

Reduction of nitrogen oxides over Ir/YSZ electrochemical catalysts

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Abstract

This study has shown that Ir/YSZ electrochemical catalysts can reach high catalytic activity for the SCR of NO by propene in the presence of oxygen. Under stoichiometric conditions, porous and thin (about 40 nm) Ir film achieves N₂ yield higher than 80% between 350 and 500 °C. However, iridium films require on-stream treatment at 500 °C in order to develop their catalytic efficiency by increasing Ir particles size and establishing an ideal Ir⁰/IrO₂ ratio. Under lean-burn conditions, the same sample presents high and durable NO conversion at 500 °C. These results confirm that magnetron sputtering is a suitable technique for synthesis of effective thin catalytic films. Furthermore, it was found that NO reduction by propene can be electrochemically promoted on Ir/YSZ electrochemical catalysts. This promotion exhibits an electrophobic NEMCA effect, the reaction rate increasing when a positive polarisation is applied. The electropromotion efficiency was found to be structure sensitive.

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1. Introduction

The automotive pollution control is an urgent need, especially due to ever more stringent future legislations. In addition to catalytic after-treatment systems of exhaust gases, there is a strong demand for a reduction in fuel consumption and CO₂ emission levels. To achieve these goals, lean-burn engines, i.e. diesel and gasoline direct injection ones, seem to be a promising way since they present significant lower fuel consumption compared to gasoline engines which are operated near the stoichiometric air/fuel ratio. Unfortunately, the development of these lean-burn engines is hindered by their NO_x emissions since no efficient and durable solution exists for NO_x removal under lean-burn conditions. Among other ways, such as NO_x storage catalysts, the selective catalytic reduction (SCR) of NO_x by hydrocarbons as reducing agents is a good candidate, especially when supported platinum is used as the catalyst. Platinum-based catalysts allow high and durable NO_x conversion in real diesel exhaust, especially at low tempera-

tures (between 200 and 350 °C) corresponding to those of such engines working in an urban cycle [1–3]. Furthermore, supported platinum catalysts are resistant to poisoning by steam or SO₂ present in the exhaust stream and exhibit a good thermal stability. However, the major drawback of platinum-based catalysts is that the majority of NO is reduced to N₂O [1–3], a greenhouse gas effect, rather than being reduced to harmless N₂. Among the family of platinum group metals, recent studies have focused on the catalytic activity of Ir for the reduction of NO. Although Tauster and Schlatter [4] have shown in 1976 that Ir can be an effective catalyst for the reduction of NO by CO under lean-burn conditions, this metal was scarcely used. Furthermore, several studies [5–7] have found opposite results by showing that supported Ir catalysts were almost inactive. In fact, recent studies [8–10] have clearly shown that iridium requires special pretreatment conditions to develop its catalytic efficiency. Catalyst activation can be achieved by high temperature hydrothermal pretreatment [8] or by in situ exposure to the feed gas at the reaction temperature [9,10]. This former conditioning seems to be the most efficient. Several studies of Wögerbauer et al. [11–13] have shown that the activation on-stream could lead to growth of Ir crystallites and to the establishment of an ideal Ir⁰/IrO₂ ratio. The ability of

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metallic Ir particle to be oxidized seems to be size dependent. Small crystallites would be easily oxidized and could favour NO oxidation into NO₂ as well as hydrocarbon oxidation. Wögerbauer et al. [14] have shown that NO reduction on Ir catalysts is structure sensitive. The capacity of Ir particles to adsorb NO strongly increases with their size. High N₂ yields were achieved with largest particle size, typically 45 nm, even in the presence of large excess of oxygen. Compared to Pt-based catalysts, the activity window of Ir takes place at higher temperatures. The maximum of the N₂ yield achieved on Ir under lean-burn conditions by using propene as a reducing agent occurs around 400 °C instead of 250 °C on Pt [1,2,11].

