# The Relationship of the Catalytic Activity and the Open-Circuit Potential of Pt Interfaced with YSZ

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**Abstract.** This study deals with the relationship between open-circuit potential and catalytic activity of the system Pt/YSZ. Temperature-programmed desorption (TPD) of oxygen was carried out in order to investigate the link between the oxygen coverage and the potential. Then, catalytic activity in parallel with the potential value was measured between 200 °C and 500 °C for NO oxidation, $C_3H_8$ combustion, $C_3H_6$ combustion and the selective catalytic reduction (SCR) of NO by $C_3H_6$ in the presence of oxygen. It was found that potential measurement can give precious information on the competitive adsorption between oxygen and other reactants. Finally, it seems to be also a good way to anticipate the NEMCA behavior for reactions, which involve oxygen.

## 1. Introduction

Platinum is an efficient catalyst for many reactions such as the abatement of nitric oxides or the combustion of light hydrocarbons. This noble metal is also used as a catalyst-electrode in a solid electrolyte cell in order to implement the electrochemical promotion of catalysis (EPOC) [1,2]. This concept, also named non Faradaic electrochemical modification of catalytic activity (NEMCA) effect, is based on the application of a current or a potential between the catalyst-electrode and a catalytically inert counter-electrode. EPOC can markedly affect the catalytic activity and the product selectivity, in a reversible and controlled way. EPOC requires low current or potential because this process is not Faradaic and thus not limited by the migration rate of ionic species in the solid electrolyte. Furthermore, EPOC enables to in-situ tune the activity of a catalyst. The system based on a platinum film deposited on yttria-stabilised zirconia (YSZ), an $O^{2-}$ conductor, has been intensively used in order to implement EPOC. Among these studies, much work concerns oxidation of light hydrocarbons such as methane, ethylene, propane, propene [3-9] and the NO reduction by propene in the presence of oxygen [10,11]. For instance, we have shown in a previous paper [9] that both propane and propene combustion on Pt/YSZ can be electrochemically promoted and that the two hydrocarbons exhibit opposite behaviours upon applied overpotentials. Propane combustion is enhanced when a positive polarisation is applied and then exhibits an electrophobic NEMCA behavior. On the contrary, the oxidation rate of propene increases under a negative voltage and presents an electrophilic NEMCA behaviour. These differences were attributed to competitive adsorption between oxygen and the hydrocarbon. Consequently, the NEMCA behaviour of a catalytic reaction which occurs on a catalyst deposited on an electrolyte conductor by oxygen ions is dependent on the oxygen coverage at OCV. The aim of this study is to in-situ evaluate catalytic reactions by the measurement of the potential and the oxygen coverage on Pt to get information about the competitive adsorption between oxygen and other reactants such as the hydrocarbons. The idea is to anticipate the NEMCA behaviour of a reaction, i.e. electrophilic or electrophobic, with respect to the temperature and the concentrations of reactants. The measurement of the open-circuit potential as a function of the temperature under different atmospheres, i.e. Solid Electrolyte Potentiometry (SEP), was proposed by C. Wagner [12] in order to probe the oxidation state of the catalyst-electrode under working condition. The equilibrium potential, $V_{WRo}$, is related to the thermodynamic activity ($a_0$) of atomic oxygen adsorbed on platinum by:

$$V_{WRo} = \frac{RT}{4F}\ln\left(\frac{a_O^2}{P_{O_2}^R}\right) \quad (1)$$

where, R is the ideal gas constant, F the Faraday constant, T the temperature in K, and $P_{O2}^R$, the partial pressure of oxygen at the reference electrode. This equation is based on the existence of equilibrium between $O^{2-}$ in YSZ and adsorbed oxygen on the platinum surface (2), according to:

$$O^{2-}_{YSZ} \rightleftarrows O_{Pt} + 2e^- \quad (2)$$

Literature is available, dealing with the evolution of $a_o$ with the temperature under reactive mixtures containing a hydrocarbon, such as methane [13], butane [14], or propene [15]. The lower temperature limit, for the use of solid electrolyte cells under equilibrium conditions with the system Pt/YSZ, has been determined at around 250 °C by comparing experimental values of $V_{WRo}$, with those calculated from the Nernst equation [16]. However, in order to deal with catalytic study demands, J. Brück et al. [16] have shown that such measurements can be performed at temperatures somewhat lower than this limit, providing that stable values of open-circuit voltage are obtained.

This study is a first approach concerning the relationship between the potential and the catalytic activity of the Pt/YSZ system. Each experiment has been done in the same tubular reactor. First, temperature-programmed desorption (TPD) of oxygen experiments were carried out in order to determine the relationship between oxygen coverage and elec-trochemical potential. Then, catalytic activity in parallel with the potential value were measured between 200 °C and 500 °C for the NO oxidation, $C_3H_8$ combustion, $C_3H_6$ combustion and the selective catalytic reduction (SCR) of NO by $C_3H_6$ in the presence of oxygen.

