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ORIGINAL PAPER

Towards a new definition of EPOC parameters for anionic electrochemical catalysts: case of propene combustion

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Abstract The electrochemical promotion of catalysis (EPOC) of propene combustion was investigated using Pt sputtered thin film on an O^{2-} conductor, 8 mol% Y_2O_3-stabilized-ZrO_2 (YSZ). In order to separate the influence of the thermal migration of the O^{2-} oxide ions from the electrolyte to the catalyst surface and the impact of an electrical polarization on the catalytic activity, several light-off experiments (cool down and heat up procedures) were successively performed under different polarizations, i.e. OCV, +2 and −2 V. These experiments have clearly shown that the presence of O^{2-} (thermally or electrochemically induced) inhibits the catalytic activity of the platinum for the propene deep oxidation. These results demonstrate the importance to define a normalized rate enhancement ratio, ρ_n, from a reference value of the catalytic rate corresponding to a Pt surface state free of O^{2-} ions.

Keywords C_3H_6 combustion · Electrochemical promotion of catalysis · EPOC · Platinum sputtered catalyst · NEMCA effect

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1 Introduction

The electrochemical promotion of catalysis (EPOC), also called Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) effect, was discovered [1] and developed [2–7] by the group of Vayenas. This process is described by the control of the catalyst work function, due to electrochemical pumping of ions (promoters or inhibiters) from a solid electrolyte [6]. EPOC can be achieved with an electrode-catalyst deposited on a dense solid electrolyte membrane, by application of an electrical potential (e.g. ±2 V) or current (e.g. ±100 μA) between the active metallic catalyst film and a counter electrode (catalytically inert) deposited on the other side of the membrane. In several technologies including, for example, burner or electrically heated catalysts [8], exhaust gas ignition [9] and hydrocarbons traps [10], the needs concerning the efficiency of the catalyst activity become more and more important. Thus, the use of electrochemistry to activate and control a reaction is an expanding domain, because it enables improvement of the catalytic performance (and the lifetime) of a metal catalyst. In previous work, we have investigated the ability of electrochemical promotion to improve the catalytic activity of Pt for C_3H_6 oxidation using YSZ [11], NASICON [12] and K-βAl_2O_3 [13] as solid electrolytes. To describe and quantify the electrochemical effect of the promoting species, some basic rules established by Vayenas et al. [14] have been introduced and are commonly used:

1. The Faradaic efficiency, Λ, defined by the following relationship:

$$\Lambda = (r - r_o)/(I/n \cdot F) = \Delta r/(I/n \cdot F) \qquad (1)$$

where r_o, in mol O/s, is the catalytic rate at open-circuit voltage (OCV), r the catalytic rate under polarization, F the Faraday constant, *n* the number of exchange electrons during the electrode reaction ($n = 2$ with O^{2-}). The variation Δr also corresponds to the acceleration of the catalytic reaction induced by a current I (A).

2. The rate enhancement ratio, ρ, defined by:

$$\rho = r/r_o. \quad (2)$$

In the case of O^{2-} conductors, the value of r_o used in the literature for the calculation of ρ and Λ corresponds to the catalytic rate at OCV before the polarization [4–7]. Considering that the presence of ionic species on the catalyst/gas interface is at the origin of the promotional effect, all these papers [15–20] assumed that the initial coverage of ionic species is negligible before polarization and does not influence the catalytic rate level measured at OCV. The objective of this study was to check this assumption. The selected reaction was propene combustion in excess oxygen and the electrochemical catalyst was Pt/YSZ. Previous studies [13, 21–23] have demonstrated that a negative voltage, above 340 °C, could promote propene deep oxidation on a Pt/YSZ electrochemical catalyst.

In this study, Pt/YSZ electrochemical catalyst was made of a continuous platinum film prepared by physical vapour deposition in order to minimize the Pt loading. This technique creates reproducible and dense films for EPOC applications [24]. Propene oxidation was investigated in lean-burn conditions (large excess of oxygen) and at low temperatures (260 °C) in order to simulate the operating conditions of a real Diesel exhaust gas [25, 26].

