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Oscillatory behavior of Rh/YSZ under electropromoted conditions

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ABSTRACT

Electrochemical induced oscillations were studied during ethylene oxidation over Rh films deposited on YSZ. Oscillations period and amplitude were for the first time analyzed depending on the applied potential or current, related with cyclic oxidation and reduction reactions and discussed on the basis of the phenomenon of the electrochemical promotion of catalysis.

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1. Introduction

Since the group of Wicke observed for the first time rate oscillations, specifically in the catalytic oxidation of CO [1], the study of oscillatory surface reactions has derived into a very active research field.

Revelation of regimes of oscillatory behavior in catalytic processes led to new insights into reaction mechanisms and achieved a better understanding of the operation and improvement of practical catalysis. Steady-state multiplicity and a stable oscillating change between two active states have been interpreted according to various reaction mechanisms, such as adsorption induced surface reconstruction, a subsurface reservoir of a reactant and a periodic formation of an oxide or a carbon layer [2].

The oscillatory behavior during catalytic oxidation reactions has been extensively investigated on supported Pt, Pd, Ir and Rh catalysts [3]. In those cases, it is generally accepted that cyclic oxidation–reduction processes are the origin of this phenomenon. Thus, the oscillations were found to be closely connected with periodic formation and destruction of surface metal oxides.

Originally proposed by Wagner [4], the technique of Solid Electrolyte Potentiometry (SEP) has been used in several cases in conjunction with kinetic measurements to study the mechanism of catalytic reactions. SEP is one of the very few techniques which can be used to extract in situ information about adsorbed species on catalyst surfaces. But this technique is particularly useful for the study of oscillatory catalytic reactions [5–11]. For instance, previous studies with Rh/YSZ [10,11] have shown the electrochemically promoted induction of self-sustained catalytic rate and potential oscillations during ethylene and methane oxidation. In both studies, the reaction rates oscillated simultaneously with the catalyst potential under closed circuit conditions. This oscillatory

behavior was observed under anodic polarization and it was explained on the basis of the electrochemically controlled backspillover of oxygen ions to the catalyst surface and the associated, via repulsive lateral interactions, decomposition of surface rhodium oxide followed by surface reoxidation to Rh_2O_3 by gaseous O_2 [12].

The aim of this study was to analyze the oscillations electrochemically induced during ethylene oxidation over Rh films deposited on YSZ (yttria-stabilized zirconia). The oscillations were studied for the first time in terms of the period and amplitude depending on the applied potential or current. The results will be discussed on the basis of the electrochemical promotion of catalysis (EPOC or NEMCA effect). This phenomenon, which was introduced and developed by the group of Professor Vayenas [12], is based on the application of low currents/potentials through the catalyst/electrolyte interface resulting in the Non-Faradaic modification of the catalyst activity and selectivity, most of the times in a reversible manner. It is well established that the EPOC phenomenon can be described using the sacrificial promoter mechanism. According to this mechanism two oxygen species or equivalently two different oxygen adsorption states exist in the catalytic system, a regular chemisorbed oxygen and a more ionic, more strongly bonded and less reactive spillover oxygen species.

Recently another mechanism was proposed by Imbihl's group for the interpretation of EPOC [13]. This mechanism based on the existence of carbonaceous CH_x adlayer inhibiting O_2 adsorption. They proposed that their data can be explained by an ignition mechanism where electrochemical O^{2-} pumping from the solid electrolyte causes an ignition from an unreactive carbon-poisoned state of the surface to an active state due to the partial removal of the inhibiting carbonaceous layer. It is worth nothing that the formation of carbonaceous layer itself under fuel rich conditions is due to the oxygen mass-transfer limitation. This alternative mechanism has been discussed already in recent works by Vernoux and Vayenas [14,15]. All the data used in the present Letter were obtained under near stoichiometric conditions. Carbon dioxide

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was the only C-containing product since CO and C2-compounds were never detected. Carbon balance was closed in all the experiments, so there was no evidence of carbon deposition. For that reason, according to our opinion this alternative mechanism based on carbonaceous layer could not interpret our results. Therefore the sacrificial promoter concept was used for the interpretation of the results.

