Methane Oxidation

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Direct Oxidation of Methane to Methanol at Low Temperature and Pressure in an Electrochemical Fuel Cell

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Methane is an abundantly available fuel whose use is mainly limited to that of a primary energy source due to its low reactivity. Methanol, on the other hand, is a useful intermediate material in many chemical manufacturing processes as well as a safe-to-handle liquid fuel for transportation and storage. There is therefore a long-standing industrial interest in producing methanol from methane effectively.[1] The conventional synthesis of methanol from methane involves multi-step processes, including the steam reforming of methane and subsequent catalytic reaction. These processes, however, require high temperatures ($<700\,^{\circ}C$) and pressures (200–300 atm) operations, respectively, which lead to high running costs.

The direct oxidation of methane to methanol has received much attention as the next step in methanol production since it avoids the above multi-step processes. However, this oxidation is regarded as a very difficult reaction, especially in the gas phase at low pressure, because of the need to operate at high temperatures ($>400\,^{\circ}C$), where methanol is quickly oxidized to formaldehyde and CO_x.[2–7] One approach for oxidizing methane at lower temperatures is to apply an electrochemical cell to the reaction system. Otsuka and Yamanaka et al., for example, have reported the selective oxidation of light alkanes to oxygenates by the electrochemically activated oxygen species[8,9] that are generated at the cathode in polymer electrolyte (PEFCs) and phosphoric acid fuel cells (PAFCs) [Eqs. (1) and (2)].

$$\text{Anode}: \; H_2 \rightarrow 2\,H^+ + 2\,e^- \qquad (1)$$

$$\text{Cathode}: \; O_2 + 2\,H^+ + 2\,e^- \rightarrow O^* + H_2O \qquad (2)$$

These active oxygen species can directly oxidize various hydrocarbons, such as ethane and propane, to oxygenates at low temperatures ($<80\,^{\circ}C$), however, there has been no report on the selective oxidation of methane to methanol in fuel-cell systems. This is because the operating temperature is too low to oxidize methane. Clearly, therefore, a fuel cell capable of working above 80 °C is necessary for methane oxidation.

Although the direct oxidation of hydrocarbons has been demonstrated in solid-oxide fuel cells (SOFCs) with stabilized zirconia[10,11] and perovskite-type oxide electrolytes,[12] these electrolytes require high temperatures above 500 °C to show high ionic conductivities. We have recently reported that 10 mol% In^{3+}-doped SnP_2O_7 ($Sn_{0.9}In_{0.1}P_2O_7$) shows high proton conductivities of above $10^{-1}\,S\,cm^{-1}$ between 100 and 350 °C under water-free conditions.[13] This material has also been used as an electrolyte in fuel cells,[14] and herein we report the selective oxidation of methane to methanol in a hydrogen-oxygen fuel cell containing $Sn_{0.9}In_{0.1}P_2O_7$ as electrolyte.

$Sn_{0.9}In_{0.1}P_2O_7$ was prepared as reported previously.[13] Pd/C, Pt/C, Rh/C, Au/C, and PdAu/C (10 wt.% metal) catalysts were tested as the cathodes. The weight ratio of Pd to Au in PdAu/C was in the range from 1 to 8. These catalysts were prepared by an impregnation method starting from the corresponding metal salts ($PdCl_2$, $H_2PtCl_6{\cdot}6\,H_2O$, $RhCl_3$, and $HAuCl_4{\cdot}4\,H_2O$). Thus, carbon powder (Black Pearls) was suspended in an ethanol/water solution and the metal salt added at about 60 °C. After drying and grinding, the catalyst powders were reduced under an H_2/Ar (10 vol.% H_2) atmosphere at 450 °C for 4 h. A commercial Pt/C anode (60 wt.% Pt) was purchased from E-TEK inc.