## 2. Experimental Procedure

*2.1. Preparation and Characterisation of Pt Film Interfaced with YSZ.* The electrolyte was Yttria Stabilised Zirconia (TOSOH powder 99.99%, average grain size: 0.3 μm), containing 8 mol percent of yttria. The schematic drawing of the reactor is shown in Fig. 1. The tubular reactor was made from a YSZ tubular sheath (outer diameter 12.7 mm, thickness 2.7 mm, length 420 mm). Both the working (W) and counter (CE) electrodes were a porous Pt film symmetrically deposited on the outer and the inner surface, respectively, of the YSZ tube by using a platinum paste (Engelhard-Clal 6926) and annealed at 800 °C for 12 hours in air. Both electrodes were placed right through the centre of the YSZ sheath for 60 mm in length in order to be in the hot zone of the oven. This enables to get a stable and homogenous temperature over the whole catalyst surface. The geometric area of the working electrode was 24 cm$^2$. The platinum quantity was 20 mg, i.e. 0.83 mg·cm$^{-2}$. The real surface area, $N_G$, expressed in moles O, was measured via isothermal surface titration of $C_3H_6$ with $O_2$ at 350 °C, as described by Vayenas et al. [2], and found to be 0.8 μmol O. Then, the Pt dispersion, i.e. the metallic fraction accessible to the gas, can be estimated lower than 1%. This very low value, compared to a powdered catalyst, is due to the calcination at 800 °C, which leads to the sintering of the Pt particles. The YSZ sheath was inserted into a quartz tube (350 mm in length), which presents an internal diameter of 14 mm. The volume of the reactor between the YSZ and quartz tubes is very low, i.e. 8 cm$^3$. The gas flow passed between the two tubes and licked the working electrode. The tubular reactor was heated by a tubular furnace (internal diameter 20 mm, length 200 mm). Torr-Seal® adhesive (Varian Vacuum Products)

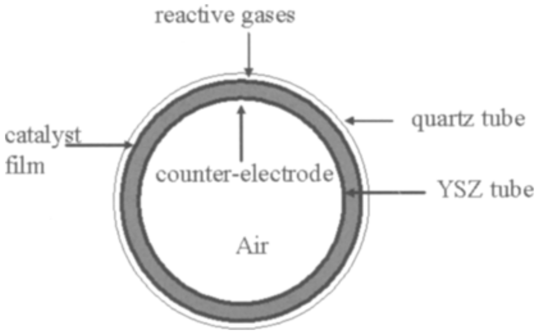

Fig. 1. Schematic drawing of the reactor.

was applied between the top of YSZ and quartz tubes in order to insure the sealing. This end part of the reactor was out of the oven. The working electrode was exposed to the reactive mixture whereas the counter electrode was only under air.

*2.2. Temperature-Programmed Desorption (TPD).* TPD experiments were carried out in the tubular reactor with a continuous He flow under atmospheric pressure. The working electrode was first reduced under $H_2$ at 300 °C for 1 h, and then temperature was increased up to 400 °C in He in order to obtain a clean Pt surface. After purged with He for 15 min at 400 °C, the Pt film was exposed to 1% $O_2$ in He (10 $L \cdot h^{-1}$) for 20 minutes or 1 h, and quickly cooled down to 200 °C under the same atmosphere. The reactor was purged with He for 20 min and the temperature was raised linearly ($\beta = 5$ $°C \cdot min^{-1}$) in order to obtain the $O_2$ TPD curves. Analysis of the gases during desorption experiments was performed by an on-line micro gas-chromatograph (VARIAN CP-2003), which enables the analysis of $O_2$ and $CO_2$ in 45 seconds with a detection limit of 1 ppm for $O_2$.

