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Electrochemical catalysis for propane combustion using nanometric sputtered-deposited Pt films

L. Lizarraga [a,*], M. Guth [a], A. Billard [b], P. Vernoux [a]

[a] Université de Lyon, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256, CNRS, Université Claude Bernard Lyon 1, 2 Avenue A. Einstein, 69626 Villeurbanne, France

[b] LERMPS – Laboratoire d'Etudes et de Recherches sur les Matériaux, les Procédés et les Surfaces, Université de Technologie de Belfort-Montbéliard, 90010 Belfort, France

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ABSTRACT

The catalytic activity of sputtered-Pt films onto Y_2O_3-stabilized ZrO_2 (YSZ) pellets was investigated on the propane combustion. Catalytic performances were compared with conventional electrochemical catalysts based on Pt-paste films. Sputtered electrochemical catalysts presented higher Pt dispersion and significantly larger intrinsic catalytic activity. Furthermore, the catalytic activity of both systems was improved when electrochemical promotion of catalysis (EPOC) was applied to them. The magnitude of the electrochemical activation was higher for sputtered electrochemical catalysts than for Pt-paste films. However, no permanent Non-faradaic Electrochemical Modification of Catalytic Activity (NEMCA) effect was observed on sputtered-Pt films. Nevertheless, the kinetic behaviour of the electrocatalytic activity exhibited temperature dependence, which may be related with the formation of PtO_x species in the bulk of the Pt film during the anodic polarization.

1. Introduction

Catalytic combustion of light hydrocarbons is a non-polluting means of heat and energy generation. Noble metals are the most effective materials for that purpose. However, these materials are very expensive and require various stages of recovery and recycling. The electrochemical promotion of catalysis (EPOC) or Non-faradaic Electrochemical Modification of Catalytic Activity (NEMCA) discovered and developed by Vayenas et al. [1,2] is an innovative concept which can be used to improve the catalytic activity. It is based on the control of the work function due to the electrochemical pumping of ions (O^{2-}) by an applied potential between a solid electrolyte (Y_2O_3-stabilized ZrO_2, YSZ) and the surface of a porous catalyst (Pt) [3,4]. The EPOC process is non-Faradaic and only requires low electrical power. EPOC has been studied for many different catalysts, such as Pt, Pd, Rh, Au, Ag, Ni, IrO_2, and RuO_2 [2]. The electrochemical promotion of C_3H_8 combustion has been investigated on the Pt/YSZ system between 300 and 500 °C and for different hydrocarbon/oxygen ratios [5–8]. Most of these studies have been performed with Pt films made from a commercial paste, typically 1–10 μm thick with a Pt particle size of the order of 1 μm. In a previous study [8], we have shown that thin sputtered-Pt films presented high activity for propane deep oxidation and can be strongly electropromoted. Recent EPOC studies have used metallic sputtered films such as Pt [8,9,16], Ir [10], Pd [11] or Rh [9]. For instance, the development of the novel monolithic electrochemically promoted reactor [9] is based on sputtered catalytic films of Pt and Rh.

In this work, sputtered-deposited films of Pt with a thickness of 60 nm are interfaced with YSZ. This type of electrochemical catalyst has a lower amount of Pt than conventional Pt-paste films. Accordingly, they may be used for practical applications of the EPOC effect [9]. This paper deals with a comparison of the catalytic activity with and without electrical polarization of these two kinds of electrochemical catalysts for the propane deep oxidation. Furthermore, we investigate the ability of sputtered electrochemical catalysts to induce "permanent" NEMCA effect. This effect is observed when a polarization is applied on the electrochemical catalyst for a long time (a few hours), and then, the polarization is interrupted. Noticeably, the catalytic activity remains higher than before the polarization [12]. The presence of this phenomenon can be interpreted with the possible formation of PtO_x species in the interface between the solid electrolyte and the catalyst surface [13–15].

2. Experimental

2.1. Catalyst preparation

Electrochemical catalysts were prepared with solid electrolyte pellets composed of 8 mol% Y_2O_3-stabilized ZrO_2. The YSZ disks

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* Corresponding author.
E-mail address: leonardo.lizarraga@ircelyon.univ-lyon1.fr (L. Lizarraga).

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presented a diameter of 17 mm and a thickness of 1.5 mm [8].