The goal of this study was to evaluate the catalytic activity of Ir thin films for SCR of NO_x by propene. Thin films of Ir were sputter-deposited on yttria-stabilised zirconia (YSZ) membranes by magnetron sputtering of an Ir target. We have shown in a previous study [15] that magnetron sputtering is a suitable technique for synthesis of catalysts coatings. The YSZ support is a solid electrolyte which is an O²⁻ ionic conductor. A continuous Ir thin film deposited on YSZ support is an electrochemical catalyst which can implement the concept of electrochemical promotion of catalysis. The electrochemical promotion of catalysis (EPOC) or non-faradaic electrochemical modification of catalytic activity (NEMCA) effect, discovered and developed by Vayenas et al. [16,17] is an innovative concept which can be used to improve the catalytic activity. This process is based on the control, by an applied potential, of the work function due to electrochemical pumping of ions between a solid electrolyte and the surface of a porous catalyst. The NEMCA effect has been observed for a wide range of reactions in the presence of metals such as Pt, Pd, Ag or Rh in contact to a solid electrolyte. Electrochemical promotion was also evidenced on IrO₂ interfaced with YSZ for the ethylene combustion [18,19]. Recent studies [20–26] have explored the utility of EPOC to promote the nitric oxide reduction by propene in the presence of oxygen. Most of them report the use of rhodium catalysts associated to YSZ or β''-Al₂O₃. These papers showed that the catalytic activity and also the selectivity of the Rh catalyst–electrode between 350 and 430 °C can be highly promoted upon varying its potential. However, in the presence of oxygen excess, the promotion efficiency drastically decreases. Using a Rh/YSZ system, Foti et al. [21] found that a simple heating from 300 to 400 °C under a reactive mixture containing 1000 ppm C₃H₆, 1000 ppm NO and 5000 ppm O₂ results in a drop of the catalytic activity due to oxidation of the Rh surface. Their results show that, at 300 °C, a positive current ($i = +5 \mu\text{A}$) enhances the catalytic activity but not the selectivity towards nitrogen. Williams et al. [22] have recently investigated a bimetallic Rh–Ag film deposited on YSZ under lean-burn conditions, i.e. C₃H₆/NO/O₂:1000 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 N₂ significantly increases from 28% to 55% upon an applied overpotential of +100 mV. The authors explain that the presence of Ag improves resistance to oxidation of the rhodium surface. We ourselves have used EPOC to promote the reduction of NO by propene in the presence of oxygen over Pt

deposited on YSZ [23] and Na super ionic conductor (NASICON), i.e. Na₃Zr₂Si₂PO₁₂, a Na⁺ conducting electrolyte [25]. We found that NO reduction by propene can be electropromoted by applying negative overpotentials. Nevertheless, the activity of the Pt/YSZ electrochemical catalyst was only electrochemically enhanced under stoichiometric conditions. Under lean-burn conditions, Pt-based catalysts are efficient at temperatures lower than 300 °C, a temperature range in which the ionic conductivity of YSZ is too low. By using a much more conductive solid electrolyte, i.e. NASICON, we found that the activity and also the selectivity to N₂ of Pt can be strongly electropromoted even under lean-burn conditions. However, the durability of a Na⁺ conducting electrolyte such as NASICON is not sufficient in the operating conditions of catalytic after-treatment because there is no Na⁺ tank contrary to O²⁻ conducting solid electrolytes, which can be continuously replenished from gaseous O₂ present in the stream. Therefore, another advantage of Ir is that it can be interfaced to YSZ because its activity temperature window is compatible with that of the ionic conductivity of this O²⁻ conducting solid electrolyte.

In this study, the catalytic activity of iridium films interfaced with YSZ, for the SCR of NO_x by propene in the presence of oxygen, was investigated between 200 and 500 °C. The influence of the film microstructure on the catalytic performances was explored by varying the thickness and the porosity of the catalytic coating. Moreover, catalytic activity measurements under closed-circuit were carried out in order to evaluate the ability of the Ir/YSZ system to implement electrochemical promotion of catalysis. The promotion efficiency was compared according to the microstructure of the Ir films.

2. Experimental

2.1. Preparation and characterization of Ir thin films

Ir thin films of various thicknesses were sputter-deposited on YSZ membranes from an Ir metallic target in argon. The electrolyte was an yttria-stabilized zirconia (TOSOH powder 99,99%, average grain size: 0,3 μm), containing 8 mol% of yttria, and sintered at 1350 °C for 2 h (densification higher than 98%). YSZ discs were 17 mm in diameter and 1 mm thick and were preliminary sand-blasted before the metallic film deposition. The experimental device, already described elsewhere [27], is a 301 sputtering chamber. The 50 mm diameter magnetron target is powered by an advanced energy dc supply equipped with a fast arc detector able to cut microarcs within 1–2 μs. In all experiments, the discharge current is maintained at a constant value of 0.2 A and the draw distance is 80 mm. Total pressure was measured using an absolute MKS Baratron pressure gauge. Coating thickness was measured using the step method with a Talysurf profilometer allowing an accuracy of about 10–20 nm or by analysing the transmittance–wavelength curves measured with a Varian Cary 5000 optical spectrometer thanks to a programme developed by PVDco Ltd. The structural features of the coatings were obtained by X-ray diffraction ($\lambda_{\text{K}\alpha\text{Co}} = 179 \text{ nm}$)