*2.3. Catalytic Activity Measurements.* The catalytic properties of the Pt film were evaluated in the tubular reactor under continuous flowing conditions at atmospheric pressure. The gas composition was controlled by mass flow controllers (Brooks, with accuracies better than 1%). In the following, the gas composition will be expressed in ppm or % and mixtures will be described as follows: $C_3H_6/NO/O_2$: 2000 ppm/2000 ppm/1 %. The vector gas was helium (Air liquid, 99.999 % purity). The reaction gases were $C_3H_6$ (Air Liquid, 7710 ± 231 ppm $C_3H_6$ in He), $C_3H_8$ (Air Products, 8000 ± 80 ppm $C_3H_8$ in He), $O_2$ (Air Liquid, 99.99 % purity) and NO (Air Liquid, 7970 ppm ± 159 ppm NO in He). Before analysis, the water produced by the catalytic reactions was trapped by an electro-gas cooler (M&C Products, ECP1000-G). For propane and propene combustion, the reactive mixture was $HC/O_2$: 2000 ppm / 1% with HC = $C_3H_8$ or $C_3H_6$. The overall gas flow rate was kept constant at 10 $L \cdot h^{-1}$ (± 0.1 $L \cdot h^{-1}$). The products of reaction were analysed by an on-line micro gas-chromatograph (VARIAN CP2003), as during $O_2$-TPD. The micro-chromatograph was composed of two modules, each one equipped with a thermal conductivity micro-detector. The first module enabled the separation of $CO_2$ and the hydrocarbon ($C_3H_6$ or $C_3H_8$) by using a Poraplot U column (10 m length and 0.32 mm in internal diameter) heated to 60 °C. The second one was equipped with a molecular sieve heated to 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. The conversion of the hydrocarbon (HC) into $CO_2$ was defined as :

$$HC_{conversion} = 100 \times P_{CO2} / (P_{CO2} + 3 \times P_{HC}) \quad (3)$$

where, $P_{CO_2}$ and $P_{HC}$ are the partial pressures of $CO_2$ and the hydrocarbon ($C_3H_8$ or $C_3H_6$) in the outlet gas, respectively. $CO_2$ is the only carbon-containing oxidation product. Carbon monoxide was not detected, according to our lower detection limit about 10 ppm.

The oxidation of NO into $NO_2$ has been carried out with a reactive mixture of 1000 ppm NO and 1% $O_2$ and an overall gas flow rate of 4 $L \cdot h^{-1}$. Analysis has been done by a VG Gasslab 300 quadrupole mass spectrometer. Signals at m/e = 16, 18, 28, 30, 32, 44 and 46 amu corresponding to $O^+$, $H_2O^+$, $N_2^+$ or $CO^+$, $NO^+$, $O_2^+$, $N_2O^+$ or $CO_2^+$ and $NO_2^+$ ions were recorded, respectively. NO conversion was defined as,

$$NO_{conversion} = 100 \times [(P_{NO})_i - (P_{NO})_o]/(P_{NO})_i \quad (4)$$

where $(P_{NO})_i$ and $(P_{NO})_o$ are the partial pressure of NO in the inlet and outlet gas, respectively.

The selective reduction of NO by propene in the presence of oxygen was also carried out on the same Pt film. The reactive mixture was composed of $C_3H_6/NO/O_2$: 2000 ppm / 1000 ppm / 1 or 5% $O_2$ and the overall gas flow was 4 $L \cdot h^{-1}$. Reactants and products were analysed by the same equipment, i.e. a quadrupole mass spectrometer. Propene and NO conversions were calculated according to eqs. (3) and (4), respectively.

Before catalytic activity measurements, whatever the chemical reaction, the Pt film was pretreated in $H_2$ at 300 °C for 1 hour in order to reduce platinum. Then, sample was cooled down to 200 °C under a flow of helium. The reactive mixture flow was switched into the reactor. Then, the sample was heated up to 500 °C with 1 °C/min heating rate. Catalyst was maintained at 500 °C for 2 h in order to stabilize the activity and then, the temperature was decreased from 500 °C to 200 °C at 1 °C/min. The catalytic activities presented in this study correspond to those recorded during the decrease of temperature.

*2.4. Solid Electrolyte Potentiometry.* Solid electrolyte potentiometry (SEP) was also carried out during the catalytic tests. The two electrodes, W (catalyst or working electrode) and CE (counter electrode) were connected to a potentiostat-galvanostat Voltalab 80 (Radiometer Analytical). The measured voltage, $\Delta V_{WCE,o}$, represents the open-circuit potential difference between the catalyst exposed to the reactive mixture and the counter electrode exposed to air, according to the following equation :

$$\Delta V_{WCE,o} = \frac{RT}{4F} \ln\left(\frac{a_O^2}{P_{O_2}^{CE}}\right) \quad (5)$$

with T, the temperature in K, $a_O$, the thermodynamic activity of oxygen on the catalyst and $P_{O_2}^{CE}$ the partial pressure of oxygen in the counterelectrode compartment, i.e. 0.21 atm. Therefore, at a given temperature, the difference between two values of $\Delta V_{WCE,o}$ is only due to the variation of the catalyst potential and then of the thermodynamic activity of oxygen on the catalyst.

