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Electrochemically induced oscillations of C_2H_4 oxidation over thin sputtered Rh catalyst films

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The electrochemically promoted induction of self-sustained catalytic rate and potential oscillations during C_2H_4 oxidation was studied over sputtered Rh thin (40 nm catalyst films interfaced with ZrO_2 (8 mol% Y_2O_3). The reaction rate oscillates simultaneously with the catalyst potential, and always in the opposite direction. The electrochemically induced oscillatory rate is typically 60 times larger than the open-circuit catalytic rate and 1000 times larger than the electrochemical rate of O^{2-} supply to the catalyst. The phenomenon is completely reversible and only observed under anodic polarization where the rate oscillates between the values corresponding to metallic Rh and surface Rh_2O_3. The oscillations are caused by the electrochemically controlled backspillover of O^{2-} to the catalyst surface and the concomitant, via repulsive lateral interactions, decomposition of surface rhodium oxide followed by surface reoxidation to Rh_2O_3 by gaseous O_2.

KEY WORDS: ethylene oxidation; Rh thin film catalysts; electrochemical promotion; Yttria-stabilized zirconia; oscillatory phenomena.

1. Introduction

Several heterogeneous catalytic systems operating near the surface oxide stability limit have often been found to exhibit oscillatory behaviour [1–5]. In most cases, oscillations in the reaction rate are observed in the transition region between the two steady-states, characterized by high and low reaction rate [1]. The nature of the catalyst bistability can be different: (i) multiple steady-states on the catalyst surface, including surface reconstruction [2,3]; (ii) multiplicity in the reactor dynamics; (iii) bistability which is connected with the kinetic and diffusion regions of the catalytic reaction. In ref. [1] it was shown that additives or impurities, which can be catalyst promoters as well as catalyst poisons can play a significant role in the induction of catalyst oscillatory behaviour. They block sites and can affect the activity of the catalyst and induce oscillations [6–9]. The impurities can even be the reason for the appearance of oscillations, if in the region of bistability they can drive the system from one state to another. One example of the influence of catalyst promoters on reaction rate oscillations was presented in [10] during CO oxidation on polycrystalline Pt where the oscillations were induced by electrochemically controlled backspillover of oxygen ions from the solid electrolyte to the catalyst surface. It was found that reaction rate oscillations can be induced by positive current and stopped by negative current application [10,11]. The results were interpreted by the electrochemically controlled backspillover of O^{2-} promoters to the catalyst surface and the concomitant formation and decomposition of surface PtO_2 [10,12,13].

The oscillatory behaviour of the oxidation of ethylene has been extensively investigated on polycrystalline Pt, Rh and Ag catalysts [4,5,12–15]. In several cases [4,5,12,13] the technique of solid electrolyte potentiometry (SEP) was used to continuously monitor the activity of oxygen on the catalyst surface during oscillations. In general, the surface oxygen activity and the rate of CO_2 production were found to oscillate simultaneously and in the opposite direction, i.e., a decrease in the activity of surface oxygen always corresponded to an increase in reaction rate. The origin of the oscillations was found to be closely connected with periodic formation and destruction of surface platinum and rhodium oxide.

The present study reports the electrochemically induced oscillatory behaviour during C_2H_4 oxidation over thin (40 nm) sputtered Rh films deposited on ZrO_2 (8 mol% Y_2O_3) solid electrolyte (YSZ). Such thin metal films with high (10–30%) metal dispersion [16] are of interest for the practical utilization of electrochemical promotion [16].

2. Experimental

The experimental set-up used in this study consists of the gas flow system, the reactor, and the gas analysis unit which includes online gas chromatography (Perkin–Elmer 300B) and IR spectroscopy (Beckman 864 CO_2 analyzer). Reactants were Messer-Griesheim-certified standards of C_2H_4 in He and O_2 in He. They could be

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further diluted in ultra pure (99.999%) He (L' Air Liquide) [16].

An atmospheric pressure single-chamber [11] quartz reactor (30 cm^3) was used for the electrochemical promotion experiments. The gas flow rate was typically 200 ml/min STP and the investigated temperature range was 300–420 °C.

The rhodium catalyst (working electrode) was deposited on one side of an yttria-stabilized zirconia (YSZ 8 mol% Y_2O_3) (Technox 802 from Dynamic Ceramic) pellet and the Au counterelectrode and reference electrode were deposited on the other side.