The anode and cathode (area: 0.5 cm^2) were attached on opposite sides of the electrolyte (thickness: 1.0 mm) and two gas chambers were set up by placing the cell assembly between two alumina tubes. The cathode and anode were supplied with a 50 vol.% methane–50 vol.% oxygen mixture and hydrogen, respectively, at a flow rate of 30 mL min^{-1}. Gas analysis was performed with online flame-ionization detector (FID) and thermal-conductivity detector (TCD) gas chromatographs. The whole gas line and the alumina tube were heated to a temperature of approximately 80 °C and the gas concentrations were obtained after the reaction steady state had been attained. Current/voltage curves for the fuel cell were measured with a galvanostat.

The ability to produce methanol from methane was first investigated with the Pd/C, Pt/C, Rh/C, and Au/C cathodes at 250 °C. The common feature of these fuel cells is their open-circuit voltage (OCV; 715–915 mV), which is lower than the theoretical OCV of 1.1 V in all cases. This result is not due to the presence of methane in the cathode gas, since there is no difference in the OCVs in the presence and absence of methane. At least two factors are responsible for the lower OCVs: 1) physical leakage of gas through the electrolyte and 2) partial electron/hole conduction in the electrolyte, which causes an internal short circuit. These fuel cells also show a large difference in the short-circuit current (140–250 mA).

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For this reason, all catalyst tests were performed at a constant current of 200 mA, unless otherwise stated.

As shown in Figures 1 a and 1 b, methanol and carbon dioxide are produced by polarization of the Pd/C cathode. No other product was observed in our GC analysis. Small amounts of methanol and carbon dioxide are also produced at the Pd/C cathode under open-circuit conditions (Figures 1 a,b). As described above, a small amount of hydrogen permeates through the electrolyte from the anode to the cathode, and we assume that this permeating hydrogen reacts with oxygen at the cathode and activates it catalytically. Furthermore, while the Pt/C and Au/C cathodes catalyze the production of carbon dioxide rather than methanol, the Rh/C cathode shows almost no activity. It has been reported that some noble metals, notably Pd, show high catalytic activity for the formation of hydrogen peroxide from hydrogen and oxygen,[4,5,15–17] which suggests that the difference in the rate of methanol formation among the tested cathodes reflects their efficiency in producing hydrogen peroxide or derivatives electrochemically.

