

Non-faradaic electrochemical modification of the catalytic activity for propane combustion of Pt/YSZ and Rh/YSZ catalyst-electrodes

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Abstract

The effect of non-faradaic electrochemical modification of catalytic activity (NEMCA effect) or electrochemical promotion (EP) was investigated in the total oxidation of propane on porous Pt and Rh catalyst-electrode films interfaced to 8 mol% Y₂O₃-stabilized-ZrO₂ (or YSZ), in the temperature range 425–520 °C and for sub-stoichiometric O₂ to propane ratios. Application of either positive or negative overpotentials resulted in non-faradaic increase of the catalytic rate, by up to a factor of 4 in the case of Rh and by up to a factor of 1350 in the case of Pt. The rate increase observed in the case of Pt is among the highest ones reported so far in NEMCA studies with oxygen ion conductors as active supports.
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1. Introduction

The catalytic properties of metal and metal-oxide porous catalyst-electrode films deposited on ionic conductors can be reversibly altered in a very pronounced and controlled manner by electrically polarizing of the catalyst-electrode via the effect of non-faradaic electrochemical modification of catalytic activity (NEMCA effect) or electrochemical promotion (EP) [1,2]. A key finding in the interpretation of the NEMCA effect is the variation of the catalyst work function upon polarization, with concomitant changes in the binding strength of chemisorbed species and reaction intermediates [1,2]. These changes result in electrochemically promoted rate changes exceeding the corresponding rate of ion transport through the ionic conductor by several orders of magnitude [1,2]. Work in this area has recently been reviewed [2].

The catalytic combustion of hydrocarbons, especially of methane and propane, is an important technology both for emission control and for energy production in an economical and less-polluting way. The combustion of alkanes in electrochemical membrane reactors [2–4] is an interesting alternative to the

conventional catalytic process, especially under conditions of electrochemical promotion [2–4]. Electrochemical promotion of the combustion of alkanes has previously been studied in the catalytic systems of methane total oxidation on Pt/YSZ [5] and Pd/YSZ [6], ethane total oxidation on Pt/YSZ [7] and, recently, propane total oxidation on Pt/YSZ [8–10] and Rh/YSZ [10]. In the case of propane total oxidation, it was found that the catalytic rate can be reversibly enhanced by more than three orders of magnitude [9,10]. The observed rate changes were non-faradaic [8–10] exceeding under certain conditions the corresponding rate of oxygen ion pumping by four orders of magnitude [8]. The appearance of sustained rate and surface oxygen activity oscillations, which were affected by applied current, was also reported [9]. The present work is a continuation of the authors' recently published work on electrochemical promotion of Pt/YSZ and Rh/YSZ catalyst-electrodes for propane total oxidation [10] including a more detailed comparison with the results of similar studies [8,9]. The work was carried out at 425–520 °C and at O₂ to C₃H₈ ratios lower than the stoichiometric ratio. The results are compared to those of earlier similar studies [8,9] and the observed promotional behavior is explained on the basis of the mechanism of the reaction and the effect of catalyst-electrode potential on the binding strength of chemisorbed reactants and on the oxidative state of the electrode surface.

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2. Experimental

Experiments were carried out in an atmospheric pressure continuous flow apparatus, which has been described previously [2,11]. Reactants and products (CO_2 and H_2O) were analyzed by on-line gas chromatography and IR spectroscopy. The carbon mass balance closure was better than 2%.

A three electrode set-up was used and two reactor configurations. In the case of Pt/YSZ, a single chamber reactor [2,11,12] was used, where both the Pt catalyst and two catalytically inert (as verified by blank experiments) Au auxiliary electrodes were deposited on an YSZ disk (Dynamic-Ceramic, 19 mm diameter, 1 mm (catalyst-electrode Pt1) to 2 mm (catalyst-electrode Pt2) thickness) and exposed to the reaction mixture in the interior of a closed at one end quartz tube of volume approximately 50 cm^3 . In the case of Rh/YSZ, a fuel cell type reactor [2,13] was used, where the Rh catalyst was deposited on the inner bottom side of a closed at one end YSZ tube (Zircoa, Inc.; 19.5 mm outer diameter, 2 mm wall thickness, 15 cm length), while two Pt auxiliary electrodes were deposited on the outer bottom side exposed to ambient air.

The electrodes were deposited on YSZ using metal pastes (Engelhard-CLAL) followed by calcination and sintering in air at specific temperatures (electrode Pt1: $840 \text{ }^\circ\text{C}$ for 30 min, electrode Pt2: $800 \text{ }^\circ\text{C}$ for 20 min, electrode Rh: $550 \text{ }^\circ\text{C}$ for 3 h). Both Pt and Rh catalyst-electrodes were porous with thicknesses on the order of a few micrometers, as shown using scanning

electron microscopy [10]. Details on electrode preparation and characterization, including surface mol N (mol of active sites) determination, can be found elsewhere [10].

