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Low temperature electrochemical catalysts using a BITAVOX electrolyte

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ABSTRACT

For the first time, electrochemical promotion (EP) was evidenced on a multi-layer electrochemical catalyst with a BIMEVOX ceramic used as an electrolyte. The electrochemical catalysts were tested for two environmental applications: selective catalytic reduction (SCR) of NOx by propene under lean-burn conditions and propene combustion. Thin Pt films were sputtered on BITAVOX.20 ($Bi_2V_{0.8}Ta_{0.2}O_{5.5-\delta}$) dense membranes. The thickness of the Pt films was less than 100 nm which led to a very small amount of Pt. First experiments revealed the formation of a Bi_xPt_{1-x} alloy, likely due to a slight reduction of the electrolyte. A new geometry was then proposed with the insertion of a YSZ barrier layer of a few nanometers between the catalyst and the electrolyte. Electrochemical promotion (EP) was evidenced for this system at low temperature (200–300 °C) under lean-burn conditions for both reactions. In the case of propene combustion, EP was maintained even in the presence of steam.

1. Introduction

One of the main challenges in environmental catalysis is the treatment of gaseous stream from automotives, such as NOx abatement (DeNOX catalysis) as well as the combustion of unburned hydrocarbons. The problem of catalytic post-treatment of NOx still remains for Diesel engines. Future legislation, such as EURO 6 standards in Europe, that will be active from 2014, requires lower NOx emission levels. One solution could be to limit the NOx 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 (HC), such as propene and carbon monoxide (CO) emissions, coupled with a decrease of the exhaust gas temperature. Therefore, this innovative technology requires efficient catalysts at low temperature. Catalysts based on supported noble metal are known as 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. One way to achieve this goal is to enhance the catalytic activity and the selectivity by using the electrochemical promotion of catalysis (EPOC), also called the non-Faradaic electrochemical modification of catalytic activity (NEMCA). NEMCA was evidenced and developed by the group of Vayenas in Patras in the eighties [1,2]. It was shown that when interfaced with a solid electrolyte as a support, the activity and selectivity of a film catalyst could be modified by the application of small potentials or currents via coupling with an electrochemical system. In case of an oxide ion conductor electrolyte for instance, a positive polarisation results in the migration of $O^{\delta-}$ species electrochemically pumped from the electrolyte on the metal surface that can modify the work function (WF) of the system [3,4]. The binding energy of species involved in the rate limiting step of the heterogeneous reaction may then be affected by the work function modification resulting in an increase or a decrease of the reaction rate.

Most of the EPOC studies were performed with catalysts based on a Pt thin film deposited on yttria stabilised zirconia (YSZ, O^{2-} conductor) or β-Al_2O_3 (Na^+ or K^+ conductor) in a usual working temperature range of 300–500 °C. Recent studies [5–12] have explored the utility of EPOC to promote the nitric oxide reduction by propene in the presence of oxygen. Most of them reported the use of rhodium catalysts and have shown that the catalytic activity and also the selectivity of the Rh catalyst–electrode between 350 and 430 °C can be highly promoted upon polarisation. However, under lean-burn conditions, the promotion efficiency drastically decreases due to oxidation of the Rh surface, as reported by Foti et al. [6] using a Rh/YSZ system. Williams et al. [8] have investigated a bimetallic Rh–Ag film deposited on YSZ under lean-burn conditions, i.e. $C_3H_6/NO/O_2$:1000 ppm/1000 ppm/5%. Their results indicate that positive overpotentials promote the catalytic activity and the selectivity to nitrogen. At 386 °C, the selectivity to N_2 significantly increases from 28% to 55% upon an applied overpotential of +100 mV. The authors explain that the

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presence of Ag improves resistance to oxidation of the rhodium surface.

Pt thin films were also used as catalyst–electrode for NOx reduction by propene in the presence of oxygen deposited on YSZ [9,13], Na super ionic conductor (NASICON), i.e. $Na_3Zr_2Si_2PO_{12}$ [10], and β-Al_2O_3 [14] both Na^+ conducting electrolytes. When Pt was interfaced on YSZ, promotional effects were only observed in stoichiometric conditions and upon negative polarisations, i.e. migration of O^{2-} species from the Pt surface to the electrolyte. Moreover, Pt was found to be efficient at temperatures lower than 300 °C, a temperature range in which the ionic conductivity of YSZ is too low. Furthermore, no activation was reported upon positive polarisations. On the contrary, when using a Na^+ conductor, NO reduction by propene can be highly electropromoted by applying negative overpotentials, i.e. backspillover of cations on the Pt surface. The selectivity to N_2 of Pt can be strongly electropromoted even under lean-burn conditions. Moreover, electrochemical promotion for the removal of N_2O was recently investigated [15] under near-real Diesel exhaust reaction conditions, excess of oxygen and water on the feed ($C_3H_6/N_2O/O_2/H_2O$: 2000 ppm/ 1000 ppm/1%/3%) on Pt/K-βAl_2O_3 electrochemical catalyst. Significant activations were reported, as for instance, at 400 °C, an increase of the N_2O reduction rate by a factor of 7.4 upon negative polarisation. However, the durability of a Na^+ and K^+ conducting electrolytes is not sufficient in the operating conditions of catalytic after-treatment because there is no Na^+ tank contrary to O^{2-} conducting solid electrolytes, which can be continuously replenished from gaseous O_2 present in the stream.

