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ORIGINAL PAPER

CGO-based electrochemical catalysts for low temperature combustion of propene

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Abstract This study has shown that the phenomenon of electrochemical promotion of catalysis or NEMCA effect can be used to activate a metal catalyst for the propene deep oxidation in the presence of water in the feed and in both stoichiometric and lean-burn conditions. The electrochemical catalysts were based on sputtered Pt films interfaced with gadolinium-doped ceria solid electrolyte. This system allows implementing NEMCA effect at quite low temperatures and electrochemical activation of propene deep oxidation was evidenced at temperatures as low as 190 °C. In addition, a new design of electrochemical catalysts was proposed by depositing a interlayer of strontium-doped lanthanum manganite between the CGO dense support and an ultra-thin coating of Pt. This concept allows to drastically decrease the Pt loading since the electronic conductivity is ensured by the perovskite layer.

Keywords Electrochemical promotion · EPOC · NEMCA effect · Electrochemical catalyst · CGO · Strontium-doped lanthanum manganite interlayer · Propene combustion · Wet condition

1 Introduction

The catalytic post-treatment of gaseous stream from Diesel automotives, such as NO_x abatement and combustion of unburned hydrocarbons, is absolutely necessary to achieve the objectives of the future international legislations, such as EURO 6 standards in Europe. One solution could be to limit the NO_x formation during the internal combustion. However, a consequence of this process, called LTC (Low Temperature Combustion) concept, is to significantly increase concentrations of unburned hydrocarbons, such as propene and carbon monoxide emissions, coupled with a decrease of the exhaust gas temperature. Therefore, this innovative technology requires efficient catalysts at low temperatures. Catalysts based on supported noble metal are known as the most effective for this type of application, however, they are very expensive and therefore a lot of efforts are made to reduce the amount of noble metal in the catalysts and/or to improve the efficiency of such catalysts.

Electrochemical catalysts based on a platinum film deposited on Yttria-Stabilised Zirconia (YSZ), an O^{2-} conductor, have been intensively studied in order to implement Electrochemical Promotion of Catalysis (EPOC) [1]. Among these studies, much work concerns oxidation of light hydrocarbons such as methane, ethylene, propane, propene [2–4]. However, the main drawback of YSZ is its low ionic conductivity at low temperatures which makes EPOC inefficient under 250 °C. A key parameter for the use of EPOC at an industrial scale is the design of efficient reactors and electrochemical catalysts. This involves the use of large specific surface area catalysts effective at low temperatures, and easy to polarize. For instance, a monolithic electrochemically promoted reactor (MEPR) consisting in a stack of 22 plates covered by sputtered Rh and Pt films was recently developed, and

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tested for NO_x reduction reaction [5–7]. Only two external electrical connections were needed to polarize the whole plates. However, the catalytic active phase is still in the form of a continuous, porous and electronically conducting film. Even if recently, the use of Physical Vapour Deposition (PVD) allowed improving the metallic dispersion up to 5–40% [5–7] these values are still far from those of conventional supported catalysts (20–90%).

This paper aims to use gadolinia doped ceria as an electrolyte in an electrochemical catalyst in order to achieve electrochemical promotion at lower temperatures than the YSZ conventional electrolyte. In addition, we propose a new design of electrochemical catalysts in which the electronic conductivity is no more ensured by the catalytic active phase but by an oxide interlayer. The double objective is to achieve electrochemical activation at low temperatures and for extremely low Pt loadings. Electrochemical catalysts were prepared from $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO) covered by a thin sputter deposited Pt layer. Furthermore, an interlayer of strontium-doped lanthanum manganite was added by PVD between the CGO dense support and an ultra-thin coating of Pt. The development of electrochemical catalysts containing an interlayer of TiO_2 was already reported in the literature [8–10]. However, most of these references have used a thick film of metallic catalyst (Pt, Cu or Rh). Therefore, the electronic conductivity was also ensured by the metallic layer. Recently, Baranova et al. [9] have investigated YSZ/TiO_2/Rh electrochemical catalysts by using the PVD technique for the Rh film deposition. However, all these Rh films ensured the electrical conductivity even the thinnest one (40 nm).

