxidation of CH_4

First, 0.4% CH_4 was passed (1.0 l/h) via a mass-flow controller, over the Pd anode at 773 K for testing the catalytic activity. 100% oxygen gas was passed (1.0 l/h) through the cathode side of the reactor, so that an oxygen pressure of 101.3 kPa was maintained during the experiments. Oxygen was pumped to the anode space through the YSZ solid electrolyte by applying the electric current. The applied current was varied to control the oxygen flux through the YSZ solid electrolyte. Before the reaction, the Pd anode was treated by the following reduction–oxidation method: the Pd anode was exposed to air at 773 K for 30 min, or further reduced with 20% H_2 in N_2 at 773 K for 1 h. In order to clarify the reactivity of the adsorbed oxygen species on the Pd surface, a 0.5 wt% Pd powder catalyst supported on YSZ (Pd/YSZ) was used as the fixed-bed catalyst. The Pd/YSZ catalyst was prepared by impregnating YSZ (Tosoh Zirconia TZ-8Y; specific surface area 16 m^2/g) with an aqueous solution of palladium acetylacetonate. The specific surface area of the 0.5 wt% Pd/YSZ catalyst was 16.2 m^2/g. Ten milligrams of catalyst diluted with 190 mg of SiO_2 (JRC-SIO-7, Reference Catalyst of Catalyst Society of Japan) was mounted in the reactor. The catalyst was pretreated in the following way: the catalyst was reduced with 20% H_2 in N_2 at 873 K for 2 h to take away the oxidized Pd or PdO, and then exposed to air at 473 K for 1 min to prepare a Pd surface covered with a monolayer of atomic oxygen.

Analysis of the effluent gas was carried out by TCD gas chromatography. Porapak Q molecular sieve 13X and 5X columns were used for the analysis of the hydrocarbons and the inorganic gases, respectively. In this work, H_2O was not quantitatively analyzed. Thus, the oxygen balance was calculated by assuming H_2O as an oxidation product under the complete oxidation of CH_4 to CO_2 and H_2O. The anode surface was characterized by X-ray diffraction (XRD) measurement and scanning electron microscopy (SEM). The XRD measurements were carried out using an MAC Science MXP 18 diffractometer with a thin film attachment at a fixed incidence angle $\theta = 5°$; SEM images were recorded by the Hitachi S-800 system.

3. Results

3.1. Cell properties

The resistance across the Pd|YSZ|Ag cell under N_2 atmosphere was measured to be 25.7 Ω at 773 K by a multimeter. One cell continuously used for 14 days was carefully dismounted, and the anode surface was characterized by a scanning electron microscope (SEM). Figure 2 shows the SEM images of the Pd anode surface of the Pd|YSZ|Ag membrane with a Pd film thickness of 0.8 μm. As shown in the image (a), the surface before the reaction was found to be rough and consisted of small Pd particles (0.4–1.2 μm). After the reaction, the Pd particles grew large, as shown in figure 2(b), due to sintering, but small pores were still present to let the CH_4 penetrate to the Pd–YSZ interface for the reaction with pumped oxygen.