2. Experimental

Rh/YSZ was used in this study as the electrochemical catalyst. The solid electrolyte cell consisted of a dense YSZ (8 mol% Y_2O_3-stabilized ZrO_2) pellet (20 mm diameter and 1 mm thickness, Henson Ceramics Ltd.), covered by three electrodes: working, counter and reference. A rhodium thin film ($\sim$2 cm^2 of geometric area), serving as the working electrode, was deposited onto one side of the YSZ pellet by application of metalorganic paste (Engelhard 8826), followed by calcination in air for 30 min at 450 °C and for 60 min at 830 °C. The resulting metal loading was 1.75 mg Rh cm^{-2}. Gold thin films were deposited on the other side of the pellet (serving as the reference and counter electrodes), by application of metalorganic paste (Engelhard 8300), followed by calcination in air for 30 min at 450 °C and for 60 min at 750 °C.

An atmospheric pressure specific tubular quartz reactor (single chamber), as described in detail elsewhere [16,17], was used for the experiments. The entire reactor was placed in a furnace (JH HEE.CC4) equipped with a heat control system (Conatec 4801). Constant potentials or currents across the cell were measured and imposed using a potentiostat–galvanostat Voltalab PGZ 301 (Radiometer Analytical). The reaction gases were Praxair certified standards of 4% C_2H_4/He, O_2, (99.99% purity), and He (99.999% purity). The gas flow was controlled by a set of calibrated mass flowmeters (Brooks 5850 E and 5850 S). The feed composition was as follows: 5800 ppm C_2H_4, 18 000 ppm O_2, He balance, and the overall flow rate was 11 L h^{-1}. Reactants and products were analyzed by a micro gas-chromatograph (Varian CP-4900).

Prior to the experiments, the rhodium film was reduced under pure hydrogen at 450 °C for 1 h. Then, the reactive mixture flow was switched into the reactor and the sample was heated to 480 °C at 1 °C min^{-1}. The catalyst was maintained at 480 °C for 1 h in order to assess the catalyst durability.

The crystalline phases of the rhodium electrode-catalyst were examined by X-ray powder diffraction (XRD) performed in a PANalytical diffractometer equipped with a X'Celerator detector with monochromatic CuK$_{\alpha1}$ radiation (λ = 1.54 Å). Particle size of Rh and Rh$_2$O$_3$ were calculated by means of Scherrer equation [18]. The structure and morphology of the film were studied by Scanning Electron Microscopy (SEM) using a JEOL 6490LV microscope.

3. Results and discussion

Figure 1 shows the XRD patterns of the electrochemical catalyst Rh/YSZ under different conditions. Rhodium oxide (with particle size equal to 152 ± 1 nm) was mainly obtained after calcination treatment under air atmosphere. On the other hand, prior to the electrocatalytic experiment, the catalyst was reduced under pure hydrogen. In this case, the XRD analysis after reduction confirmed that Rh was mainly present under reduced state, indicating that the presence of metals oxides was almost negligible. Nevertheless, one can observe that after working conditions both metallic and rhodium oxide coexisted on the surface. This means that under the used reaction conditions (i.e. in presence of oxygen and positive polarization), it is possible that part of the surface metallic Rh to be oxidized again to rhodium oxide. The size of the metallic
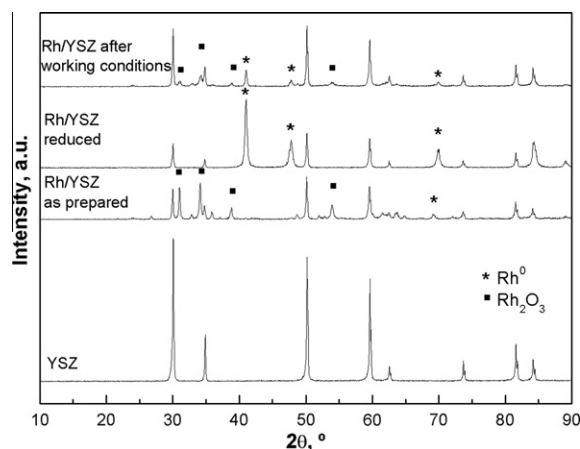

Figure 1. XRD patterns of Rh films deposited on YSZ.

rhodium particles was found to be 58.5 ± 0.3 nm from the XRD patterns of the reduced sample (Figure 1). This value seemed to be independent of the total catalyst loading since analysis of double loading samples gave particles with the same size (data not shown).

