# Electrochemical modification of the catalytic activity of TiO$_2$/YSZ supported rhodium films

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The electrochemical activation of ethylene oxidation was studied over rhodium catalysts of different thickness (40, 100 and 160 nm) sputtered on top of a thin layer of TiO$_2$ deposited on YSZ. The strong relationship between catalytic activity and oxidation state of rhodium was confirmed. Under open-circuit operation the catalyst potential appears as a suitable indicator of the surface oxidation state of rhodium allowing a prediction of the catalytic behavior from solid electrolyte potentiometric measurements. Under closed-circuit conditions the catalyst potential was used as a tool to tune the catalytic activity of rhodium which showed increasing promotional efficiency with decreasing catalyst film thickness.

KEY WORDS: electrochemical promotion; ethylene oxidation; rhodium catalyst; catalyst film thickness; catalyst potential.

## 1. Introduction

The catalytic activity of a rhodium catalyst strongly depends on its oxidation state which, in turn, is closely related to its potential [1]. The latter can be suitably measured in an electrochemical cell where the catalyst film (working electrode), and also the catalytically inert counter and reference electrodes usually made of gold, are deposited on a solid electrolyte. This electrochemical cell configuration allows not only for the measurement of the open-circuit catalyst potential with respect to that of the reference electrode in a solid electrolyte potentiometric (SEP) experiment [2,3], but also for the application of a potential (or current) to the catalyst [4]. In this closed-circuit operation, the applied potential or current is an independent variable used to tune the activity and/or the selectivity, which results in a marked, and very often highly non-faradaic, change in the catalytic reaction rate. The phenomenon [5] is called electrochemical promotion of catalysis (EPOC) or non-faradaic electrochemical modification of catalytic activity (NEMCA effect) [4].

Ethylene oxidation on Rh catalysts exhibits a sudden transition between regions of low and high reaction rate depending on the reacting gas composition. The reason for this is that, unlike other noble metals of group VIII, rhodium easily forms surface oxides, which poison surface reactions [6,7]. In a net oxidizing environment, the surface of a rhodium catalyst is composed mainly of surface Rh$_2$O$_3$, whereas treatment with a net reducing stream yields predominantly metallic rhodium at the surface [7,8].

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From thermodynamic point of view, the transformation between oxidized and reduced states is expected to occur at a given open-circuit catalyst potential, or equivalently, at a given surface activity of atomic oxygen, $a_O$, at the three-phase boundary (tpb):

$$U^o_{WR} = \frac{RT}{4F} ln\left(\frac{a_O^2}{P_{O_2}}\right) \quad (1)$$

where $P_{O_2}$ is the partial pressure of oxygen at an ideal reference electrode. The underlying assumptions are that the electrodes are pure electron conductors while the solid electrolyte is pure ion conductor, and that the only charge transfer reaction defining the potential is

$$O_2(gas) + 4e^-(cat) \leftrightarrows 2O(tpb) + 4e^-(cat) \leftrightarrows 2O^{2-}(YSZ) \quad (2)$$
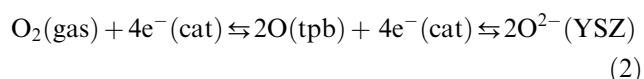
In a previous work [1] solid electrolyte potentiometry of Rh/YSZ was performed in a simplified one-chamber cell, where the gold reference electrode was exposed to the reacting gas mixture of varying composition. The catalytic reaction was the oxidation of propylene with oxygen at 375 °C. The qualitative agreement found between the surface oxidation state estimated from potential measurements and the observed catalytic activity was satisfactory, taking into account that $a_O$ is a property of the "tpb" while the reaction rate reflects the average of the whole gas- exposed catalyst surface.

In the present work, the relation between catalyst potential and catalytic performance is studied under open-circuit and closed-circuit conditions. For this purpose the Rh catalyst-electrodes with a thickness of 160, 100 and 40 nm were sputtered on YSZ previously covered by a thin layer (4 µm thick) of TiO$_2$. The method of sputtering has several advantages compared

to other methods of thermal decomposition of suitable precursors or commercial organo-metal paste deposition [9]: (i) deposition of pure metallic film (no oxidation during deposition) of high dispersion; (ii) deposition of very thin films with precise control of thickness; (iii) good adhesion of the metal film to the substrate. In the present work the ethylene oxidation over Rh/TiO₂/YSZ catalysts with different Rh film thickness is taken as a model reaction.