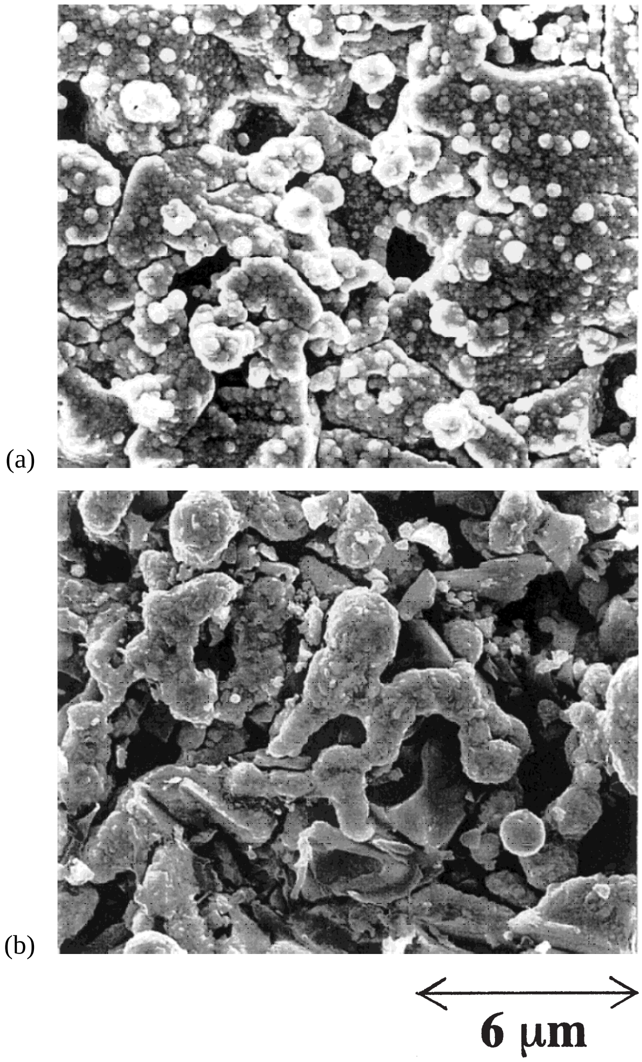

Figure 2. SEM images of the Pd anode in the Pd|YSZ|Ag electrochemical reactor: (a) before, (b) after the reaction.

3.2. Partial oxidation of CH_4 in the Pd|YSZ|Ag system

Upon introducing the diluted CH_4 (0.4%) and the O_2 (100%) gas into the anode and the cathode spaces, respectively, H_2 and CO were produced over the anode surface under the open circuit condition, namely without electrochemically pumping oxygen to the anode space through the YSZ. In addition, the electrochemical reactor gave a stable cell voltage (EMF) of 920 mV, indicating the formation of a fuel cell type system.

Applying an electric current of 5 mA (O_2 0.047 mmol/h) to the reaction cell resulted in an increase in the amount of the products, CO and H_2. Figure 3 shows the formation rates of oxidation products as a function of reaction time. It is clear that the formation rates of CO and H_2 decreased with reaction time. No evolution of molecular oxygen was observed during the reaction. Assuming that water was another oxidation product, the oxygen balance between the electrochemical oxygen supply and the oxygen-containing compounds formed was estimated to be almost 100%. The formation rates of CO and H_2 were 0.405 and 0.207 mmol/h after 60 min of the reaction, respectively, where the conversion of CH_4 was 27%. The selectivity to CO was quite high ($S_{CO} = 94.4\%$, $S_{CO_2} = 5.6\%$), which was higher than that obtained using the Rh|YSZ|Ag membrane reactor ($S_{CO} = 85\%$, $S_{CO_2} = 15\%$). However, the amount of H_2 obtained in this study was smaller than that expected from equation (1) because of the production of H_2O.

The H_2 treatment of the anode surface at 773 K for 1 h drastically reduced the rate of H_2 production, as shown in figure 4. The H_2 production was initially slightly observed by applying an electric current to the reaction cell, but the amount was quickly decreased. The CO_2 selectivity

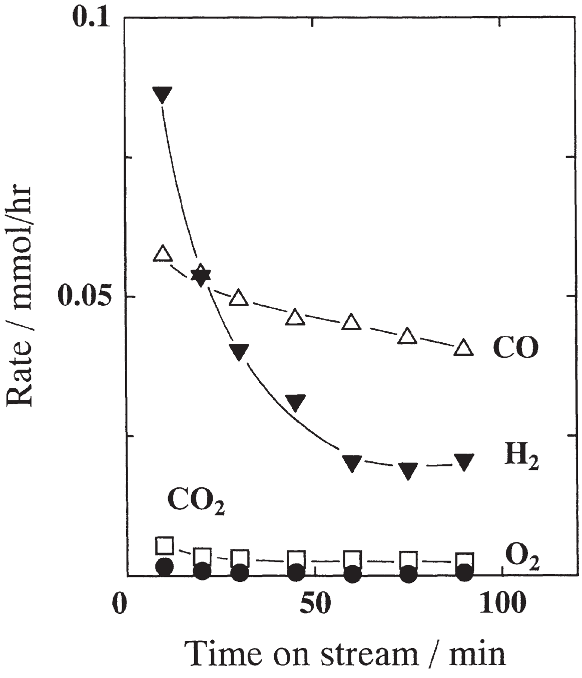

Figure 3. Partial oxidation of CH_4 at 773 K using the Pd|YSZ|Ag electrochemical reactor after air treatment.