## 3. Results and Discussion

*3.1. TPD of $O_2$.* Figure 2 (a) shows the $O_2$-TPD spectra after adsorption of 1% $O_2$ at 400 °C for 20 minutes and 1 hour. For both experiments, oxygen starts to desorb at low temperature, i.e. from 300 °C, and spectra present a broad and non-symmetrical peak with a maximum at $T_p$ = 390 °C. By fitting this peak, it may be possible to consider two peaks, one centred around 390 °C (denoted as $\alpha_1$) and a second one around 440 °C (denoted as $\alpha_2$). Similar TPD of oxygen has been obtained with a powdered catalyst composed of platinum dispersed on $\gamma$-$Al_2O_3$. This catalyst presented a very low Pt dispersion comparable to that of the Pt particles [17]. Indeed, several studies [18,19] have demonstrated that the $O_2$ desorption temperature was lower on large Pt particles relative to small ones. Therefore, peaks of oxygen TPD that we observed can be assigned to oxygen adsorbed from the gas phase onto Pt particles. With the extension of exposure time to 1% $O_2$ atmosphere, the amount of oxygen adsorbed on Pt increases. If one consider the true surface area, $N_G$ = 0.8 μmol O, which corresponds to the total number of Pt sites available and the dissociative adsorption of $O_2$ onto Pt, then we can estimate the oxygen coverage over Pt film This oxygen coverage increases from 0.083 to 0.165 with exposure time prolonged from 20 min to 1 h. Fig. 2 (a) also shows that with the decrease of oxygen coverage, desorption peak slightly shifts toward lower temperature.

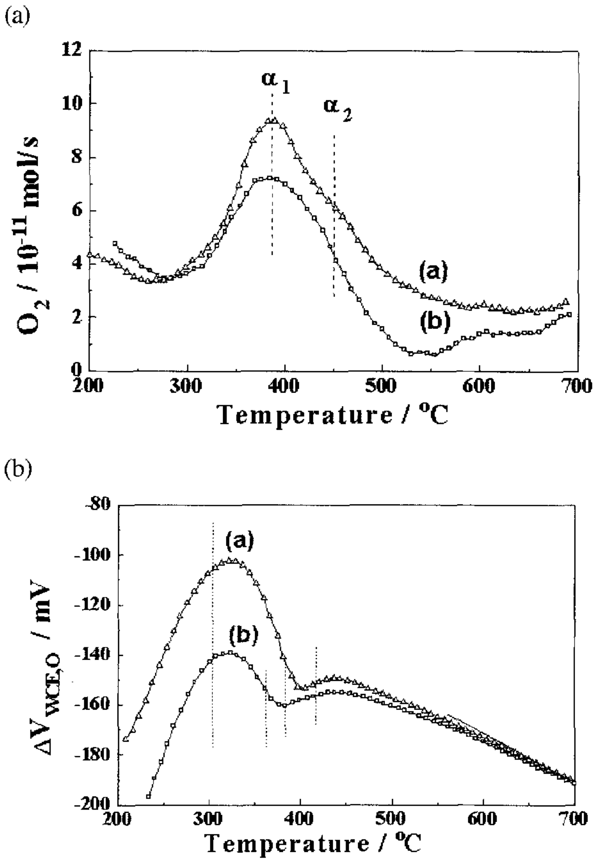

Fig. 2(a). Profiles corresponding to $O_2$ detection during TPD after preliminary adsorption of 1% $O_2$ for 1 hour (a) or 20 minutes (b). (b) Variation of potential during $O_2$-TPD after preliminary adsorption of 1% $O_2$ for 1 hour (a) or 20 minutes (b).

Figure 2 (b) presents transient behavior of potential $\Delta V_{WCE,o}$ of Pt film recorded during the two oxygen TPD runs. One can consider three distinct parts in the curve of potential variation versus temperature: before, during and after the $O_2$ desorption. Nevertheless, over the whole range of temperature, $\Delta V_{WCE,o}$ is negative because the oxygen partial pressure in counterelectrode compartment is always higher than for working electrode. Below 300 °C, the beginning of the desorption, $\Delta V_{WCE,o}$ increases with temperature and then does not follow the Nernst eq. (5). This is certainly because the electrode reaction is not at the equilibrium. The comparison between the two TPD experiments is very interesting because, below 300 °C, $\Delta V_{WCE,o}$ variations versus temperature follow the same trend but the potential for a short exposure time is significantly lower. These two experiments have been done with the same sample and operating conditions. Therefore, this potential difference can only be explained by the oxygen coverage on Pt which is lower after 20 minutes of adsorption, i.e. 0.083 than after one hour, i.e. 0.165. When the oxygen desorption occurs, $\Delta V_{WCE,O}$ abruptly decreases due to the concomitant drop of $a_O$ and the increase of temperature. Let us note that, the higher the initial oxygen coverage, the higher the potential drop. From 380 °C or 400 °C corresponding to short and long adsorption time, respectively, $\Delta V_{WCE,O}$ variation shows a slight increase. One can think that a part of the oxygen species released from $\alpha_1$-related sites re-adsorbs over $\alpha_2$-related ones, leading to an increase of $a_O$. This result seems to confirm the co-existence of two different sites for oxygen adsorption on Pt. After the maximum of $\alpha_2$ peak, potential continuously decreases. From 550 °C, after the oxygen desorption, $\Delta V_{WCE,O}$ only varies with the temperature according to the eq. (5) since the oxygen activity remains very low and stable. The slopes of both experimental lines and theoretical values predicted by eq. (5) are similar, i.e. $-2 \times 10^{-4}$ K/V. Values of $\Delta V_{WCE,O}$ for the two experiments with short or long adsorption time are identical since the Pt surface state in this temperature domain is the same, i.e. clean Pt surface. This result clearly confirms that the value of the potential can be compared at a given temperature between two different operating conditions at the working electrode.