The sputtered-Pt films were obtained via a deposition of a polycrystalline Pt film on one side of the YSZ pellets by means of DC-magnetron sputtering at low pressure. The sputtering device consisted on a 40 L chamber filled with Ar at a pressure of 0.3 Pa. The substrates were positioned at 30 mm from the target axis, at a draw distance of 100 mm. The target was mounted on an unbalanced magnetron and was powered by a 1.5 kW Advanced Energy DC supply. In the coatings, the discharge current was maintained at a constant value of 0.2 A (for more details see Ref. [16]). The nanometric-Pt film presented a thickness of 60 nm and a Pt total mass of 0.2 mg. The thickness was determined by optical transmission spectroscopy in the visible range, using a fitting software developed by PVDco s.a.r.l. [17].

The micrometric Pt films were prepared by painting one side of the YSZ pellet with platinum paste (Engelhard-Clal 6926). The paste only contained fritted glass and was free of Bi. The YSZ disks with the Pt paste were annealed at 550 °C for 4 h. The mass of Pt deposited on the YSZ pellet was 6 mg.

In both electrochemical catalysts, the Pt films were used as working electrode. Two gold films were deposited on the opposite side of the Pt-coating in order to act as counter and reference electrodes, respectively. Gold was selected because of its negligible catalytic activity in propane oxidation, as verified through blank experiments under our experimental conditions. The reference electrode was deposited close enough (about 3 mm) to the counter-electrode avoiding any electrical perturbation. Voltage and current were applied and measured according to the procedure generally used in conventional three-electrode electrochemical cells. The catalyst potential V_{WR} was measured between the working electrode (Pt) and the reference electrode (Au) which may be considered as a pseudoreference since we have checked that its potential does not vary significantly with the composition of the gaseous mixture.

2.2. Catalytic activity

The electrochemical catalysts were tested in a quartz reactor. The latter was designed to facilitate the connection between the electrodes and the potentiostat and to allow the reactive mixture to reach the electrocatalyst surface (for more details see Ref. [7]). A potentiostat–galvanostat Voltalab PGP 201 was used in order to apply and measure both potential and current in the electrochemical catalyst. The reaction gases were mixtures of C_3H_8 (Air Liquide, 8000 ± 80 ppm), O_2 (Air Liquide, 99.95%), and He (Air Liquide, 99.999%) as the vector gas. The gas composition was controlled by mass flow controllers (Brooks), with accuracy of 1%.

The true surface area, N_G, of the sputtered-Pt films expressed in mol O, was measured, after the pretreatment at 550 °C, via isothermal surface titration of C_3H_8 with O_2 at 300 °C, as described by Vayenas et al. [2], and found to be 50 nmol O. The value of Pt dispersion can be estimated at 5%. This dispersion value is much higher than the value reported for Pt-paste films (<1%) [19].

The catalytic properties of the sputtered-Pt films were tested at an overall flow rate of 3 L h^{-1} and the reactive mixture was composed of C_3H_8/O_2: 2300 ppm/1.2% using He as carrier. The paste-Pt films electrochemical catalysts were analyzed at an overall flow rate of 6 L h^{-1} with the same composition of the reactive mixture. Before measuring the catalytic activity, sputtered-Pt and paste-Pt electrochemical catalysts were pretreated for 10 h at 550 °C in the presence of the reactive mixture in order to stabilize the Pt film morphology. The reaction products were analyzed by an on-line micro gas-chromatograph (R3000 SRA Instruments) and a CO_2 IR analyzer (Horiba VA 3000). The propane conversion into CO_2 was defined as:

$$\text{Propane conversion} = 100 \times \frac{P_{CO_2}}{P_{CO_2} + 3P_{C_3H_8}}$$

where P_{CO_2} and $P_{C_3H_8}$ are the partial pressures of CO_2 and C_3H_8 in the outlet, respectively. Carbon dioxide and propane were the only products detected.

The polarization effect on the catalytic reaction is characterized by the rate enhancement ratio (ρ) defined as $\rho = r/r_o$, where r_o, in mol O/s, is the catalytic rate after a negative polarization (−1 V) for 1 h, and r the catalytic rate under polarization. The magnitude of the electrochemical promotion effect is described by the Faradaic efficiency, Λ, which is defined as: $\Lambda = (r - r_o)/(I/nF)$ where n is the number of exchanged electrons during the electrode reaction, in this case equal to 2. A catalytic reaction exhibits the NEMCA effect when $|\Lambda| > 1$. A reaction which is accelerated by a negative current or overpotential (oxygen removed from the catalyst surface) exhibits an electrophilic NEMCA behaviour and corresponds to a value of Λ lower than −1. In contrast, when the catalytic reaction is promoted by a positive current or overpotential (oxygen supplied to the catalyst surface), its NEMCA behaviour is called electrophobic ($\Lambda > 1$).