was slightly enhanced by the H_2 treatment of the Pd anode (5.6–11%), indicating that the H_2 treatment enhances the activity for the complete oxidation of CH_4, namely H_2O and CO_2 formation. The selectivity was considered to be controlled by the oxidation state of Pd particles on the anode. Figure 5 shows XRD diffraction lines of Pd and ZrO_2 (YSZ) for a fresh anode (a), an air-treated anode (b), and H_2-treated anode (c). Among these samples, the PdO species is only included in the oxidized anode (b). Only the peak of metallic Pd was observed for samples (a) and (c). The reversible change between Pd and PdO thus controls the selectivity to CO/H_2 or CO_2/H_2O, that is, the production of H_2 is enhanced on the oxidized Pd anode including PdO species.

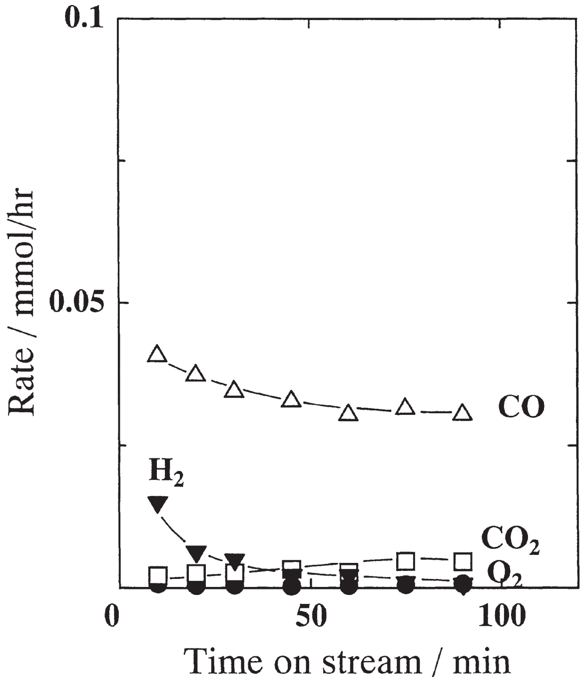

Figure 4. Partial oxidation of CH_4 at 773 K after H_2 treatment. Pretreatment: air treatment (500 °C, 30 min) → 20% H_2 treatment (500 °C, 1 h) → reaction.

3.3. CH_4 oxidation with gaseous oxygen over the Pd anode

Our previous results [11–13] have indicated that the active oxygen species for the partial oxidation of hydrocarbons are electrochemically pumped at the electrode–solid electrolyte (YSZ)–gas-phase boundary, namely the triple-phase boundary. In the partial oxidation of CH_4 using the Rh|YSZ|Ag reactor, the oxygen species appearing at the triple-phase boundary were found to migrate onto the Rh surface and then react with CH_4 producing the synthesis gas. Here, it is interesting to examine the difference in the reactivity with CH_4 between oxygen species electrochemically pumped from the triple-phase boundary and that supplied from the gas phase. To clarify this, the reaction of CH_4 (0.4%) with O_2 (0.1%) on the Pd anode was carried out after treatment of the Pd with air (773 K, 30 min) and then