The rhodium catalyst was deposited on YSZ by sputtering. Prior to Rh deposition, the YSZ support was cleaned as described in detail elsewhere [16]. After cleaning, the support was introduced into the sputtering chamber filled with pure argon, then rhodium (Rh 99.8, Lesker) was deposited onto the substrate (YSZ support) at 50 °C. The sputtering conditions were the following: direct-current (dc) mode with a discharge of 305 V, argon pressure of 0.5 Pa. Under these conditions the deposition rate is 0.25 nm/s. The film thickness was measured by calibration with smooth silicon samples processed simultaneously. The thickness of the sputter-deposited rhodium film was 40 nm. The geometric surface area of the catalyst film was 0.5 cm^2. The metal dispersion of the Rh/YSZ film was estimated to be 8% (±3%) using the galvanostatic transient technique [16].

The counter and reference electrode consisted of porous gold film deposited onto the YSZ by thermal decomposition of a gold paste (Gwent C70219R4); the calcination temperature was 550 °C [17,18]. Current or potential application was made using a scanning potentiostat (Model 362, EG & G Princeton Applied Research).

The magnitude of electrochemical promotion is usually described by two parameters: (a) the rate enhancement ratio (ρ), defined as [11,19]:

$$\rho = r/r_o \qquad (1)$$

where r_o is the catalytic rate at open circuit and r the catalytic rate under polarization and (b) the apparent Faradaic efficiency, M, defined as [11,19]:

$$\Lambda = \Delta r/(I/2F) \qquad (2)$$

where I is the applied current, F is the Faraday constant, and $I/2F$ equals the rate of O^{2-} supply to the catalyst.

3. Results

A typical example of rate and catalyst potential oscillations obtained at a constant partial pressure of oxygen of 0.5 kPa and increasing $P_{C_2H_4}/P_{O_2}$ ratios is shown on figure 1. Under open-circuit conditions the catalyst is originally at a stable, low reaction rate steady-state, showing no oscillations. Upon positive current application the reaction rate increases (figure 1a) and, when the $P_{C_2H_4}/P_{O_2}$ ratio is sufficiently high, the system exhibits oscillatory behaviour (figure 1b–1f). In all cases after current interruption the catalyst returns to its initial steady-state. Increasing ethylene partial pressure leads to an increase in the oscillation frequency and to a decrease in the oscillation amplitude (figure 1b–1f). At $P_{C_2H_4}/P_{O_2}$ above about 2 the amplitude vanishes and the oscillations disappear. The catalyst is maintained at stable active state, characterized by a high ethylene oxidation reaction rate. The catalyst potential oscillates simultaneously with the rate of CO_2 production but in the opposite direction, i.e. increasing rate corresponds to decreasing catalyst potential as in the case of C_2H_4 and CO oxidation on Pt [4,10]. It can be seen in figures 1 and 2, that the rate and catalyst potential are oscillating between the values corresponding to a reduced (low potential) Rh surface and those corresponding to an oxidized (high potential, surface Rh_2O_3 [16]) Rh surface.

Figure 2 is based on the data of figure 1 and shows the effect of the $P_{C_2H_4}/P_{O_2}$ ratio on the rate of C_2H_4 oxidation. Three curves can be distinguished on the figure: One (open symbols) corresponds to the reaction rate under open-circuit conditions, corresponding to very low catalytic activity. The two others (filled symbols) correspond to the upper and lower limit of the oscillations induced by the applied current of +50 μA. Increasing $P_{C_2H_4}/P_{O_2}$ ratio causes a decrease in the amplitude of the oscillations until the oscillations vanish at $P_{C_2H_4}/P_{O_2} \approx 2$. At this point the lower limit of the oscillations has reached the upper limit corresponding to catalytic oxidation on Rh metal. The electrochemically promoted reaction rate is up to 61 times larger than the unpromoted open-circuit rate ($\rho \approx 61$ (Point B, figure 2)) and up to 1400 times larger than the rate, $I/2F$, of O^{2-} supply (backspillover) from YSZ to the catalyst surface, where M equals 1398, i.e. each O^{2-} supplied to the catalyst causes, on the average, 1398 chemisorbed oxygen atoms to react with C_2H_4, forming CO_2 and H_2O.

