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Electrochemical Promotion of RuO_2 Catalysts for the Gas Phase Combustion of C_2H_4

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Abstract

The influence of the polarisation of the RuO_2/YSZ *interface on the electrochemical promotion of* RuO_2 *catalysts was studied by temperature programmed desorption and high temperature cyclic voltammetry measurements. The desorption activation energy of adsorbed oxygen is decreasing from 2·32 eV at 380 mV to 7·26 eV at 600 mV by polarizing of the* RuO_2/YSZ *interface. A higher oxide (*RuO_3*) might be formed at the* RuO_2/YSZ *interface during anodic polarisation. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: electrochemical promotion, interfaces, surfaces, electrical properties, ionic properties.

1 Introduction

The combustion of volatile organic compounds (VOC) is getting more and more important with the increasing emission of them in the environment. Emission sources are wide spread and reach from industrial waste air to motor vehicle exhaust gases.

Low temperature heterogeneous catalysis is still the most common way for the gas phase combustion of VOCs. Recently, it has been found that the catalytic activity of thin metal oxide films[1–3] (MO_2 with $M = Ru$, Ir) can be modified in a controlled manner by polarisation of the catalyst in an electrochemical cell of the type

$$\text{reactants, } MO_2\,|\,\text{solid electrolyte}\,|\,\text{Au, reactants}$$

This modification is known from the literature as electrochemical promotion[1,4] or as non–faradaic electrochemical modification of catalytic activity (NEMCA-effect).[5–7]

Temperature programmed desorption (TPD) of oxygen from RuO_2 films and high temperature cyclic voltammetry of RuO_2 films in vacuum were used for the investigation of the electrochemical promotion.

2 Experimental Details

The electrochemical cell consisted of a tubular ZrO_2-6%mol Y_2O_3 (YSZ) specimen (outer diameter 26 mm, inner diameter 20 mm) which was used as solid electrolyte, an O^{2-} conductor, on which the electrodes were directly deposited. A conventional three electrode configuration with the counter and the reference electrode on the inside and the working electrode on the outside of the tube was used. Counter and reference electrode consisted of gold deposited onto the YSZ at 850°C by thermal decomposition of a gold paste (Engelhard, A-1118). The working electrode consisted of RuO_2 deposited on the YSZ by thermal decomposition[8] of a solution of 53·7 mg $RuCl_3{\cdot}xH_2O$ (Johnson Matthey, 191000) in 1·66 ml 2-propanol (Fluka, 59309 puriss) (0·13 M in Ru) at 550°C. The working electrode had a superficial surface area of 1 cm^2, the counter electrode of 1 cm^2 and the reference electrode of 0·5 cm^2.

The experiments were carried out in an ultrahigh vacuum chamber (base pressure $1{\cdot}3\times10^{-8}$ mbar after baking) equipped with a quadrupole mass spectrometer (Balzers QMG 420) and a differentially pumped gas inlet system. The sample was heated radiatively using an Osram Xenon lamp located inside the YSZ tube. The temperature was varied by using an Eurotherm programmable temperature controller.

Oxygen adsorption was carried out by either introduction of ultra pure oxygen into the vacuum chamber ('gas phase adsorption') or by adsorption of electrochemically produced oxygen, formed at the three phase boundary during anodic polarisation ('electrochemical adsorption'). Both gaseous and electrochemical adsorption were carried out at 300°C followed by cooling of the sample to 240°C.

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The thermal desorption was carried out between 240 and 500°C with different linear heating rates (0·5–2°C s^{-1}).

Electrochemical measurements were carried out by applying of a constant current between the working and the counter electrode (galvanostatic operation) or by applying of a constant potential between the reference and working electrode (potentiostatic operation) with a galvano-potentiostat (AMEL 553). The same potentiostat in conjunction with an AMEL 567 function generator was used for the cyclic voltammetric experiments.

The experimental set-up for the TPD measurements[9] and the atmospheric pressure continuous flow reactor used for the catalytic measurements[3] are shown elsewhere.

3 Results and Discussion

Figure 1 shows a typical temporal evolution of the catalytic reaction rate and the catalyst potential relative to the reference electrode (V_{WR}) during a galvanostatic step of 50 μA ($I > 0$, O^{2-}-ions are pumped to the catalyst) during 60 min. A sharp increase of the reaction rate just after current application was followed by a slow increase which led to a new steady state after 60 min. The reaction rate decreased rapidly after current interruption before relaxing to its initial open circuit value.

The electrochemical promotion is characterised by three main factors, the rate enhancement factor ρ, the enhancement factor Λ and the open circuit enhancement factor γ.