The impact of the electrical polarizations on the conversion of propene was carried out with different propene/oxygen ratios and in the presence of steam for both electrochemical catalysts designs, conventional and with the conductive oxide interlayer.

2 Experimental

2.1 Preparation of electrochemical catalysts

The dense electrolyte membranes (relative density > 95) were prepared as follow: the CGO powder (supplied by Rhodia) was shaped into disks pressed by uniaxial pressing followed by isostatic pressing at 1,700 bar, the as-obtained pellets were then sintered at 1,550 °C for 2 h with heating and cooling rate of 5 °C min^{-1}. Conductivity versus temperature was measured for a smaller CGO dense pellets (10 mm in diameter and approximately 4 mm in thickness) sintered in the same conditions. A Solartron 1255 frequency analyser was used with a 40 mV amplitude signal in the 1 Hz–1 MHz frequency range with stabilization time of 1 h between each temperature. As expected, the ionic conductivity of CGO is, at least, 10 times higher than that of YSZ in the temperature window of the catalysis, i.e. 200–400 °C (Fig. 1).

CGO/Pt electrochemical catalysts were composed of a thin Pt film interfaced on a CGO dense pellet. Pt thin films were sputter-deposited at low argon pressure (0.3 Pa) on 1 mm-thick CGO membrane. The deposition device was a 30 L sputtering chamber equipped with a rotating substrate holder. The 50 mm diameter magnetron target was powered by an Advanced Energy DC supply and its axis was off-centred by 6 cm from that of the substrate holder. In all experiments, the discharge current was maintained at a constant value of 0.2 A and the draw distance was 50 mm. The thicknesses of the coatings were determined by analysing the transmittance-wavelength curves measured with a Varian Cary 5000 optical spectrometer thanks to a programme developed by PVDco Ltd [13, 14] using a similar layer deposited on a glass substrate. Before depositing the Pt layers by PVD on one side of the electrolyte, gold counter and reference electrodes were deposited on the opposite side of the pellet from a gold paste (Metalor A1644) annealed at 800 °C under air for 2 h. The Pt thickness was estimated around 22 nm (Table 1). In addition the Pt film loading, estimated from the bulk density of Pt considering dense films, was found to be 32 µg cm^{-2}.

CGO/LSM/Pt electrochemical catalysts were also prepared by reactive magnetron sputtering in the same chamber as that used for the deposition of Pt films. Strontium-doped lanthanum manganite ($La_{0.7}Sr_{0.3}MnO_3$) thin films were sputtered on similar CGO pellets than those used for the CGO/Pt electrochemical catalysts. In that case,

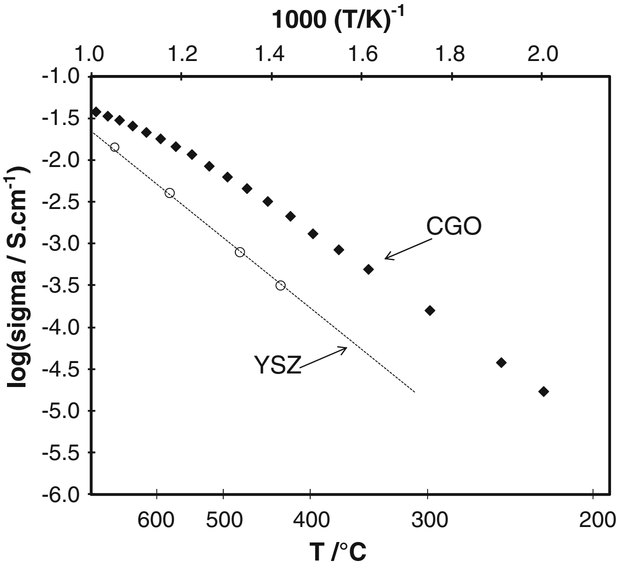

Fig. 1 Arrhenius plots of CGO ($Ce_{0.9}Gd_{0.1}O_{1.95}$) ceramic compared to YSZ ($Zr_{0.92}Y_{0.08}O_{1.96}$) [12]