The aim of this study was to develop electrochemical catalysts effective for catalytic combustion of propene as well as NOx abatement in conditions of Diesel exhaust; i.e. under lean-burn conditions, in the presence of large quantity of steam and at low temperature (200–300 °C). Since YSZ conductivity in this range of temperatures is too low, the possibility of using BIMEVOX oxide ion conductor as an electrolyte was investigated. These materials are well known for their high oxide ion conductivity at moderate temperature, about two orders of magnitude higher than YSZ below 400 °C (Fig. 1). They derive from the parent compound $Bi_4V_2O_{11}$ by partial substitution for vanadium with a metal [16]. The acronym BIMEVOX.x is used for compositions of the general formula $Bi_2V_{1-x}Me_xO_z$. A wide range of metals can be introduced into the vanadium site. Most of them have been found to stabilise at low temperature the γ-type $Bi_4V_2O_{11}$ phase which is most attractive for its electrical property. For instance γ-BICUVOX.10 is obtained by partial substitution of vanadium with 10% of copper. This composition exhibits the best ionic conductivity ($\sigma \sim 10^{-1}$ S cm^{-1} at 500 °C). However it is not stable at low temperature. Indeed, the γ-BIMEVOX forms, stabilised at room temperature, show some ordering of oxygen vacancies at temperatures lower than 500 °C, which leads to an increase in activation energy. They are termed γ′ in this temperature domain. In the case of BICOVOX.10 and BICUVOX.10 compositions, Watanabe et al. [17] showed a sluggish transformation of these γ′ forms into a more ordered α-related polymorph when annealed for several hundred hours at 450 °C. The evolutions observed on the Me^{II} BIMEVOX are reversible on heating; however they compromise the use of these materials on applications at low temperature. Later, after long time annealing at 450 °C, some of us confirmed this modification for doped BIMEVOX with divalent metals but better stability was observed for BIMEVOX doped with pentavalent metals such as BISBVOX.15, BINBVOX.25 and BITAVOX.20 [18]. Therefore, in this paper, a BITAVOX.20 electrolyte was used due to the better thermal stability of the Me^V BIMEVOX. Electrochemical catalysts, consisting in BITAVOX.20 electrolyte covered by a thin sputter-deposited Pt film, were considered for two catalytic reactions: selective catalytic reduction (SCR) of NOx by propene and propene combustion.

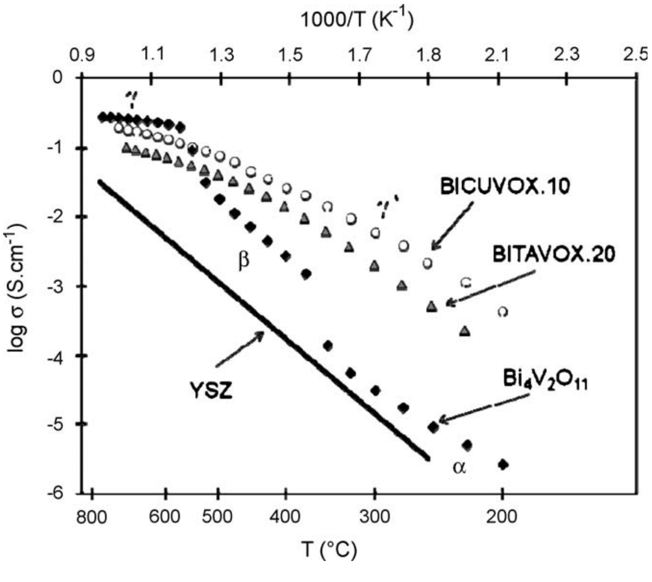

Fig. 1. Arrhenius plots of $Bi_4V_2O_{11}$ and BIMEVOX ceramics compared to YSZ.

2. Experimental

BITAVOX.20 ($Bi_2V_{0.8}Ta_{0.2}O_{5.5-\delta}$) powders were prepared by solid state route as described in Ref. [19]. The powder was attrition milled (Netzsch PE 075) and shaped into disks pressed by uniaxial pre-pressing followed by isostatic pressing at 1700 bar. The membranes were then sintered at 875 °C for 2 h with heating and cooling rates of 5 °C/min. Dense membranes were obtained (15 mm in diameter, 1.5-mm thick, relative density >95%). Pt films were sputter-deposited onto the membranes pellets from a Pt metallic target at low argon pressure. Samples with a YSZ thin film diffusion barrier were also prepared, by sputtering, using a $Zr_{0.84}Y_{0.16}$ metallic target under argon/oxygen atmosphere. Gold counter and reference electrodes were also sputter-deposited onto the opposite side of the electrolyte disk using adequate masks. Gold was selected because of its non-activity under NOx reduction and propene oxidation under the operating conditions. The reference electrode was deposited close to the counter-electrode, but at a sufficient distance to avoid any electrical perturbation.

The deposition reactor, described in details elsewhere [20], is mainly composed of a 40-L stainless steel cylinder equipped with two 50-mm diameter magnetron targets separated from each other by about 120 mm and a rotating substrate holder parallel to the targets at a distance of about 50 mm. A suction system consisting in a primary oil pump and a secondary turbomolecular pump ensures a base vacuum of about 10^{-4} Pa before refilling with argon and eventually oxygen to the desired pressure. The flow rates of both gases are controlled by MKS mass flowmeters and the resulting pressure is determined using a Baratron absolute gauge. The targets are powered using Advanced Energy 5 kW pulsed DC supplies. The parameters for the deposition of YSZ diffusion barrier derive from an earlier study [21]. The main deposition conditions of the different coatings are summarized in Table 1.

The thickness of the Pt and YSZ coatings is determined from interferometric measurements performed by fitting the transmittance of the coating deposited on a glass slide using a model developed by Perry and co-workers [22]. The transmittance curves are measured in the visible range (380–780 nm) using a Varian Cary 500 spectrophotometer.