The rate enhancement factor ρ [eqn (1)] is defined by the ratio of the promoted catalytic reaction rate r ($t = 60$ min) to the initial open circuit reaction rate r_o (before polarisation, $t = 0$) and gives an information about the level of the promotion.

$$\rho = r/r_o \tag{1}$$

ρ values of up to 115 were observed for RuO_2 catalysts.

The enhancement factor Λ [eqn (2)], or the current efficiency, is defined by the ratio of the observed reaction rate increase to the maximal possible electrochemical rate increase

$$\Lambda = (r - r_o)/(I/(2 \cdot F)) \tag{2}$$

where I is the applied current, F the Faradaic constant and $I/(2 \cdot F)$ the rate of O^{2-} applied to the catalyst ($I > 0$). Values of up to 4000 were observed.

The open circuit enhancement factor γ [eqn (3)] describes the reversibility of the electrochemical promotion and is defined by the ratio of the steady state open circuit catalytic reaction rate r' after polarisation ($t > 100$ min) to the initial open circuit catalytic reaction rate r_o ($t = 0$ min) before polarisation

$$\gamma = r'/r_o \tag{3}$$

The γ factor was under all studied reaction conditions equal to 1 and the electrochemical promotion is termed reversible.

Figure 2 compares oxygen desorption spectra after gas phase adsorption and after electrochemical adsorption. A broad desorption peak at 360°C was observed after gas phase adsorption. The desorption spectrum after electrochemical adsorption shows a sharper peak at 345°C. No additional desorption peak corresponding to a back spillover oxygen species was observed after

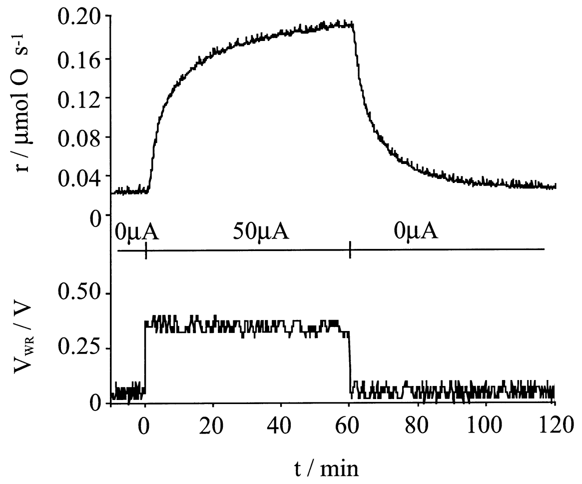

Fig. 1. Temporal evolution of the catalytic reaction rate (r) and the catalyst potential relative to the reference electrode (V_{WR}) during a galvanostatic step of 50 μA during 60 min. T = 380°C, $P_{C_2H_4}$ = 0·114 kPa, P_{O_2} = 17·7 kPa, V = 175 ml min^{-1} STP.

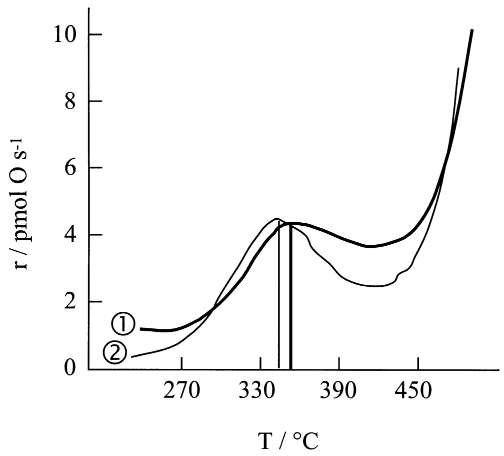

Fig. 2. Comparison of oxygen desorption spectra after gas phase adsorption ① and after electrochemical adsorption ②. Gaseous oxygen dosing at 300°C during 300 s, P_{O_2} = 4·9×10^{-7} mbar. Electrochemical oxygen adsorption during 2400 s, I = 3 μA.

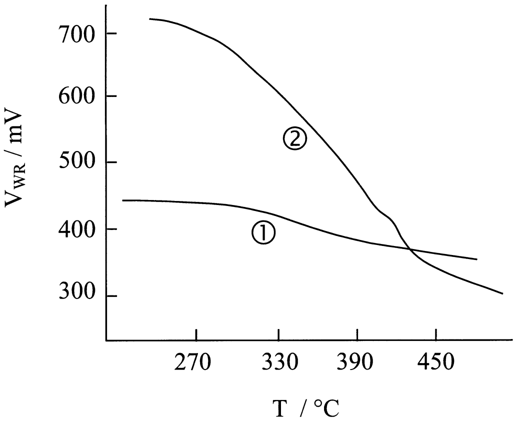

Fig. 3. Comparison of the potential changes during oxygen desorption after gas phase adsorption ① and after electrochemical adsorption ②. Same conditions as Fig. 2.

electrochemical adsorption as it was the case for Pt-films.[9] Above 410°C the decomposition of the ruthenium oxide became dominant. The lowering of the desorption temperature after electrochemical treatment shows nevertheless that the binding strength of adsorbed oxygen has been decreased during polarisation of the RuO_2/YSZ interface.