The effect of the $P_{C_2H_4}/P_{O_2}$ ratio on the electrochemically induced oscillatory behaviour of the Rh catalyst was also studied at 310, 350 and 420 °C (figure 3) and it was found that in all cases the reaction rate exhibits oscillations under positive current application. Increasing temperature causes a narrowing of the $P_{C_2H_4}/P_{O_2}$ domain, where the reaction rate and catalyst potential oscillations take place (figure 3). The oscillations follow the same trends, i.e. increasing $P_{C_2H_4}/P_{O_2}$ ratio causes a decrease in the period, T_p, of the oscillation frequency and a decrease in the amplitude. As shown in figure 3 the frequency, $1/T_p$, of the oscillations, increases near linearly with the $P_{C_2H_4}/P_{O_2}$ ratio similarly to the case of C_2H_4 oxidation on Pt [4,12].

Figure 4 shows the effect of temperature on the rate oscillations induced by constant anodic current application at fixed gaseous composition. In this and subsequent figures only the rate oscillations are shown

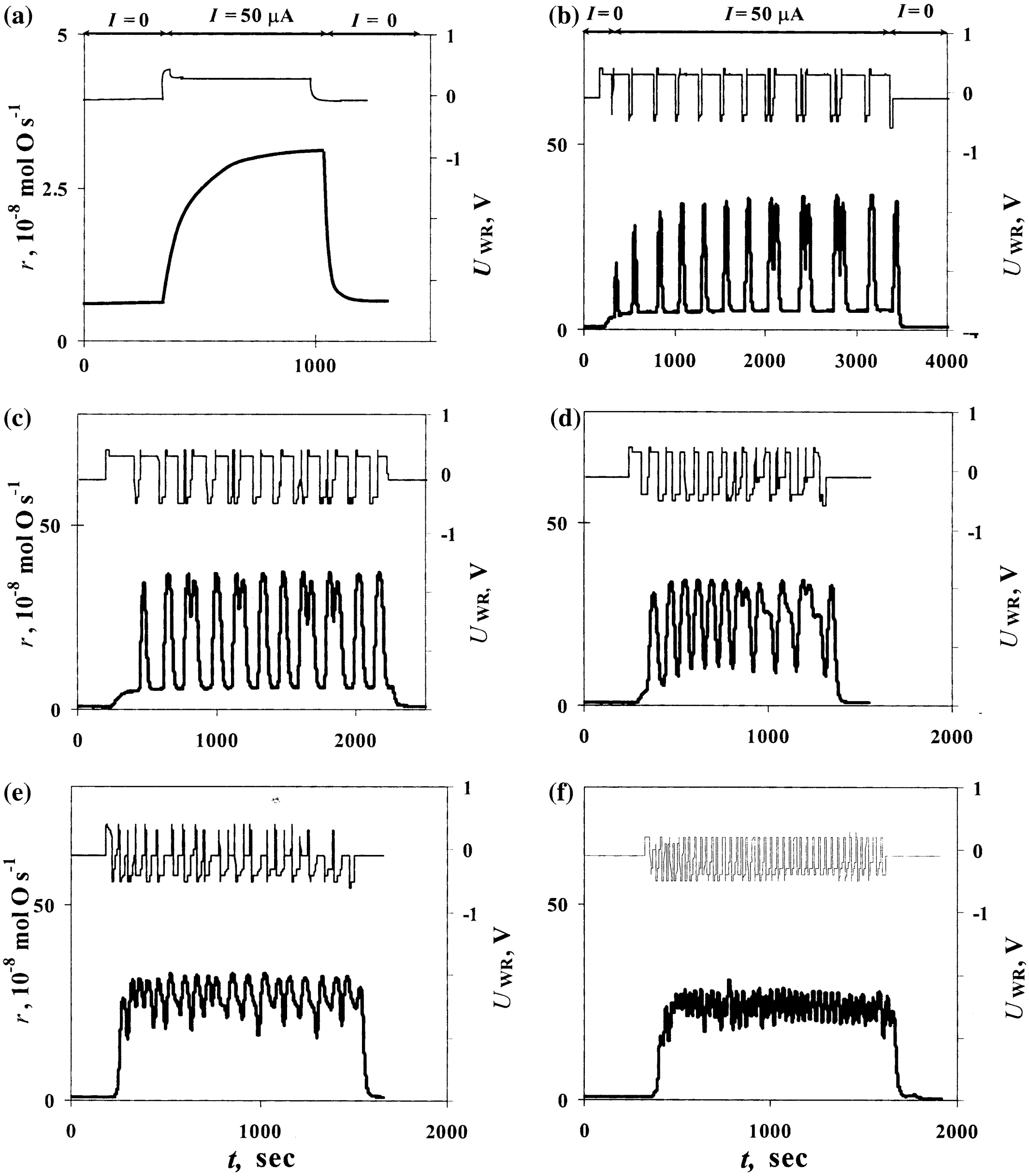

Figure 1. Response of ethylene oxidation reaction rate and corresponding catalyst potential to a step change in applied current +50 μA on Rh(40 nm)/YSZ at T = 390 °C. Gas composition: $P_{C_2H_4}$ (variable)/P_2 (0.5 kPa). Flow rate 200 ml/min. (a) $P_{C_2H_4}/P_{O_2} = 0.86$; (b) $P_{C_2H_4}/P_{O_2} = 1.02$; (c) $P_{C_2H_4}/P_{O_2} = 1.10$; (d) $P_{C_2H_4}/P_{O_2} = 1.24$; (e) $P_{C_2H_4}/P_{O_2} = 0.51$; (f) $P_{C_2H_4}/P_{O_2} = 1.80$.

for simplicity, as the potential oscillations are, as already shown, in opposite phase with the rate oscillations. Increasing temperature from 350 to 470 °C causes a near 5-fold increase in oscillation frequency (figure 5).

