ELSEVIER

Catalysis Today 42 (1998) 337–340

CATALYSIS TODAY

Syngas production from methane in an electrochemical membrane reactor

V.A. Sobyanin*, V.D. Belyaev, V.V. Gal'vita

Boreskov Institute of Catalysis, 630090, Novosibirsk-90, Russian Federation

Abstract

Electrocatalytic conversion of methane over Ag-, Pt-, Ni- and Pt+CeO_2-based electrode-catalysts in a cell with a solid oxygen conducting electrolyte:

$$CH_4, \text{electrode-catalyst}|0.9ZrO_2 + 0.1Y_2O_3|Pt + PrO_2, \text{air}$$

was studied at 660–850°C and the ratio of methane and electrochemically pumped oxygen flows of 0.8–2.0. Unlike Ag and Pt+CeO_2 electrodes, the Ni and Pt electrodes were found to be active electrode-catalysts for partial oxidation of methane to syngas with the concentration ratio of $[H_2]/[CO]\approx 2$.

Keywords: Methane; Partial oxidation; Syngas; Solid oxide electrolyte cell

1. Introduction

This paper is a brief review of our current research activity on electrocatalytic oxidation of methane to synthesis gas over Ag-, Pt-, Ni-, and Pt+CeO_2-based electrode-catalysts in an electrochemical reactor with an yttria stabilized zirconia (YSZ) electrolyte-membrane. Schematically, such a reactor is similar to the solid oxide fuel cell (SOFC):

$$CH_4 + N_2, \text{metal electrode-catalyst}|YSZ|Pt, \text{air}.$$

At electrocatalytic oxidation of methane in the SOFC system, the methane flow did not contain oxygen. It was fed directly into the reaction zone by passing anodic current through the cell. In this case oxygen ions O^{-2} are formed at the air electrode (cathode). Then, these ions transfer to the electrode-catalyst (anode) through the YSZ electrolyte-membrane. On the anode they can either discharge to produce O_2 or oxidize methane.

The electrocatalytic oxidation of CH_4 in SOFC system is a new way for syngas production from methane. The way provides a number of advantages over the catalytic oxidation of methane to syngas [1,2]. The studies in this field are interesting both for elucidation of a feasibility of electrocatalytic conversion of methane to syngas and for development of natural gas fueled SOFC capable of cogenerating electricity and syngas [3].

2. Experimental

An electrochemical membrane reactor was a YSZ electrolyte tube with two porous metallic electrodes

---

*Corresponding author. Fax: +7 383 2 355756; e-mail: sobyanin@catalysis.nsk.su

0920-5861/98/$32.00 © 1998 Elsevier Science B.V. All rights reserved.
PII S0920-5861(98)00111-4

deposited on its inner and outer surfaces. An electrode-catalyst was inside the YSZ tube and the Pt+PrO_2 air electrode was outside it. The geometrical area of the electrodes was 3 cm^2 and their thickness was ca. 10–30 µm. The cell design was similar to that used in [2].

Electric current (I) passing through the cell was controlled by a potentiostate. Oxygen flow through the electrolyte was calculated by the equation: $V_{O_2} = I/4F$, where F is the Faraday constant. Details of electrochemical measurements are given elsewhere [4].

Electrocatalytic conversion of methane was studied at 660–850°C, atmospheric pressure and the rate of feeding of the CH_4–N_2(He) mixture of 0.36–2 cm^3/s. The concentration of methane was varied from 3.5 to 12 vol%. The inlet ratio of methane and electrochemically supplied oxygen flows (CH_4/O_2) was varied from 0.8 to 2. The compositions of the inlet and outlet gas mixtures were analyzed by on-line gas chromatography [2].

3. Results and discussion

Electrocatalytic oxidation of methane to syngas was achieved over Pt [1,2], Fe [5] and Rh [6] electrode-catalysts. Table 1 presents CH_4 conversions and CO yields produced by electrocatalytic oxidation of methane over Ag, Pt–CeO_2, Pt, Ni and Fe electrode-catalysts. These values were obtained at the inlet ratio of the methane and oxygen flows close to the stoichiometry ($CH_4/O_2 \approx 2 \pm 0.2$). Methane diluted with inert gas ($[CH_4]_O \leq 12$ vol%) was used in the most cases, the inlet flow of 100 vol% of methane was tested only in [1]. Practically complete conversion of electrochemically pumped oxygen was observed on all the electrodes except Ag.

