Oxidation of methane over platinum in a solid proton-conducting electrolyte cell

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Studies of the complete oxidation of methane on a Pt electrode-catalyst in the cell with a solid proton-conducting electrolyte ($CH_4 + O_2$, Pt | $SrCe_{0.92}Dy_{0.08}O_3$ | Pt, $H_2O + N_2$) were carried out. The non-Faradaic effect of electrochemical hydrogen pumping on the rate of methane oxidation has been demonstrated. The induced change in the reaction rate at anodic polarization of a Pt electrode-catalyst was over two orders of magnitude higher than the rate of hydrogen pumping from the reaction zone through the electrolyte.

Keywords: oxidation of methane; platinum electrode-catalyst; proton-conducting solid electrolyte

1. Introduction

In heterogeneous catalysis much attention is focused on the catalytic behavior of platinum in the oxidation of methane [1–3]. Recently, this reaction has been studied [4–6] on a Pt electrode-catalyst in a solid oxygen-conducting electrolyte cell of the type

$$CH_4 + O_2, Pt \mid ZrO_2 + 8-10\ \mathrm{mol}\%\ Y_2O_3 \mid Pt, O_2 .$$

The current passing through the cell (oxygen flow through the electrolyte) was found to change remarkably and reversibly the catalytic activity of platinum. The induced change in the catalytic rate far exceeded the rate of oxygen pumping through the electrolyte. This phenomenon, referred to as the non-Faradaic electrochemical modification of catalytic activity (NEMCA) [4], is of great interest to heterogeneous catalysis since the current passing through the cell or electrode potential allows the control of catalytic activity of the electrode supported on the electrolyte.

This paper is devoted to investigation of the influence of electrochemical hydrogen pumping on CH_4 oxidation on the platinum electrode-catalyst in the cell with the solid proton-conducting electrolyte based on $SrCeO_3$:

$$CH_4 + O_2, Pt \mid SrCe_{0.92}Dy_{0.08}O_3 \mid Pt, H_2O + N_2 .$$

The experiment is shown schematically in fig. 1. Flows of gas mixtures $CH_4 + O_2 + N_2$ and $H_2O + N_2$ were fed to an electrode-catalyst and a counter electrode, respectively. With an open circuit in the cell a typical heterogeneous catalytic reaction occurs on the electrode-catalyst:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O . \tag{1}$$

Upon passing current through the cell the electrode-catalyst can be, depending on the polarity of the applied current, either anode or cathode which results in hydrogen pumping from or to the reaction zone through the electrolyte. The effect of electrochemical pumping of hydrogen on the CH_4 oxidation rate was the subject for study.

Note that the doped strontium cerate $SrCe_{1-x}M_xO_{3-x}$ (where $x = 0.05$–0.1 and $M = Yb, Sr, Y, Nb, Sm, Dy$) was shown in refs. [7–9] to possess a high protonic conductivity and is widely used as a proton-conducting electrolyte in hydrogen sensors [9], fuel cells [10,11] and steam electrolysers [12].

2. Experimental

The electrochemical cell was a tube made of yttria-stabilized zirconia. A solid hydrogen-conducting electrolyte disk of composition $SrCe_{0.92}Dy_{0.08}O_{3-x}$ was cemented with a glue to one of the tube ends. Porous platinum electrodes were deposited onto each face of the disk. A working electrode was inside the tube, and a counter electrode outside of it. The disk was 12 mm in diameter and 1.5 mm in

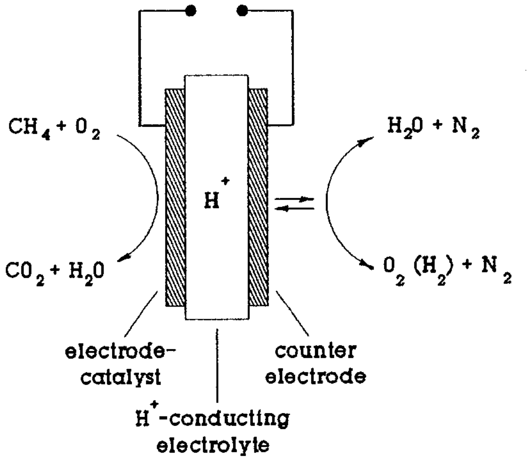


Fig. 1. Schematic diagram for the oxidation of methane in an electrochemical cell with solid proton-conducting electrolyte.

thickness. Geometrical areas of the electrodes were ca. 0.5 cm^2. There was 10 mg Pt loading in an electrode. A quartz jacket, equipped with gas supply lines, covered the tube to provide a controllable atmosphere above the counter electrode.