Figure 6 shows the effect of gas flowrate, and thus residence time in the catalytic reactor, on the oscillatory behaviour. Increasing flowrate by a factor of three causes a more than 2-fold increase in rate oscillation frequency (Figure 7), again similarly to the case of C_2H_4 oxidation on Pt [4,12]. This is because the reactor is operated at constant feed composition, thus increasing flowrate causes a decrease in conversion, thus an increase inP_{O_2} which enhances the rate of catalyst surface reoxidation [4,12] while as can be seen, e.g. in figure 4, the decomposition of surface Rh_2O_3 is almost instantaneous.

4. Discussion

The present results show that the electropromoted catalytic rate oscillates between an upper limit corresponding to a reduced Rh surface (low catalyst potential, i.e. low surface oxygen activity [11] (figure 1)), and a lower limit corresponding to an oxidized surface (high catalyst potential, i.e. high surface oxygen activity ([11], figure 1).

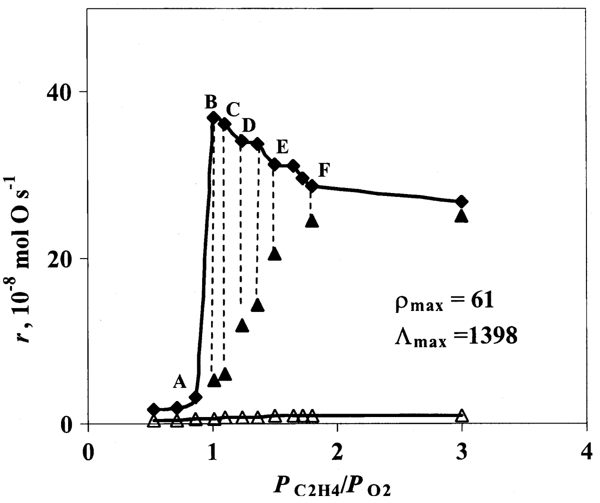

Figure 2. The C_2H_4 oxidation reaction rate on Rh/YSZ as a function of $P_{C_2H_4}/P_{O_2}$ ratio under open-circuit conditions (open symbols) and closed circuit ($I = +50$ μA) (filled symbols) at $T = 390$ °C. Gas composition: $P_{C_2H_4}$ (variable)/P_{O_2} (0.5 kPa). Flow rate 200 ml/min. Diamonds and triangles connected by dashed line show the upper and lower limit of the rate oscillations.

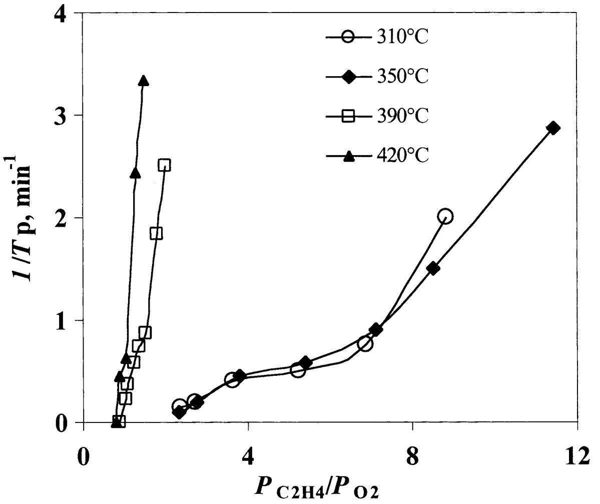

Figure 3. Frequency of the rate and potential oscillations obtained under current application ($I = +50$ μA) versus the ratio of partial pressures $P_{C_2H_4}/P_{O_2}$ at different temperatures. Gas composition: $P_{C_2H_4}$ (variable)/P_{O_2} constant. For 310 and 350 °C: $P_{O_2} = 0.2$ kPa; for 390 and 420 °C: $P_{O_2} = 0.5$ kPa.