SEM pictures from the top view and from the cross section of the electrochemical catalyst are shown in Figure 2a and b, respectively.
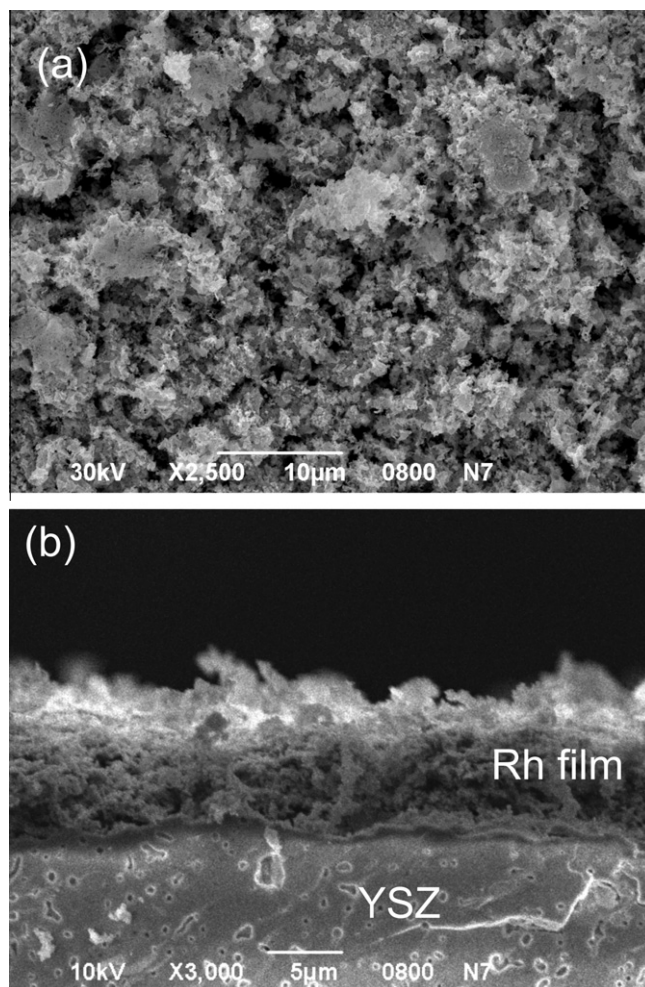

Figure 2. SEM micrographs of Rh/YSZ (a) top view and (b) cross section.

It can be observed (Figure 2a) that the preparation technique led to a continuous rhodium film, porous enough to allow the access of reactants and products. Both the morphology and structure of the sample obtained were similar to those reported for other pasted catalysts-electrodes like Pt/YSZ [19] and Ag/YSZ [20]. The thickness of the catalyst film (calculated by the cross section micrograph, Figure 2b) was ranged from 5 to 10 μm, which is usual for films prepared by applying metalorganic pastes [12].

In order to evaluate the electrochemical promotion phenomenon, a galvanostatic transient was carried out. Figure 3 shows the response of the catalyst-electrode potential and CO_2 formation reaction rate upon imposition of a constant positive current between the rhodium film and the counter electrode. For the first hour, no current was applied in order to stabilize the catalyst. Then, a constant current of +20 μA was applied, so that O^{2-} ions were transferred from the solid electrolyte to the catalyst at a rate given by Fadaray's law, I/2F. Polarization effect on the catalytic reaction was characterized by the main parameters commonly used in NEMCA studies [12], the rate enhancement ratio (ρ) and the Faradaic efficiency (Λ), both defined as:
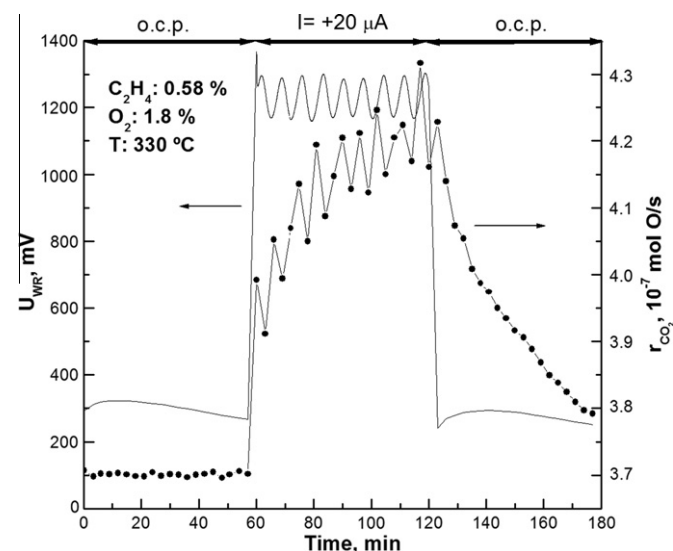
$$\rho = r/r^0 \qquad (1)$$
$$\Lambda = (r - r^0)/(I/nF) = \Delta r/(I/nF) \qquad (2)$$