Table 1 List and main characteristics of electrochemical catalysts

Electrochemical catalysts	Pt loading ($\mu g\ cm^{-2}$)	Pt layer thickness (nm)	LSM layer thickness (nm)
CGO/Pt	32	22	–
CGO/LSM/Pt	2.2	2	80

the coatings were deposited by co sputtering of $La_{0.7}Sr_{0.3}$ and Mn metallic targets (50 mm diameter and 3 mm thick) in Ar-O_2 reactive gas mixture following a procedure described in details elsewhere [15]. The convenient deposition parameters to obtain amorphous $La_{0.85}Sr_{0.15}MnO_3$ coating were 1 A dissipated on the $La_{0.85}Sr_{0.15}$ target and 0.45 A dissipated on the Mn target at an argon pressure of 0.3 Pa and an oxygen flow rate of 10 sccm which ensures the total oxidation of both targets. The deposition time to obtain a 80 nm-thick LSM coating was 10 min. This amorphous LSM layer was further annealed in air at 850 °C for 2 h in order to achieve the perovskite phase structure. An ultra-thin Pt coating was deposited by PVD onto the LSM layer. The thickness was of the order of 2 nm, even if the Pt layer did not cover the whole surface. The Pt loading of the CGO/LSM/Pt electrochemical catalysts was estimated to be 2.2 $\mu g\ cm^{-2}$ which corresponds to an extremely short sputtering time of Pt of 5 s in the conditions described previously for Pt. Table 1 summarizes the list and main characteristics of the electrochemical catalysts.

2.2 Catalytic performance measurements

The catalytic activity measurements of Pt film sputter-deposited on CGO membranes were carried out within a specific quartz reactor which was described in a previous study [3]. The reaction gases were mixtures of C_3H_6, O_2, H_2O and helium which was used as the vector gas. The gas composition was controlled by mass flow controllers (Brooks, with accuracy better than 1%). The reactive mixture contains 1,500–1,660 ppm of propene, 1–6.5% of oxygen and 5% of water vapour. The overall gas flow rate was kept constant at 10 L h^{-1}. The reactants and products were analyzed by an on-line micro gas-chromatograph (Varian CP2003). Prior to the catalytic measurements, the CGO/Pt electrochemical catalysts were stabilised by maintaining them for 1 h at 700 °C under the reactive gas mixture.

The conversion of propene into CO_2 was defined as:

$$C_3H_6\,\text{conversion} = 100 \times P_{CO_2}/(P_{CO_2} + 3 \times P_{C_3H_6}) \qquad (1)$$

where, P_{CO_2} and $P_{C_3H_6}$ are the partial pressures of CO_2 and the C_3H_6 in the outlet gas, respectively. CO_2 was the only carbon-containing oxidation product.

The polarization effect on the catalytic reaction rate is characterised by the rate enhancement ratio (ρ) defined by $\rho = r/r_o$, where r_o (in mol/s) is the catalytic rate at OCV (Open-Circuit Voltage) and r the catalytic rate under polarization. The magnitude of the EPOC effect is described by the Faradaic efficiency [19], defined by $\Lambda = \Delta r/(I/F)$, where $\Delta r = r - r_o$ is the electrochemically induced change in catalytic rate, I the current, and F the Faraday constant.