Under open-circuit and low $P_{C_2H_4}/P_{O_2}$ ratios (<0.8) the rate corresponds to that of the oxidized surface (figure 2) while for high $P_{C_2H_4}/P_{O_2}$ ratios (>2) and positive applied current the steady-state rate corresponds to that of the reduced Rh surface. Recent work [16] has shown that thin Rh (40 nm) catalyst films deposited by sputtering onto a TiO_2 sublayer supported on YSZ (Rh/TiO_2/YSZ) has two similar stable oxidation states under open circuit: Rh metal and surface Rh oxide, depending on the gas composition. In the case of Rh/YSZ thin films the variation in gas composition and temperature under open circuit does not change the stable oxidized state (figure 2). The present results confirm the electrophobic nature (increase of reaction rate with positive current application) of ethylene oxidation on Rh [20,21]. Positive current supplies backspillover O^{2-} ions to the catalyst/surface which act as sacrificial promoters, since they are less reactive than normally chemisorbed O [11]. The backspillover O^{2-} ions spread over the entire gas-exposed catalyst surface [11,18,22] and are accompanied by their image charge in the metal catalyst, thus forming an overall neutral double layer at the catalytically active surface which increases in general the catalyst work function [11]. The increase in work function weakens the binding strength of chemisorbed oxygen [11] and via repulsive lateral interactions of O_{2-} with the oxygen of the surface oxide can cause surface oxide decomposition [11]. Thus the backspillover O^{2-} species acts as a sacrificial promoter [11]. Spent O^{2-} is continuously replenished via reduction of gaseous O_2 at the counter electrode [11].

The observed dependence of oscillation frequency on $P_{C_2H_4}/P_{O_2}$ and temperature is almost identical to that observed during C_2H_4 oxidation on Pt [4,12], the oscillation frequency increases significantly with temperature (figure 4) and near linearly with$P_{C_2H_4}/P_{O_2}$ ratio (figure 3) and with gas flowrate (figure 7). Also in both cases, the oscillations were found to occur under fuel-rich gas compositions and to disappear above a certain temperature-dependent critical $P_{C_2H_4}/P_{O_2}$ ratio (figure 3). Thus the same physical [4] and mathematical [12] model used to successfully describe the rate and potential oscillations during C_2H_4 oxidation on Pt, based on the periodic formation and reduction of a surface oxide, can be applied here. In terns of this general model [14] the origin of self-sustained rate and potential oscillations presented here is the following: under open circuit the surface Rh oxide is stable but upon anodic polarization and concomitant O^{2-} supply to the catalyst the surface rhodium is decomposed due to repulsive lateral interactions with O^{2-} [11,16], thus oxygen previously associated with Rh_2O_3 becomes available for reaction with C_2H_4. This causes an abrupt decrease in the ($P_{C_2H_4}/P_{O_2}$) ratio above the catalyst. When this ratio falls below a critical $(P_{C_2H_4}/P_{O_2})^*$ ratio, formation of surface Rh_2O_3 by gaseous O_2 is thermodynamically favoured and takes place again. This, however, causes an increase in the $P_{C_2H_4}/P_{O_2}$ ratio, due to the extra consumption of gaseous O_2, and the oxide becomes unstable again, thus repeating the cycle [11,16].

This type of oscillatory mechanism bears several similarities with the mechanisms and models discussed by Franck and FitzHugh [23] and by Rush and Newman [24] for aqueous electrochemical systems displaying passivation behaviour, where the oscillation have been shown to be due to spontaneous transitions between the active and passive state [23,24]. These models also address the important question of coherence which is