Table 1
Main deposition conditions of the different coatings.

	Au	YSZ	Pt (dense)	Pt (porous)
Base vacuum (Pa)	10^{-4}	10^{-4}	10^{-4}	10^{-4}
Ar flow rate (sccm)	30	30	30	60 + throttling
O_2 flow rate (sccm)	0	5	0	0
Ar pressure (Pa)	0.3	0.3	0.3	2
Target material	Au	Zr–16 at.%Y	Pt	Pt
Discharge current (A)	0.5	0.6	0.2	0.2
Deposition rate (μm/h)	2.5	0.25	0.36	0.28

The three electrodes (working, counter-electrode and reference) were connected to a potentiostat–galvanostat Voltalab 80 (Radiometer analytical). To check the electrochemical promotion, a current or a potential bias was applied. The current was going through the working electrode (Pt) and the counter-electrode and the potential measured or applied between the working electrode (Pt) and the reference electrode.

The catalytic properties of these electrochemical catalysts were investigated for the selective catalytic reduction (SCR) of NOx by propene and for propene combustion. The cell described in Ref. [23] was used for catalytic tests. The overall gas flow rate was kept constant at 10 L h^{-1} and the reactive mixture compositions were C_3H_6 700 ppm/NO 1000 ppm/O_2 10%/He and C_3H_6 1800 ppm/O_2 18%/H_2O 5%/He for SCR and propene combustion, respectively. The gas composition was controlled by mass flow controllers (Brooks). The reagents and products were analysed by a NOx (NO and NO_2) analyser (Cosma, TOPAZE 3000) an on-line microgas-chromatograph (Varian CP2003). The micro-chromatograph was made of two modules, each one equipped with its own thermal conductivity micro-detector. The first module enabled the separation of CO_2 and C_3H_6 by using a Poraplot U column (10 m length and 0.32 mm in internal diameter) heated at 60 °C. The second one was equipped with a molecular sieve heated at 90 °C (10 m length and 0.32 mm in internal diameter) preceded by a back flush column. This module analysed O_2, N_2 and CO. The overall duration of one analysis was only 110 s. Before these analyses, the water produced by the catalytic reactions, was trapped by an electro-gas cooler (M&C Products, ECP1000-G). The conversion of the propene into CO_2 was defined as:

$$\text{propene conversion} = 100 \times \frac{PCO_2}{PCO_2 + 3PC_3H_6} \tag{1}$$

where, PCO_2 and PC_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 NO conversion was defined as the percentage conversion of NO to N_2 and N_2O on a N-atom basis. We also calculated the selectivity to N_2 as follows:

$$\text{selectivity to } N_2 = 100 \times \frac{PN_2}{PN_2 + PN_2O} \tag{2}$$

where PN_2 and PN_2O are the partial pressures of N_2 and N_2O in the outlet gas, respectively. Carbon monoxide was not detected according to our lower detection limit at about 10 ppm. Carbon and nitrogen mass balances were found to be within 2%. Blank experiments have shown that the fritted quartz was catalytically inert up to 500 °C.The catalyst polarisation 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 polarisation. The magnitude of the electrochemical promotion effect is described by the Faradaic efficiency, 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.

X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB 220XL spectrometer.

3. Results and discussion

3.1. Selective catalytic reduction of NOx by propene on Pt/YSZ/BITAVOX

3.1.1. Catalytic activity measurements at open circuit voltage

3.1.1.1. Pt/BITAVOX catalyst. The first electrochemical catalyst consisting on a dense 100-nm thick Pt film deposited on BITAVOX.20 was tested at open circuit for SCR of NOx by propene. The sample was heated at 295 °C under oxygen (13% O_2 in He) and the reactive mixture was then introduced. The evolution of the catalytic activity as a function of time is given in Fig. 2. C_3H_6 and NO conversions of 60% and 17%, respectively, were initially measured but rapidly decreased with time, indicating a loss of activity of the catalyst. The surface of the catalyst before and after catalytic test was characterised by XPS. As shown in Fig. 3, it revealed bismuth metal in the Pt film (Bi 4f peaks) after test. This indicates that, even at low temperature and in the presence of oxygen, Bi^{3+} was likely reduced to metallic bismuth at the Pt–BIMEVOX interface which reacted with platinum to form a Pt_x–Bi_{1-x} alloy with a low catalytic activity. Bismuth based materials are known for their sensitivity towards bismuth III reduction in bismuth metal under reductive atmosphere. Because of the high oxygen concentration (more than 10%) in the SCR and propene combustion, a good stability of the electrolyte was expected. A low oxygen activity at the electrolyte surface is likely responsible for a slight reduction of the electrolyte.

To avoid the contamination of the Pt film with Bi, the design of a new electrochemical catalyst was then decided: a YSZ layer was deposited by sputtering between the BITAVOX electrolyte and the Pt film to act as a Bi diffusion barrier.