The measurements presented in this work were performed with the following protocol in order to obtain reproducibility: first, a cathodic potential was applied for 1 h on the working electrode to eliminate the O^{2-} species from the Pt surface [18]. This negative polarization was used in order to remove oxygen ionic species which can migrate onto the Pt film by thermal migration as established in the reference [18]. Then, different anodic currents were applied for 3 h in order to promote ionic species on the Pt surface; and finally, the anodic current was interrupted, and the electrochemical catalyst was kept in OCV conditions.

3. Results and discussion

3.1. Comparison of catalytic activity at open-circuit voltage

Fig. 1 shows SEM images of the Pt-sputtered films (1.a) and Pt-paste films (1.b) after their exposure to the reactive mixture for 10 h at 550 °C. The images show that both Pt films studied present a porous Pt network structure. However, the Pt-sputtered films consist of a 2D network of Pt grains with an average size of 50 nm, whereas Pt-paste films present a multilayer 3D structure with Pt branches of 2 μm average size. This difference may explain the high dispersion value of 5% determined for Pt-sputtering films by isothermal surface titration. Noticeably, sputtered films present a lot of holes, zones in which the YSZ substrate are not covered by the Pt network.

Fig. 2 presents the variation of the catalytic activity for the propane oxidation between 150 and 500 °C, corresponding to the sputtered and paste-Pt films in rate unities of μmol C_3H_8 s^{-1} g^{-1} Pt. It is remarkable the difference between the two curves. The reaction rate for Pt-sputtered films reaches 200 μmol C_3H_8 s^{-1} g^{-1} Pt, whereas the rate for Pt-paste films only achieves 5 μmol C_3H_8 s^{-1} g^{-1} Pt. The higher activity of the former per gram of Pt is related to the higher dispersion value of these films in agreement with the morphology of the films (Fig. 1).

3.2. Comparison of the catalytic activity under closed-circuit

Fig. 3 displays the changes in the propane conversion at 390 °C with the applied potential (V_{WR}) on the sputtered-Pt electrochemical catalyst. First, the catalytic activity was measured at OCV for 1 h. Then, a negative polarization of −1 V was applied, and the propane conversion decreased from 8% to 2.5%. After that, OCV condition was applied for 15 min in order to stabilize the potential before apply-

