Conversion of methane to synthesis gas over Pt electrode in a cell with solid oxide electrolyte

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Electrochemical conversion of methane has been studied over a Pt electrode in a solid oxygen conducting electrolyte cell at 800°C. It was found that the Pt electrode is an active electrode-catalyst in the partial oxidation of methane to syngas. Carbon monoxide selectivity and yield of 85 and 65% respectively were reached. Potentialities of the electrochemical route for production of syngas from methane against the conventional catalytic way are briefly discussed.

Keywords: methane partial oxidation; syngas; solid oxide fuel cell

1. Introduction

Catalytic steam reforming of methane is a main industrial way to produce syngas [1]. Recently however, the attention is attracted to alternative processes for syngas production, i.e. the partial catalytic oxidation of methane:

$$CH_4 + 0.5O_2 \rightleftharpoons CO + 2H_2$$

The studies involved are presented in many papers well reviewed in ref. [2]. CH_4 partial oxidation to syngas is usually performed at high temperatures (700–800°C) on supported metal catalysts, including platinum-containing systems [3–5].

In the present study we report the results of electrochemical oxidation of methane to syngas over a Pt electrode-catalyst in a high temperature cell with a solid oxygen conducting electrolyte, viz. yttria stabilized zirconia (YSZ). Schematically such a cell is similar to the solid oxide fuel cell (SOFC):

$$CH_4, Pt \mid 0.9ZrO_2 + 0.1Y_2O_3 \mid Pt, air$$

In the electrochemical oxidation of methane in the SOFC system the methane flow did not contain oxygen. Oxygen was fed directly into the reaction zone by passing an anodic current through the cell. In this case oxygen ions, O^{2-}, are formed on the air electrode (cathode) according to the reaction:

$$0.5O_2 + 2e \rightarrow O^{2-}$$

Then, these ions transfer to the electrode-catalyst (anode) through the YSZ electrolyte. On the anode they can either discharge forming O_2 or oxidize methane:

$$O^{2-} \rightarrow 0.5O_2 + 2e$$

$$CH_4 + O^{2-} \rightarrow CO + 2H_2 + 2e$$

Note that recently syngas production by electrochemical CH_4 oxidation was proved to occur in the SOFC system on Rh [6] and Fe [7] electrode-catalysts. Oxidized Rh was found to be more active than reduced Rh in the production of syngas. Iron exhibited an opposite behavior, and formation of carbon on the Fe electrode-catalyst took place.

2. Experimental

Fig. 1 shows a draft of the SOFC system. It consisted of a tube of YSZ electrolyte closed at one end. The electrolyte tube was 100 mm in length, 10 mm in diameter and had a wall thickness of 0.6 mm. The Pt electrodes are

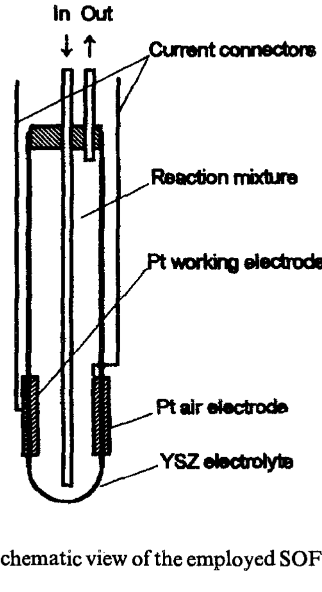

Fig. 1. Schematic view of the employed SOFC system.

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supported on the inner and outer surface of the tube. The geometrical area of the electrodes was 3 cm^2. The Pt amount was 10 mg/cm^2.

The outer surface of the tube was blown with air. A mixture of methane and He or N_2 was fed inside. The electric current flowing through the cell was controlled by a potentiostat. The techniques used for the electrochemical measurements have been described in detail elsewhere [8]. The composition of the gas mixture before and after passing through the cell was analyzed by on-line gas chromatography with a molecular sieve and Porapak-Q columns.

