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Effect of hydrogen pumping on the rate of methane oxidation over a platinum electrode

V.D. Belyaev [a], V.A. Sobyanin [a], V.P. Gorelov [b], V.V. Gal'Vita [a]

[a] *Boreskov Institute of Catalysis, 630090 Novosibirsk, Russia*
[b] *Institute of Electrochemistry, 620219 Ekaterinburg, Russia*

Abstract

The effect of electrochemical pumping of hydrogen on the rate of methane oxidation on a Pt electrode catalyst in the solid proton conducting electrolyte cell has been demonstrated. The induced changed in the reaction rate at the anodic polarization of a Pt electrode was two orders of magnitude higher than the rate of hydrogen pumping from the reaction zone through the electrolyte.

1. Introduction

Recently [1–2] the oxidative conversion of methane has been studied on a Pt electrode in a cell with solid oxygen conducting electrolyte:

$$CH_4 + O_2, Pt | ZrO_2(8\text{–}10 \text{ mol-\% } Y_2O_3) | \text{metal}, O_2$$

It was found that during the oxidation of CH_4 the catalytic activity of the Pt electrode can be altered dramatically and in a reversible manner by passing the electric current through the cell (a flow of oxygen anions through the electrolyte). The induced change in the catalytic rate was one order of magnitude higher than the rate of oxygen pumping through the electrolyte.

The present paper deals with the influence of electrochemical hydrogen pumping on CH_4 oxidation on a platinum electrode catalyst in a cell with solid conducting electrolyte:

$$CH_4 + O_2, Pt | SrDy_{0.08}Ce_{0.92}O_{3-x} | Pt, N_2 + H_2O$$

2. Experimental

The electrochemical cell was an yttria stabilized zirconia tube. A solid proton conducting electrolyte disk of a composition $SrCe_{0.92}Dy_{0.08}O$ was cemented with glue to one of the tube ends. Porous platinum electrodes were deposited on each face of the disk. A working electrode was inside the tube, and the counter one outside it. To isolate the counter electrode from ambient air, the cell was enclosed in a quartz tube. The geometrical areas of the electrodes were 0.5 cm^2. The CH_4 oxidation reaction was studied at atmospheric pressure and temperatures 600–750°C. A flow of CH_4, O_2 and N_2 was fed to a working Pt electrode at 0.3–1 cm^3/s. The counter electrode was blown with a $N_2 + H_2O$ mixture. The concentrations of methane and oxygen in the gas mixture were varied in the range 3–16 vol.-% and 20–84 vol.-%, respectively.

The electric current flowing through the cell was controlled by a potentiostat. The composition

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of the gas mixture before and after passing through the cell was analyzed by chromatography.

Conversion of the reagents was insignificant in all experiments. In a blank test without deposition of the platinum electrode on a H^+ conducting electrolyte the rate of CH_4 oxidation was $\langle 5\%$ of the rate obtained with Pt.

3. Results and discussion

When the CH_4 oxidation is performed in the temperature range 600–700°C the products are almost exclusively carbon dioxide and water. The effect of passing a current through the cell on the CO_2 formation rate during methane oxidation at 600°C is shown in Fig. 1. All results reported here were obtained under halvanostatic mode of cell operation and after the achievement of steady-state potential and rate values. It is seen that the cathodic current $(I \langle O)$ causes almost no change in the reaction rate with respect to its open circuit value. Application of an anodic current $(I \rangle O)$ increases the reaction rate. A sharp enhancement is observed upon a minor increase of the anodic current up to 10^{-2} mA and with a further increase of the current the rate goes to plato.

Analysis of the data presented in Fig. 1 shows that if the anodic current is applied, the enhancement of the reaction rate $\Delta r = r - r_o$ (where r and r_o are reaction rate at $I \rangle 0$ and $I = 0$, respectively) is far above the rate of hydrogen pumping from the reaction zone through the electrolyte calculated by Faraday's law $(I/(2F))$. A rate enhancement ratio defined as $\Lambda = \Delta r/(I/2F)$ decreases from 330 to 10 with an increase of the applied anodic current. Thus, H^+ pumping from the Pt electrode catalyst was found to cause non-Faradaic changes of NEMCA effect in the methane oxidation rate. A non-Faradaic increase of the rate of CO_2 formation upon applying the anodic current was observed under all the experimental conditions used in the present work.

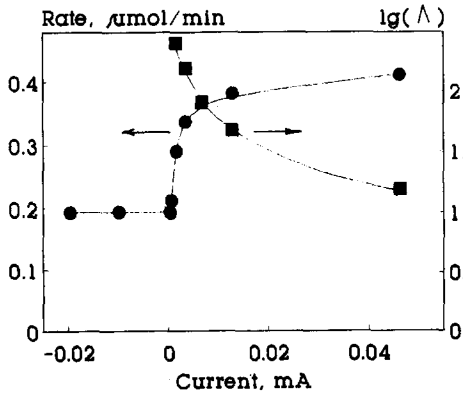

Fig. 1. Effect of applied current on the rate of CO_2 formation and on the rate enhancement factor (Λ) under methane oxidation. T = 600°C; $[O_2]$ = 56 vol.-%; $[CH_4]$ = 16 vol.-%.

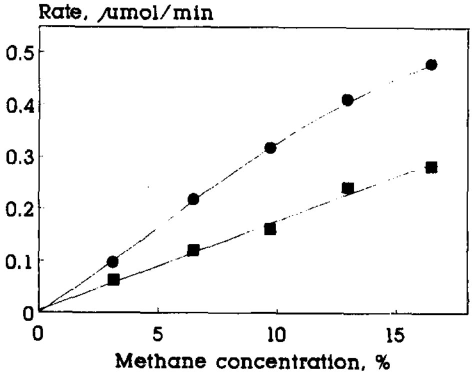

Fig. 2. Effect of methane concentration on the rate of CO_2 formation under open circuit conditions and under a constant anodic current application. T = 600°C; $[O_2]$ = 84 vol.-%; (■) I = 0; (●) I = 0.05 mA.

The induced changes in catalytic reaction rate were reversible (upon current interruption the rate returned to its open circuit value). At a higher temperature (700–750°C) water, carbon dioxide and C_2 hydrocarbons were detected. However the selectivity of C_2 hydrocarbons appeared to be low (10–20%) and the current passing through the cell does not change the rate of C_2 hydrocarbons formation with respect to its open circuit value.

It should be noted that although hydrogen pumping from the platinum electrode affects the CO_2 formation rate, it has no effect on the reaction orders in methane and oxygen. As is shown in Fig. 2, the reaction order in methane is 1. The reaction order in oxygen, as experimentally observed, decreases from 0.5 to 0.2 with increasing oxygen concentration.

The origin of the NEMCA phenomenon was discussed in a number of publications [1–3] and very different ideas were proposed. From our point of view the anodic current-induced enhancement of the catalytic CH_4 oxidation rate is caused by the change in surface state of the solid proton conducting electrolyte. As shown before [4], electrolytes based on $SrCeO_3$ can possess proton- and hole-type conductivities simultaneously. We assume that under anodic polarization of the Pt electrode catalyst, the concentration of electron holes in the electrolyte is higher than its open circuit value. If the electron holes are catalytically active sites, the application of anodic current should increase the methane oxidation rate. When the anodic current is turned off, the concentration of the electron holes decreases. The latter can be accompanied by the relaxation of the catalytic oxidation rate, thus providing reversibility of the current effect on the reaction rate.

4. Acknowledgements

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5. References

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