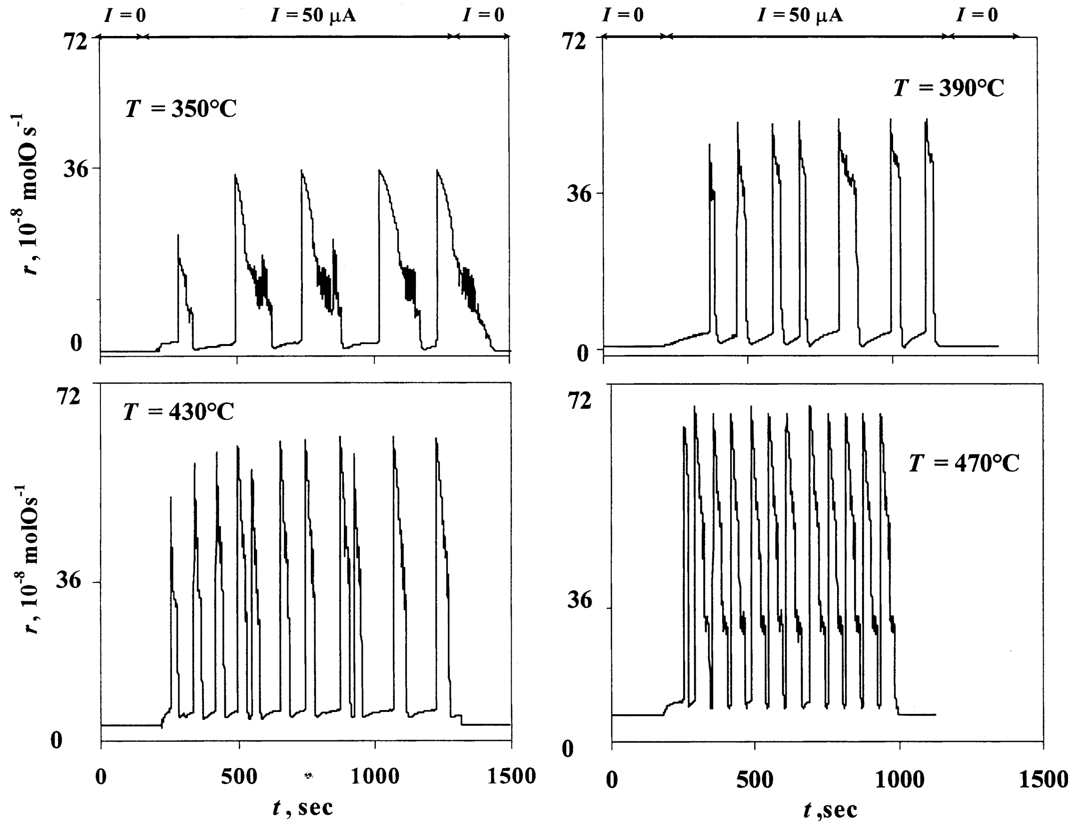

Figure 4. Response of ethylene oxidation reaction rate to step change in applied current $+50$ μA on Rh(40 nm)/YSZ at different temperatures. Gas composition: $P_{C_2H_4} = 2$ kPa, $P_{O_2} = 0.69$ kPa. Flow rate 200 ml/min.

accounted for in the model for catalytic C_2H_4 oxidation oscillations via the fast gas phase diffusion and resulting spatial uniformity in the gas phase composition in contact with the catalyst [12].

The mathematical model presented in [12] consists for four differential mass balances for gaseous C_2H_4 and O_2 and for surface chemisorbed oxygen and metal oxide. The latter becomes unstable above the critical $(P_{C_2H_4}/P_{O_2})^*$ ratio. Numerical integration in time of these four differential equations shows periodicity and describes semiquantitatively the observed nearly linear increase in oscillation frequency with temperature, with $P_{C_2H_4}/P_{O_2}$ ratio and with gas flowrate for the case of C_2H_4 oxidation on Pt [12], thus can be applied directly to the present case too. The novelty of the present work is that in ref. [12] the oscillations on the Pt catalyst occur under open-circuit conditions while here the oscillatory behaviour is observed only under anodic electrochemical promotion conditions, while under open circuit the Rh catalyst remains to its inactive surface Rh_2O_3 state. This is due to the higher propensity of Rh than Pt for surface oxidation.

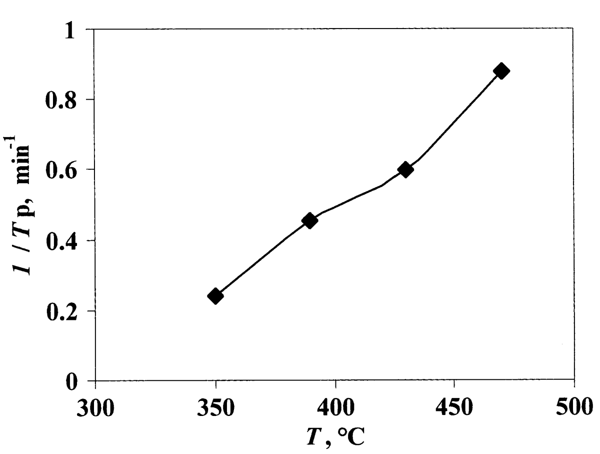

Figure 5. Frequency of the rate oscillations obtained under current application ($I = +50$ μA) versus temperature at constant gas composition: $P_{C_2H_4} = 2$ kPa, $P_{O_2} = 0.69$ kPa. Flowrate 200 ml/min.