The experiments were performed at 800°C, atmospheric pressure and a fixed rate of CH_4 + He (N_2) flow of 0.5 cm^3/s. The methane concentration varied from 3.6 to 14 vol%. The anodic current flowing through the cell was also fixed and equaled 0.5 A, which corresponds to 1.3 μmol O_2/s of electrochemical oxygen supply to the reaction zone.

The Pt electrodes were prepared by calcination of a Pt paste, containing 5 wt% of YSZ, deposited on the surface of the tube in air at 950°C. To obtain stable electrochemical cell characteristics, the electrodes were pretreated with both the anodic and cathodic current in air at 850°C for 20 h. According to the data obtained by SEM, the Pt electrodes were porous and their thickness was ca. 10 μm.

3. Results and discussion

Fig. 2 shows the conversion of CH_4 and outlet concentrations of CO, CO_2 and H_2 as functions of the inlet methane concentration, $[CH_4]_{in}$, in the electrochemical methane oxidation. The conversion of oxygen electrochemically pumped into the reaction zone was almost complete, its outlet concentration being low (< 0.05 vol%) and not shown in fig. 2.

Obviously, as the inlet methane concentration increases from 3.6 to 11.5 vol% (corresponding to inlet ratios of the CH_4 and O_2 flows, F_{CH_4}/F_{O_2}, of ca. 0.5–1.7), CH_4 conversion decreases from 100 to 75%, and the outlet CO_2 concentration decreases from 3.2 to 1.2 vol%. Meanwhile, the outlet concentrations of CO and H_2 increase, their ratio $[H_2]_{out}/[CO]_{out}$ being close to 2.

Using the data of fig. 2, we calculated the selectivity of CO formation, $S_{CO} = 100[CO]_{out}/([CO]_{out} + [CO_2]_{out})$, and CO yield, $Y_{CO} = 100[CO]_{out}/([CO]_{out} + [CO_2]_{out} + [CH_4]_{out})$. Fig. 3 shows CO selectivity and yield versus the inlet CH_4 concentration. Obviously, as $[CH_4]_{in}$ (or F_{CH_4}/F_{O_2}) increases, S_{CO} grows from 0 to 85% and Y_{CO} increases from 0 to 65%.

Therefore, in the electrochemical methane oxidation the Pt electrode can behave as an active electrode-catalyst of both deep methane oxidation (low ratio $F_{CH_4}/F_{O_2} \approx 0.5$) and of partial methane oxidation to syngas (high ratio $F_{CH_4}/F_{O_2} \approx 1.7$) depending on the operation conditions.

However (see fig. 3), the experimental values of S_{CO} and Y_{CO} are lower than expected from the thermodynamic equilibrium ones calculated assuming that the equilibrium composition is determined by the reactions

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Moreover, note that for $[CH_4]_{in}$ higher than 11.5 vol% coking of the Pt electrode does occur. This is evidenced from the following observations. At $[CH_4]_{in}$ < 11.5 vol% there is no imbalance with respect to carbon, in a 100 h operation neither does the electrode-catalyst lose its activity nor do the current–voltage characteristics of the cell change. At $[CH_4]_{in}$ > 12 vol%, however, we observe

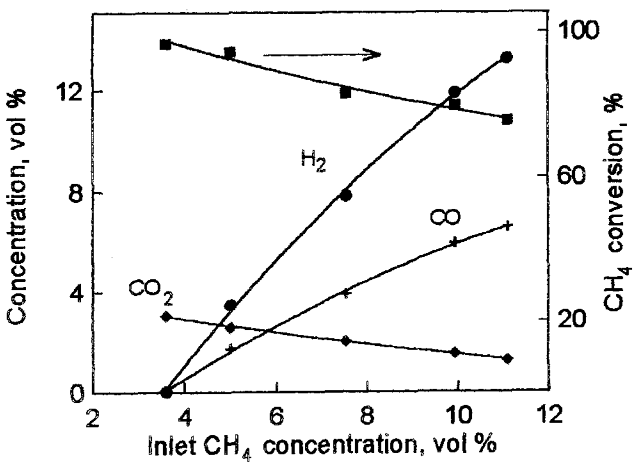

Fig. 2. Methane conversion and outlet concentrations of H_2, CO and CO_2 versus inlet CH_4 concentration in the electrochemical oxidation of CH_4. T = 800°C; anodic current = 0.5 A.