2 Experimental

2.1 Electrochemical catalyst preparation

Pt thin coatings were sputter-deposited on yttria-stabilized zirconia (YSZ) membranes (Kerafol Gmbh) from a Pt metallic target in argon. The experimental device, described previously [27], was a 40 L sputtering chamber. The 50 mm diameter magnetron target was powered by an advanced energy dc supply equipped with a fast arc detector able to cut microarcs within 1–2 µs. In all experiments, the discharge current was maintained at a constant value of 0.1 A and the draw distance was 50 mm. Total pressure was measured using an absolute MKS Baratron pressure gauge. Coating thickness was measured by analysing the transmittance-wavelength curves measured with a Varian Cary 5000 optical spectrometer based on a programme developed by PVDco Ltd [28, 29]. The electrochemical catalyst consisted of a dense and continuous thin Pt film (geometric area of 1.5 cm^2, Pt loading of 65 $\mu g\ cm^{-2}$) deposited on one side of the YSZ disc (17 mm in diameter and 0.5 mm thick). The thickness of the Pt films was found to be 32 ± 3 nm. X-ray diffraction measurements (Philips model PW-1711) using $K\alpha_{(Cu)}$ have shown by using the Scherrer equation that the Pt particle size varied from 8 nm for fresh catalyst to 13 nm for aged (after thermal pretreatment). Gold counter and reference electrodes were deposited on the opposite side of the YSZ membrane also by physical vapour deposition from an Au metallic target.

2.2 Catalytic activity measurements for C_3H_6 combustion

The catalytic activity measurements were performed at atmospheric pressure in a specific quartz reactor, as described previously [30, 31]. The reaction gases were Praxair certified standards of 4% C_3H_6/He, O_2 (99.99% purity), and He (99.999% purity), which was used as the vector gas. The gas composition was controlled by mass flow controllers (Brooks). The reactive mixture (RM) was as follows: O_2/C_3H_6: 10%/1,800 ppm. The overall gas flow rate was kept constant at 10 L h^{-1}. A thermal pretreatment was carried out in order to stabilize the morphology of the platinum film. This consisted of three steps:

- introduction of the reactive mixture at 100 °C,
- heating from 100 to 400 °C at 5 °C min^{-1},
- plateau at 400 °C for 2 h.

Reactants and products were analysed using an on-line micro gas-chromatograph (Varian CP-4900). The three electrodes, W (catalyst-electrode or working electrode, the Pt sputtered film), R (reference, Au sputtered film) and CE (counter-electrode, Au sputtered film) were connected to a potentiostat-galvanostat Voltalab 21 (Radiometer Analytical). A reaction accelerated by a negative current or overpotential (oxygen removed from the catalyst surface to the membrane) presents electrophilic NEMCA behaviour, corresponding to a value of Λ lower than -1. In parallel, a reaction promoted by a positive current or overpotential (oxygen supplied from the membrane to the catalyst surface) is named electrophobic ($\Lambda > 1$). In this study, the usual r_o determined as the catalytic rate at Open Circuit Voltage (OCV) was substituted by r_{ref} corresponding to a Pt surface state free of ionic species. To obtain this state for YSZ electrolyte, an O^{2-} ionic conductor, r_{ref} was defined by the catalytic rate upon a negative voltage of -2 V for 1 h. This cathodic polarization generates the migration of O^{2-} ionic species from the Pt surface toward the electrolyte, leaving a free Pt surface without any ionic species. Thus, before each polarization a cleaning step was implemented, i.e. an overpotential of -2 V (including the ohmic drop) was applied for 10 min. This step assures the same Pt surface state before each polarization. The electrochemical catalyst was successively polarized for 1 h at −2 V (reference state), −1.5, −1, −0.5, 0, +0.5, +1, +1.5, +2 V. Between two polarizations, the cleaning step was systematically performed. The catalytic rate values were recorded at the end of each polarization. To evaluate the influence of temperature on the impact of polarization, two temperatures were chosen, 260 and 280 °C.

3 Results and discussion

3.1 Light-off curves

After keeping the electrochemical catalyst at 400 °C for 2 h, catalytic activity measurements were carried out by using a specific thermal procedure, consisting in a rapid cooling from 400 to 200 °C followed by heating from 200 to 400 °C (heating ramp: 5 °C min^{-1}) under reactive mixture (RM). This procedure was performed four times consecutively. For each thermal procedure, various polarizations, OCV, +2 and −2 V were applied during the cooling process from 400 to 200 °C. The light-off curves, i.e. propene conversion variations versus temperature, were successively recorded without polarisation during the heating. The ranking of the experiments was as follows: OCV, +2 V, and −2 V. The last experiment corresponding to −2 V was realized twice and named −2 V (a) and −2 V (b) to check the reproducibility. These consecutive light-off measurements demonstrate the difference between no prior polarization of the electrochemical catalyse (OCV, where O^{2-} can only migrate to the Pt surface by thermal migration), an anodic overpotential (+2 V, where O^{2-} can migrate both thermally and electrochemically) and a cathodic polarization (−2 V, where O^{2-} cannot migrate to the Pt surface).