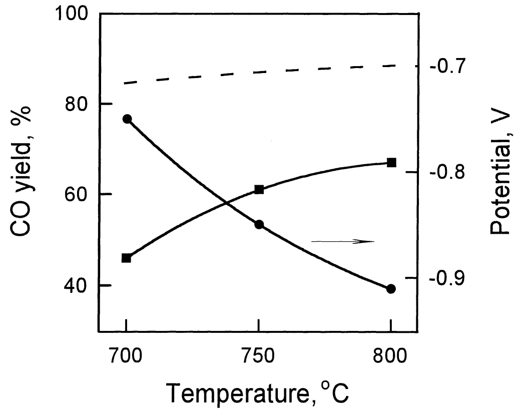

Fig. 1. Effect of temperature on CO yield and electrode potential at electrocatalytic oxidation of CH_4 over Pt electrode. $[CH_4]_O$= 6.5 vol%; I=0.3 A; flow rate=0.43 cm^3/s; CH_4/O_2=1.5. Solid lines – experiment; dashed line – calculated thermodynamic equilibrium values of CO yield.

Table 1 indicates low yields of CO on Ag and Pt–CeO_2 electrodes and considerable yields of CO on Pt, Ni and Fe electrodes. The high electrocatalytic activity of Pt, Ni and Fe electrodes in formation of syngas is quite natural since those metals are known as good catalysts for regular catalytic oxidation of methane to syngas.

So, the electrodes made of catalytically active metals for syngas production possess high electrocatalytic activity, too. Let us discuss the effects of temperature and current on electrocatalytic oxidation of methane to syngas over Pt and Ni electrodes.

In Figs. 1 and 2 the CO yield are plotted against temperature at electrocatalytic oxidation of CH_4 over Pt and Ni electrodes. Practically complete conversion

Table 1
Different electrode-catalyst performance in the electrocatalytic oxidation of methane

Electrode	T (°C)	CH_4 conversion (%)	CO yield (%)	Ref.
Ag	800	19	~0	This work
Pt-2 wt% CeO_2	800	28	~1	This work
Pt	800	75	69	[2] and this work
	1100	~100	97	[1]
Ni	800–850	93	82–88	This work
Fe	950	74.5	73	[5]

The table does not show the data on Rh electrode [6]. They indicate formation of syngas at as low temperature as 500°C, only.

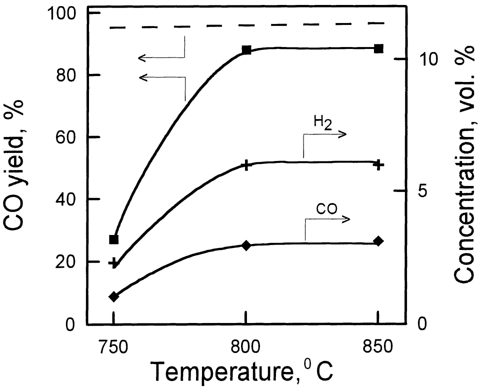

Fig. 2. Effect of temperature on CO yield and concentrations of H_2 and CO at electrocatalytic oxidation of CH_4 over Ni electrode. $[CH_4]_O$=3.5 vol%; I=0.11 A; flow rate=0.36 cm^3/s; CH_4/O_2=1.8. Solid lines – experiment; dashed line – calculated thermodynamic equilibrium values of CO yield.

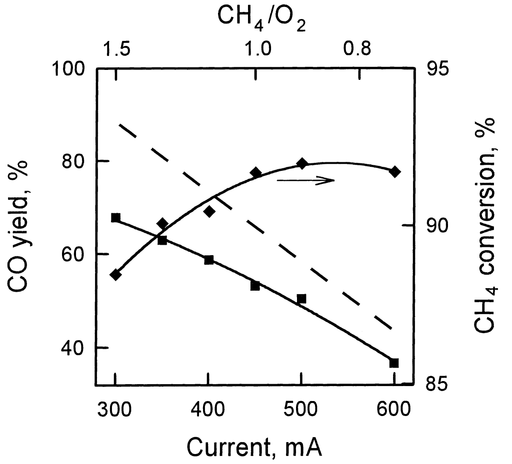

Fig. 3. Effect of current on CO yield and CH_4 conversion at electrocatalytic oxidation of CH_4 over Pt electrode. T=800°C; $[CH_4]_O$=6.5 vol%; flow rate=0.43 cm^3/s. Solid lines – experiment; dashed line – calculated thermodynamic equilibrium values of CO yield.