Table 1
Main properties of Ir coatings in relation with their deposition condition

Samples	Deposition duration (min)	P_{Ar} (Pa)	Thickness (nm)	Ir loading estimation (mg)	Ir particle size ^a (nm)	V_{WRO} at 500 °C (mV) vs. Au
Ir-20-LP	1.5	0.3	20–30 os	0.1	19	+77
Ir-40-HP	1.5	10	30–45 os	0.16 (porosity 20%)	24	+193
Ir-90-LP	10	0.4	90 p	0.46	30	+134
Ir-150-HP	5	4	150 p	0.6 (porosity 20%)	30	+179

os: determined by optical spectroscopy, p: determined by profilometry.

^a After the activation procedure (determined by XRD).

using an INEL diffractometer. Their morphology was observed via scanning electronic spectroscopy. The coating porosity was modified by varying the argon pressure in the sputtering chamber; the higher the Ar pressure during the deposition stage, the higher the film porosity [28]. The other parameter during the deposition process is the duration which allows controlling the thickness of the film. This former varies from 20 to 150 nm with two different microstructures, i.e. dense and porous. The Ir loading of each electrochemical catalyst was estimated from the theoretical bulk density of Ir, i.e. 22.421 g cm⁻³ (Table 1). In the sample designation, such as Ir-40-HP, the number means the thickness in nanometers and HP and LP mean high and low porosity, respectively. The Ir-40-HP sample was investigated by XPS before and after the on-stream treatment at 500 °C. The XPS spectra were recorded on a RIBER SIA 200 multitechnique (XPS, AES, ISS) spectrometer, equipped with a MAC2 analyser. For all XPS analyses, the take-off angle of analysed photoelectrons was 70° with respect to the sample plane. We used non-monochromatised Al K α radiation (1486.6 eV), from a dual anode (Mg/Al) system. Residual pressure in the analysis chamber was lower than 2×10^{-9} Torr at the beginning of each analysis. The photoelectron energy scale was calibrated according to the Au 4f 7/2 peak. The maximum of the C1s peak envelope corresponding to carbon atoms bonded to other carbon and hydrogen atoms was assumed to be at 285.1 eV.

2.2. Catalytic activity measurements

Catalytic testing was performed at atmospheric pressure in a specific quartz reactor described in a previous study [29]. The electrochemical catalyst was placed on a fritted quartz, 18 mm in diameter, with the catalyst–electrode side facing the fritted quartz. The gas flow passed through the porous disk from below and then licked the catalyst. An inner quartz tube was pressed onto the sample in order to ensure electric contacts. A K-type thermocouple was located near the electrochemical catalyst. The reaction gases were mixtures of NO (Air Liquide, 7970 ppm \pm 160 ppm NO in He), O₂ (Air Liquide, 99.99% purity), C₃H₆ (Messer, 7780 ppm \pm 230 ppm C₃H₆ in He) and He (Air Liquide, 99.999% purity) which was used as the vector gas. 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 %. The reactive mixture (RM) is containing C₃H₆/NO/O₂: 2000 ppm/2000 ppm/1 or 5%. The overall gas flow rate was

kept with He constant at 10 L h⁻¹ (\pm 0.1 L h⁻¹). The electrochemical reactor was heated at 200 °C under He and then exposed to RM. Catalytic activity measurements were performed between 200 and 500 °C. First, performances were investigated during heating from 200 to 500 °C with a ramp of 1 °C min⁻¹. Then, the catalyst was maintained at 500 °C for 5 h on stream and the catalytic activity was recorded during the cooling down (1 °C min⁻¹). The reactants and products were analysed by a NO_x (NO and NO₂) analyser (Cosma, TOPAZE 3000) and an on-line micro gas-chromatograph (VARIAN CP2003). Before these analyses, the water produced by the catalytic reactions, was trapped by an electro-gas cooler (M&C Products, ECP1000-G). The micro-chromatograph was composed of two modules, each one equipped with a thermal conductivity micro-detector. The first module enabled the separation of CO₂, N₂O and the hydrocarbon (C₃H₆) 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 O₂, N₂ and CO. The overall duration of one analysis was only 110 s. Carbon and nitrogen mass balances were found to be within 2%. Blank experiments have shown that the fritted quartz was catalytically inert up to 600 °C. We have also investigated the catalytic performances of the gold counter and reference electrodes.