### *3.2. Catalytic Activity Measurements.*

*3.2.1. NO Oxidation.* The NO conversion to $NO_2$ starts from 225 °C. Then, the reaction rate increases with temperature and passes through a maximum at 480 °C with a NO conversion of 17% (Fig. 3). The feature of this activity curve is related to the thermodynamic equilibrium since the $NO_2$ production is thermodynamically favoured at low temperatures. The $\Delta V_{WCE,O}$ variation versus temperature follows the same trend with the NO conversion. Below 225 °C, the potential (Table 1) is higher than that observed during $O_2$-TPD certainly due to the dissociative adsorption of NO on Pt (6). Indeed, atomic oxygen adsorbed on Pt can come from gaseous oxygen (7) and/or from the dissociative adsorption of NO (6).

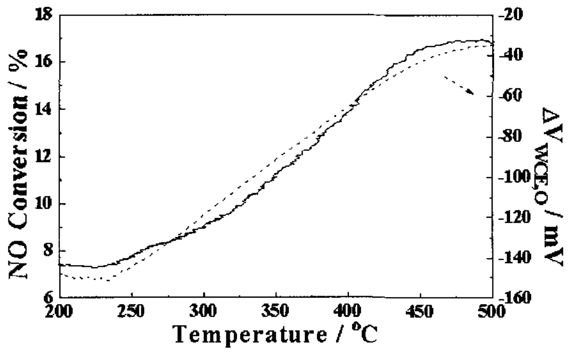

Fig. 3. NO conversion and potential variation versus temperature. Reactive mixture: $NO/O_2$: 1000 ppm/ 1 %.

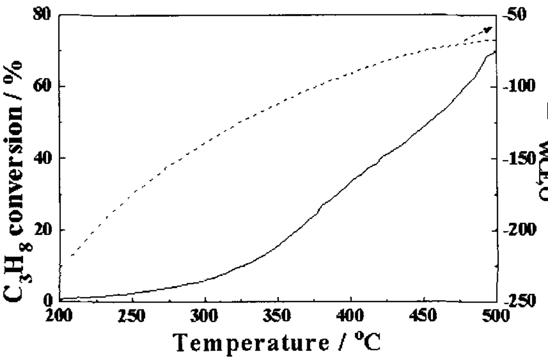

Fig. 4. Propane conversion and potential variation versus temperature. Reactive mixture: $C_3H_8/O_2$: 2000 ppm / 1 %.

$$NO(g) \rightarrow NO\text{-}Pt \rightarrow N\text{-}Pt + O\text{-}Pt \qquad (6)$$

$$O_2(g) \rightarrow 2\ O\text{-}Pt \qquad (7)$$

Potential increases from 225 °C and reaches its maximum when the NO conversion is optimal. This indicates that the oxygen activity on Pt gradually increases in parallel with the NO conversion. Therefore, the in-situ measurement of the potential seems to be a suitable indication of the catalytic behaviour. At 500 °C, $\Delta V_{WCE,O}$ is very high (Table 1), suggesting that the Pt surface is mainly covered by oxygen. Let us note that the $\Delta V_{WCE,O}$ variation versus the temperature does

Table 1. Values of $\Delta V_{WCE,O}$ (mV) at 200 °C and 500 °C.

| | $O_2$-TPD* | NO / $O_2$ | $C_3H_8$ / $O_2$ | $C_3H_6$ / $O_2$ | $C_3H_6$ / NO / 1%$O_2$ | $C_3H_6$ / NO / 5% $O_2$ |
|---|---|---|---|---|---|---|
| 200 °C | -174 | -148 | -222 | -784 | -504 | -445 |
| 500 °C | -158 | -35 | -67 | -129 | -87 | -29 |

* Adsorption under 1% $O_2$ in He for 1 hour.

never follow the Nernst eq. (5). Consequently, the prevailing factor is the oxygen activity change induced by the catalytic reaction and not the increase of temperature.