3.1.1.2. Pt/YSZ/BITAVOX electrochemical catalyst. An electrochemical catalyst with a 50 nm thick YSZ layer (Pt(100)–YSZ(50)–BITAVOX) was prepared by PVD technique. To evaluate the stability of this system, measurements of the catalytic activity under open circuit voltage were performed during a thermal treatment

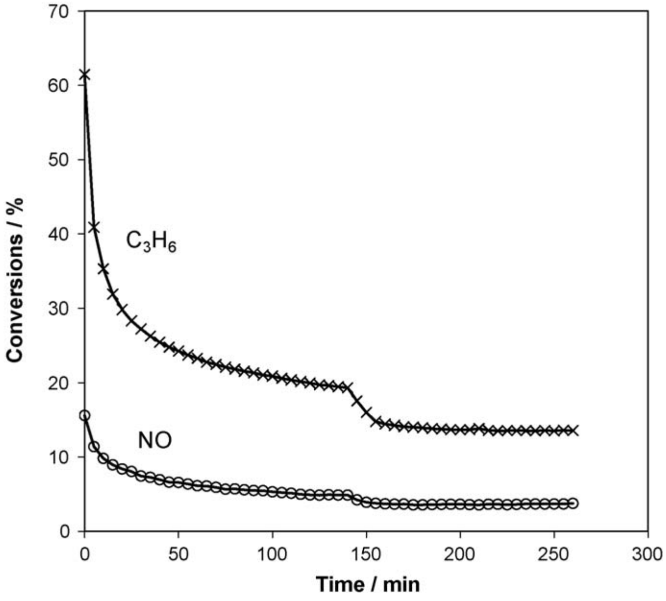

Fig. 2. Variation of the C_3H_6 and NO conversions at 295 °C as a function of time under open circuit. Electrochemical catalyst: Pt(100)–BITAVOX. Reactive mixture: C_3H_6 700 ppm/NO 1000 ppm/O_2 10%/He. Overall flow rate: 10 L h^{-1}.

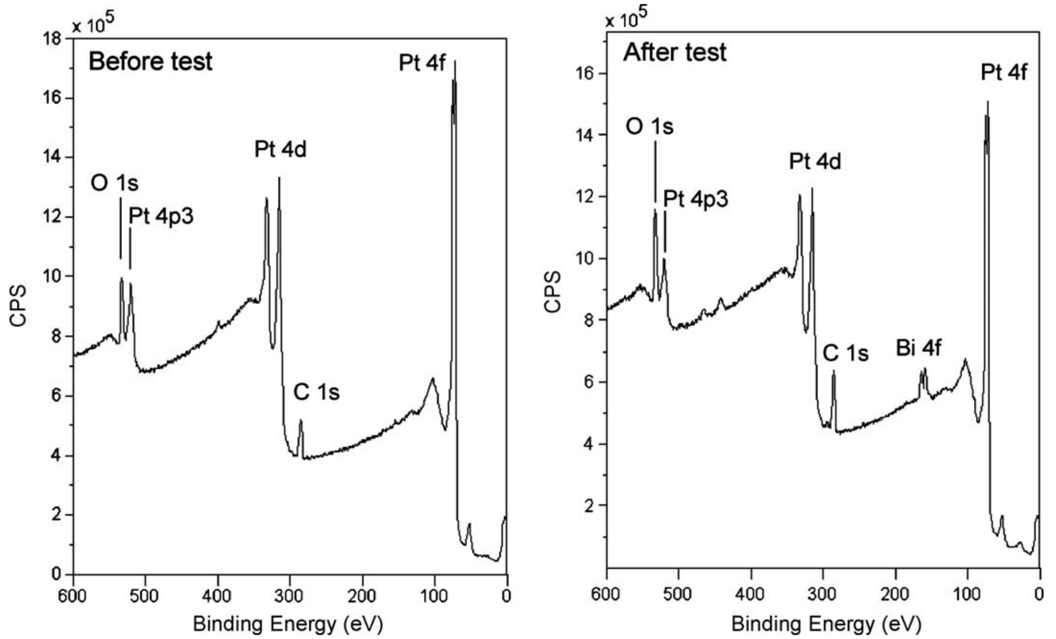

Fig. 3. XPS performed on the Pt(100)–BITAVOX catalyst before SCR and after SCR at 295 °C under C_3H_6 700 ppm/NO 1000 ppm/O_2 10%/He as reactive mixture under open circuit.

consisting of 10 cycles of heating and cooling between 150 and 300 °C with a heating and cooling rate of 2 °C/min. The results, presented in Fig. 4 and Table 2, show a slight deactivation of the catalyst. The maximum propene conversion was reached at 284 °C for the tenth cycle instead of 264 °C for the first one and, in parallel, a shift was observed for the NO conversion with a decrease of the maximum of conversion (denoted as T_{max}, Table 2) from 18% (263 °C) to 14% (283 °C). The T_{20} and T_{50}, temperatures corresponding to 20 and 50% of propene conversion, respectively, increased of around 15 °C between the first and the tenth cycles (Table 2). This deactivation is significantly weaker than the one obtained with the system without YSZ layer and can be rather explained by a sintering of the platinum layer than by bismuth diffusion to the surface. Indeed, Pt films were prepared by PVD techniques at room temperature and were not pretreated before implementing the first thermal cycle. One can assume that this slight loss of activity is due to the stabilisation of the Pt film morphology. Therefore, one can conclude that the YSZ barrier layer is effective to avoid Bi reduction and contamination of Pt active film.

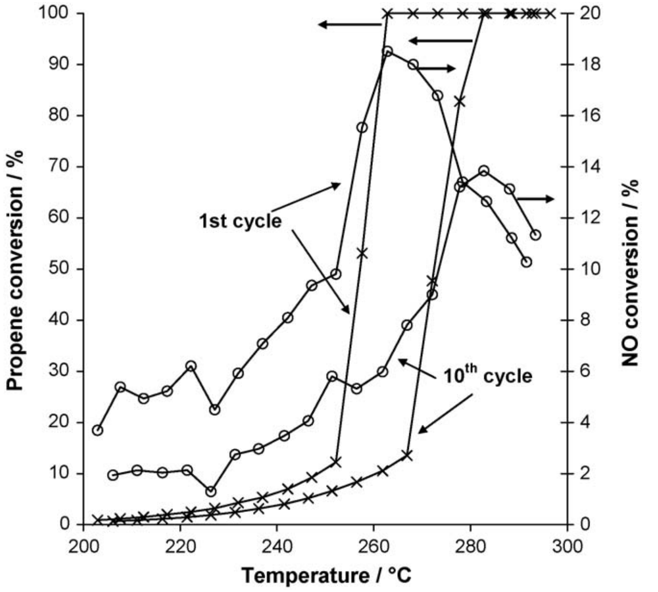

Fig. 4. Variation of the C_3H_6 and NO conversions as a function of the temperature under open circuit. Electrochemical catalyst: Pt(100)–YSZ(50)–BITAVOX. Reactive mixture: C_3H_6 700 ppm/NO 1000 ppm/O_2 10%/He. Overall flow rate: 10 L h^{-1}.