Figure 1 shows that prior negative polarization leads to the most effective catalyst for propene combustion. The value of T_{20} which corresponds to the temperature for 20% of conversion was found to be 303 °C. When the spillover of ionic species is removed or limited by an initial negative polarization, the catalyst gives its highest performance. On the other hand, after anodic pretreatment (+2 V), the catalyst exhibits the lowest performance with a value of T_{20} of 332 °C. This demonstrates the inhibiting effect of O^{2-} ions for the propene deep oxidation on Pt. The catalytic behaviour recorded without previous polarization was intermediate with a value of T_{20} of 321 °C. The initial O^{2-} coverage on Pt without any polarization is only due to thermal migration of ions from YSZ to the Pt surface as already demonstrated [32, 33]. Thus, one can assume that the O^{2-} coverage corresponds to an intermediate value between that after anodic pretreatment (high O^{2-} coverage) and that after cathodic treatment (negligible O^{2-} coverage). Therefore, the OCV curve does not represent a reference state because it depends on the initial O^{2-} coverage on Pt, i.e. on the thermal story of the sample.

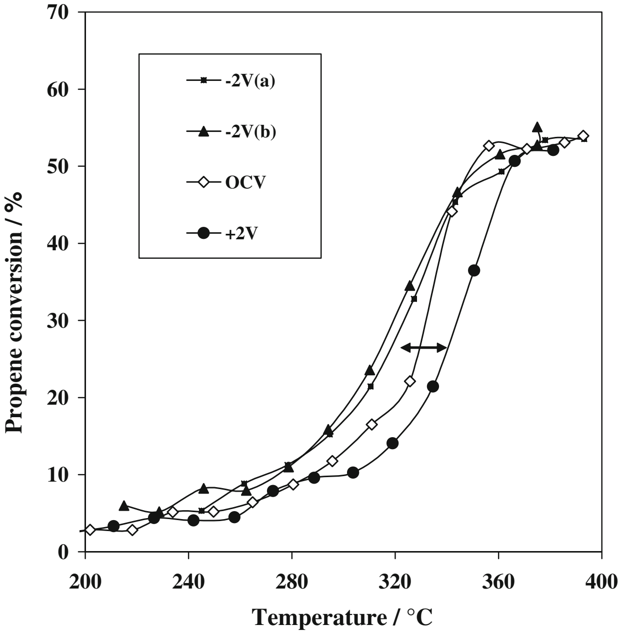

Fig. 1 Propene conversion variations versus temperature recorded after different polarizations during the cooling down process (OCV, −2 V, +2 V). Feed composition: O_2/C_3H_6: 10%/1,800 ppm

By comparing curves −2 V (a) and −2 V (b), it is possible to check that the sintering was avoided by the initial thermal pretreatment since these two light-off curves are similar.

3.2 Potentiostatic transient NEMCA experiments

Figure 2 presents the impact of negative polarization (−4 V) at 260 °C on propene conversion; the current measured was −60 µA. When cathodic polarization was applied, the propene conversion rapidly increased from 8% to 13.5% and stabilized after 35 min at 12%. The Faradaic efficiency was found to be −250, demonstrating that the polarization impact on the catalytic activity is clearly non-Faradaic, exhibiting an electrophilic NEMCA behaviour. When the current was stopped, the conversion returned to its initial value. The rapid response of activity with applied overpotential is characteristic of sputtered catalytic thin films as already shown in a previous paper [25]. These results confirm the inhibiting effect of ionic species on propene conversion. Indeed, the negative polarization leads to the removal of ionic inhibiters. However, the magnitude of the polarization depends on the initial level of O^{2-} coverage on Pt. This former is linked to the magnitude of thermal migration and on the thermal history of the electrochemical catalyst.