3 Results and discussion

3.1 CGO/Pt electrochemical catalysts

EPOC characterisations were first performed at 250 °C in a near stoichiometric reactive gas mixture containing large excess of steam (5%). Figure 2 presents the evolution of the catalytic rate as a function of the applied current at 250 °C. The initial open circuit voltage value was −146 mV. This value is lower than that obtained without water as steam has been identified as an electron donor adsorbate like propene [16, 17] in these reaction conditions. At 250 °C, the propene conversion is extremely low, less than 1%. Nevertheless, for both negative and positive bias, a slight increase of the propene conversion is observed, with equivalent Faradaic efficiencies, Λ, of −2 and +2, respectively. This result is in good agreement with our previous study in similar operating conditions on Pt/YSZ/BITAVOX electrochemical catalyst [18]. The addition of steam in the feed considerably modifies the adsorbates coverage on Pt. Propene coverage decreases in favour of both O_2 and H_2O adsorptions. One can suggest that coverage of all the adsorbates is low. Therefore, positive polarizations, which favour propene and H_2O adsorptions, can enhance the activity while negative polarizations which can promote oxygen chemisorption can also increase the catalytic performances. The Faradaic efficiency values indicate that the activation of the catalytic process is not Faradaic. According to Vayenas et al. [19], the Faradaic efficiency is linked to the initial catalytic rate and the exchanged current:

$$\Lambda = 2Fr_o/i_o \qquad (2)$$

with r_o is the initial catalytic rate and i_o is the exchanged current at the Pt/CGO interface. Therefore, one can assume that Faradaic efficiency values, measured in this study, are low due to extremely small initial propene conversions. For similar reasons, the rate enhancement ratios are low but slightly higher under cathodic currents ($\rho = 1.3$) than upon positive ones ($\rho = 1.2$). In addition, we observed a decrease of propene conversion during positive polarizations, suggesting that opposite phenomena occur after long-term polarization as already observed with Pt/YSZ/BITAVOX electrochemical catalyst [18]. Nevertheless, these results show that the electrochemical activation of propene deep oxidation occurs in the presence of steam under these operating conditions.

A second set of experiments was performed in the presence of an excess of oxygen at lower temperature (220 °C), still in the presence of large quantity of steam. Figure 3 reveals that, as expected, the propene conversion is much higher than that observed in stoichiometric conditions. The value of the open-circuit voltage is -156 mV. Both positive and negative currents promote the propene conversion. The Faradaic efficiency is higher for positive bias ($\Lambda = +6$) than for negative one ($\Lambda = -2$). The rate enhancement ratio is (slightly) higher for positive polarization ($\rho = 1.3$) than for negative (or cathodic) ones ($\rho = 1.1$). No decrease of the propene conversion during positive polarisations was observed, in opposition with the results obtained in stoichiometric conditions. These results confirm, as already demonstrated by using Pt/YSZ/BITAVOX electrochemical catalyst [18], that electrochemical promotion of propene deep oxidation can take place even in lean-burn conditions and with large quantity of steam in the feed. On Figs. 2 and 3, the propene conversion did not return to its initial value but in a lower one after the cathodic polarization. This is certainly due to the thermal ionic migration that can easily take place by using thin sputtered film of Pt [11]. Therefore, the O^{2-} coverage on Pt is higher before the cathodic polarization than after. As the presence of oxide ions on the Pt surface has a promoting effect on the catalytic activity (Figs. 2 and 3), the propene conversion is lower after the cathodic polarization than before.

The use of CGO instead of BITAVOX [18] or YSZ [3] allows decreasing the operating temperature. Under the same reactive mixture, both positive and negative currents were applied at 190 °C (Fig. 4). At this low temperature, extremely small conversion occurs of the order of 0.8%. The open-circuit voltage is very negative, i.e., -286 mV. This suggests a strong adsorption of steam on Pt surface which inhibits the catalytic activity. No significant effect on the propene conversion was observed upon negative polarisation. On the other hand, a positive current led to a gradual improvement with time of the propene conversion up to 1% (Fig. 4). This enhancement is non-Faradaic with a Λ value equal to 1.7. This positive polarization could improve the propene coverage on Pt. Let us note that the decrease of the propene conversion, when the current was turned off, was quite slow maybe due to the fact that consumption of ionic promoter species already present on Pt is extremely slow at this temperature. This could indicate that, in this low temperature range, a continuous polarization is not necessarily required for promoting the activity.