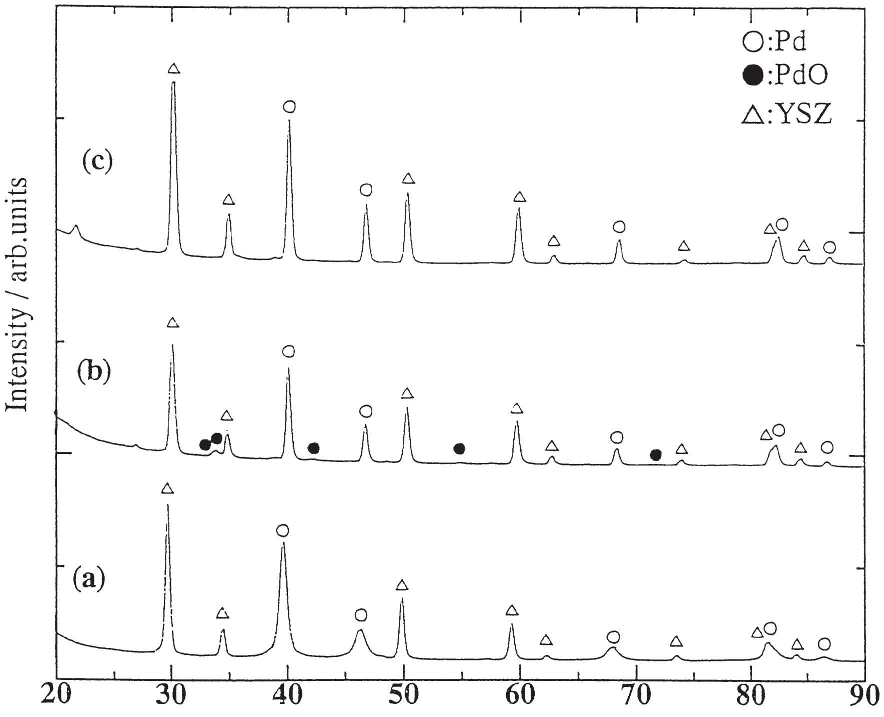

Figure 5. X-ray diffraction diagrams of the Pd anode in the electrochemical reactor before and after the pre-treatment: (a) before reaction, (b) after the air treatment (773 K, 30 min) → H_2 treatment (773 K, 1 h) → air treatment (773 K, 1 h), (c) after the air treatment (773 K, 30 min) → H_2 treatment (773 K, 1 h).

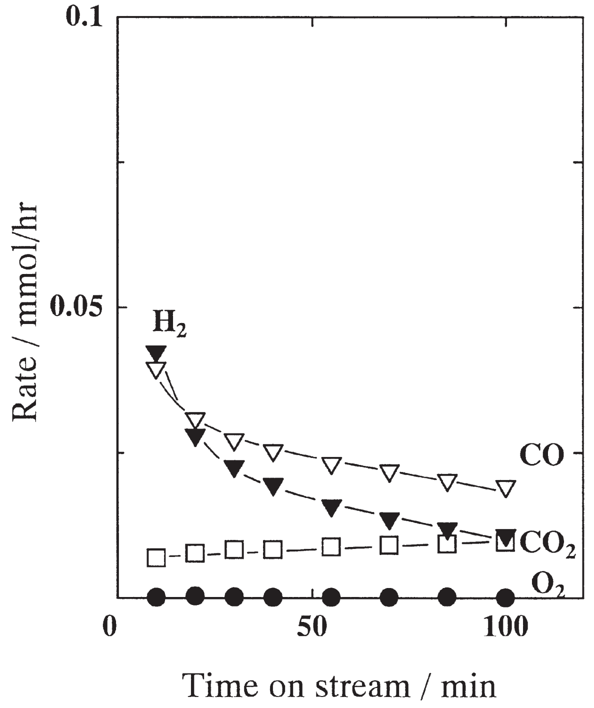

Figure 6. CH_4 oxidation with the molecular oxygen over the Pd anode. Pre-treatment: air treatment (500 °C, 30 min) → 20% H_2 treatment (500 °C, 1 h) → reaction.

20% H_2 (773 K, 1 h). Figure 6 shows the result of the CH_4 oxidation with gaseous oxygen over the Pd anode without the electrochemical oxygen pumping. Clearly, a significant amount of CO_2 was detected as the product of the complete oxidation of CH_4, which is quite different from the results of pumping oxygen (figures 3 and 4). The CO selectivity obtained in the CH_4 oxidation with gaseous oxygen was 84%, and its value was lower than that (94%) obtained in the CH_4 oxidation under electrochemical oxygen pumping conditions (figure 3). In contrast, CO_2 selectivity increased from 6 to 16%. These results indicate that complete oxidation of CH_4 was accelerated using the gaseous oxygen as an oxidant. Therefore, it is likely that the oxygen species over the Pd catalyst, which was derived from the gaseous phase, have low catalytic activity for the selective oxidation of CH_4 to synthesis gas.

3.4. Partial oxidation of CH_4 with O_{ad} over the Pd/YSZ catalyst

The partial oxidation of CH_4 with the adsorbed oxygen species was carried out on the Pd supported on YSZ at 773 K to examine the reactivity of adsorbed oxygen provided from gaseous O_2 onto the Pd surface. Immediately after the reaction started, the formation of synthesis gas was recognized, as shown in figure 7. The conversion of CH_4 was 0.32%. Note that no significant formation of CO_2 was observed here. The amount of the adsorbed oxygen species over the Pd catalyst was estimated to be 1.23 μmol by the amount of the oxidation products. That value corresponded to a monolayer of atomic oxygen covering the Pd surface.