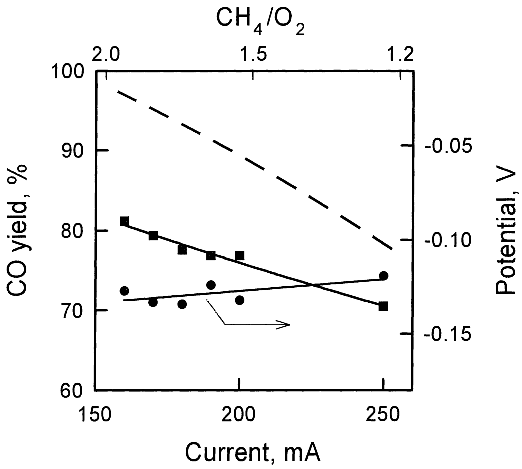

Fig. 4. Effect of current on CO yield and electrode potential at electrocatalytic oxidation of CH_4 over Ni electrode. T=800°C; $[CH_4]_O$=5.4 vol%; flow rate=0.36 cm^3/s. Solid lines – experiment; dashed line – calculated thermodynamic equilibrium values of CO yield.

of electrochemically pumped oxygen was observed. Elevation of temperature is seen to cause an increase in CO yield. In particular, CO yield of 65% and 85% were reached over Pt and Ni electrode, respectively. The ratio of the outlet concentrations of H_2 and CO ($[H_2]/[CO]$) was close to 2 for Ni electrode (Fig. 2) and the same for Pt electrode [2]. The experimental values of CO yields are lower than those expected from the thermodynamic equilibrium (Figs. 1 and 2), calculated assuming that the equilibrium composition is determined by the reactions:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

$$CH_4 + H_2O = CO + 3H_2$$

$$CO + H_2O = CO_2 + H_2$$

Figs. 3 and 4 show CO yield versus anodic current at CH_4 electrocatalytic oxidation over Pt and Ni electrodes. The inlet concentration of methane was kept constant, so that an increase in current was equivalent to a decrease in the inlet ratio of the methane and oxygen flows (CH_4/O_2). Variations in this ratio are plotted in Figs. 3 and 4. The conversion of oxygen was close to 100% at all values of current.

Increasing current or decreasing the CH_4/O_2 ratio are seen to cause a decrease in CO yields (Figs. 3 and 4), and a slight increase in CH_4 conversions (Fig. 3). The experimental dependencies of Y_{CO} on current are seen to run somewhat below than their thermodynamic equilibrium ones, however they behave in the same manner as those expected from thermodynamic equilibrium consideration.

The electrocatalytic way of production of syngas from methane in SOFC system is able to cogenerate electricity and chemicals ($CO+H_2$). The results presented in Figs. 1 and 4 support this conclusion. One can see that under the conditions of syngas formation Pt and Ni electrode potentials versus air electrode are negative values.

Finally, it should be mentioned, that no change in the electrocatalytic activity of Pt and Ni electrodes, no imbalance with respect to carbon (with ±5% accuracy) and current–voltage characteristics of the SOFC systems were observed during electrocatalytic oxidation of methane (ca. 100 h, 700–850°C, inlet ratio of methane and electrochemically pumped oxygen flows (CH_4/O_2) ranging between 1.2 and 1.9). The observations allow us to conclude that the Pt and Ni electrodes are stable under conditions of syngas formation.

Based on the results obtained SOFC systems with Pt- and Ni-based electrode-catalysts seem rather promising to electrocatalytic syngas formation from methane.

Acknowledgements

The authors are grateful to INTAS (project 94-3056) for supporting a part of this research.

References

[1] T.J. Mazanec, T.L. Cable, J.G. Frege Jr., Solid State Ionics 53 54 55 56 (1992) 111.

[2] V.V. Gal'vita, V.D. Belyaev, V.N. Parmon, V.A. Sobyanin, Catal. Lett. 39 (1996) 109.

[3] C.G. Vayenas, S. Bebelis, I.V. Yentekakis, H.G. Lints, Catalysis Today 11 (1992) 303.

[4] O.A. Mar'ina, V.A. Sobyanin, V.D. Belyaev, Elektrochimija 26 (1990) 1413.

[5] H. Alqahtany, D. Eng, M. Stoukides, J. Electrochem. Soc. 140 (1993) 1677.

[6] K. Sato, J. Nakamura, T. Uchijima, T. Nayakawa, S. Hamakawa, T. Tsunoda, K. Takehira, J. Chem. Soc., Faraday Trans. 91 (1995) 1655.