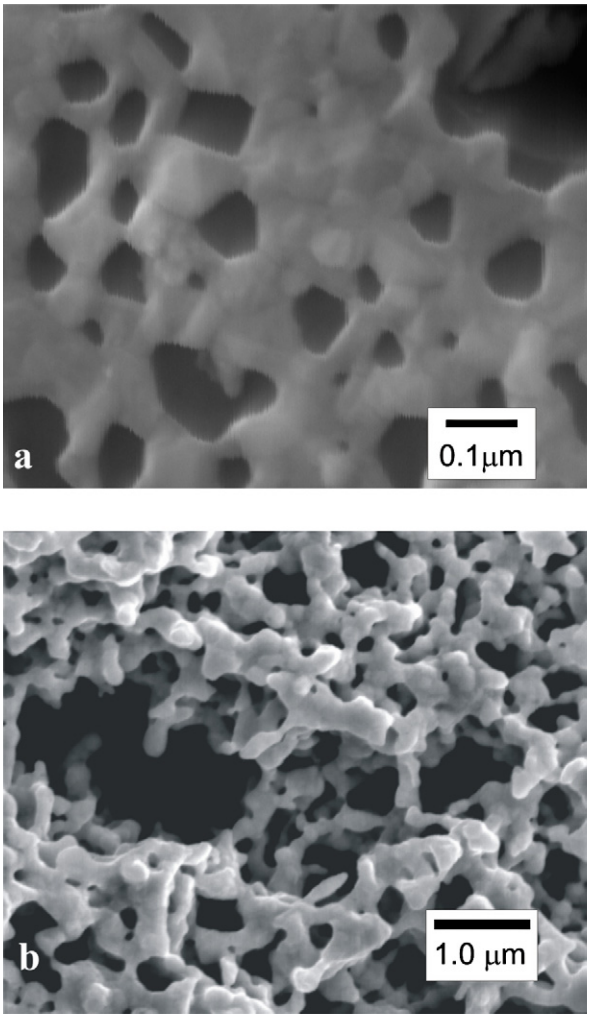

Fig. 1. Top view SEM images of the Pt–YSZ electrochemical catalysts after the stabilization treatment of 10 h at 500 °C in presence of the reactive mixture (a: Pt-sputter electrochemical catalyst; b: Pt-paste electrochemical catalyst).

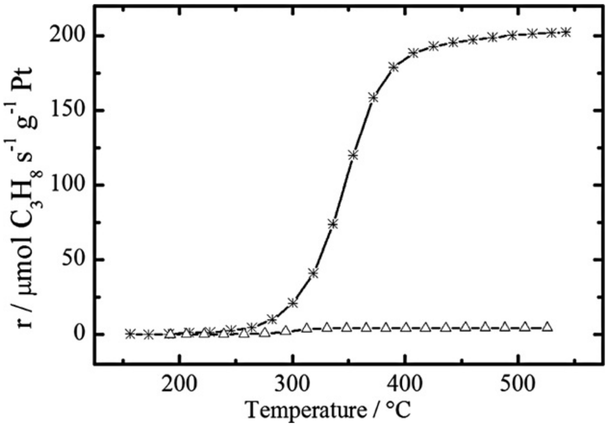

Fig. 2. Propane conversion and open-circuit voltage variations versus temperature for Pt-sputter films (*) and Pt-paste films (△). Reactive mixture: C_3H_8/O_2: 2300 ppm/1.2%. Total flow: 3 L h^{-1}.

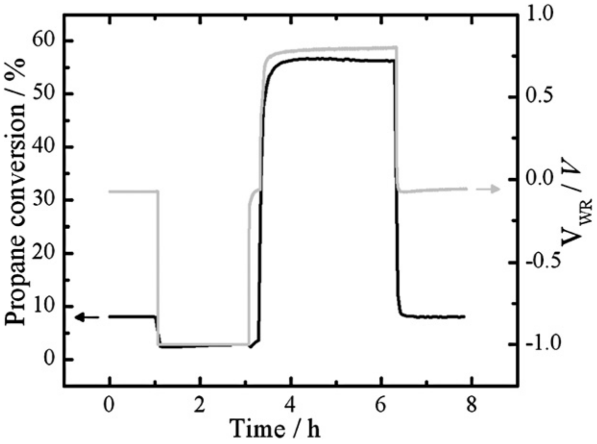

Fig. 3. Propane conversion and potential V_{WR} responses to step changes in applied polarization on the Pt-sputter electrochemical catalyst at 390 °C. Reactive mixture: C_3H_8/O_2: 2300 ppm/1.2%. Total flow: 3 L h^{-1} (black solid line: propane conversion; grey solid line: V_{WR}).

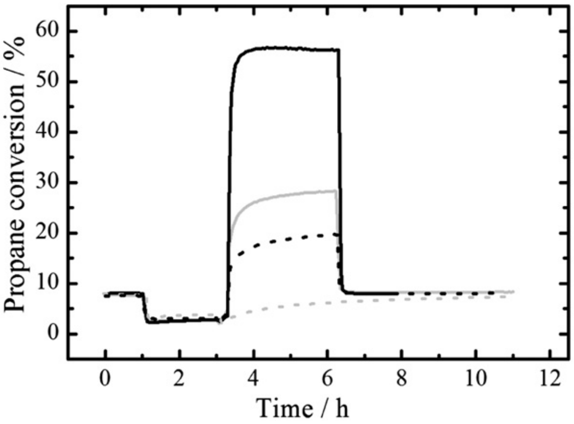

Fig. 4. Propane conversion obtained when different anodic polarization currents were applied on Pt-sputter the electrochemical catalyst at 390 °C. Reactive mixture: C_3H_8/O_2: 2300 ppm/1.2%. Total flow: 3 L h^{-1} (black solid line: +500 μA; grey solid line: +100 μA; black dash line: +50 mA; grey dash line: OCV).

ing the positive polarization. Subsequently, an anodic current of +500 μA was applied for 3 h, and the potential reached the value of +0.8 V. At that moment, the propane conversion was increased up to 56%. The propane oxidation presented an electrophobic enhancement because the reaction rate of propane oxidation decreased when a negative polarization was applied; and it increased when a positive polarization was applied [19].