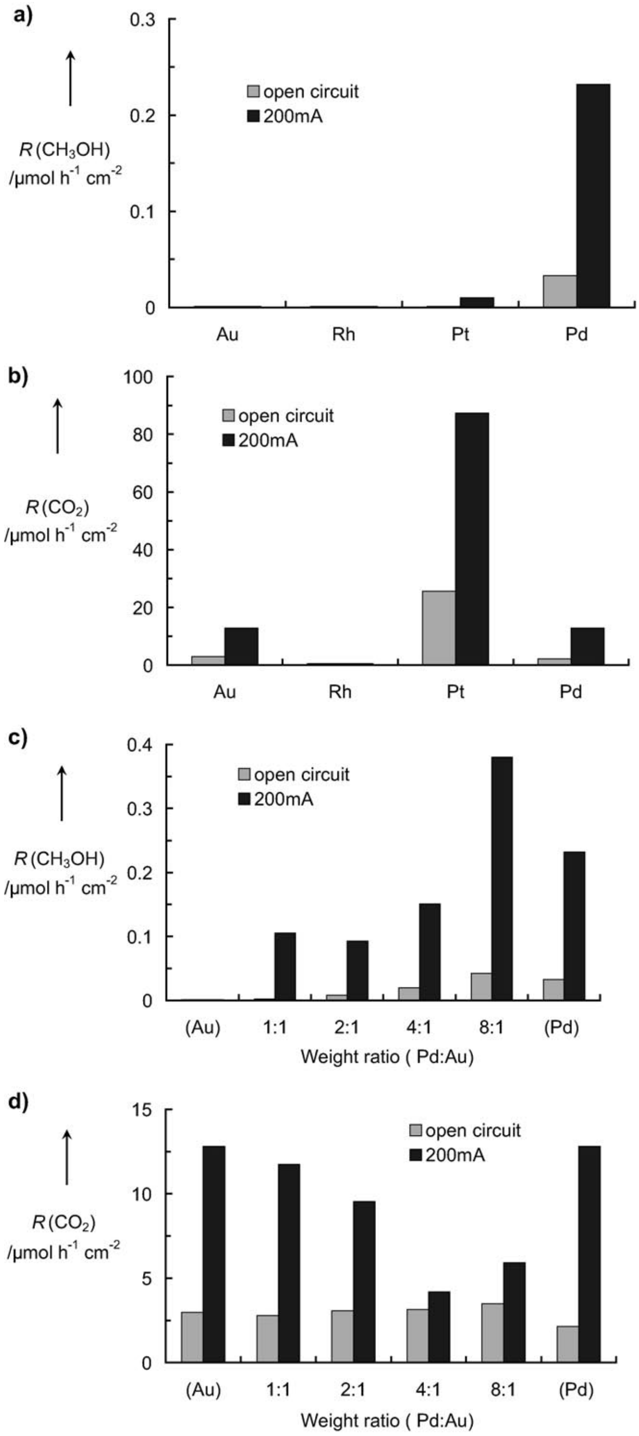

Figure 1. Rates of a) methanol and b) carbon dioxide formation at various metal/C cathodes at 250 °C. Rates of c) methanol and d) carbon dioxide formation at PdAu/C cathodes with various compositions. A mixture of 50 % methane and 50 % oxygen was supplied at a rate of 30 mL min^{-1} to all the cathodes.

Although the direct oxidation of methane to methanol is possible at the Pd/C cathode, the rate of methanol formation is far from satisfactory. Landon et al.[18,19] and Ishihara et al.,[20] for example, have reported that the catalytic formation of hydrogen peroxide from hydrogen and oxygen is enhanced by the addition of Au to Pd. This method was therefore applied in the present study. It can be seen from Figures 1 c and 1 d that the highest rate of methanol formation is achieved at a Pd/Au ratio of 8:1. Another important result is that the rate of carbon dioxide formation is relatively low at this Pd/Au ratio. The resulting selectivity toward methanol reached 6.03 %, which is about three times higher than the value obtained for the Pd cathode.

To better understand these reactions at the PdAu/C cathode, both fuel cell and catalyst tests were performed under various conditions. Figure 2 shows the cell voltage–current density curves of the fuel cell with the PdAu/C cathode in the temperature range 50–250 °C. A positive effect on the cell performance is seen upon addition of Au to Pd. For example, the OCV at 250 °C is 727 mV for the Pd/C cathode and 740 mV for the PdAu/C cathode, and the short-circuit current at 250 °C is 140 mA for the Pd/C cathode and 230 mA for the PdAu/C cathode. This effect is ascribed to a reduction of the polarization resistance of the cathode. Figures 3 a and 3 b show the rates of methanol and carbon dioxide formation,

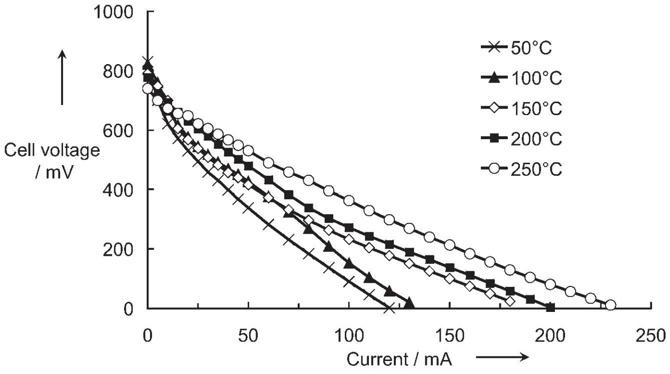

Figure 2. Cell voltage–current density curves of the fuel cell with a PdAu/C (Pd/Au = 8:1) cathode between 50 and 250 °C: H_2, Pt/C | $Sn_{0.9}In_{0.1}P_2O_7$ (1 mm) | PdAu/C, 50 % O_2 + 50 % CH_4.