The catalytic performances of the fresh Pt/YSZ/BITAVOX electrochemical catalyst are similar to those observed on Pt/NASICON [24]. This last sample prepared from a commercial Pt paint presented, under similar reactive mixture, a maximum NO conversion of 18% at 319 °C. However, the Pt loading of this last sample was 3 mg cm^{-2} instead of 0.2 mg cm^{-2} in the BITAVOX based electrochemical catalyst. This clearly confirms that PVD technique can achieve suitable metallic thin films for catalytic applications.

The selectivity to N_2 of the Pt/YSZ/BITAVOX (first cycle) was found to be 40% at the temperature corresponding to the maximal conversion of NO, i.e. at 263 °C (Table 2). This value is higher than that reported for conventional Pt-supported catalysts under lean-burn conditions which is around 30% [25].

3.2. Catalytic activity measurements under closed circuit

To evaluate the effect of an electrical polarisation on the catalytic performance of the Pt(100)–YSZ(50)–BITAVOX catalyst, a current i = +100 μA was applied and an eleventh thermal cycle was carried out. The variations of both C_3H_6 and NO conversions as a function of temperature under polarisation and open circuit (tenth cycle under OCV) are compared in Fig. 5. The continuous positive polarisation during the cooling-down improves the catalytic activity (Fig. 5, Tables 3 and 4). The value of T_{max} decreases of about 8 °C while the maximum of NO conversion rises from 14% to 19%, i.e. higher than the conversion observed on the fresh sample (first cycle, Table 2). The electrochemical promotion efficiency is very pronounced in a wide temperature range between 210 and 290 °C. These promotional effects are non-Faradaic with values of ΛC_3H_6 calculated from the propene consumption reaching 580 at 270 °C (Table 4). Values of the rate enhancement ratios are around 2 both for NO and C_3H_6 conversions.

Table 2
Comparison of the T_{20}, T_{50} (propene conversion) and T_{max} (NO conversion) values for the Pt(100)–YSZ(50)–BITAVOX electrochemical catalyst between the first and the tenth cycles during the thermal treatment under OCV. Reactive mixture: C_3H_6 700 ppm/NO 1000 ppm/O_2 10%/He. Overall flow rate: 10 L h^{-1}.

	C_3H_6 conversion, T_{20} (°C)	C_3H_6 conversion, T_{50} (°C)	NO conversion, T_{max} (°C)
First thermal cycle	253	257	263
Tenth thermal cycle	268	273	283

Table 3
Comparison of the T_{20}, T_{50} (propene conversion) and T_{max} (NO conversion) values for the Pt(100)–YSZ(50)–BITAVOX electrochemical catalyst under OCV (tenth thermal cycle) and +100 μA. Reactive mixture: C_3H_6 700 ppm/NO 1000 ppm/O_2 10%/He. Overall flow rate: 10 L h^{-1}.

	C_3H_6 conversion T_{20} (°C)	C_3H_6 conversion T_{50} (°C)	NO conversion T_{max} (°C)
OCV	268	273	283
+100 μA	252	261	275

The effect of an electrical polarisation was also investigated at a constant temperature by using another sample (Pt(20)–YSZ(50)–BITAVOX) with a much thinner platinum layer, i.e. 20 nm instead of 100 nm. The morphology of this sample was first stabilised under the reactive mixture for 1 h at 300 °C and then tested at 254 °C. This temperature was selected because it corresponds to a low conversion domain without any diffusion limitations. The electrophobic NEMCA effect was confirmed (Fig. 6) with rate enhancement ratios still close to 2 (ρNO = 1.9, ρC_3H_6 = 1.9) and with a Faradaic efficiency ΛC_3H_6 = 41. However, the N_2 selectivity was found to slightly decrease under positive polarisations from 62% to 55%.

All these results evidence that O^{2-} ionic species can promote the Pt activity for selective catalytic reduction of NO by propene under lean-burn conditions. This is in contradiction with previous studies on Pt/YSZ electrochemical catalysts made from commercial Pt paint [9] or by electrostatic spray deposition (ESD) [13]. Indeed, promotional effects were only observed in stoichiometric conditions and upon negative polarisations, i.e. migration of O^{2-} species from the Pt surface to the electrolyte. Propene deep oxidation was investigated on sputtered films of Pt interfaced with YSZ [26] and promotional effects were also evidenced only upon negative polarisations. In all these cases, the enhancement of the activity was explained by a decrease of the propene coverage on Pt in favour of O_2 and NO adsorption. Indeed, it has been established that in a propene-rich reactive mixture, the Pt surface is covered by propene-derivated species. The opposite NEMCA behaviour results reported in this study suggest that propene coverage is significantly lower because the reactive mixture contains an extremely large excess of oxygen. Indeed, the atomic ration O/C is equal of 95 instead of 37 in Ref. [26] and 3.6 in Refs. [9,13]. In this oxygen-rich condition, one can suggest that O_2 coverage is high. The application of a positive polarisation induces an enhancement of the Pt work function. Then, chemical bonds with electron-donor adsorbates, such as C_3H_6, are strengthened whereas those with an electron-acceptor, such as O_2 and NO, are weakened. Thus, the strengthening of the Pt–C_3H_6 bond promotes the propene adsorption and then the catalytic activity. At the same time, the reactions of adsorption and dissociation of NO are not favoured by the weakening of the Pt–NO bond, and consequently the strengthening of the N–O one, which results in a decrease of the N_2 selectivity, as experimentally observed.