The catalytic activities presented in this study correspond to those recorded during the decrease of temperature. We calculated the production of N₂, N₂O and NO₂, which were defined as the percentage of NO converted to these products. The selectivity to N₂ represented the amount of N₂ production compared to that of N₂O.

The three electrodes, W (catalyst–electrode or working electrode), R (reference) and CE (counter-electrode) were connected to a potentiostat–galvanostat Voltalab 80 (Radiometer Analytical). Voltage or current was applied and measured according to the procedure generally used in conventional three-electrode electrochemical cells. The enhancement factor or faradaic efficiency, Λ , was defined by

$$\Lambda = \frac{r - r_o}{I/nF} = \frac{\Delta r}{I/nF} \quad (1)$$

where r_o , in mol O/s, is the catalytic rate at OCV, r the catalytic rate under polarisation, n the number of exchanged electrons during the electrode reaction ($n = 2$ with an O²⁻ conductor) and

Δr is the catalytic reaction rate change induced by a current I . A catalytic reaction exhibits the NEMCA effect when $|\Lambda| > 1$. A reaction which is accelerated by a negative current or overpotential (oxygen removed from the catalyst surface) exhibits an electrophilic NEMCA behaviour and corresponds to a value of Λ lower than -1 . In parallel, when the catalytic reaction is promoted by a positive current or overpotential (oxygen supplied to the catalyst surface), its NEMCA behaviour is called electrophobic ($\Lambda > 1$).

3. Results

3.1. Change in activity during on-stream treatment

Fig. 1 represents the variation of the Ir-40-HP catalytic activity versus temperature between 200 and 500 °C. The feed composition is near to the stoichiometry, i.e. containing 1% of O₂. Catalytic activity starts from 280 °C with a concomitant conversion of propene and production of N₂ and N₂O. We observed an extremely low NO₂ production over the whole temperature range. Main products were CO₂, H₂O, N₂ and N₂O. However, from 350 °C, we have measured a small production of CO at a level about 100 ppm. During the first heating cycle, propene conversion gradually increases to reach 90% at 500 °C while N₂O yield passes through a maximum of 11% at 375 °C. The variation of N₂ yield with temperature is very different since this parameter starts to reach 15% at 382 °C and then, from 420 °C, significantly increases with temperature. During the plateau at 500 °C for 5 h, the N₂ yield drastically increases to reach values higher than 80%. During the cooling down, N₂ yield remains higher than 80% down to 370 °C and then drops to recover values similar to those observed during the heating. The propene conversion is maximum, i.e. 87%, down to 380 °C and then abruptly decreases to reach values lower than those

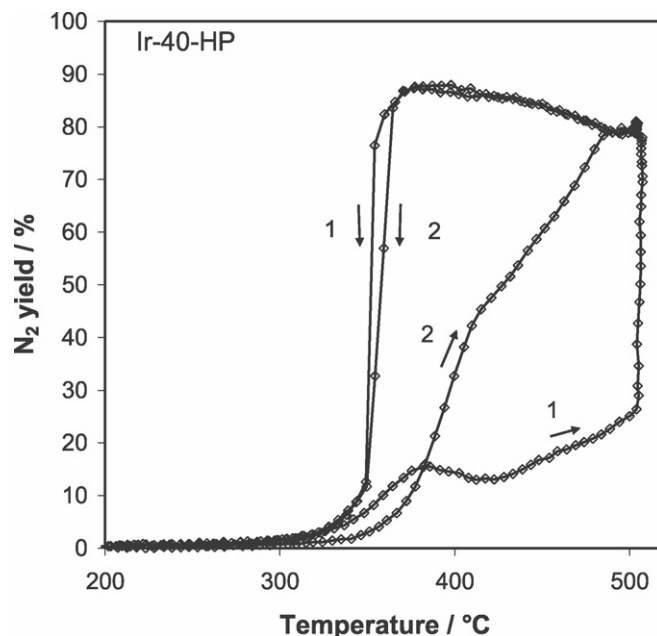


Fig. 2. N₂ yield variation vs. temperature on Ir-40-HP during two successive heating cycles. Feed composition: C₃H₆/NO/O₂: 2000 ppm/2000 ppm/1%.

