Partial Oxidation of Methane: Continuous Production of Synthesis Gas over Rh/YSZ/Ag under Oxygen Supply

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Partially oxidized rhodium metal showed remarkable and stable activity for the partial oxidation of methane into synthesis gas by oxygen species transported through Rh/YSZ/Ag under 1 atm and at a low temperature of 773 K.

Recently, partial oxidation of methane into synthesis gas has been studied as a promising method for methane conversion.[1] Metals in group VIII such as Rh, Ni, Ru, Pt, Ir and Pd are active catalysts for the reaction (1).

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad (1)$$

This reaction is basically composed of reactions including complete oxidation of methane, reforming of methane by H_2O and CO_2, and the water gas shift reaction. The partial oxidation of methane into synthesis gas is normally performed at 800–1000 K, because the reforming reactions are highly endothermic. At 900 K, the equilibrium conversion of CH_4 to CO and H_2 is approximately 90% at 0.01–1 atm.

Schmidt *et al.*[2] recently suggested the possibility of the direct oxidation of methane to synthesis gas by using a Rh- or Pt-coated monolith catalyst at a short residence time, where Rh is superior to Pt because of the higher activation energy for OH formation from adsorbed hydrogen and oxygen on Rh (20 kcal mol^{-1}) (1 cal = 4.184 J) than on Pt (2.5 kcal mol^{-1}). We (U. T. group)[3] have studied the reaction pathway of eqn. (1), and found that adsorbed oxygen species on Rh/SiO_2 from gaseous oxygen can oxidize methane directly into synthesis gas. Further, an incorporation of oxygen from SiO_2 *via* Rh surface into the reaction products was observed in the reaction of adsorbed ^{18}O on Rh/SiO_2 with CH_4 at 673–873 K, *i.e.* spillover mechanism. Another of the authors (NIMC group) has studied solid electrolyte-aided oxidation of hydrocarbons using 8 mol% yttria-stabilized zirconia (YSZ) where $M_1|YSZ|M_2$ serves as an oxygen pump through which oxide ions can be transported from the cathode (M_2) to the anode (M_1).[4] When Au was used as the anode, propene and ethane were partially oxidized into acrylaldehyde and acetaldehyde, respectively, over an inert Au anode film under the oxygen pumping; this suggests that the oxygen species transported through YSZ onto Au surface was active for the selective oxidation.[4a,d] Here we report the behaviour of oxygen species generated on the Rh anode surface for the partial oxidation of methane under the oxygen pumping through Rh|YSZ|Ag.

An electrochemical reactor was constructed from an YSZ disc of diameter 32 mm and thickness 1 mm. Thin compact films of Ag (2.1 μm thick) and Rh (0.81 μm thick) were prepared as the cathode and the anode, respectively, on each face of the disk by vacuum evaporation.[4a] The two electrodes of the disk were connected with gold wires to an electrical circuit for controlling the oxygen transfer flux from the Ag cathode to the Rh anode across the YSZ by changing the applied voltage. An oxygen pressure of 101.3 kPa was maintained on the cathode of the cell. A gaseous mixture of methane and nitrogen was passed over the anode side for testing the activity of oxygen species generated on the Rh anode film. The products in the effluent gas were analysed by GC using a thermal conductivity detector.