5. Conclusion

The catalytic activity of Rh for ethylene oxidation on thin sputtered Rh catalyst films deposited on YSZ can be enhanced very significantly ($\rho = 60$, $\Lambda = 1400$) via positive current application. The electrochemically promoted state is oscillatory for low $P_{C_2H_4}/P_{O_2}$ ratios where the reaction rate oscillates simultaneously with catalyst potential. The minimum rate value corresponds to an oxidized Rh surface (Rh_2O_3) and the maximum rate to reduced Rh.

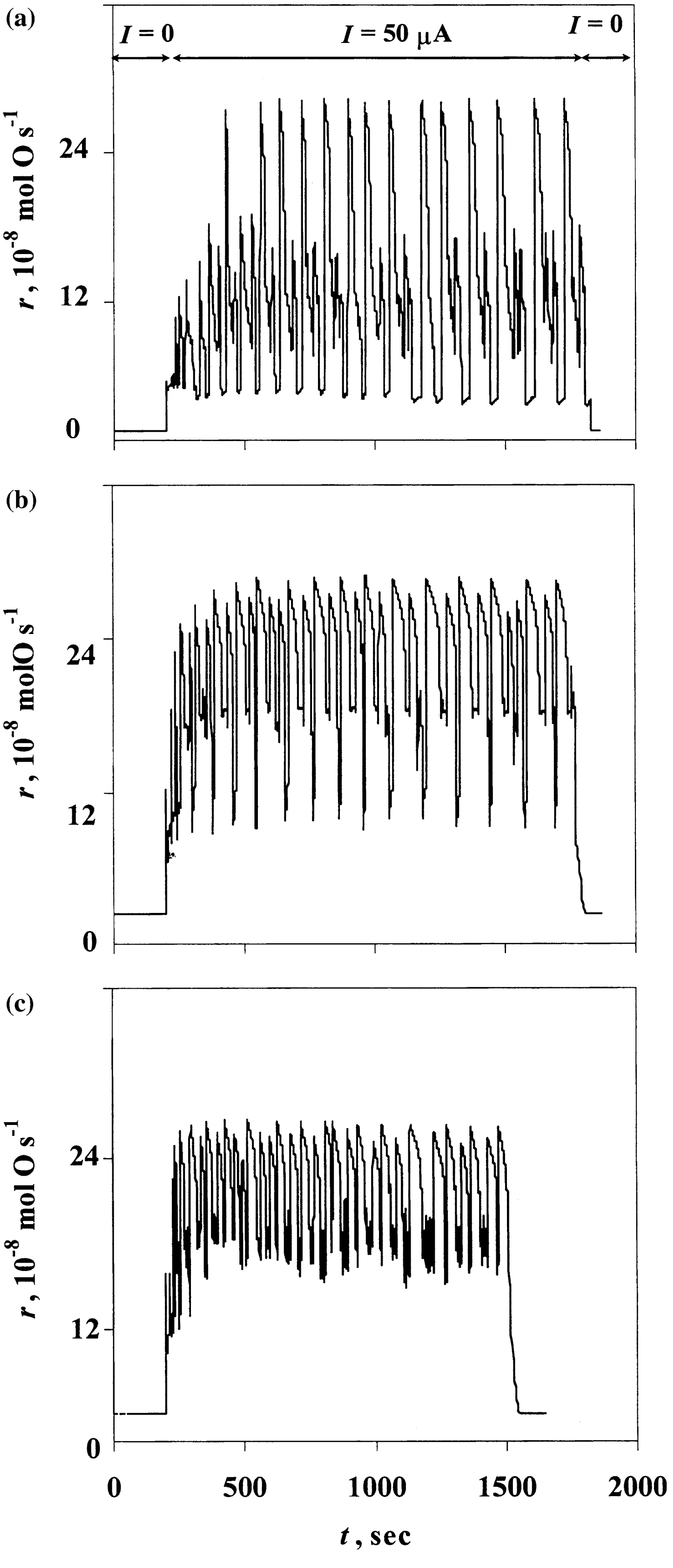

Figure 6. Response of ethylene oxidation reaction rate to step change in applied current +50 μA on Rh(40 nm)/YSZ at different gas flowrates: (a) 200 ml/min; (b) 400 ml/min; (c) 600 mil/min. Gas composition: $P_{C_2H_4} = 2$ kPa,$P_{O_2} = 0.4$ kPa. $T = 350$ °C.