where r^0 is the catalytic reaction rate under open circuit conditions, r is the reaction rate under polarization, n is the number of charge carried by the ions ($n = 2$ with an O^{2-} conductor), Δr is the catalytic reaction rate change induced by a current I, and F the Faraday's constant. The presence of transferred oxygen ions into rhodium film catalyst led to a small rate enhancement up to 15% and a Faradaic efficiency of 523. It is worth noting that in all the experimental the conversion of the ethylene was less than 10%.
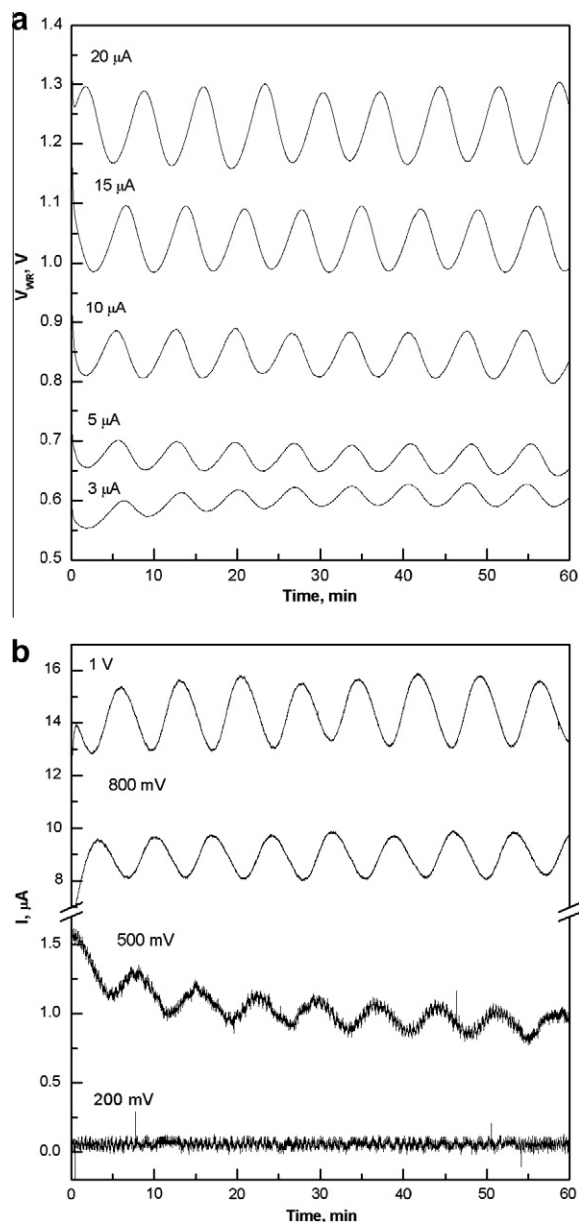
On the other hand, it is interesting to note that during the polarization, oscillations were induced in contrast with open circuit conditions in which both the catalytic activity and the open circuit potential were stable; as it was already observed by Baranova et al. [10]. Those authors explained that the oscillatory behavior is 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. Thus, positive polarization supplied backspillover oxygen ions to the catalyst

film, which acted as sacrificial promoters. These ions spread over the entire gas-exposed catalyst surface and were accompanied by their image charge in the metal catalyst, thus forming an overall neutral double layer at the active surface, which increased the catalyst work function [21]. The increase in the work function weakened the binding strength of chemisorbed oxygen. Moreover, the repulsive lateral interactions of oxygen promoters with the oxygen of the surface oxide led to rhodium oxide decomposition followed by surface reoxidation by gaseous oxygen. These results confirmed once again that the electrophobic behavior of ethylene oxidation on Rh, which has been already established and discussed in previous studies [22]. Similar behavior has been also observed during potentiostatic transient as well as at lower temperature (290 °C).