Cyclic voltammetries were carried out under various atmospheres in the anode room; electric current shows the transportation rate of oxide ions *via* 4 electrons reduction–oxidation steps across the YSZ, which in turn inform us about the catalytic activity of the Rh anode. In a blank test where nitrogen gas alone flowed on the Rh anode at 773 K, a sigmoidal *i–E* curve was observed, *i.e.* electric current appeared at 0.25 V, increased at about 0.5–0.8 V, and then reached a constant value above 1.25 V. Thus, in contrast to the linear *i–E* dependency observed over the inert Au anode of Au|YSZ|Ag system,[4a] a clear over-potential was observed over the Rh anode in Rh|YSZ|Ag system, suggesting that O_2 associative desorption is the rate-determining step. When the methane (0.37%)–nitrogen mixture was passed at a rate of 1 l h^{-1} across the Rh anode at 773 K, the anodic overpotential disappeared; a large increase in the current was observed only by closing the electric circuit without no applied potential. In the cyclic voltammogram, a clear hysteresis was observed; when the potential was decreased, the current did not retrace the pathways observed during the initial potential increase but showed higher values at the potentials below 1 V. The lower level of oxygen transportation during the initial potential increase might be due to either an elimination of deposited carbon over Rh or the oxidation of Rh surface during the oxygen pumping. When the Rh anode surface was treated with air (1 l h^{-1}) for 30 min at 773 K, a remarkable increase in the current as well as the activity for synthesis gas production was observed together with an enhanced hysteresis at the potentials below 1 V.

Product distributions together with the amount of CH_4 during the cyclic voltammetry after the air treatment are shown in Fig. 1. When the potential increased, the production rates of CO_2, CO and H_2 increased. At the potential of 0.035 V, each production rate of CO_2, CO and H_2 was 0.012, 0.010 and 0.017 mmol h^{-1}, respectively, and reached 0.062, 0.017 and 0.034 mmol h^{-1} at 2.0 V. When the potential decreased from 2.0 to 0 V, the production rate of CO_2 decreased to 0.023 mmol h^{-1} as expected, while those of CO and H_2 increased to 0.036 and 0.084 mmol h^{-1}, respectively, in spite of the decrease in the current. The final values at 0 V correspond to 25.0% of H_2 yield, 21.7% of CO yield and 13.5% of CO_2 yield

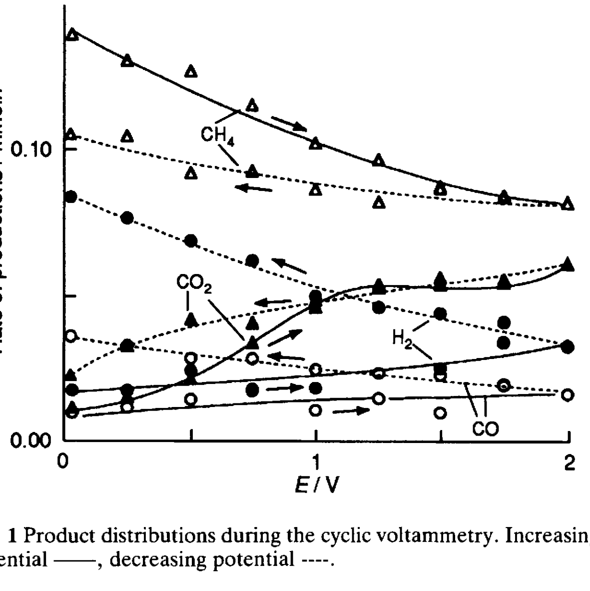

Fig. 1 Product distributions during the cyclic voltammetry. Increasing potential ——, decreasing potential ----.

at 37.0% of CH_4 converson. The potential dependency of the production rate of CO_2 showed a hysteresis similar to that of the electric current, suggesting that CO_2 is directly produced by the oxygen species pumped through the YSZ.

It is most likely that oxygen evolves through the three phase boundary, *i.e.* Rh-YSZ-atmosphere, and then migrates to the Rh surface by a reverse spillover mechanism. The fact that both the air pretreatment and the oxygen pumping caused an increase in the activity for synthesis gas production strongly suggests an important role of the adsorbed oxygen species over the Rh surface in the synthesis gas production. This well coincides with the result previously obtained by us,[3] the adsorbed oxygen species over Rh metal is definitely important in the synthesis gas production from CH_4. A moderate supply of oxygen species through the YSZ to the Rh surface is the most effective for the synthesis gas production. It has thus been found that the partially oxidized Rh anode catalyses continuously the direct oxidation of CH_4 into synthesis gas by the oxygen species supplied through the Rh|YSZ|Ag cell system.

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