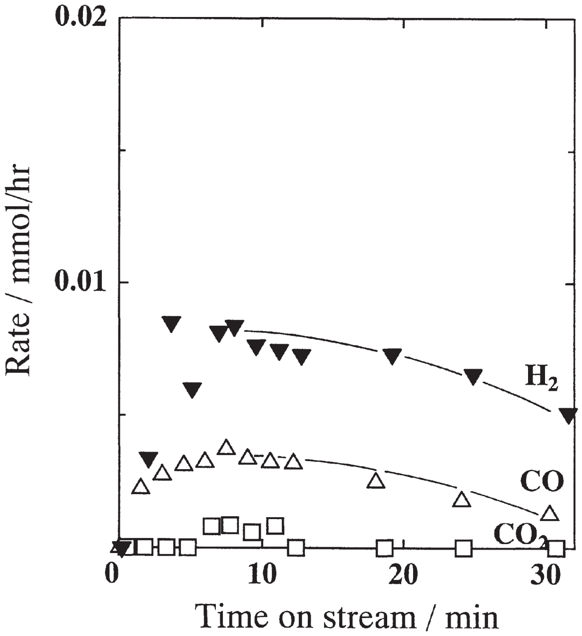

Figure 7. CH_4 oxidation with the adsorbed oxygen species over the 0.5 wt% Pd/YSZ catalyst diluted with SiO_2. Pre-treatment: 20% H_2 treatment (600 °C, 2 h) → air treatment (200 °C, 1 min) → reaction.

The H_2/CO molar ratio was two, suggesting that the formation of synthesis gas is not ascribed to the reforming of CH_4 with H_2O or CO_2, but ascribed to the direct partial oxidation of CH_4. The decrease in the formation rate of both CO and H_2 with the reaction time after 18 min was due to a decrease in the amount of the adsorbed oxygen species on the Pd metal. The formation of H_2 was still observed after 30 min, which may be due to the thermal cracking of CH_4 over the Pd/YSZ catalyst.

4. Discussion

4.1. Active oxygen species for the electrochemical oxidation of CH_4

Cullis and Willat have studied the kinetics of CH_4 oxidation over Pd catalyst supported on a number of metal oxides using a pulse-flow microreactor technique at 500–800 K [20]. They reported that the adsorbed oxygen over the Pd catalysts reacted with CH_4 to produce CO above 700 K. Recently, Matsumoto et al. [18,19] have reported that the Pd–Y zeolite catalyst activated by a reduction–reoxidation treatment shows excellent activity and selectivity in the oxidation of CH_4 to CO and H_2 under oxygen deficient conditions at 800–1000 K. They suggested that a small cluster of Pd species formed on the zeolite by the treatment catalyzed the direct oxidation of CH_4 with oxygen species on the Pd cluster to synthesis gas. These results are consistent with those of the present study in that the adsorbed oxygen species provided by either gas phase or electrochemically pumping partially oxidized CH_4 to CO (figures 3, 4 and 6).

As previously reported on the Rh(anode)|YSZ|Ag (cathode) electrochemical membrane system [14], oxygen species appearing at the triple-phase boundary of the Rh|YSZ|atmosphere migrated to the surface of the Rh metal anode, namely the reverse spill-over mechanism, and they played an important role as the active oxygen species for the direct conversion of CH_4 to synthesis gas. This mechanism is valid for the partial oxidation of CH_4 using the Pd|YSZ|Ag reactor, because oxygen species on Pd reacted with CH_4 to form CO and H_2 (figure 7). Namely, the oxygen species, generated electrochemically at the triple-phase boundary and migrated on the Pd surface, demonstrate catalytic activity for the selective oxidation of CH_4.

On the other hand, CH_4 oxidation with gaseous oxygen over the Pd anode resulted in the enhancement of the CO_2 formation (figure 6). This may be due to the deep oxidation of Pd metal, that is, the reaction pathway of the oxidation of CH_4 to CO and/or to CO_2 is probably determined by the concentration of the surface oxygen on the Pd catalyst. Thus, the moderate oxidation of the Pd surface is effective for the partial oxidation of CH_4 to CO.