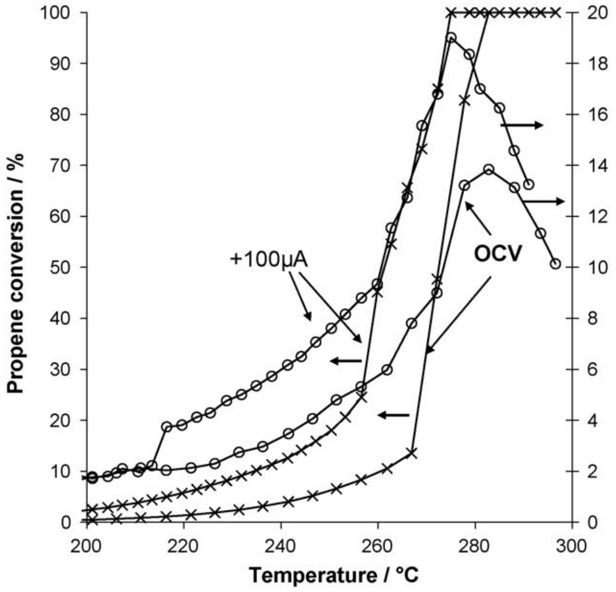

Fig. 5. Comparison of the evolution of the C_3H_6 and NO conversions as a function of the temperature under open circuit and electrical bias. Electrochemical catalyst: Pt(100)–YSZ(50)–BITAVOX. Reactive mixture: C_3H_6 700 ppm/NO 1000 ppm/O_2 10%/He. Overall flow rate: 10 L h^{-1}.

3.3. Propene combustion on Pt/YSZ/BITAVOX

The electrochemical promotion on propene oxidation was also investigated in lean-burn conditions in the presence of steam in order to simulate the operating conditions of LTC Diesel motorisations exhaust gas.

3.3.1. Catalytic activity measurements under open circuit voltage

The propene combustion was investigated on electrochemical catalysts with a 55 nm thick Pt film and an YSZ diffusion barrier of 12 nm. Two samples were studied with two different morphologies of the Pt layer: one with a low porosity (LP) denoted as Pt(55-LP)–YSZ(12)–BITAVOX and another with a high porosity (HP) denoted as Pt(55-HP)–YSZ(12)–BITAVOX. The porosity of the Pt film was modified by the variations of Ar pressure inside the sputtering chamber. Indeed, increasing the argon pressure decreases the mean free path of sputtered particles which impinge the substrate with a lower energy [27]. The resulting lower diffusivity of ad-atoms then favours the deposition of columnar and porous coatings which hence present a higher specific area [28]. The propene conversion and open circuit voltage variations as a function of temperature for the low porosity sample are plotted in Fig. 7. As already reported in the literature on YSZ-based electrochemical catalysts [29], the variations of ΔV°_{WR} follow the same trend than that of the conversion. Variations of ΔV°_{WR} correspond to modifications of the oxygen thermodynamic activity on Pt, probably linked to the oxygen coverage. This last is highest when hydrocarbon conversion is maximal. Values of OCV are therefore an indicator of the catalyst activity and could be used as a sensor for the *in situ* following of the catalytic process. However,

Table 4
Promotional parameters for the Pt(100)–YSZ(50)–BITAVOX electrochemical catalyst under a positive polarisation ($i = +100\ \mu A$).

Temperature	240 °C	270 °C
ρNO	1.9	2
ρC_3H_6	2.75	2.18
ΛC_3H_6	96	580

when a porous layer was used, the correlation between the evolution of the open circuit voltage and the sample activity was not so clear, likely because of low electronic conductivity. The catalytic performances of the two samples are compared in Fig. 8. It can be noticed that the propene conversion does not reach 100% and that the maximum conversion is different from one catalyst to the other. This is explained by a bypass of a part of the reactive gas mixture which is never in contact with the Pt film. This bypass is more important for the porous sample because of a smallest Pt film diameter. Nevertheless, the porous catalyst exhibits lower values of T_{20} and T_{50} (Fig. 8). Therefore, the catalytic activity is strongly related to the morphology of the Pt film. In the case of the porous film a better dispersion of the Pt particles could explained the higher catalytic activity but this could be also related to the thermal migration of oxides ions which is favoured in this case.

3.4. Catalytic activity measurements under closed circuit

3.4.1. Dry reactive mixture

We chose to study the effect of the electrical polarisation on the Pt(55-HP)–YSZ(12)–BITAVOX sample (porous catalyst), which exhibited the best catalytic performances (Fig. 8). The composition of the reactive gas mixture was C_3H_6 1600 ppm/O_2 10% (atomic ratio O/C = 41.6) in Helium with an overall flow rate of 10 L h^{-1}. The EP characterisations were performed at 279 °C by applying successive polarisations, both negative and positive, of 1 h. Before the first polarisation, the open circuit voltage was −90 mV suggesting a low oxygen coverage on Pt. Fig. 9 shows that negative bias induces a slight activation whereas positive polarisation has no impact. Upon negative currents, the propene conversion increases from 7.7% to 8.1% ($\rho = +1.05$). Effects are reproducible and non-Faradaic with Faradaic efficiency values of −8. These results are in good agreement with those recently obtained on Pt/YSZ electrochemical catalysts, also prepared by PVD [26]. Under this operating condition, i.e. an atomic ratio O/C equal to 20.8, propene is strongly adsorbed on the Pt surface and inhibits oxygen adsorption. The migration of O^{2-} ionic species 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.