recorded during the first heating cycle. For instance, at 350 °C, the propene conversion was 34% during the heating and only 18% during the cooling down. During the cooling step, the maximum of N₂O yield shifted to lower temperatures, from 375 to 350 °C but remained constant at 11%. These experiments clearly show that, during the on-stream treatment at 500 °C, the catalytic activity of Ir-40-HP for the reduction of NO by propene into nitrogen drastically increases. With the same sample, a second heating cycle was performed. Fig. 2 compares the N₂ yield variation versus temperature during these two successive heating cycles. One can observe significant difference between the two heating ramps whereas catalytic activities recorded during the two cooling down steps are fairly similar. During the second heating ramp, N₂ production starts at higher temperature and becomes much more important from 380 °C. The temperature corresponding to propene half conversion (T₅₀) increases from 363 to 382 °C. One can suggest that the treatment at 500 °C under RM leads to a sintering of the Ir particles. The same trend was observed for the N₂O production since its maximum was reached at 395 °C instead of 375 °C. Except for N₂O production, the catalytic activity during the temperature increase is significantly lower than during the decrease. One can suggest that the treatment on stream at 500 °C is necessary to activate the catalyst. A similar activation on-stream at 500 °C was observed for all samples whatever their microstructure. For instance, Fig. 3 represents the catalytic activity of Ir-90-LP during temperature cycle. The morphology of this electrochemical catalyst is different to that of Ir-40-HP since it exhibits a higher thickness and a lower porosity. The N₂ yield on Ir-90-LP was also significantly promoted after the on-stream treatment at 500 °C. Let us note that, contrary to Ir-40-HP, the N₂O yield and the C₃H₆ conversion were not affected. These observations exclude a relationship between the hysteresis loop recorded for N₂ yield

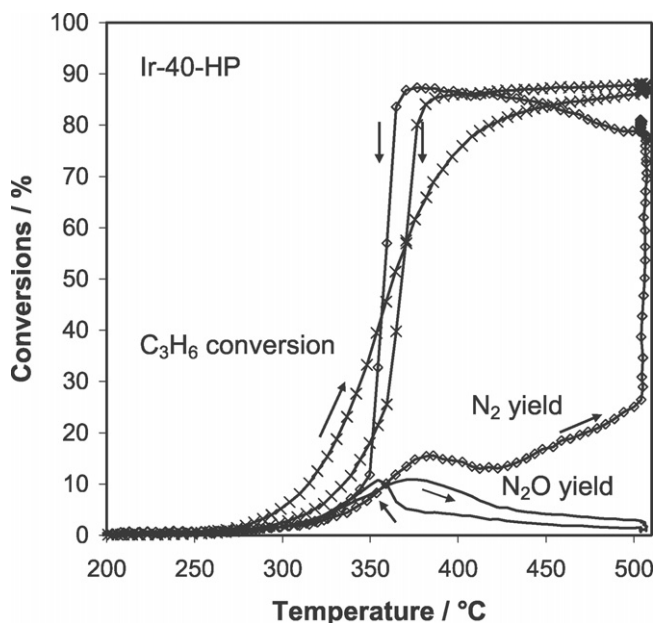


Fig. 1. C₃H₆ conversion, N₂ and N₂O yields on Ir-40-HP vs. temperature. Feed composition: C₃H₆/NO/O₂: 2000 ppm/2000 ppm/1%.

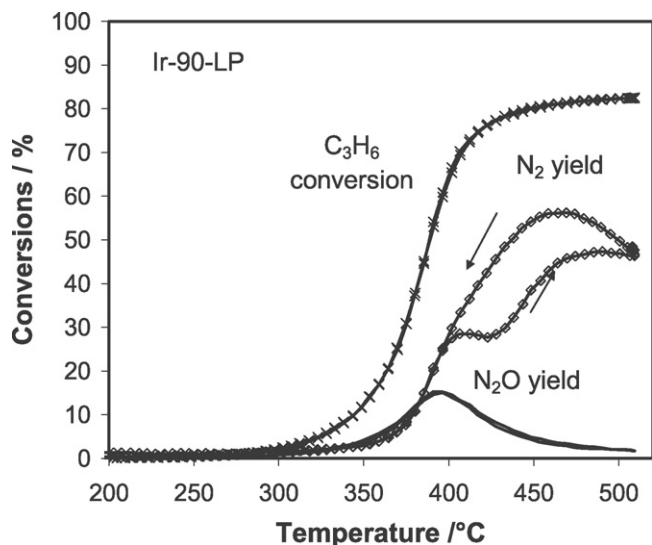


Fig. 3. C_3H_6 conversion, N_2 and N_2O yields on Ir-90-LP vs. temperature. Feed composition: $C_3H_6/NO/O_2$: 2000 ppm/2000 ppm/1%.