3.2 CGO/LSM/Pt electrochemical catalysts

The Pt loading of the CGO/LSM/Pt electrochemical catalyst was extremely low, i.e. 2.2 µg Pt cm^{-2}, at least 30 times lower than that of CGO/Pt sample. Regarding the Pt

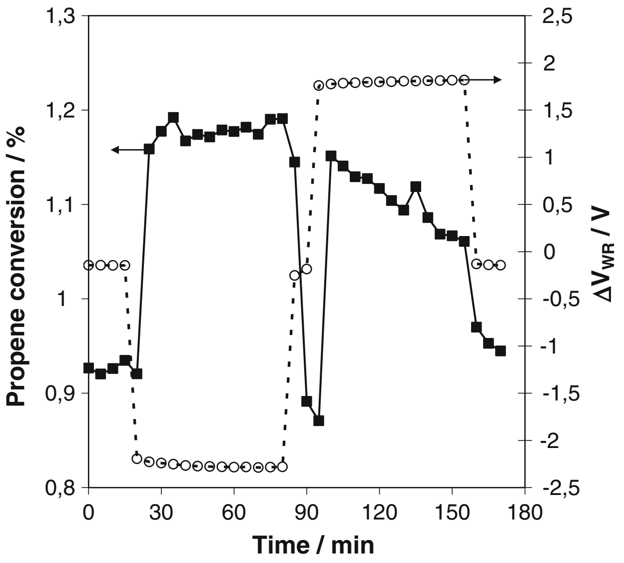

Fig. 2 Effects of the application of ±200 µA on propene conversion at 250 °C. Electrochemical catalyst: CGO/Pt. Reactive mixture: $C_3H_6/O_2/H_2O$: 1,500 ppm/1%/5%

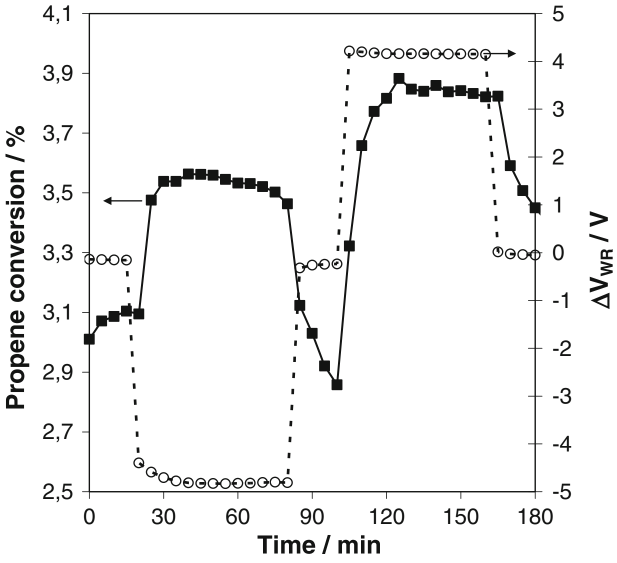

Fig. 3 Effects of the application of ±200 µA on propene conversion at 220 °C. Electrochemical catalyst: CGO/Pt. Reactive mixture: $C_3H_6/O_2/H_2O$: 1,500 ppm/6.5%/5%

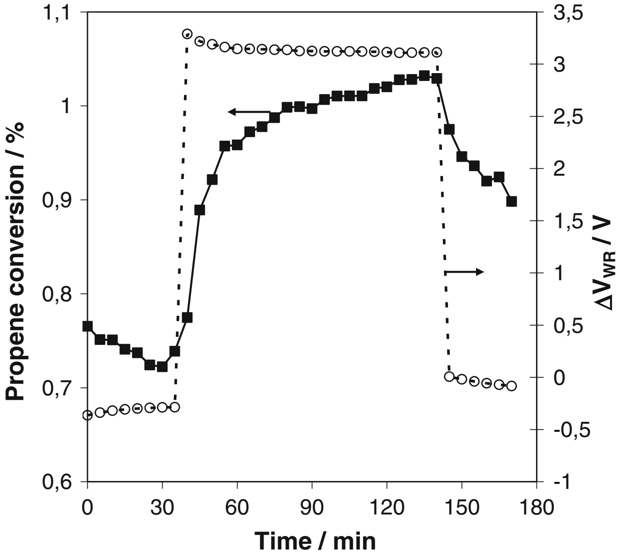

Fig. 4 Effects of the application of +500 μA on propene conversion at 190 °C. Electrochemical catalyst: CGO/Pt. Reactive mixture: $C_3H_6/O_2/H_2O$: 1,500 ppm/6.5%/5%