*3.2.2. Propane Combustion.* Figure 4 shows propane oxidation and transient potential behavior versus temperature from 200 °C to 500 °C. Propane conversion slowly increases until 300 °C, and then reaction rate becomes more important and, finally, conversion reaches maximum of 70% at 500 °C. During propane oxidation, as already observed in $NO/O_2$, potential variation with temperature does never follow the Nernst equation, but the potential continuously increases suggesting that the oxygen coverage increases with the catalytic activity. Nevertheless, the potential variation does not present a slope change when the reaction rate accelerates. The value of $\Delta V_{WCE,o}$ at 200 °C is slightly lower than that recorded during TPD measurements (Table 1). This means that the oxygen coverage on Pt is also slightly lower due to the competitive adsorption between propane and oxygen.

*3.2.3. Propene Combustion.* As already observed [9], propene is much more easily oxidised than propane (Fig. 5). Full conversion is reached at only 275 °C with a very abrupt increase of activity between 200 °C and 275 °C. The value of $\Delta V_{WCE,o}$ at 200 °C is very negative and much more lower than under $C_3H_8/O_2$, $NO/O_2$ or during TPD measurements. This observation confirms that propene is strongly adsorbed on Pt and the oxygen coverage is negligible before the propene activation. The potential rapidly increases with temperature from 200 °C to 360 °C with a slope three times higher than that observed during propane oxidation. This slope decreases strongly from 360 °C after a full conversion was reached. At 500 °C, the value of $\Delta V_{WCE,o}$ remains lower than that recorded under $NO/O_2$ and $C_3H_8/O_2$. It indicates that, even at full propene conversion, the oxygen coverage is still very low.

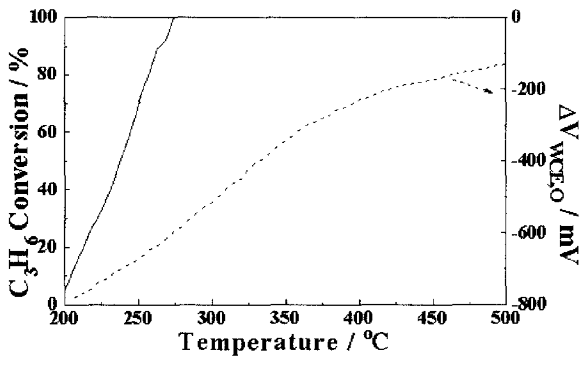

Fig. 5. Propene conversion and potential variation versus temperature. Reactive mixture: $C_3H_6/O_2$: 2000 ppm / 1 %.

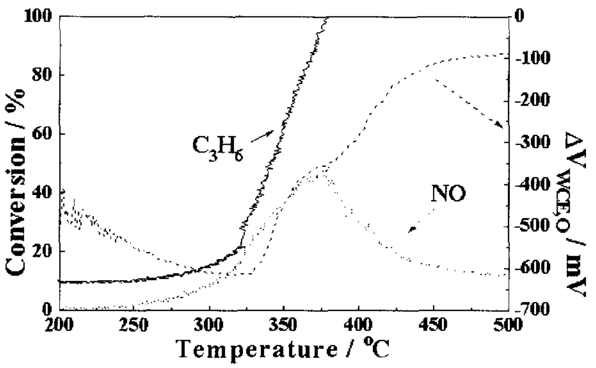

Fig. 6. Propene and NO conversions as well as potential variation versus temperature. Reactive mixture: $C_3H_6/NO/O_2$ : 2000 ppm / 1000 ppm / 1%.

*3.2.4. Selective Catalytic Reduction (SCR) of NO by Propene in the Presence of Oxygen.* This reaction has been carried out for two concentrations of oxygen, 1% of $O_2$, i.e. near to the stoichiometry and 5% of $O_2$, i.e. under lean-burn conditions.