during the temperature cycles and a thermal effect due to the strong exothermicity of the propene combustion. X-ray diffraction measurements have been performed for all samples before and after the activation procedure at 500 °C under RM. For instance, Fig. 4 presents XRD spectra of Ir-150-HP recorded before and after the activation procedure at 500 °C. XRD spectrum of fresh samples contains three broad peaks attributed to three crystallographic faces of Ir^0 and fine peaks which correspond to YSZ. After the activation procedure, we clearly observed the apparition of a new peak at 28.45° corresponding to IrO_2 . Furthermore, the three peaks attributed to Ir^0 are much thinner, then demonstrating that there was a sintering of Ir particles sizes during the activation procedure. The Ir particle size was estimated with the Scherrer formula

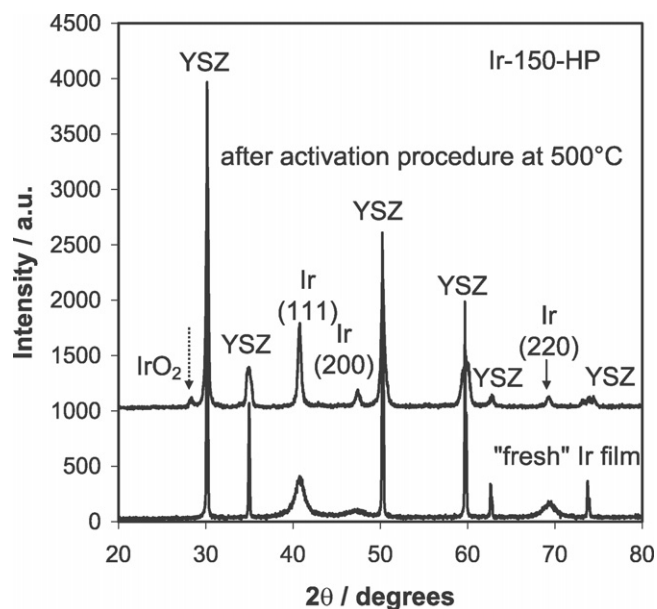


Fig. 4. XRD diagrams of Ir-150-HP recorded before and after the activation procedure at 500 °C.

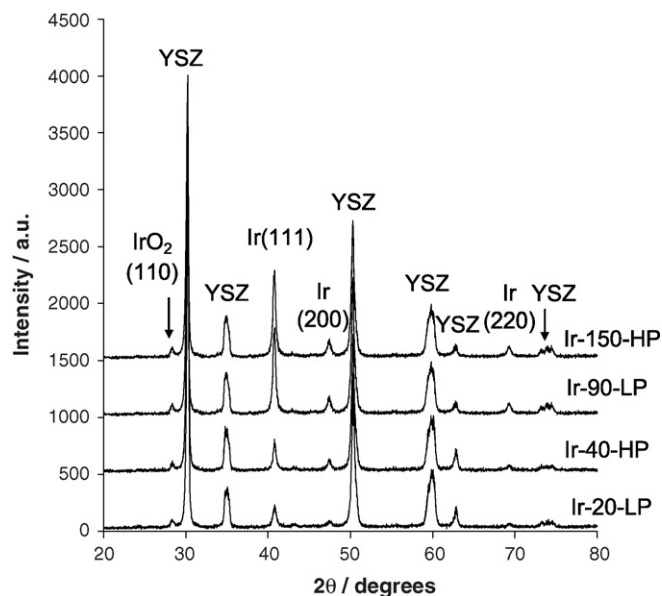


Fig. 5. XRD spectra of all samples (Ir-150-HP, Ir-90-LP, Ir-40-HP and Ir-20-LP) after on-stream treatment at 500 °C.