Figure 3 shows the potential changes during oxygen desorption. A higher potential change was observed after electrochemical adsorption than after gas phase adsorption for a similar initial coverage which shows clearly the modification of the RuO_2/YSZ interface.

The dependence of the desorption activation energy on the polarisation potential during electrochemically oxygen adsorption is shown in Fig. 4. The desorption activation energy was determined from the modified Redhead equation of Falconer and Madix.[9,10] It can be seen that the desorption activation energy decreases with increasing polarisation potential.

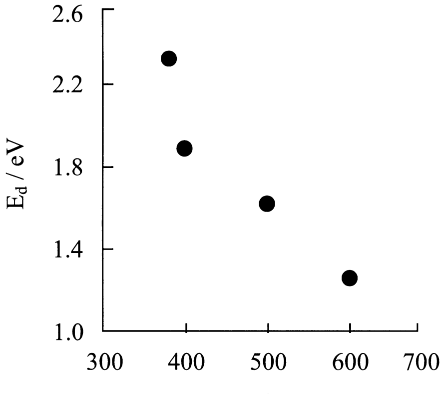

Fig. 4. Dependence of the polarisation potential (V_{WR}) on the desorption activation energy (E_d).

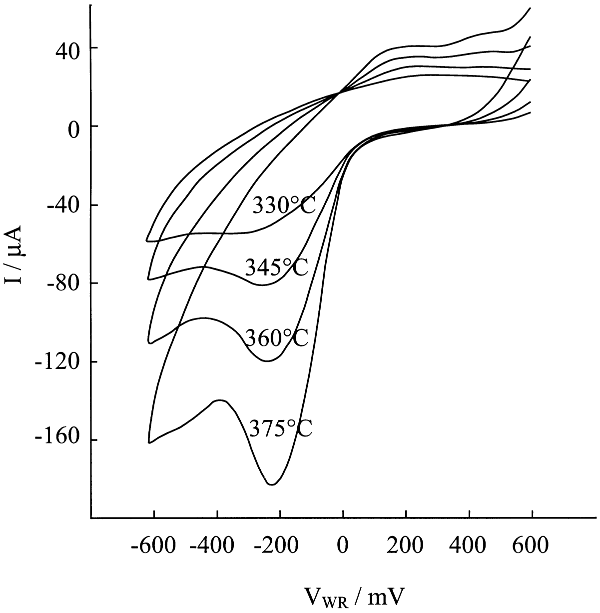

Fig. 5. Temperature dependence of the cyclic voltammogram of RuO_2 film in vacuum after anodic polarisation at 600 mV during 1 min. Sweep rate $30\,mV\,s^{-1}$.

The modification of the RuO_2/YSZ interface and the related increase of oxygen activity was also shown by high temperature cyclic voltammetry measurements. Figure 5 shows cyclic voltammograms at different temperatures after anodic polarisation of the catalyst at 600 mV (V_{WR}) during 1 min. A reduction peak at around −220 mV was observed over the whole studied temperature range (330–375°C). The appearance of the reduction peak at temperature higher than the desorption temperature of electrochemically adsorbed oxygen (345°C, Fig. 2) leads to the assumption that another species than adsorbed oxygen is involved. It is assumed that the O^{2-}-ions which are transported to the RuO_2/YSZ interface are even oxidized or are interacting with the RuO_2 at the YSZ/RuO_2 interface forming an electrochemical double layer. In the former case two atomic oxygen react at the three phase boundary (tpb, RuO_2/YSZ/gas phase) to gaseous oxygen and in the latter case a higher oxide might be formed according to eqn (4)

$$RuO_2 + O^{2-} \rightarrow RuO_3 + 2e^- \qquad (4)$$

The higher oxide is supposed to be reduced during the cathodic potential sweep leading to the observed reduction peak.

4 Conclusion

The desorption activation energy of adsorbed oxygen can be affected by polarizing of the RuO_2/YSZ interface and is decreasing from 2·32 eV at 380 mV to 1·26 eV at 600 mV. The possible formation of a higher ruthenium oxide (RuO_3) at the RuO_2/YSZ interface was shown with high temperature cyclic voltammetry measurements in vacuum. This electrochemical modification of the RuO_2/YSZ interface influences the catalytic activity on the gas exposed surface of the RuO_2 film as shown in Fig. 1. This is in good agreement with the already found interaction of the two interfaces during work function measurements.[3]

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