The reaction of methane oxidation was studied at ambient pressure and 600–700°C. The methane concentration varied from 3 to 16 vol% and O_2 concentration was kept constant (20 or 84 vol%). A flow of gas mixture $CH_4 + O_2 + N_2$ was fed to the Pt working electrode (inside the tube) at the velocity 0.3–1 cm^3/s, while the counter electrode was fed with a $N_2 + H_2O$ mixture. The electric current (I) flowing through the cell was controlled by a potentiostat. The composition of the gas mixture before and after passing through the cell was analyzed by chromatography. Carbon dioxide and water were observed among the reaction products. Conversion of both methane and oxygen in the course of all the runs was low, not exceeding 5%. The rate of the formation of carbon dioxide W (µmol/min) was calculated by

$$W = 25CV ,$$

where C is the CO_2 concentration, in vol%, and V is the space velocity of the gas mixture, in cm^3/s.

The hydrogen flow through the electrolyte (V_{H_2}) upon passing current I through the cell was determined as

$$V_{H_2} = I/2F , \tag{2}$$

where F is the Faraday constant. This equation is true provided that the electrolyte possesses conductivity with the proton transfer number being equal to unity. Though, as shown before [7–9], electrolytes based on $SrCeO_3$ can possess proton- and hole-type conductivities simultaneously under certain experimental conditions. In this respect the electrolyte used in our work is not an exception. Among others, the results we obtained in studies of steam electrolysis in the same cell as that used for methane oxidation argue in favor of this conclusion.

The steam electrolysis experiments were as follows. A flow of N_2 was fed to one of the electrodes and a flow of the $N_2 + H_2O$ mixture to the other one. The electrode blown with N_2 was then cathodically polarized. The hydrogen evolution rate was calculated from the concentration of hydrogen (determined chromatographically) and the flow rate of nitrogen. Fig. 2 shows the hydrogen evolution rate as a function of current passing through the cell. The hydrogen evolution rate is close to the theoretical value calculated from the Faraday law, eq. (2), (solid line) in the low current limit for a proton transport number equal to unity. At high current ($\sim$ 10 mA) the hydrogen evolution rate deviates from its theoretical value. The proton transport number (the ratio of the observed value of hydrogen evolution to the theoretical one) was above 0.90 at I = 10 mA.

By analogy with refs. [7–9,12], we think the oxygen evolved during electrolysis brings about hole-type conductivity, e.g. due to the formation of holes by the reaction:

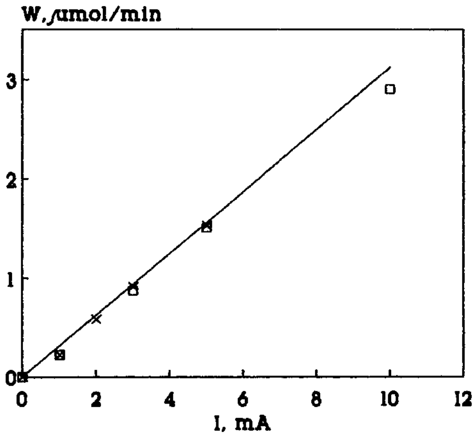


Fig. 2. Hydrogen evolution rate versus current under electrolysis of steam. (×) 600°C; (□) 700°C. Solid line shows the theoretical rate.

$$O_2 + 4H_v^+ \rightleftharpoons 2H_2O + 4h_v^+ , \qquad (3)$$

where H_v^+ and h_v^+ are a proton (a hydrogen defect) and an electron hole in the bulk of an electrolyte, respectively.

Thus our results prompt us to propose that the real flow of hydrogen through the electrolyte may be less than that calculated from Faraday's law.

3. Results and discussion

Fig. 3 shows the galvanostatic transient rate of CO_2 formation at CH_4 oxida-

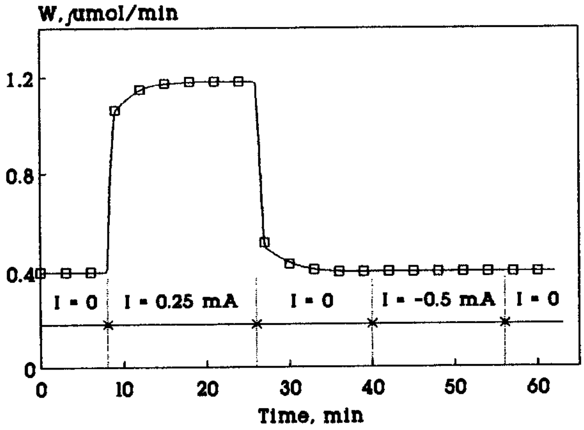


Fig. 3. Transient galvanostatic effect of applying an anodic current of 0.25 mA and a cathodic current of −0.5 mA on the rate of CO_2 formation under methane oxidation, $T = 645$°C, $[O_2] = 20$ vol%, $[CH_4] = 14$ vol%.