from the $Ir(1\ 1\ 1)$ peak at 40.78° which is the most intensive one. XRD spectra of all samples recorded after the on-stream treatment at 500 °C are exposed on Fig. 5. The Ir particle size increases from about 10 nm to 30 nm after the on-stream treatment. Table 1 gives values of Ir particle size after the activation procedure; the higher the thickness, the larger the particles of Ir. Let us also mention that the intensity of the $Ir(1\ 1\ 1)$ peak at 40.78° increases with the thickness of the film. Fig. 6 shows SEM picture of Ir-40-HP after the activation procedure. This picture confirms the porosity of this film which is composed of small Ir particles with a diameter lower than 50 nm. Sample Ir-40-HP was investigated by XPS prior to and after on-stream treatment at 500 °C. Corresponding wide-range spectra are shown in Fig. 7(a) and (b), respectively. Narrow-range spectra of Ir 4f 5/2, 7/2 peaks were also recorded with a better resolution (not shown here). The XPS spectrum of fresh Ir-40-HP sample exhibits characteristic peak of iridium (Ir 4s, Ir 4p, Ir 4d 3/2, 5/2 and Ir 4f 5/2, 7/2), oxygen (O1s and also Auger peak OKLL) and carbon. Initial carbon contamination is detected but the level remains very low, indicating a good initial

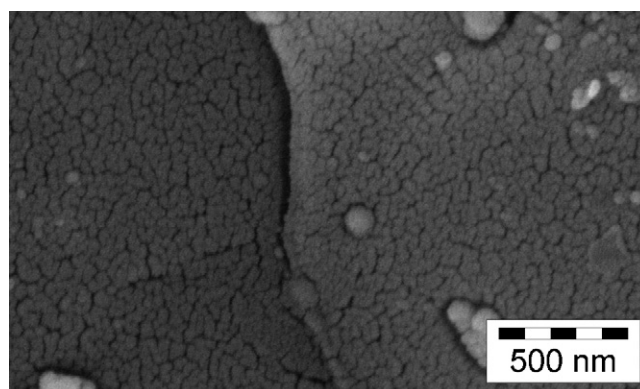


Fig. 6. SEM picture of Ir-40-HP after the activation procedure.

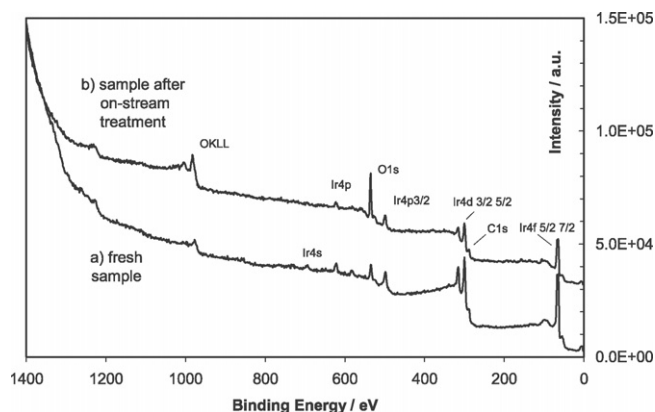


Fig. 7. XPS wide scan spectra of catalyst 40-HP prior to (a) and after (b) on-stream treatment at 500 °C.

cleanliness of the coating. Narrow range Ir 4f 5/2, 7/2 spectrum indicates that iridium is mainly present as metallic Ir⁰ (4f 5/2 peak at 64.0 eV BE and $\text{os} = 2.8$ eV). The spectrum recorded after the on-stream treatment at 500 °C is slightly different, as shown on Fig. 7(b). The O1s/Ir 4p 3/2 intensity ratio is increased by a factor of about three, Ir 4s peak is no longer detected and OKLL peak is also clearly enhanced. Narrow range Ir 4f 5/2, 7/2 spectrum now exhibits some features characteristics of Ir⁴⁺ (4f 5/2 peak at 65.0 eV BE) but metallic iridium is still the prevailing species. This observation confirms the formation of IrO₂ at the surface of the electrochemical catalyst after the activation procedure. Nevertheless, this oxide layer is very thin and can be estimated close to 2 nm of a continuous layer. Furthermore, it is interesting to note that XPS spectrum did not reveal the presence of additional carbonaceous species on Ir coating surface after the on-stream treatment.