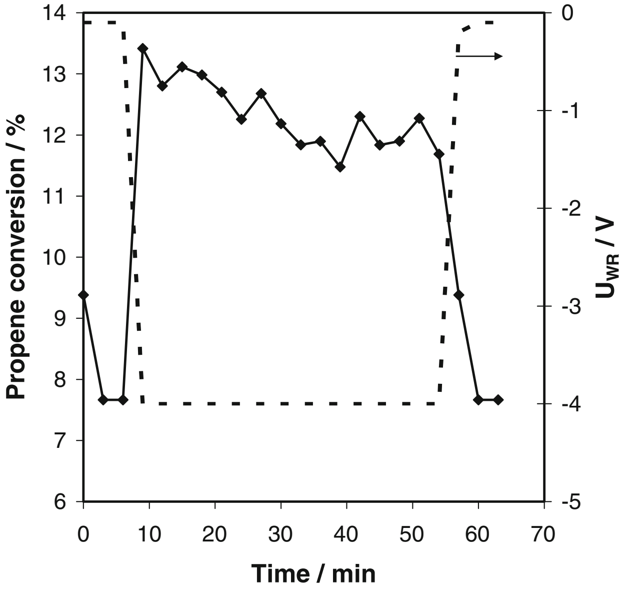

Fig. 2 Potentiostatic transient experiment at 260 °C upon $U_{WR} = -4$ V. Feed composition: O_2/C_3H_6: 10%/1,800 ppm

Figure 2 shows a slight decrease in propene conversion with time under cathodic polarization. This can be attributed to local reaction temperature increase on the catalyst surface due to the heat release from the reaction. The large increase in propene combustion under application of negative polarization led to an increase in the local temperature of the Pt particles that produces an additional increase in catalytic activity. However, as long as the heat is progressively dissipated over the whole catalyst surface, after 35 min, the conversion is almost constant.

In order to evaluate the real impact of the polarization on propene conversion, transient NEMCA experiments were carried out at two different temperatures, i.e. 260 and 280 °C. We calculated a normalized rate enhancement ratio, ρ_n, and a normalized Faradaic efficiency, Λ_n using the following relationships:

1. The normalized rate enhancement ratio, ρ_n defined by:

   $$\rho_n = r/r_{\mathrm{ref}} = r/r_{(-2\,\mathrm{V\,during\,1\,h})} \tag{3}$$

   where r_{ref} is not the open-circuit catalytic rate (r_o) which depends on the sample thermal story but the catalytic rate corresponding to a reproducible Pt-free surface (r_{ref}), i.e. with a negligible O^{2-} coverage on Pt. Value of r_{ref} is obtained after 1 h of polarization at −2 V. This value of potential difference was selected because the observed impact on propene conversion was exactly the same as that recorded at a more negative voltage, i.e. −4 V (see Fig. 2).
2. A new definition is given for the normalized Faradaic efficiency Λ_n taking into account this reference state. Therefore the value of current (i_{ref}) during polarization at −2 V is integrated in the equation 2:

   $$\Lambda_n = (r - r_{\mathrm{ref}})/((i - i_{\mathrm{ref}})/n \cdot F). \tag{4}$$

Figures 3 and 4 show the variation at 260 and 280 °C of propene conversion and of the normalized rate enhancement ratio (ρ_n) versus the applied polarization. These figures clearly confirm the inhibiting effect of O^{2-} species on propene conversion since ρ_n decreases from 1 at −2 V, to 0.55 at +0.5 V. This means that the propene conversion can be divided by two when ionic species can migrate onto the Pt surface. In addition, Fig. 4 suggests that at a polarization of +0.5 V, the impact on propene conversion is constant, i.e. O^{2-} ion coverage is maximal.

Table 1 summarizes the normalized enhancement factor values calculated at different temperatures. At 260 and 280 °C, for +0.5 V applied for 1 h, high values of Λ_n are achieved, close to −780 and −680, respectively. The sign of Λ_n values is always negative (electrophilic behaviour for all the range of applied overpotentials) confirming the inhibiting rule of the O^{2-} species on propene conversion. The thermal migration of O^{2-} species from the electrolyte to the Pt surface can be avoided or limited by the negative polarization. In our case, as we considered the reference state upon a negative polarization of −2 V, the electrochemical migration (from Pt to YSZ) rate of O^{2-} ions at 260 and 280 °C is higher than thermal migration which occurs in the opposite direction. However, for lower negative applied overpotentials, thermal migration is faster than electrical leading to an increase in the O^{2-} species on the Pt surface.