Under stoichiometric conditions (Fig. 6), propene and NO conversions simultaneously start from 320 °C. It is far higher than that observed without the presence of NO (Fig. 5). One can think that the addition of NO still decreases the oxygen coverage on Pt. This assumption is not confirmed by the value of $\Delta V_{WCE,o}$ at 200 °C which is higher than that observed under $C_3H_6/O_2$. Nevertheless, this higher value of the potential could be explained by the NO dissociation on Pt (6). Below 320 °C, the potential decreases with temperature, from –504 mV at 200 °C to –616 mV at 320 °C, suggesting that the oxygen coverage still decreases. This behaviour was not observed under $NO/O_2$, $C_3H_8/O_2$ or $C_3H_6/O_2$. One can suggest that NO dissociation (6) is more favoured at 200 °C than at 320 °C. This is in good agreement with the fact that, at 320 °C, the predominant reaction is the NO reduction by $C_3H_6$. Between 320 °C and 375 °C, the $C_3H_6$ conversion increases from 20% to 100%. NO conversion goes through a maximum at a temperature corresponding to the total hydrocarbon conversion, i.e. 48% at 375 °C. This catalytic behaviour is similar to that reported in the literature for platinum deposited on $\gamma$-$Al_2O_3$ [20,21] or $SiO_2$ [22,23], and also for a similar Pt film deposited on YSZ [10]. The behaviour of $\Delta V_{WCE,o}$ versus temperature is very interesting because it presents an abrupt change at 320 °C, temperature of the activation of NO reduction by $C_3H_6$. Furthermore, $\Delta V_{WCE,o}$ starts abruptly to increase with temperature from 320 °C and then presents a significant shoulder in a temperature range corresponding to the maximum NO conversion. After 100% $C_3H_6$ conversion, i.e. 375 °C, the potential again rapidly increases and stabilizes from 450 °C. At 500 °C, the value of $\Delta V_{WCE,o}$ (Table 1) is intermediate between that obtained under $NO/O_2$ and $C_3H_6/O_2$.

Under lean-burn conditions (Fig. 7), the catalytic curves present similar feature than under stoichiometric conditions but are shifted to lower temperatures. Indeed, propene full combustion occurs at lower temperature, i.e. 308 °C and the maximum NO conversion decreases from 47% to 37%. As already observed [10], NO reduction by propene is hindered by the increase of oxygen concentration. After 100% propene conversion, we observed a production of $NO_2$ arising from the oxidation of NO. The behaviour of $\Delta V_{WCE,o}$ is also similar to that recorded under stoichiometric conditions but, as expected, potential presents higher values over the whole temperature domain.

*3.3. Discussions.* The aim of this study was to find relationships between the potential of the Pt and its catalytic activity. If considering that the electrode reaction (2) is at the equilibrium, according to the Nernst equation (5), the Pt potential is linked to the thermodynamic activity of oxygen on Pt and the temperature. $O_2$-TPD experiments have clearly shown that this potential could also be directly linked to the oxygen coverage because the Pt potential:

- is dependent on the amount of oxygen atoms previously adsorbed on Pt, before the temperature of oxygen desorption,
- decreases when oxygen desorbs,
- and only varies with temperature when all oxygen atoms are desorbed.

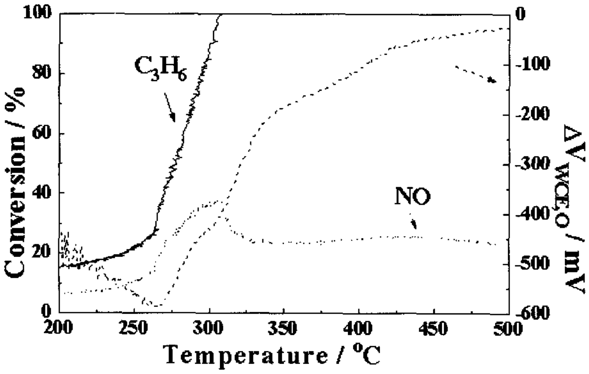

Fig. 7. Propene and NO conversions as well as potential variation versus temperature. Reactive mixture: $C_3H_6/NO/O_2$ : 2000 ppm / 1000 ppm / 5%.

Therefore, one can assume that the measurement of the Pt potential is an in-situ estimation of the oxygen coverage. We have followed the variation of the Pt potential versus temperature under various atmospheres, i.e. $NO/O_2$, $C_3H_8/O_2$, $C_3H_6/O_2$ and $C_3H_6/NO/O_2$. For all these experiments, between 200 °C and 500 °C, the potential variation versus temperature does never follow the Nernst eq. (5). These results show that the predominant factor is the oxygen activity change induced by the catalytic reaction and not the influence of temperature. Catalytic reactions are driven by a competitive adsorption on Pt atoms between the different reactants, according to the Langmuir-Hinshelwood model. Therefore, if the Pt surface is mainly covered by one reactant, the adsorption of other ones is hindered and the catalytic activity is low. So, for reactions involving oxygen, the coverage in such a species is a good parameter in order to get in-situ information on the competitive adsorption between oxygen and the others reactants. The presence of propene in the reactive mixture drastically decreases the potential over the whole temperature range. This confirms that propene is strongly adsorbed on Pt and then significantly decreases the oxygen coverage. If we compare values of $\Delta V_{WCE,o}$ between $C_3H_8/O_2$ and $C_3H_6/O_2$ atmospheres, it clearly appears that propene is much more strongly adsorbed than propane as already observed by TPD in a previous study [9]. Under $NO/O_2$ atmosphere, values of the potential are high, suggesting that oxygen is more strongly adsorbed than NO. Nevertheless, a part of the adsorbed oxygen can originate from the NO dissociation (6). This reaction also takes place under $C_3H_6/NO/O_2$ and could be at the origin of the decrease of the potential that we observed at low temperature. From a general view, the variation of the potential with temperature follows the catalytic activity and then can provide a correct in-situ evaluation of the conversion. For NO oxidation, propene oxidation and SCR, the potential gives a good indication of the temperature corresponding to the beginning of the conversion. Furthermore, for the SCR, the potential is an accurate sensor for the temperature related to the maximum NO conversion and the full propene conversion. For propane combustion, direct relationship between the propane conversion and the potential are less obvious. Indeed, the increase of the catalytic rate is not followed by a strong increase of the potential but, on the contrary, to an attenuation of its rise. One can assume that, for propane oxidation, the key factor is not oxygen coverage but the propane one. Therefore, if the Pt surface is not entirely covered by both reactants, i.e. oxygen and propane, the estimation of the oxygen coverage by the measurement of the potential could not give correct information on the competitive adsorption.