Fig. 4 presents the different profiles obtained for propane conversion for different anodic currents (+500 μA, +100 μA and +50 μA) following the protocol described before (Fig. 3) on the electrochemical catalyst at 390 °C. As well, Fig. 4 shows propane conversion evolution when OCV conditions were established after 2 h of negative polarization (without the anodic current step). It is clear in Fig. 4 that the catalytic performance strongly increased when the anodic current was applied. All profiles reached a plateau with Λ values superior to 150 and high ρ values were determined (see Table 1). The Λ and ρ values obtained indicate an important NEMCA effect in the studied reaction for this type of electro-

Table 1
NEMCA parameters obtained when positive polarizations were applied on the Pt-sputter and the Pt-paste electrochemical catalysts.

Electrocatalyst	Anodic current (μA)	Λ	ρ
Pt-sputter films	500	153	22.4
	100	361	11.2
	50	480	7.8
Pt-paste films	500	109	1.4
	100	274	1.2

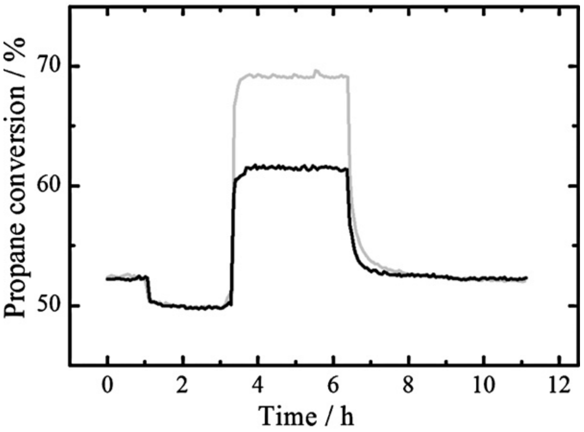

Fig. 5. Catalytic activity profile obtained when applying a polarization current of +500 μA at 390 °C (black solid line) and 430 °C (grey solid line).

chemical catalysts. The sputtered Pt/YSZ electrochemical catalysts presented reproducible results at 390 °C along approximately 20 NEMCA experiments with no decrease in the catalytic activity.

Fig. 5 shows the NEMCA effect results for the electrochemical catalyst composed of Pt-paste films. The profiles obtained, when anodic polarization of +500 μA and +100 μA were applied, are similar to those observed for sputtered-Pt films (Fig. 4). However, the values of Λ for sputtered-Pt films were 50% higher than for Pt-paste films. The low ρ values obtained for Pt-paste films were due to the high OCV conversion. According to Vayenas et al. [2], the absolute value of the Faradaic efficiency may be approximated by:

$$|\Lambda| = \frac{2Fr_o}{I_o}$$

where r_o is the unpromoted rate and I_o is the exchange current of the Pt film–YSZ interface. The unpromoted rate under negative polarization at 390 °C is much higher on paste-films than on sputtered electrochemical catalysts (Figs. 4 and 5). Therefore, it is possible that the exchange current is significantly greater on paste films than on sputtered ones, suggesting that sputtered electrochemical catalysts are highly polarizable. The magnitude of I_o is proportional to the tpb (triple phase boundary) length [20,21]. Then, in spite of much larger Pt grain size, it seems that the tpb length of the Pt-paste film interfaced with YSZ is higher than that of the sputtered electrochemical catalyst. That could be due to the extremely low loading of Pt used in the case of sputtered films which leads to holes and a completely covered surface of the YSZ substrate.