The catalytic rate is a factor of 60 higher on the reduced than in the surface Rh_2O_3 state. Electrochemically induced backspillover of O^{2-} to the oxidized catalyst surface does not lead to further oxidation. Instead, it causes surface Rh_2O_3 decomposition. This confirms the role of backspillover O^{2-} as an effective anionic catalyst promoter.

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References

[1] M.M. Slin'ko and N.I. Jaeger, in: *Studies in Surface Science and Catalysis*, B. Delmon and J.T. Yates eds. (Elsevier, Amsterdam, 1994).

[2] K. Krischer, M. Eiswirth and G. Ertl, Surf. Sci. 251–252 (1991) 900.

[3] M. Bär, M. Falcke, C. Zülicke, H. Engel, M. Eiswirth and G. Ertl, Surf. Sci. 269–270 (1992) 471.

[4] C.G. Vayenas, B. Lee and J.N. Michaels, J. Catal 66 (1980) 37.

[5] I.V. Yentekakis, S. Neophytides and C.G. Vayenas, J. Catal. 111 (1988) 152.

[6] A.K. Galwey, P. Gray, J.F. Griffiths and S.M. Hasko, Nature 313 (1985) 668.

[7] T. Lamb, R.P. Scott, P. Watts, B. Holland, S. Gentry and A. Jones, J. Chem. Soc. Chem. Commun. 23 (1977) 882.

[8] R.C. Yeates, J.E. Turner, A.J. Gellman and G.A. Somorjai, Surf. Sci. 149 (1985) 175.

[9] K.E. Keck and B. Kasemo, Surf. Sci. 167 (1986) 313.

[10] I.V. Yentekakis and C.G. Vayenas, J. Catal. 111 (1988) 170.

[11] C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda and D. Tsiplakides, *Electrochemical Activation of Catalysis. Promotion, Electrochemical Promotion, and Metal-Support Interaction* (Kluwer Academic/Plenum Publishers, New York, 2001).

[12] C.G. Vayenas, C. Georgakis, J.N. Michaels and J. Tormo, J. Catal. 67 (1981) 348.

[13] C.G. Vayenas and J.N. Michaels, Surf. Sci. 120 (1982) L405.

[14] D.J. Kaul and E.E. Wolf, Chem. Eng. Sci. 41 (1986) 1101.

[15] S.D. Dhalewadikar, N.M. E and A. Varma, Chem. Eng. Sci. 41 (1986) 1743.

[16] E.A. Baranova, A. Thursfield, S. Brosda, G. Fôti, C. Comninellis and C.G. Vayenas, J. Electrochem. Soc. 152(2) (2005) E40.

[17] G. Fóti, S. Wodiunig and C. Comninellis, Current topics in Electrochemistry 7 (2000) 1.

[18] G. Fóti, I. Bolzonella and C. Comninellis, in: *Modern Aspects of Electrochemistry*, C.G. Vayenas eds. (Kluwer Academic/Plenum Publisher, New York, Boston, Dordrecht, London, Moscow, 2003) p. 310.

[19] C.G. Vayenas, S. Brosda and C. Pliangos, J. Catal. 216 (2003) 487.

[20] C. Pliangos, I.V. Yentekakis, X.E. Verykios and C.G. Vayenas, J. Catal. 154 (1995) 124.

[21] C. Pliangos, I.V. Yentekakis, V.G. Papadakis, C.G. Vayenas and X.E. Verykios, Applied Catalysis B: Environmental 14 (1997) 161.

[22] C.G. Vayenas, M.M. Jaksic, S.I. Bebelis and S.G. Neophytides, in: *Modern Aspects of Electrochemistry*, J.O.M. Bockris, B.E. Conway and R.E. White eds. (Plenum Press, New York, 1996) p. 57.

[23] U.F. Franck and R. FitzHugh, Z. Elektrochem. 65 (1961) 156.

[24] B. Rush and J. Newman, J. Electrochem. Soc. 142(11) (1995) 3770.