## 2. Experimental

The experimental set-up used in this study consisted of the gas flow system, the reactor, and the gas analysis unit [10]. Reactants were Carbagas certified standards of $C_2H_4$ (99.95%) and $O_2$ (99.95%) supplied as 12,5% and 20% mixtures in He (99.996), respectively. The balance was Helium. The experiments were performed in an atmospheric pressure single-chamber reactor made of quartz (volume 150 mL); the flow rate was 500 ml/min STP and the temperature was 350 °C. The temperature in the reactor was measured with a K-type (NiCr–Ni) thermocouple placed close to catalyst. At the reactor outlet, $C_2H_4$ and $CO_2$ were monitored with online infrared (NDIR) analyzers (Ultramat 5E-2R; Siemens), analysis of $O_2$ was made with an offline gas chromatograph (GC-A8, Shimadzu, detector TCD, column packed with molecular sieve 13X). Current or potential application was made in the direct polarization mode (the catalyst served as working electrode and the gold film as counter electrode) using a scanning potentiostat (Model 362, EG&G Princeton Applied Research).

The electrochemical cell was of the single-pellet type, where the rhodium working electrode or catalyst was deposited on one side of an yttria-stabilized zirconia (YSZ 8 mol%) (Technox 802 from Dynamic Ceramic) pellet; the counter electrode and the reference electrode were deposited on the other side.

Rh thin film-electrodes were deposited by sputtering. Prior to deposition, the YSZ support was sandblasted for 10 s with the purpose to increase the roughness of the surface. Then the support was carefully cleaned in order to avoid the presence of impurities on the support surface that would interfere with film growth. The cleaning was executed as described elsewhere [11]. A micropipette was used to deposit 2.5 μL of a slurry of 20 % TiO₂ (1 g TiO₂ Degussa P25 in 20 ml EtOH:H₂O 1:1) on a 0.5 cm² YSZ surface area followed by evaporation at 60 °C for 10 min and thermal treatment at 450 °C in air for 30 min. The loading of the TiO₂ layer was 1 mg/cm². The apparent density of the TiO₂ was 2 g/cm³ and the estimated layer thickness was about 4 μm. Then the TiO₂/YSZ support was introduced into the sputtering chamber, filled with pure argon, and rhodium (Rh 99.9, Engelhard) was sputtered onto the substrate (TiO₂/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 was 0.25 nm/s. The thickness of the deposited film was varied by varying the time of sputtering and it was measured by the Alphastep method on smooth silicon samples processed simultaneously. Rhodium films with three different thicknesses were produced: 40, 100 and 160 nm. The counter and reference electrode consisted of porous gold films deposited onto the YSZ by thermal decomposition of a gold paste (Gwent C70219R4); the deposition temperature was 550 °C [10].

Scanning electron micrographs (JSM-6300F, JEOL) of Rh catalyst films deposited on TiO₂/YSZ supports with a thickness of 40, 100 and 160 nm are shown in figure 1. Increasing Rh film thickness leads to formation of compact film with decreasing catalyst porosity.

The effect of current or potential on the catalytic activity is characterized by the rate enhancement ratio ($\rho$) defined as [12,13]:

$$\rho = r/r_o \qquad (3)$$

where $r_o$ is the catalytic rate at open circuit and $r$ the catalytic rate under polarization. The apparent Faradaic efficiency, $\Lambda$, is defined as [4,14]:

$$\Lambda = \Delta r/(I/2F) \qquad (4)$$

where $\Delta r$ ($= r - r_o$) is the increase in catalytic reaction rate due to polarization, $I$ is the applied positive current, $F$ is Faraday's constant, and $I/2F$ equals the rate of $O^{2-}$ supply to the catalyst.