3. Results and discussion

Fig. 1a shows the response of the catalyst-electrode potential U_{WR} and of the rate r of propane oxidation (expressed in mol O s^{-1}) and turnover frequency TOF upon application of a constant positive current $I=1.5 \text{ mA}$ between the catalyst-electrode Pt1 ($N=1.0 \times 10^{-7} \text{ mol Pt}$) and the Au counter electrode, at $425 \text{ }^\circ\text{C}$ and at fixed $P_{\text{O}_2}/P_{\text{C}_3\text{H}_8}$ ratio in the feed ($P_{\text{O}_2}/P_{\text{C}_3\text{H}_8} \approx 0.5$, hydrocarbon-rich mixture). It also shows the transient effect of constant current application on the enhancement ratio $\rho=r/r_o$, where r_o denotes the open-circuit rate, and on faradaic efficiency or enhancement factor $A=(r-r_o)/(I/2F)$ [1,2], where F is the Faraday constant. Upon current application, the rate starts increasing, stabilizing after approximately 15 min to a value which is 49 times higher than its open-circuit value ($\rho=r/r_o=49$). The rate increase $\Delta r=r-r_o=4.77 \times 10^{-7} \text{ mol O s}^{-1}$ is 61 times larger than the rate $I/2F$ of O^{2-} supply to the Pt catalyst ($I/2F=7.8 \times 10^{-9} \text{ mol O s}^{-1}$), that is, A is equal to 61. The observed changes in rate and catalyst-electrode potential are reversible, as upon current interruption they both return practically to their initial open-circuit values.

Fig. 1b shows a similar galvanostatic transient ($I=3.5 \text{ mA}$) for catalyst-electrode Pt2 ($N=6 \times 10^{-7} \text{ mol Pt}$) at a higher

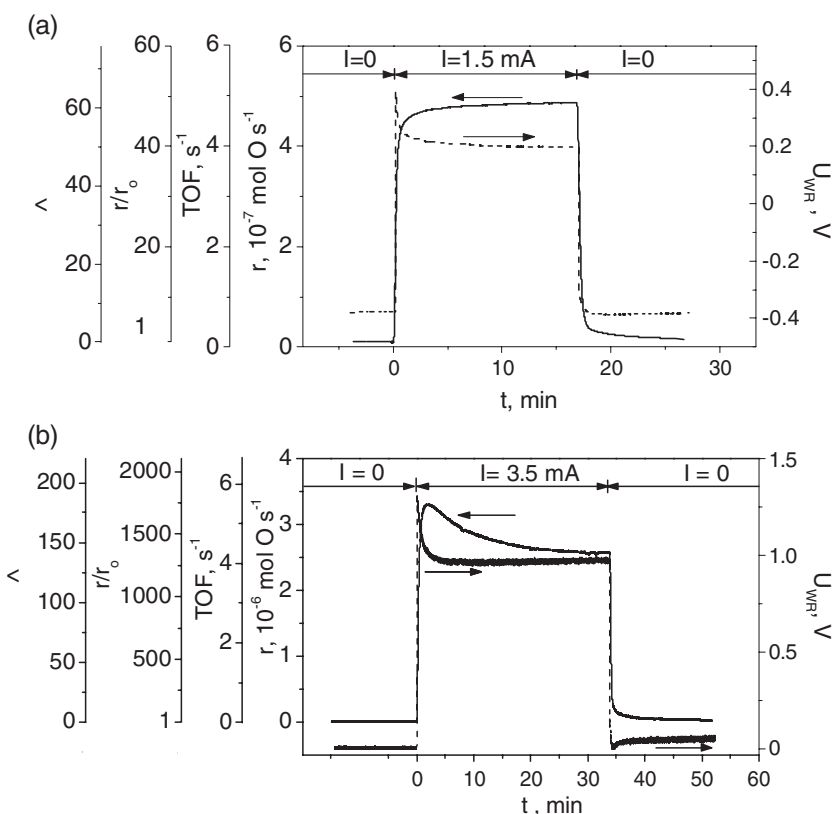


Fig. 1. Rate r , turnover frequency TOF, rate enhancement ratio r/r_o , faradaic efficiency $A=(r-r_o)/(I/2F)$ and catalyst potential U_{WR} response to a step change in applied positive current. (a) Catalyst Pt1, $T=425 \text{ }^\circ\text{C}$, feed composition: $P_{\text{O}_2}=0.92 \text{ kPa}$, $P_{\text{C}_3\text{H}_8}=1.95 \text{ kPa}$, flow rate: $101 \text{ cm}^3 \text{ (STP) min}^{-1}$. (b) Catalyst Pt2, $T=480 \text{ }^\circ\text{C}$, feed composition: $P_{\text{O}_2}=4.7 \text{ kPa}$, $P_{\text{C}_3\text{H}_8}=1.4 \text{ kPa}$, flow rate: $483 \text{ cm}^3 \text{ (STP) min}^{-1}$.

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