tion on Pt electrode upon applying anodic ($I = 0.25$ mA) and cathodic ($I = -0.5$ mA) currents. One can see that the cathodic current, i.e. hydrogen pumping to the reaction zone through the electrolyte, brings about no change in the rate of CO_2 formation with respect to its open-circuit value ($I = 0$). Anodic current, i.e. hydrogen pumping from the reaction zone through the electrolyte, leads to an enhancement of the reaction rate. Upon applying an anodic current of 0.25 mA the reaction rate increases from 0.4 μmol/min at $I = 0$ to a new steady-state value equal to 1.2 μmol/min. This new value of the reaction rate was kept during the longest period of current action (180 min). After the anodic current passing through the cell had been turned off, the reaction rate returned to its initial value at $I = 0$. Turning the current on again resulted in the same phenomenon as just discussed. Therefore, there is a reversible effect of current on the reaction rate. The increase of the reaction rate upon applying an anodic current was observed under all the experimental conditions employed in the present work.

Figs. 4 and 5 show examples of the effect of current passing through the cell on the CO_2 formation rate during methane oxidation at 600°C ($[O_2]/[CH_4] \approx 6.5$) and at 645°C ($[O_2]/[CH_4] \approx 1.4$). All results reported here were obtained under galvanostatic mode of cell operation and after the achievement of steady-state potential and rate values. It is seen that the cathodic current ($I < 0$) causes nearly no change in the reaction rate with respect to its open circuit value. Application of anodic current ($I > 0$) leads to the enhancement of the reaction rate at both 600°C (fig. 4) and 645°C (fig. 5). A sharp enhancement is observed upon minor increase of the anodic current upto 0.001 mA at 600°C and upto 0.05 mA at 645°C. With further increase of the anodic current the rate changes only slightly and goes to a plateau.

Let us discuss the effect of anodic current on the reaction rate in more detail.

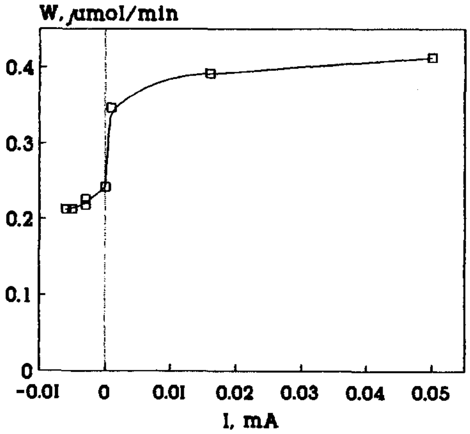


Fig. 4. Effect of the applied current on the rate of CO_2 formation under methane oxidation. $T = 600$°C, $[O_2] = 84\%$, $[CH_4] = 13$ vol%.

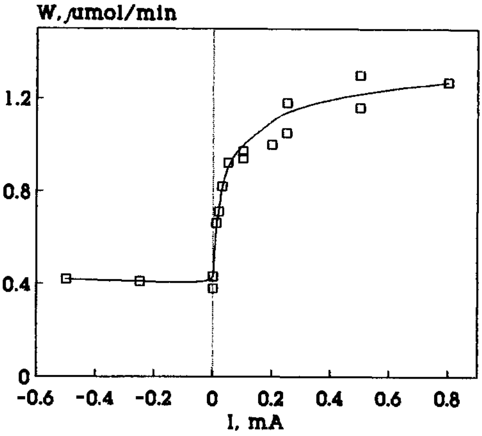


Fig. 5. Effect of the applied current on the rate of CO_2 formation under methane oxidation. $T = 645°C$, $[O_2] = 20\%$, $[CH_4] = 14$ vol%.

Under anodic polarization of the Pt electrode-catalyst the catalytic methane oxidation (eq. (1)) is coupled with electrochemical oxidation of hydrogens to protons:

$$H_s \rightarrow H_V^+ + e, \qquad (4)$$

where H_s is an adsorbed hydrogen atom and H_V^+ is a proton in the bulk of solid electrolyte. Note that hydrogen atoms H_s can be generated by dissociative adsorption of CH_4 on the electrode. The protons formed are then transferred through the electrolyte towards the counter electrode where they are reduced to hydrogen:

$$2H_V^+ + 2e \rightarrow H_2 .$$

Hydrogen pumping from the reaction zone through the electrolyte is thus achieved.