## 3. Results and discussion

The first series of catalytic measurements were made under open-circuit condition at 350 °C. The reaction rate of $CO_2$ production and the catalyst potential were measured at varying feed composition with a constant flow rate of 500 ml/min in the atmospheric reactor. The partial pressure of ethylene was varied from zero to 2 kPa, while the oxygen partial pressure of 0.2 kPa was kept constant. The results are shown in figure 2 (open symbols), where the reaction rate and catalyst potential are plotted as a function of the ethylene partial pressure at the reactor outlet. This figure also shows closed-circuit behavior (applied anodic current +50 μA, full symbols), which will be discussed further.

All catalysts exhibited slow but increasing reaction rate at low ethylene content (first regime). The abrupt transition from the first regime to the second, observed at higher ethylene content and characterized by a much higher and slightly decreasing reaction rate, is dictated mainly by the change in the oxidation state of the catalysts, rhodium oxide being a poor catalyst and metallic rhodium being an efficient catalyst. For the
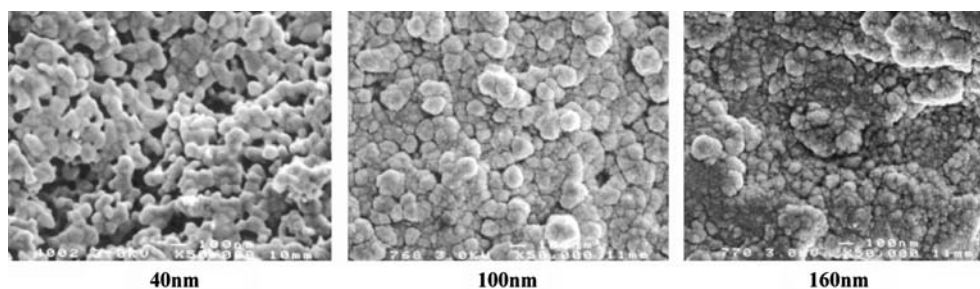
Figure 1. Scanning electron micrographs (top view) of the Rh film deposited on TiO$_2$ interlayer on YSZ; rhodium film thicknesses: 40, 100 and 160 nm. Enlargement: see scale on the photographs.
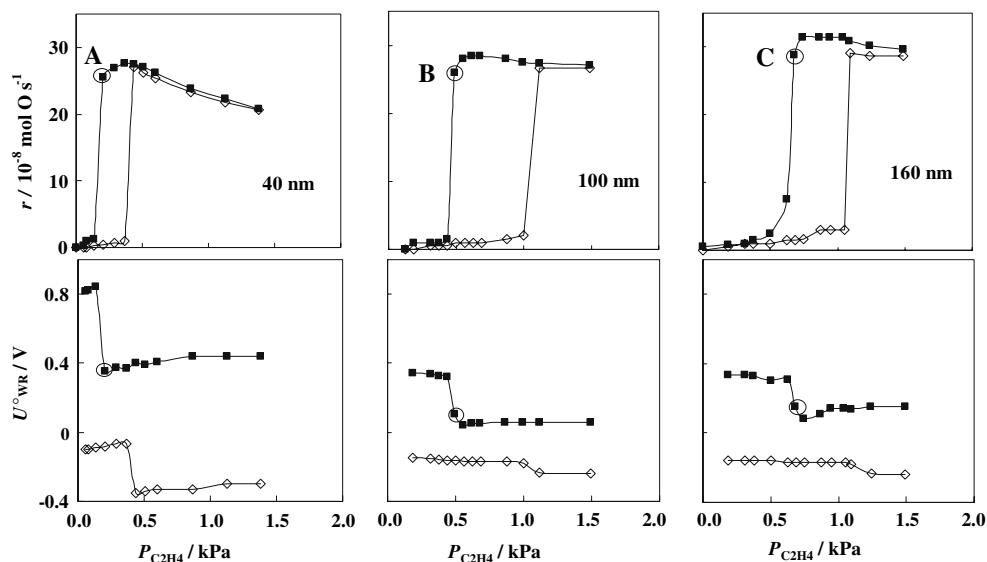