Figure 4 shows the induced oscillations during different galvanostatic and potentiostatic anodic polarizations. In the first case (Figure 4a) constant currents between +3 and +20 μA were applied during 60 min to the catalyst system at 330 °C whereas in the second case (Figure 4b) constant potentials between +200 and

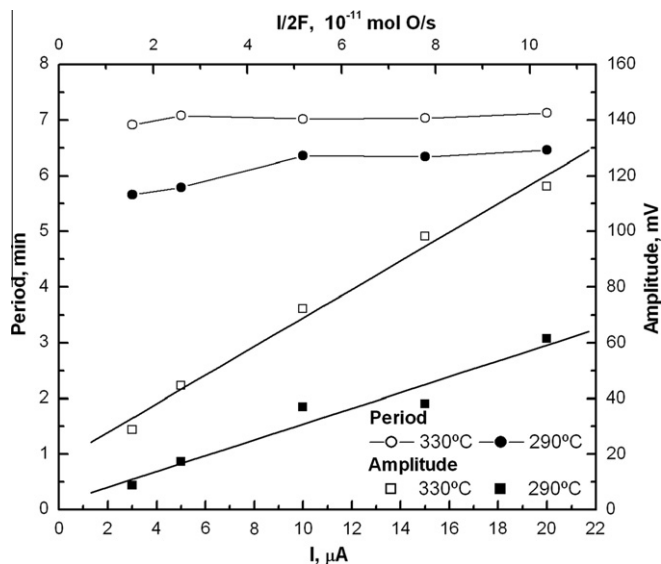**Figure 4.** Time evolution of oscillatory behavior on Rh catalyst electrode during (a) galvanostatic and (b) potentiostatic polarization. $T = 330$ °C.

Figure 3. Time evolution of the catalytic activity and catalyst potential during galvanostatic polarization. $T = 330$ °C.

Figure 5. Influence of the applied current on the oscillations period and amplitude at two different temperatures.
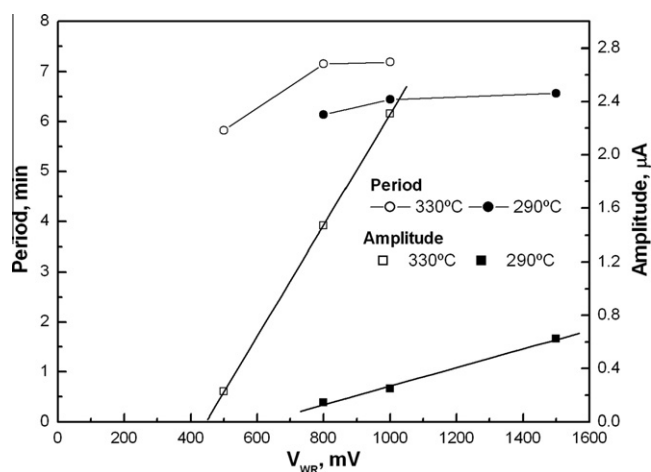
Figure 6. Influence of the applied potential on the oscillations period and amplitude at two different temperatures.

+1000 mV were also imposed at the same conditions. The observed dependence of oscillation period and amplitude on applied current and potential for two different temperatures is shown in Figures 5 and 6, respectively. Amplitude was defined as the oscillation height in mV or µA under galvanostatic or potentiostatic conditions, respectively, and period as the time in min between two consecutive peaks maxima.

For both temperatures, amplitude is a linear function of current (Figure 5) or potential (Figure 6). This could be related to the increased backspillover oxygen coverage of the surface under increased current or potential application. An increase in the positive polarization led to an increase in the amount of decomposed rhodium oxide; and, consequently, in the amount of following reduced Rh surface. In addition, the amplitude increased with temperature, which could be ascribed both to the higher conductivity of YSZ and to the enhanced oxidation-reoxidation processes at elevated temperatures.

It is worth noting that under constant application of 1000 mV (Figure 5) the amplitude at 330 °C was one order of magnitude higher than at 290 °C. On the other hand, the period tended to be constant (approximately 6–7 min) for all the cases except for low applied currents or potentials, which was slightly lower. This means that the transformation rate between rhodium oxide and metallic rhodium was always the same and independent of the amount of decomposed rhodium. The higher values of period observed at 330 °C could be related to the higher fraction of rhodium oxides, which were reduced (or metallic rhodium being oxidized).

4. Conclusions

The electrochemically induced oscillatory phenomena were investigated on Rh films during ethylene oxidation. It was found that the oscillations amplitude increased linearly with the applied current or potential whereas the period, which expresses the reaction rate between rhodium oxide decomposition and rhodium metallic oxidation, remained almost constant (6–7 min). This behavior was related to the presence of the backspillover oxygen on the surface, which affected both the stability of the rhodium oxide and the bond strength of the adsorbed species as well. Besides, under reaction conditions, a continuous cycle of oxidation and reduction reactions took place resulting in an oscillatory behavior. The effect of temperature was also studied; it was observed that the amplitude of the oscillations was strongly dependent on the temperature due to the changes of the YSZ conductivity and the enhanced oxidation-reoxidation processes at elevated temperatures.

Acknowledgements

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