These relationships between the Pt potential and its catalytic activity can be used in order to predict the NEMCA behaviour, i.e. electrophilic or electrophobic, of the considered reaction. The origin of the electrochemical promotion of catalysis has been established by Vayenas et al. [1,2]. They have shown that a change in the electrode overpotential $\Delta V_{WR}$ results in a modification of the work function $e\Phi$ of the gas-exposed surface of the porous catalyst-electrode film:

$$\Delta(e\Phi) = e\Delta V_{WR} \tag{8}$$

The theoretical validity of the Equation has been discussed in the literature and confronted to experimental results [24-28]. The variation of the Pt work function (WF) alters the strength of the chemical bonds between the metal and the adsorbates and then modifies the competitive adsorptions between the reactants. A decrease of the Pt WF induced by a negative polarization increases the electronic density of Pt and weakens the Pt chemical bonds with electron-donor adsorbates, such as $C_3H_6$ and $C_3H_8$, and strengthens those with electron-acceptor ones, such as $O_2$ and NO [29]. On the contrary, the Pt WF may be increased by applying anodic overpotentials, which induce a positive charge on the metal. The decrease of the Pt electronic density weakens the Pt-O and Pt-NO bonds and strengthens the Pt-$C_3H_6$ and Pt-$C_3H_8$ ones. A reaction, which is electrochemically promoted by either a positive or a negative polarisation, exhibits an electrophobic or an electrophilic behaviour, respectively. Referring to our results, propene is strongly adsorbed on Pt either in $C_3H_6/O_2$ or $C_3H_6/NO/O_2$ atmospheres. Before the temperature corresponding to the propene activation, the oxygen coverage on Pt is extremely low. Therefore, if a negative polarization, which strengthens the Pt-O and Pt-NO bonds and weakens the Pt-$C_3H_6$, is applied, $O_2$ and NO coverage would increase and $C_3H_6$ one decrease. The catalytic activity should be promoted. This is in a good agreement with previous studies, which have clearly shown the electrophilic behaviour of propene combustion [7,9] and SCR of NO by propene [10,11]. Considering propane combustion, our results seem to indicate that the key factor is the increase of the propane coverage. Therefore, propane combustion should be promoted by a positive polarization, which can strengthen the Pt-$C_3H_8$ bond and weaken the Pt-O one, as it has been experimentally shown [9]. Under $NO/O_2$ atmosphere, high values of the open-circuit potential seem to indicate that the oxygen coverage is high. A positive polarization, as in $C_3H_8/O_2$ atmosphere, could decrease it. Unfortunately, anodic voltage should also weaken the Pt-NO bond since O and NO are both electron-acceptors and then no NEMCA effect could be observed. This is what we have experimentally confirmed. Indeed, any promotional or inhibiting effect has been observed when applying positive and negative polarizations.

Therefore, the measurement of the Pt open-circuit voltage seems to be a good indication in order to anticipate the NEMCA behaviour for reactions, which involve oxygen.

## 4. Conclusion

This study demonstrates that the measurement of open-circuit voltage of platinum interfaced with YSZ can be efficient to get in-situ information on the competitive adsorption between oxygen and the others reactants. $O_2$-TPD experiments have clearly shown that the Pt potential can be directly linked to the oxygen coverage on platinum. For NO oxidation, propene oxidation and selective catalytic reduction (SCR) of NO by propene, the potential is a good indicator for the temperature corresponding to the beginning of the conversion. Furthermore, for the SCR, the potential is an accurate sensor of the temperature related to the maximum NO conversion and the full propene conversion. It seems the measurement of the Pt open-circuit voltage is also a good way to anticipate the NEMCA behaviour for reactions, which involve oxygen.

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