Analysis of the data presented in figs. 3–5 shows that with the anodic current applied the increase of the reaction rate ($\Delta r = r - r_0$, where r and r_0 are reaction rates at $I \neq 0$ and $I = 0$, respectively) is far above the rate of electrochemical oxidation of hydrogen or, that is the same, the rate of hydrogen pumping from the reaction zone through the electrolyte calculated by eq. (2). The $\Delta r/(I/2F)$ ratio decreases with the increase of the anodic current and, from data presented in figs. 4 and 5, varies from 330 to 10 and from 70 to 3, respectively. Thus, hydrogen pumping from the reaction zone was found to cause non-Faradaic changes, or the NEMCA effect, in the CH_4 oxidation rate on the Pt electrode-catalyst deposited on the solid proton-conducting electrolyte.

The nature of the NEMCA effect was discussed in a number of publications. According to ref. [4], the essence of the NEMCA effect consists in the fact that, during polarization of the metal electrode deposited on the solid oxygen-conducting electrolyte, i.e. when current is passing through the cell, the electrode work function changes. This leads to changes in the strength of the chemisorptive bond of adsorbed oxygen and, hence, in catalytic properties of the electrode for oxidation reactions. We consider this idea questionable since the strength of the chemisorptive bond of adsorbed oxygen on the electrode was shown, using the oxygen isotope exchange technique, not to change under the electrode polarization [13].

The non-Faradaic effect of current on the rate of CO oxidation on Pt and Au electrode-catalysts in a cell with a solid oxygen-conducting electrolyte was discussed [14] in terms of a chain reaction mechanism involving electrochemically generated oxygen species during polarization of the electrode.

In the case of methane oxidation on the Pt electrode supported on the solid oxygen-conducting electrolyte the NEMCA effect was attributed to current-induced changes of the chemical state of the electrode–electrolyte system [5,6]. That leads to the appearance of new catalytically active sites and, consequently, to enhancement of catalytic activity.

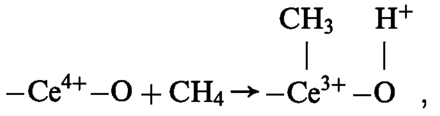
Every one of the discussed NEMCA concepts might be applicable to the present work taking into account that, in our case, a proton-conducting electrolyte was used. However, we think it plausible that the anodic current-induced enhancement of the catalytic CH_4 oxidation rate is caused by a change in the surface state of the solid proton-conducting electrolyte. Indeed, compared to the open circuit conditions, the anodic polarization of the Pt electrode-catalyst leads to stronger oxidative conditions. As discussed before, not only electrochemical oxidation of hydrogen (reaction (4)) but also appearance of electron holes (e.g. by reaction (3)). In other words, this means the transformation of the electrolyte from a less oxidized state at the open circuit conditions to a more oxidized one at passing anodic current. Schematically, the process can be presented as follows:

$$-\,Ce^{3+}\underset{(I)}{-O-}H^{+} \xrightleftharpoons{\text{gaseous oxygen}} -\,Ce^{4+}\underset{(II)}{-}O + \tfrac{1}{2}H_2O$$

$$-Ce^{3+}-O-H^{+} \xrightleftharpoons{\text{anodic current}} -Ce^{4+}-O + \tfrac{1}{2}H_2\,,$$

where I and II are hydrogen defect and electron hole, respectively. Note that hydrogen generated in the second reaction is evolved on the counter electrode (cathode).

Thus, the above considerations permit us to assume that under anodic polarization of the Pt electrode-catalyst the concentration of electron holes in the electrolyte (in the bulk and on surface) is higher than its open circuit value. If the electron holes are catalytically active sites, for instance, they activate methane by the reaction:



$$-Ce^{4+}-O + CH_4 \rightarrow -\overset{\displaystyle CH_3}{\overset{|}{Ce^{3+}}}-\overset{\displaystyle H^{+}}{\overset{|}{O}}\ ,$$

the anodic current application should give rise to the increase of the rate of CH_4 oxidation. Upon turning off the anodic current, the hole concentration decreases to its open circuit value. Apparently, this can be accompanied by the relaxation of the catalytic oxidation rate to its open circuit value, thus providing reversibility of the influence of the anodic current on the reaction rate.

The cathodic polarization of the Pt electrode-catalyst (hydrogen pumping to the reaction zone through the electrolyte) seems to cause no changes in the states of interfaces of Pt electrode–solid proton-conducting electrolyte system and, naturally, does not affect the catalytic reaction rate, as was observed experimentally (figs. 3–5).

The nature of the observed phenomenon, viz. the non-Faradaic effect of electrochemical hydrogen pumping from the reaction zone on the rate of CH_4 oxidation on the Pt electrode deposited on the solid proton-conducting electrolyte, is still unclear. Only tentative explanation is given in this work, and further experimental elucidation is needed. It would be interesting to find the analytical dependence of the reaction rate on the electrode potential and achieve more information on the state of interfaces in the electrode–solid electrolyte system using in situ surface science techniques.

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