3.4.2. Wet reactive mixture

Experiments were then carried out in the presence of steam in the feed. The composition of the reactive gas mixture was C_3H_6

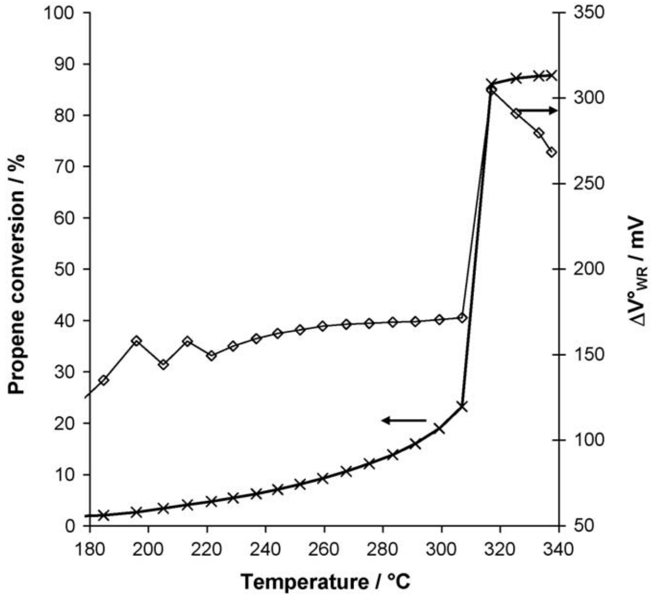

Fig. 7. Variations of the propene conversion and the open circuit voltage versus temperature. Electrochemical catalyst: Pt(55-LP)–YSZ(12)–BITAVOX. Reactive mixture: C_3H_6 1650 ppm/O_2 10%/H_2O 5%/He. Overall flow rate: 10 L h^{-1}.

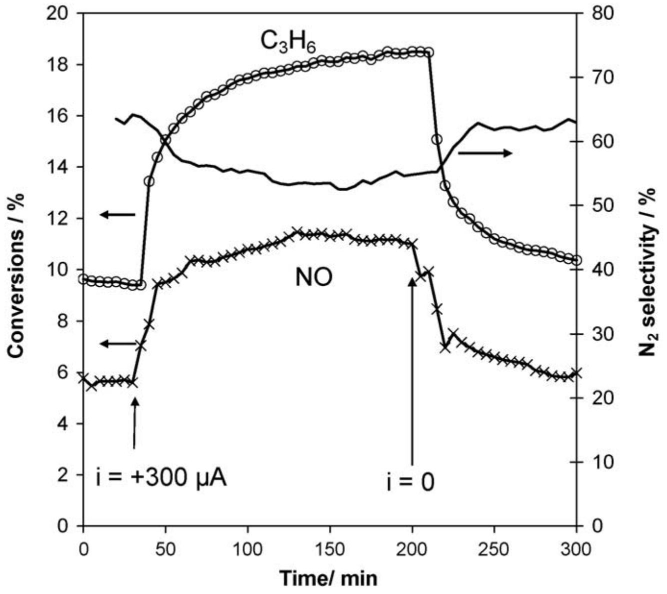

Fig. 6. Effect of a positive current ($i = +300\ \mu A$) on propene and NO conversions and N_2 selectivity. Electrochemical catalyst: Pt(20)–YSZ(50)–BITAVOX. Temperature: 254 °C. Reactive mixture: C_3H_6 700 ppm/NO 1000 ppm/O_2 10%/He. Overall flow rate: 10 L h^{-1}.

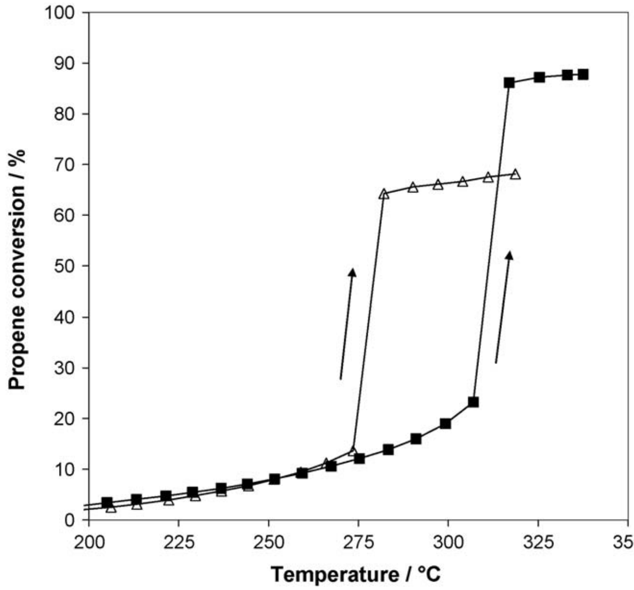

Fig. 8. Propene conversion variations versus temperature. Electrochemical catalysts: Pt(55-LP)–YSZ(12)–BITAVOX (square) and Pt(55-HP)–YSZ(12)–BITAVOX (triangle). Reactive mixture: C_3H_6 1650 ppm/O_2 10%/H_2O 5%/He. Overall flow rate: 10 L h^{-1}.