This thermal migration effect cannot only be interpreted by the ionic conductivity of YSZ but most probably by the

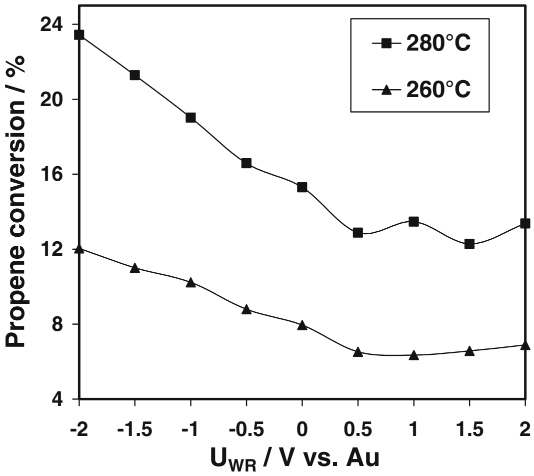

Fig. 3 Influence of the polarization on the propene conversion for Pt/YSZ at low temperatures. Feed composition: O_2/C_3H_6: 10%/1,800 ppm

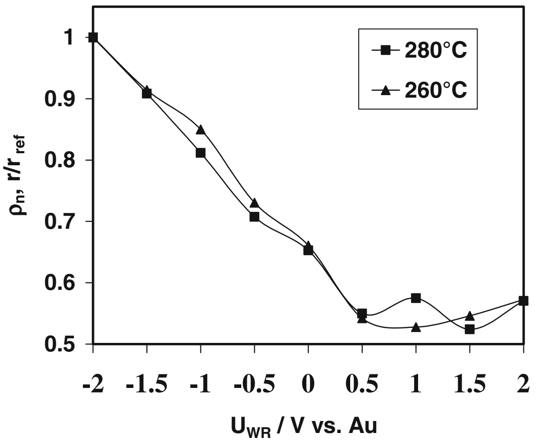

Fig. 4 Influence of the polarizations on the normalized rate enhancement ratio (ρ_n) for Pt-YSZ at low temperatures. Feed composition: O_2/C_3H_6: 10%/1,800 ppm

Table 1 Normalized enhancement factor (Λ_n) and current intensity as a function of voltage differences for different temperatures: 260 and 280 °C

Voltage difference (V)	260 °C		280 °C	
	Intensity (μA)	Λ_n	Intensity (μA)	Λ_n
−2 (reference)	−25	0	−53.1	0
−1.5	−17	−491	−34.8	−419
−1	−12	−495	−20.8	−486
−0.5	−5.7	−599	−9.2	−556
0	−2.8	−656	−3.4	−583
+0.5	0.2	−779	2.3	−678
+1	3.5	−711	12.4	−542
+1.5	7.7	−595	17.9	−559
+2	12	−495	24.1	−464

Feed composition: O_2/C_3H_6: 10%/1,800 ppm

morphology of the electrochemical catalyst. Indeed, the migration of O^{2-} species from YSZ is promoted by a very thin and dense sputtered Pt layer (very low internal diffusion) compared to porous and thick films usually obtained from a commercial paste.

The inhibiting effect of O^{2-} species on propene conversion can be explained from the modification of the Pt work function. Indeed, polarization inducing the migration of O^{2-} ions from the electrolyte to the Pt surface strengthens the Pt–C_3H_6 chemical bonds (electron-donor) and weakens the Pt–O bonds (electron-acceptor) [5, 11, 34]. Considering that at low temperatures, C_3H_6 is strongly adsorbed on the Pt surface (low oxygen coverage) as already shown in previous studies [11–13, 21–23], positive polarization inhibits oxygen adsorption, thus, as predicted by the Langmuir-Hinshelwood model, decreasing propene conversion.

4 Conclusion

The electrochemical promotion of catalysis (EPOC) of propene combustion was investigated using Pt sputtered thin film on YSZ. Results have clearly demonstrated that thermal migration of O^{2-} species from YSZ to the Pt surface can occur in the temperature range 200–400 °C. The O^{2-} coverage on Pt, which depends on the thermal history of the electrochemical catalyst, can strongly affect catalytic activity. Therefore, in order to evaluate the real impact of polarization on the catalytic activity, we calculated normalized rate enhancement ratio (ρ_n) and Faradaic efficiency (Λ_n), not from the open-circuit catalytic rate (r_o) which depends on the sample thermal story, but from the catalytic rate corresponding to a Pt surface free from O^{2-} (r_{ref} and i_{ref}), i.e. with a negligible O^{2-} coverage on Pt. Thus, modifications of the catalytic rate induced by polarization can be investigated without the contribution of thermal migration.

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