film prepared by painting [20, 21], the Pt content was about 3 orders of magnitude lower. The electronic conductivity of the catalyst electrode was here ensured by the strontium-doped lanthanum manganite interlayer deposited by PVD and annealed at 850 °C for 2 h. The Pt ultra-thin layer was further deposited on the crystallised LSM surface by PVD at room temperature. Blank experiments were performed on similar LSM layer interfaced on YSZ. We found that LSM layers prepared by PVD had negligible catalytic activity for propene combustion. This is certainly due to the extremely low specific area developed by this kind of film (lower than 0.5 m^2 g^{-1}) associated with a weak quantity of perovskite. In a first step, the catalytic performances of this CGO/LSM/Pt electrochemical catalyst were carried out at 370 °C in dry and near-stoichiometric conditions, i.e. with a reactive mixture containing C_3H_6/O_2: 1,660 ppm/1%. We observed a gradual decay of the propene conversion with time, probably due to the Pt particles growing. The low specific area and porosity of the LSM layer seem to strongly strengthen this phenomenon. The value of the open-circuit voltage was around −45 mV for an un-promoted propene conversion of 11%. Figure 5 shows the impact of a cathodic polarization on the propene conversion at 371 °C. In spite of a continuous decrease of the activity due to the Pt sintering, the imposition of −100 μA rapidly increased the propene conversion from 10.3 up to 12.3%. This activation corresponds to a maximum value of the Faradaic efficiency of −56 which must be only considered as indicative considering the unstable conditions of these experiments. The propene conversion still decreased upon negative polarizations due to the Pt sintering but abruptly dropped when turning off the current to reach a propene conversion lower than 9%. A successive experiment was performed by applying a positive current of +100 μA (Fig. 6). We observed an opposite behaviour since the propene conversion decreased from 8.8 down to 7.5%, corresponding to a maximum Faradaic efficiency indicative value of −44. In spite of unstable conditions, these results are in good agreement with those recently obtained on Pt/YSZ [11] and Pt/YSZ/BiTaVOx [18] electrochemical catalysts, also prepared by PVD. In addition, previous studies using Pt films prepared from commercial paints exhibited similar behaviours [3, 22]. Under this operating condition, i.e. an atomic ratio O/C equal to 2, propene is strongly adsorbed on the Pt surface and inhibits oxygen adsorption. The migration of O^{2-} ionic species (positive polarization) on Pt induces an increase of the Pt work function which again enhances the propene coverage by strengthening the Pt–C_3H_6 chemical bond. This consequently decreases the propene conversion. A negative current induces the opposite effect.

The CGO/LSM/Pt electrochemical catalyst was maintained in the reactive mixture at 370 °C for 12 h in order to stabilize the morphology of the Pt ultra-thin layer. The propene conversion achieved 7.8% and the open-circuit voltage was fairly unchanged (−50 mV). After this stabilisation time, a negative polarisation ($i = -500$ μA) was applied (Fig. 7) and as previously observed, this cathodic polarization had a very pronounced promoting impact on the catalytic performances since the propene conversion abruptly increased up to 11.3%. This electrochemical