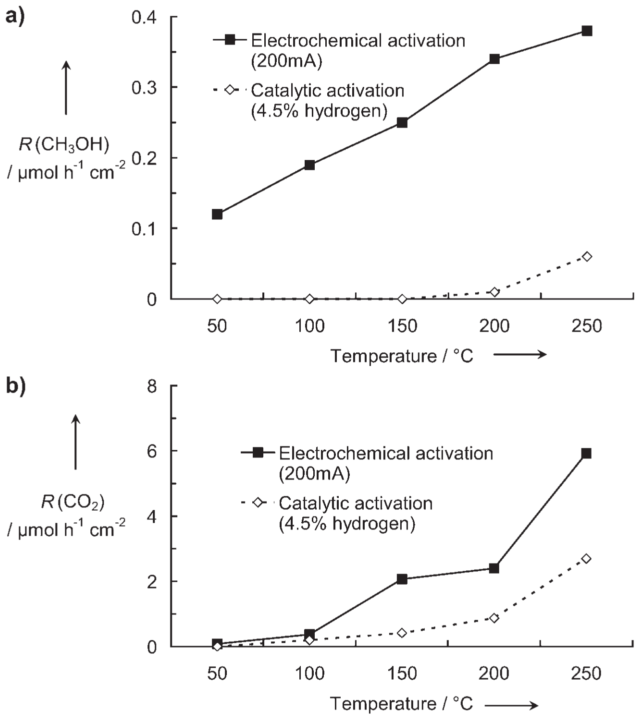

Figure 3. Rates of a) methanol and b) carbon dioxide formation at a PdAu/C (Pd/Au = 8:1) cathode between 50 and 250 °C. This figure includes the results for the catalytic reaction between gas-phase hydrogen, oxygen, and methane at the open-circuit voltage.

respectively, between 50 and 250 °C. The rates of formation of these gases increase with increasing temperature, although the temperature dependence is somewhat larger for carbon dioxide than for methanol. Consequently, the selectivity towards methanol becomes higher as the temperature decreases: 6.03 % (CH_4 conversion: 0.38 %) at 250 °C, 10.8 % (CH_4 conversion: 0.14 %) at 150 °C, and 60.0 % (CH_4 conversion: 0.012 %) at 50 °C.

It would be useful to compare the electrochemical activation of oxygen with the catalytic activation of oxygen, therefore gaseous hydrogen was added to the cathode gas outside the system. A hydrogen concentration of 4.5 % is equivalent to the amount of hydrogen produced by passing a current of 200 mA through the cell. The results of these studies are also included in Figures 3 a and 3 b. The rates of methanol and carbon dioxide formation with gas-phase hydrogen at the OCV were found to be considerably lower than those obtained by applying a current of 200 mA. In particular, no methanol was produced with gas-phase hydrogen at or below 150 °C. The difference observed between the two hydrogen species is indicative of a higher efficiency for electrochemical activation of oxygen than for its catalytic activation. One possible explanation for this difference is a shift of the cathode potential toward more negative voltages during the electrochemical activation—the cathode potentials at 200 mA are in the range −0.7 to 0.06 V (vs. normal hydrogen electrode (NHE)), which is more negative than the oxidation potential of hydrogen peroxide (0.68 V vs. NHE). Thus, it is possible that hydrogen peroxide is more stable under polarization conditions than under open-circuit conditions, which results in an enhancement of methanol formation.

In conclusion, this study has demonstrated that methane can be converted directly into methanol by raising the reaction temperature to above 80 °C. However, as shown in Figure 3, methanol is produced even at 50 °C, which suggests that low-temperature proton conductors, such as Nafion, could also be used as the electrolyte under similar conditions. Indeed, an electrochemical cell containing Nafion produces methanol and carbon dioxide at 50 °C, although only about half the amount produced with $Sn_{0.9}In_{0.1}P_2O_7$. This result means that the $Sn_{0.9}In_{0.1}P_2O_7$ electrolyte has no specific effect on methanol production other than allowing high proton conductivities above 80 °C and also suggests that this PdAu/C electrode can be utilized with various electrolytes.

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