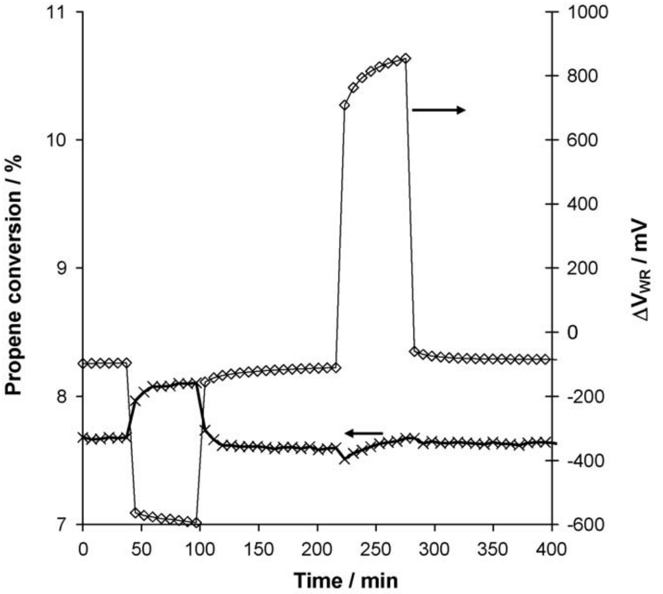

Fig. 9. Effect of the electrical polarisations ($i = \pm 300$ μA) on propene conversion. Electrochemical catalyst: Pt(55-HP)–YSZ(12)–BITAVOX. Temperature = 279 °C. Reactive mixture: C_3H_6 1600 ppm/O_2 10%/He. Overall flow rate: 10 L h^{-1}.

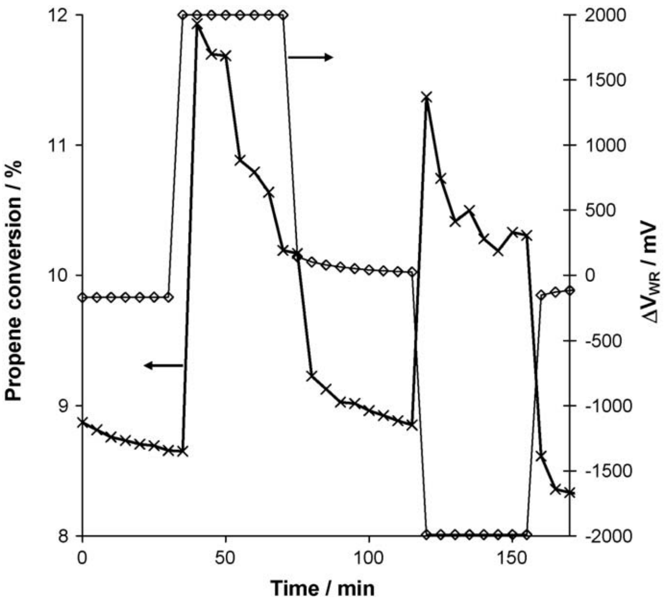

Fig. 10. Effect of the electrical polarisation on propene conversion with $V = \pm 2$ V. Electrochemical catalyst: Pt(55-HP)–YSZ(12)–BITAVOX. Temperature = 279 °C. Reactive mixture: C_3H_6 1600 ppm/O_2 10%/H_2O 5%/He. Overall flow rate: 10 L h^{-1}.

1600 ppm/O_2 10%/H_2O 5% in Helium (atomic ratio O/C = 52) with an overall flow rate of 10 L h^{-1}. In the presence of steam, the propene conversion is slightly higher than the initial one. A promotion of the catalytic properties under steam conditions was systematically observed and seems to indicate the role of water as a promoter.

To characterise the catalyst behaviour under an electrical bias, electrical polarisations were applied (Fig. 10) at 279 °C. The initial open circuit voltage value was −168 mV, this value is lower than the one obtained without water as steam has been identified as an electron-donor adsorbate like propene [15,30]. An anodic polarisation was first applied and resulted in a sudden increase of the conversion from 8.6% to 12% followed by a decrease to 10% after 1 h of polarisation. During the cathodic polarisation, the conversion increased from 8.8% to 11.3% and stabilised at 10.3% after 1 h of polarisation. In contrast to experiments performed under dry conditions, in the presence of steam, the effects were very similar for the anodic and cathodic polarisation with NEMCA parameters of the same order of magnitude ($\rho = +1.1$ and $|\Lambda| = 14$). 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, a positive polarisation, which favours both propene and H_2O adsorption, can enhance the activity whereas a negative one which can promote oxygen chemisorption. However, these NEMCA effects are not stable in time suggesting that opposite phenomena occur after long-term polarisation. Nevertheless, the presence of steam does not inhibit the electrochemical activation of propene deep oxidation and even better seems to enhance the effects, under these operating conditions.

4. Conclusions

Electrochemical promotion was evidenced on a bilayer electrochemical catalyst with a BIMEVOX ceramic used as an electrolyte combined with a YSZ diffusion barrier between the electrolyte and the Pt active film. PVD technique allows to develop electrochemical catalysts containing very low Pt loading with different morphologies. Moreover, EPOC was evidenced on this system at low temperature (200–300 °C) under lean-burn conditions for selective catalytic reduction of NO by propene and for propene deep oxidation reactions. For propene combustion, the addition of steam in the feed does not inhibit the electrochemical activation and even better seems to enhance the NEMCA effects. The possibility to control the catalyst activity by measuring the cell voltage (open circuit voltage) was also demonstrated and foreshadows the possibility to use this catalyst as a sensor. However the necessity to add a diffusion barrier between the electrolyte and the catalyst remains a drawback.

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