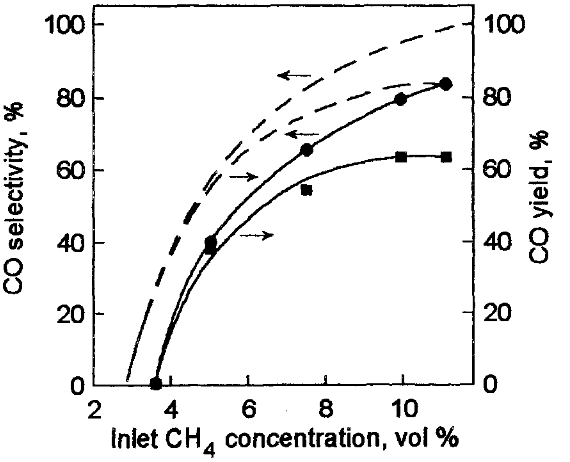

Fig. 3. CO selectivity and yield versus inlet CH_4 concentration in the electrochemical oxidation of CH_4. T = 800°C; anodic current = 0.5 A. (—) Experiment; (– – –) calculated thermodynamic equilibrium values.

a carbon imbalance, the electrode-catalyst activity falls, and the electrochemical cell characteristics become worse.

The data obtained do not allow us to judge about the mechanistic scheme of the electrochemical oxidation of methane to syngas, i.e., whether it is a "combustion and reforming reaction mechanism" or a "direct partial oxidation mechanism" [2]. Further investigations are required for this purpose.

Nevertheless, we would like to point out some expected advantages of the electrochemical oxidation of methane to syngas in comparison to the conventional partial catalytic methane oxidation to syngas. So, at electrochemical oxidation of methane to syngas in SOFC systems (i) it is possible to produce not only syngas but electricity as well, thus, the SOFC is able to cogenerate chemicals ($CO + H_2$) and electricity; (ii) the probability of the reaction mixture to explode decreases, since fed methane and air are separated by the electrolyte, and it is easy to control the oxygen amount in the reaction zone by regulating the electric current passing through the SOFC system; (iii) when air is used as an oxidant, no nitrogen accumulates in the reaction zone, since oxygen is separated from the other components of air just at the stage of its electrochemical supply to the reaction zone.

Lastly, note that it is possible to use water vapors and carbon dioxide in the electrochemical oxidation of methane to syngas, e.g., by arranging the following SOFC systems:

$$CH_4, \text{electrode} \mid \text{YSZ} \mid \text{electrode}, H_2O$$

$$CH_4, \text{electrode} \mid \text{YSZ} \mid \text{electrode}, CO_2$$

In these systems, the cathodic polarization of electrodes blown with H_2O and CO_2 will cause the electrolysis of these gases:

$$H_2O + 2e \rightarrow H_2 + O^{2-} \qquad (1)$$

$$CO_2 + 2e \rightarrow CO + O^{2-} \qquad (2)$$

The O^{2-} ions formed will transfer through YSZ to the anode (the electrode blown with CH_4), where they will oxidize methane to syngas:

$$CH_4 + O^{2-} \rightarrow CO + 2H_2 + 2e \qquad (3)$$

Obviously, summed-up the semireactions (1) + (3) and (2) + (3) represent the overall chemical reactions of steam and carbon dioxide reforming of methane. According to refs. [1,2] it is possible to perform these reactions in a conventional catalytic way. However, their electrochemical performance allows arranging the required ratio CO/H_2 in the syngas via mixing outlet gas flows from the anodic and cathodic compartments of the SOFC system.

Taking all the above into consideration, we believe that the electrochemical oxidation of CH_4 to syngas in SOFC systems is rather promising. It is reasonable to focus the efforts on the study of the mechanism of electrochemical CH_4 oxidation and to look for more perfect electrode-catalysts.

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