4.2. Dependence of the oxidation state of Pd on H_2 production

Generally, Pd catalysts have been employed in the combustion of hydrocarbons because of the high activity to oxidize hydrocarbons completely to CO_2 and H_2O. In the present study, the production of H_2 in the oxidation of CH_4 was found to strongly depend on the pre-treatment condition of the Pd anode (figures 3 and 4). The XRD results (figure 5) showed that the reduction of the Pd anode by H_2 led to a change in the oxidation state of the Pd surface from PdO to Pd metal. Corresponding to the change, the selectivity to H_2 decreased to almost zero, as shown in figure 4. The absence of H_2 indicates the combustion of H_2 to H_2O occurring on the reduced Pd anode, that is, a moderately oxidized Pd surface hinders the combustion of H_2, which also explains the results of figures 3 and 6. It should be noted that the H_2/CO ratio was not 2, even when the Pd electrode treated by air was used. This may be due to the Pd metal surface remaining on the Pd anode.

The particle size of Pd is considered to be a factor in controlling the selectivity of H_2 and/or H_2O in the membrane system. The average particle size of the Pd metal on the anode was estimated to be 119–197 Å from the XRD measurement of the Pd anode, as shown in table 1. As for the Pd catalyst supported on YSZ, no peak due to the Pd metal or PdO was detected in the XRD measurement, suggesting that the average of Pd particle size over the YSZ is less than the limit size of 50 Å, which is reported to be the limitation of the XRD measurement [21]. The part of the Pd metal in the anode formed by the H_2 reduction was thus much greater than that of the Pd/YSZ catalyst. It is thought that the large size of the Pd metal particle on the anode is responsible for the high activity of the conversion of H_2 to H_2O because, in the electrochemical membrane system, the oxygen species are electrochemically pumped continuously to the triple-phase boundary and migrate to cover the surface of the Pd anode. The partial oxidation of CH_4 to synthesis gas probably occurs at the partially oxidized Pd around the triple-phase boundary, while the combustion of H_2, produced by the partial oxidation of CH_4, occurs consecutively at the Pd metal surface, except for the triple-phase boundary. Thus, the oxygen species generated at the triple-phase boundary cannot migrate enough to cover the entire Pd surface with increasing particle size. As a result, the conversion of H_2 to H_2O with unreacted oxygen species, e.g., adsorbed oxygen species migrated onto the Pd surface or molecular oxygen generated at the triple-phase boundary, takes place consecutively on the Pd surface away from the triple-phase boundary.

Table 1
Average of the Pd metal on the YSZ solid electrolyte estimated from the XRD patterns of Pd metal under various pre-treatments.

Treatment	Average of the Pd metal (Å)
Fresh	119
Air treatment (773 K, 1 h)	188
H_2 treatment (773 K, 1 h)	197

On the other hand, in the fixed-bed catalyst, oxygen is supplied to the entire Pd anode surface from the gas phase. The fact that production of H_2 was observed in the reaction with oxygen supplied from gaseous O_2 is ascribed to the uniform coverage of the Pd surface with adsorbed oxygen, where the oxygen hinders the conversion of H_2 to H_2O.

5. Conclusions

Partial oxidation of CH_4 has been carried out using an electrochemical membrane system (Pd|YSZ|Ag), and the Pd anode prepared by the electroless plating method has shown a remarkable activity for the selective oxidation of CH_4 to CO. It is considered that CO is produced by the reaction of CH_4 with the oxygen species over the Pd anode (PdO), which was electrochemically generated at the triple-phase boundary and then migrated on the Pd surface. The oxygen species derived from PdO showed a similar activity for the CO production to the adsorbed one on the Pd, Pd–O_{ad}, on supported YSZ powder catalyst (Pd/YSZ). However, the ratio of H_2/CO was not 2, and H_2 formation strongly depended on the pre-treatment of the Pd anode. These phenomena were explained as follows: the partial oxidation of CH_4 to synthesis gas ($CO + H_2$) occurred around the triple-phase boundary, while the combustion of H_2 to H_2O which occurred at the Pd metal surface with unreacted oxygen species, e.g., adsorbed oxygen species migrated onto the Pd surface or molecular oxygen generated at the triple-phase boundary. This difference observed in the catalytic activity for H_2 production between the pumped oxygen and the adsorbed oxygen can be ascribed to the differences in the size of the Pd particles and in the way of the oxygen supply to the Pd surface.

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