Figure 2. Effect of $P_{C_2H_4}$ and applied current on the rate of C$_2$H$_4$ oxidation on Rh/TiO$_2$/YSZ and corresponding catalyst potential for 40 nm, 100 nm and 160 nm catalyst thicknesses. Open symbols: open circuit; full symbols: closed circuit with $I = +50$ μA. $T = 350$°C, $P_{O_2} = 0.2$ kPa, flow rate 500 ml/min.

three catalysts the change occurred at different gas compositions. The smaller the catalyst thickness the less reducing the environment required for the rhodium catalyst to enter its high activity regime. It can be concluded that decrease of the catalyst thickness has positive effect on its catalytic activity and stability showing that Rh (40 nm) can be easily reduced (activated) at lower C$_2$H$_4$ content than Rh (100 nm) and Rh (160 nm).

Assuming that there is only one single charge transfer reaction (Eq. 2) and it is in equilibrium at both rhodium and gold electrodes, one can use the Equation 1 in order to calculate the activity of atomic oxygen at the three-phase boundary (tpb) of the catalyst. The gold reference electrode fairly well satisfies these assumptions, having a reasonably high exchange current and showing a steady-state current-potential behavior independent of the presence of reactive hydrocarbons [15]. Assuming that the same ideal behavior is valid also for the catalyst electrode, the oxygen activity at the "tpb" at a nominal oxygen partial pressure of 0.2 kPa and at 350 °C is calculated as:

$$\ln(a_O^2) = \frac{4F}{RT}\left[U_{WR}^o + \frac{RT}{4F}\ln(P_{O_2})\right] \quad (5)$$

Figure 3 shows the stability limits of bulk rhodium oxides, in terms of surface oxygen activity, $\ln(a_O^2)$, at the temperature of measurements (350 °C) [16]. The figure allows comparison of the bulk stability limits with the experimental $\ln(a_O^2)$ values calculated with Eq. 5 from the open circuit potential measurements in the immediate proximity of the abrupt potential changes. The oxygen activity of the three oxidized catalysts fall in the region of Rh$_2$O$_3$ stability while after reduction only the Rh (40 nm) catalyst was deeply reduced and the oxygen activity was shifted into the metallic Rh region. The Rh (100 nm) and Rh (160 nm) catalysts did not exhibit a shift big enough to enter the metallic Rh region, so they remained partially oxidized after reduction.

Despite of the several limitations when SEP measurements are performed by using a one-chamber cell where the reference electrode is not separated from the reacting gas of varying composition [1], the open-circuit
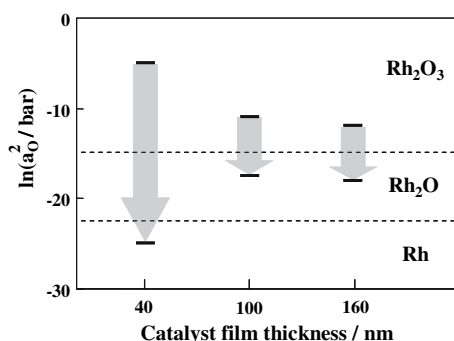
Figure 3. Activity of atomic oxygen, $a_O$, at the three-phase boundary of Rh/TiO₂/YSZ catalyst with different thicknesses in the potential domain of high and low reaction rate shown in Figure 2, in comparison with the stability limits of bulk rhodium oxides in terms of $\ln(a_O^2)$ at 350 °C. Arrows indicate direction of shift during surface reduction.

catalyst potential appears as a sensitive in situ indicator of the average oxidation state, hence also of the catalytic activity, of rhodium catalysts deposited on TiO₂/YSZ support.

Also in closed-circuit operation (figure 2, full symbols) the catalyst potential well indicates the oxidation state of the Rh/TiO₂/YSZ catalyst. For intermediate $P_{C_2H_4}$ values close to the transition region, positive current application causes a pronounced increase in the reaction rate relative to its open-circuit value. It is manifested by decrease in the critical partial pressure of ethylene ($P_{C_2H_4}^*$), where, according to the catalyst potential, decomposition of Rh oxide is occurring. In active state of the catalyst $P_{C_2H_4} > P_{C_2H_4}^*$ the reaction rate is almost the same for the three catalysts and almost unaffected by positive current application (figure 2).