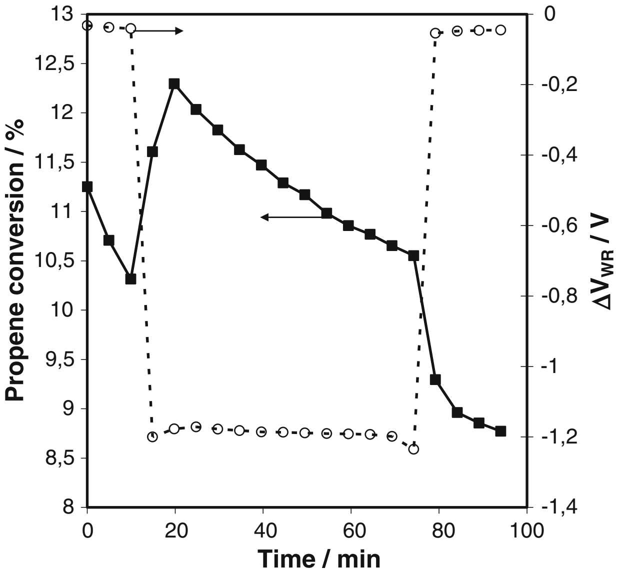

Fig. 5 Effects of the application of −100 μA on propene conversion at 370 °C. Electrochemical catalyst: CGO/LSM/Pt. Reactive mixture: C_3H_6/O_2: 1,660 ppm/1%

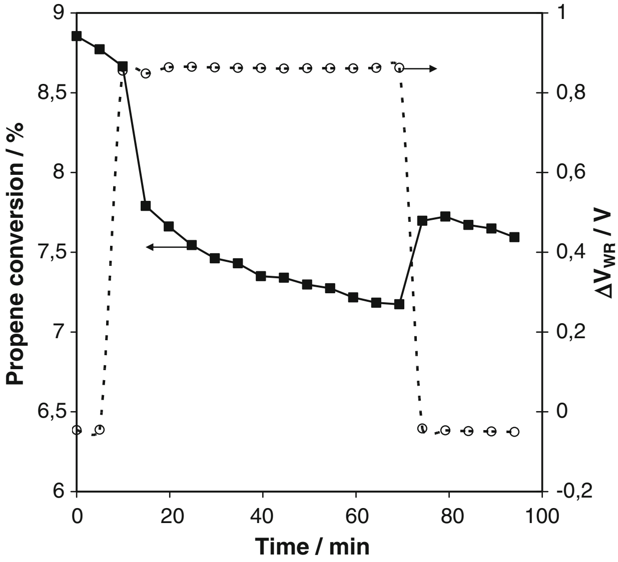

Fig. 6 Effects of the application of +100 μA on propene conversion at 370 °C. Electrochemical catalyst: CGO/LSM/Pt. Reactive mixture: C_3H_6/O_2: 1,660 ppm/1%

activation is non-Faradaic since the value of Faradaic efficiency is −25.

EPOC experiments were also performed in the presence of steam in the feed, still near stoichiometric conditions at 370 °C. When the steam was introduced in the feed, the unpromoted propene conversion dropped from 7.8 down to 4.2%. This seems to indicate that the addition of steam, which is an electron donor, decreases the oxygen coverage. The effect of the addition of steam on the catalytic activity of CGO/Pt and CGO/LSM/Pt electrochemical catalysts was opposite. The addition of steam had a promoting effect on the propene conversion on CGO/Pt while it had an inhibiting impact on the performances of CGO/LSM/Pt. This suggests that the coverage of the adsorbates was different, mainly due to the size of the Pt particles. Indeed, one can assume that the Pt particles size is much higher on CGO/Pt than on CGO/LSM/Pt, mainly because the CGO/Pt electrochemical catalyst was stabilized at 700 °C on stream for 1 h.

In spite of this strong variation of the propene conversion, the open-circuit voltage remained unchanged at −50 mV. This result demonstrates that the catalyst-electrode potential is not fixed by the ultra-thin Pt layer but by the electronically conducting LSM interlayer. Figure 8 displays the impact of polarizations on the propene conversion in the presence of steam at 370 °C. The propene oxidation exhibits similar electrophilic EPOC properties than those observed in dry conditions; i.e., a negative current or potential can enhance its rate while a positive one can inhibit it. The Faradaic efficiency values are −4 and −14 for positive and negative currents, respectively. Therefore, the EPOC magnitude was less pronounced in the presence of steam, due to lower unpromoted rates. The CGO/Pt electrochemical catalyst exhibits an inverted volcano behavior with applied potential while the CGO/LSM/Pt electrocatalyst shows an electrophilic one. This difference of chemisorption properties due to different Pt particle sizes between the two electrochemical catalysts associated with two different operating temperatures (250 °C for CGO/Pt instead of 370 °C for CGO/LSM/Pt) could explain the various NEMCA behaviours.