The thermal migration of ionic species from the YSZ electrolyte to the Pt surface was also compared between the two kinds of electrochemical catalysts. Regarding the propane conversion profile on the sputtered-Pt film when OCV conditions were applied immediately after the cathodic potential (without the anodic current step), a slow and gradual increase of the conversion back to its initial value was observed. This confirms the electrophobic behaviour of the propane combustion and that thermal migration of ionic species occurs even at 390 °C. At this temperature, the two electrochemical catalysts were firstly negatively polarized at −1 V for 1 h in order to remove ionic species already present on the metallic surface. These ionic species could spillover on the Pt surface during the pretreatment at 550 °C for 10 h in the feed. Upon negative polarization at 390 °C, the current decreases with time and vanishes to zero when all ionic species are removed. Therefore, the overall charge during this process gives a good indication of the concentration of ionic species which were able to thermally migrate. The value of this charge was estimated to be 2 C for sputtered-films and only 3 mC for paste-films. Therefore, the thermal migration is 3 orders of magnitude faster on the sputtered electrochemical films. This property could be used for the elaboration of self-electropromoted catalytic films [22].

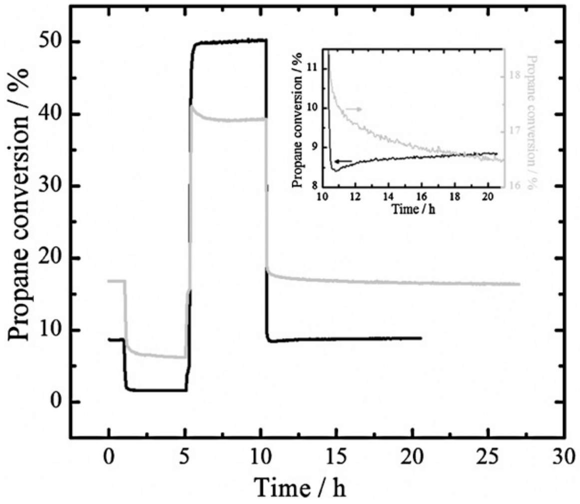

Fig. 6. Propane conversion obtained when different anodic polarization currents were applied on the Pt-paste electrochemical catalyst at 390 °C. Reactive mixture: C_3H_8/O_2: 2300 ppm/1.2%. Total flow: 6 L h^{-1} (black solid line: +500 μA; grey solid line: +100 μA).

3.3. *Investigation of permanent NEMCA on Pt-sputtered electrochemical catalysts*

Fig. 4 shows that, at 390 °C, after 3 h of anodic polarization there was no evidence of permanent NEMCA effect because propane conversion is not enhanced respect to the non applied current case. Absences of permanent NEMCA effect in the Pt-sputtered film electrochemical catalysts were also observed at 430 °C and when 20 h of polarization were applied at 390 °C (figure not shown). These results are in agreement with the study of Jaccoud et al. [15] at 450 °C.

Fig. 6 presents the catalytic activity profiles obtained at two temperatures, 390 and 430 °C. Both measurements were performed applying a polarization current of +500 μA using the protocol previously described. Propane conversion variations with time presented differences according to the temperature values. Although the NEMCA effect was present for both temperatures, different kinetic profiles were observed. At 430 °C the propane conversion increased up to a maximum value when the anodic current was applied. Afterwards, propane conversion decreased and reached a plateau. This behaviour was not observed at 390 °C. The catalytic activity sharply decreased at both temperatures when the polarization was interrupted. At 390 °C it reached a plateau whereas at 430 °C the catalytic performance slowly and gradually decreased (see the inset of Fig. 6). The decrease of catalytic activity under anodic polarization at 430 °C may be due to the presence of PtO_x species on the surface of the Pt film. Besides, the small rate of decrease observed after the anodic polarization may be induced by migration of O^{2-} species to the Pt surface from PtO_x species formed during the anodic polarization in the Pt/YSZ interface or in the Pt bulk [13,14]. Nevertheless, theses PtO_x species do not induce “permanent” NEMCA effect as suggested by Falgairette et al. [13,14]. This could be due to a fast consumption of these oxides by propane due to the relatively high metallic accessible fraction of this kind of thin sputtered electrochemical catalysts.

4. Conclusion

Electrochemical catalysts based on Pt-sputtered films over YSZ were successfully used in the catalysis of propane oxidation. Combustion of propane was strongly improved when anodic currents were applied, due to the NEMCA effect. The sputtered-Pt electrochemical catalysts presented better characteristics for the electrochemical promotion of catalysis than Pt-paste electrochemical catalysts, due to their greater dispersion value and higher polarizability. There was no evidence of a permanent NEMCA effect when working at 390 or 430 °C. However, changes in the kinetic profile were observed at 430 °C respect to 390 °C, which may be associated with the production of PtO_x species in the electrochemical catalyst during the anodic polarization.

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