Thus positive current application leads to destabilization of the surface oxide. This point is at first somewhat surprising, but it is well documented and confirmed in the electrochemical promotion literature [4], where this effect is attributed to oxygen backspillover from the solid electrolyte. The presence of the backspillover oxygen species on the gas-exposed catalyst surface causes weakening of the chemisorptive bond strength of electron acceptor adsorbates (e.g. oxygen) making easier the reduction of surface oxides to metallic rhodium [17,18]. This fact is well confirmed by the catalyst potential recorded during a galvanostatic (constant imposed current of +50 μA) transient of C₂H₄ oxidation on the Rh catalysts deposited on TiO₂/YSZ (figure 4). The shown transients were obtained for the three catalysts at the gas compositions, temperature and flow rate that correspond to the points A, B, C on figure 2.

The transient behavior of the potential shown in figure 4 is similar for the three catalyst thicknesses. Before current application the catalyst potential is stable and corresponds to the oxidized Rh surface. Under applied positive current it firstly jumps toward the
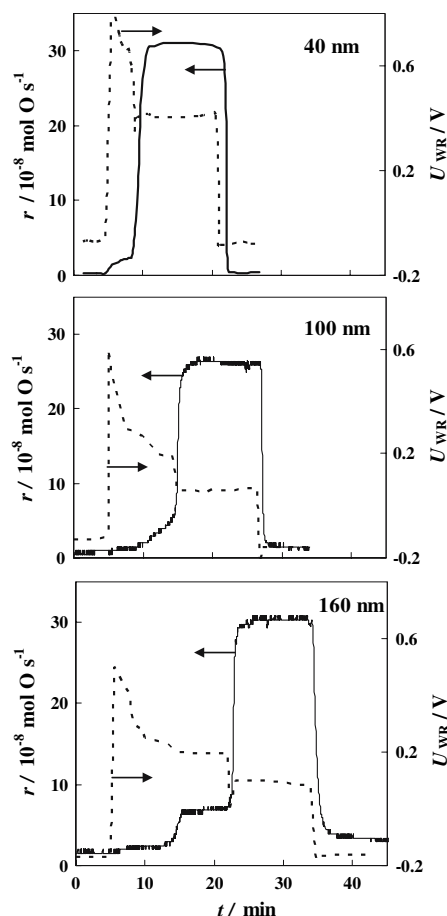


Figure 4. Rate and catalyst potential responses to a step change in applied current of +50 μA at 350 °C and $P_{O_2} = 0.2$ kPa on Rh/TiO₂/YSZ. For Rh film thickness of 40, 100 and 160 nm $P_{C_2H_4} = 0.21$, 0.49 and 0.69 kPa, respectively (see points A, B and C in Figure 2). Flow rate 500 ml/min.

potential of the Rh₂O₃ surface under polarization. Then without being stabilized at this condition the catalyst potential drops suddenly followed by a slow gradual decrease until reaching a steady-state value which remains stable until current interruption. During the slow potential decrease the reaction rate is increasing to reach a stable electropromoted state when the catalyst potential corresponds to metallic Rh surface.

The observed effect is completely reversible and the catalyst returns to its initial state upon current interruption. Decrease of Rh thickness has positive influence on electrochemical promotion. The thinner the Rh catalyst film the less reducing the gas composition required for induction of its stable electropromoted state. Another influence of the catalyst thickness on EPOC is that the time required for the reaction rate to reach stable EPOC decreases with decreasing catalyst film thickness (figure 4).