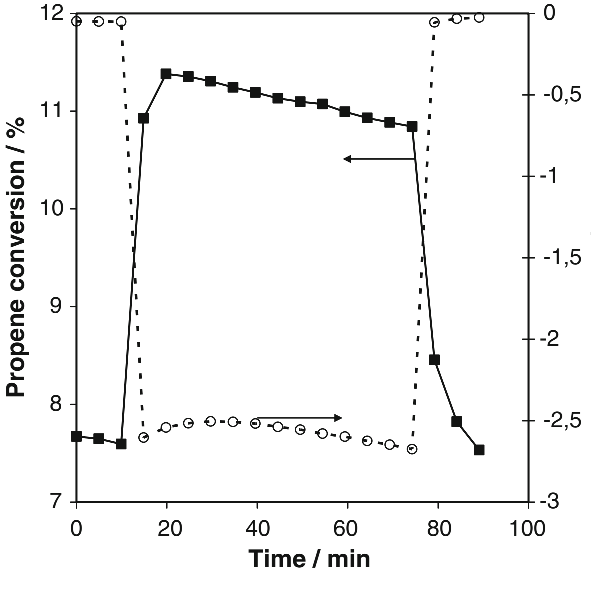

Fig. 7 Effects of the application of −500 μA on propene conversion at 370 °C. Electrochemical catalyst: CGO/LSM/Pt. Reactive mixture: C_3H_6/O_2: 1,660 ppm/1%

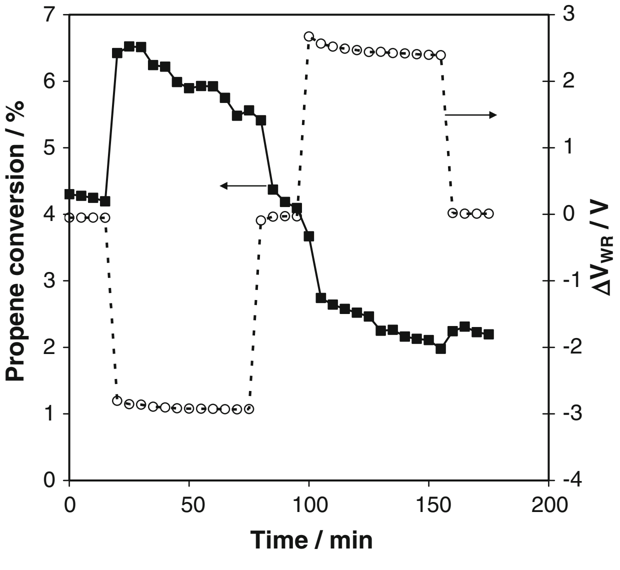

Fig. 8 Effects of the application of −500 and +500 μA on propene conversion at 370 °C. Electrochemical catalyst: CGO/LSM/Pt. Reactive mixture: $C_3H_6/O_2/H_2O$: 1,600 ppm/1%/5%

All these experimental results demonstrate that the catalytic activity of an ultra-thin layer of Pt deposited on an electronically conducting interlayer of perovskite can be electropromoted even in the presence of steam in the feed.

4 Conclusions

Electrochemical promotion of propene deep oxidation was performed on CGO/Pt electrochemical catalysts with large quantity of steam in the feed and extremely low loading of Pt. Activation of propene conversion was evidenced both in stoichiometric and lean-burn conditions with Faradaic efficiency slightly higher than one. CGO electrolyte allowed implementing NEMCA effects at temperatures lower than 200 °C even in the presence of steam in the feed. In addition, a new design of electrochemical catalysts was prepared by adding a sputtered interlayer of strontium-doped lanthanum manganites between the CGO dense support and an ultra-thin coating of Pt. The catalytic activity of this ultra-thin layer of Pt deposited on the electronically conducting interlayer of perovskite can be electropromoted even in the presence of steam in the feed. This result is of great interest for future industrial applications of EPOC.

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