Figure 5 shows the rate enhancement factor, $\rho$, and the apparent Faradaic efficiency, $\Lambda$, as a function of the catalyst thickness of Rh/TiO₂/YSZ catalysts at 350 °C
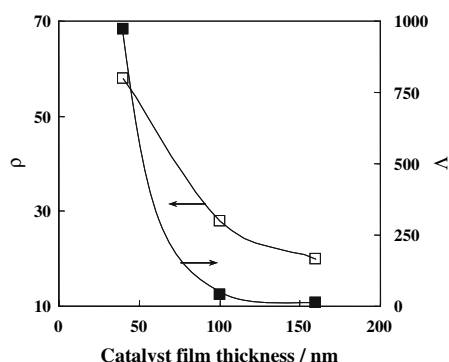
Figure 5. Rate enhancement factor ($\rho$) and Faradaic efficiency ($\Lambda$) values as a function of the Rh catalyst thickness. As $\rho$ values are given the highest rate enhancement factors obtained in ethylene oxidation over Rh/TiO₂/YSZ catalysts at $P_{O_2} = 0.2$ kPa and at $P_{C_2H_4} = 0.21$, 0.66 and 0.73 kPa for Rh film thickness of 40, 100 and 160 nm, respectively. $\Lambda$ values refer to constant gas composition of $P_{O_2} = 0.2$ kPa and $P_{C_2H_4} = 0.2$ kPa. $T = 350$ °C, flow rate 500 ml/min.

and $P_{O_2} = 0.2$ kPa. The three catalysts show strong electrochemical promotion and this effect is highly nonfaradaic in all cases resulting in $\Lambda$ values of 10, 40 and 970 for the Rh (160 nm), Rh (100 nm) and Rh (40 nm) catalyst, respectively. The origin of this high promotion is the anodic polarization of the catalyst/TiO₂ interface, which generates $O^{2-}$ spillover species at the tpb. The polarizability of the catalyst/TiO₂ interface indicates that the Rh-TiO₂ contact is not purely ohmic due to the mixed electronic-ionic conductivity of TiO₂. Hence, TiO₂ may act as an efficient $O^{2-}$ donor as established in previous works [11,17]. Spreading out of these species over the gas-exposed, hence catalytically active, surface decreases the rhodium-oxygen binding energy, thus it assists also to the decomposition of surface rhodium oxide at a gas composition where, under open-circuit conditions, the rhodium oxide surface sites appear stable. EPOC was found the most efficient with the Rh(40 nm) catalyst since both $\rho$ and $\Lambda$ parameters increase with decreasing Rh catalyst thickness.

It can be concluded that increase of the catalyst thickness hinders ion backspillover from the TiO₂ to the rhodium surface. Common promotional kinetics [4] assumes fast backspillover of the promoting species relative to its desorption or reaction resulting in its uniform distribution over the entire catalytic surface. In the present case, it is probable that with increasing thickness of the catalyst film the point is reached where the rate of desorption and/or reaction on the growing gas-exposed catalyst surface become comparable to that of ion backspillover which, far from the tpb, cannot maintain anymore the surface coverage uniform [20,21]. This leads to a decrease in the mean coverage of the promoting species on the catalyst surface, and as seen in Figure 5, to a decrease in parameters $\rho$ and $\Lambda$.

## 4. Conclusion

The potential of Rh film catalysts sputtered on top of a thin layer of TiO₂ deposited on YSZ was found to be a suitable indicator of the oxidation state of the catalyst surface under open-circuit as well as under closed circuit catalyst operation. Therefore, from catalyst potential measurements one can predict the catalytic behavior of the rhodium catalyst. Under open-circuit a good qualitative agreement was found between oxygen activity, $a_O$, which is the property of the three-phase boundary, and reaction rate of ethylene oxidation which reflects the average of the entire gas-exposed catalyst surface. Under closed-circuit conditions the potential of the catalyst appears to be a convenient tool to tune the catalytic activity. At intermediate partial pressure of ethylene, where the Rh catalyst was close to the limit of surface reduction, electrochemical promotion was highly nonfaradaic. Under positive current application, the catalyst surface got partially reduced due to electro-generated $O^{2-}$ spillover toward the gas-exposed catalyst surface, which is known to weaken the rhodium-oxygen binding strength. The efficiency of EPOC strongly depended on the Rh film thickness following the order Rh (40 nm) > Rh (100 nm) > Rh (160 nm), and the thinner the Rh catalyst film the less reducing the gas composition required to transform the catalyst to its stable electropromoted state.

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