The open-circuit voltage, V_{WRO} , has been measured during the activation procedure at 500 °C for 5 h. The measured voltage, ΔV_{WRO} , represents the open-circuit potential difference between the catalyst potential and that of the gold reference, both exposed to RM, according to the following equation:

$$\Delta V_{\text{WCE,o}} = \frac{RT}{4F} \ln \left(\frac{a_{\text{o,Ir}}^2}{a_{\text{o,Au}}^2} \right) \quad (2)$$

with T , the temperature in K, $a_{\text{o,Ir}}$ and $a_{\text{o,Au}}$ the thermodynamic activity of oxygen on the catalyst and on gold reference electrode, respectively. The Au electrode may be considered as a pseudoreference (R) since its potential does not vary significantly with the composition of the gaseous mixture, as checked by blank experiments. We have shown in previous studies [30] that the in situ measurement of the potential can give a direct evidence of the catalytic activity. For instance, for NO oxidation, propene oxidation and selective catalytic reduction (SCR) of NO by propene on Pt film interfaced with YSZ, the potential measurement is a good indicator of the temperature corresponding to the beginning of the catalytic conversion. The variation of the Ir-40-HP open-circuit potential during the plateau at 500 °C under RM is given on Fig. 8. The potential slowly decreases from +193 mV versus Au to +143 mV versus

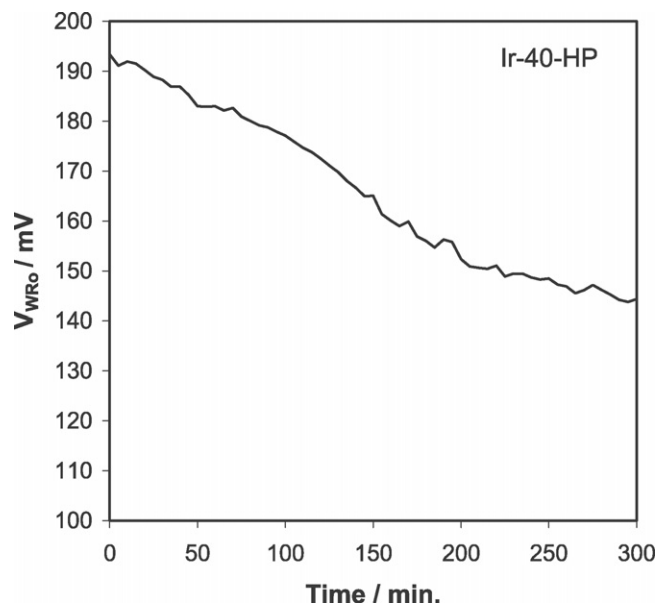


Fig. 8. Open-circuit voltage vs. time during the plateau at 500 °C for 5 h on stream. Sample: Ir-40-HP. Feed composition: C₃H₆/NO/O₂: 2000 ppm/2000 ppm/1%.

Au. The same trend was observed for all the samples. The decrease of $\Delta V_{\text{WCE,o}}$ corresponds to a decrease of the oxygen thermodynamic activity on Ir and then, most probably, of the oxygen coverage on Ir. Moreover, the value of the open-circuit voltage at the beginning of the activation procedure is positive (Table 1), suggesting that the oxygen coverage is high.

3.2. Catalytic activity measurements at open-circuit voltage

Catalytic activity of all samples was compared after the on-stream treatment at 500 °C during the temperature decrease. It was found that the production of NO₂ was extremely low under our operating conditions. N₂ and N₂O yields as well as C₃H₆ conversion variations versus temperature are plotted on Fig. 9a–c, respectively. The feed composition was near to the stoichiometry, i.e. containing 1% of O₂. Catalytic activity strongly depends on the microstructure, i.e. thickness and porosity, of the electrochemical catalyst. This suggests that the NO reduction by propene on Ir is structure sensitive, in good agreement with the study of Wögerbauer et al. [14]. The most efficient catalyst for the reduction of NO into harmless N₂ is Ir-40-HP. This electrochemical catalyst exhibits high N₂ yields, up to 80%, over a wide temperature window, between 330 and 500 °C. The production of N₂O is low with a maximum conversion of only 8.9% at 349 °C, leading to a very high N₂ selectivity, larger than 90%. As expected, the propene conversion variation versus temperature follows that of N₂ yield. Similar results were reported by Wögerbauer et al. [11] on unsupported Ir black by using high partial pressure of propene as a reducing agent. These observations demonstrate that the main reaction is the NO reduction by propene into N₂. From these results, one can suggest that the most suitable Ir thickness is around 40 nm and that the most active film is the

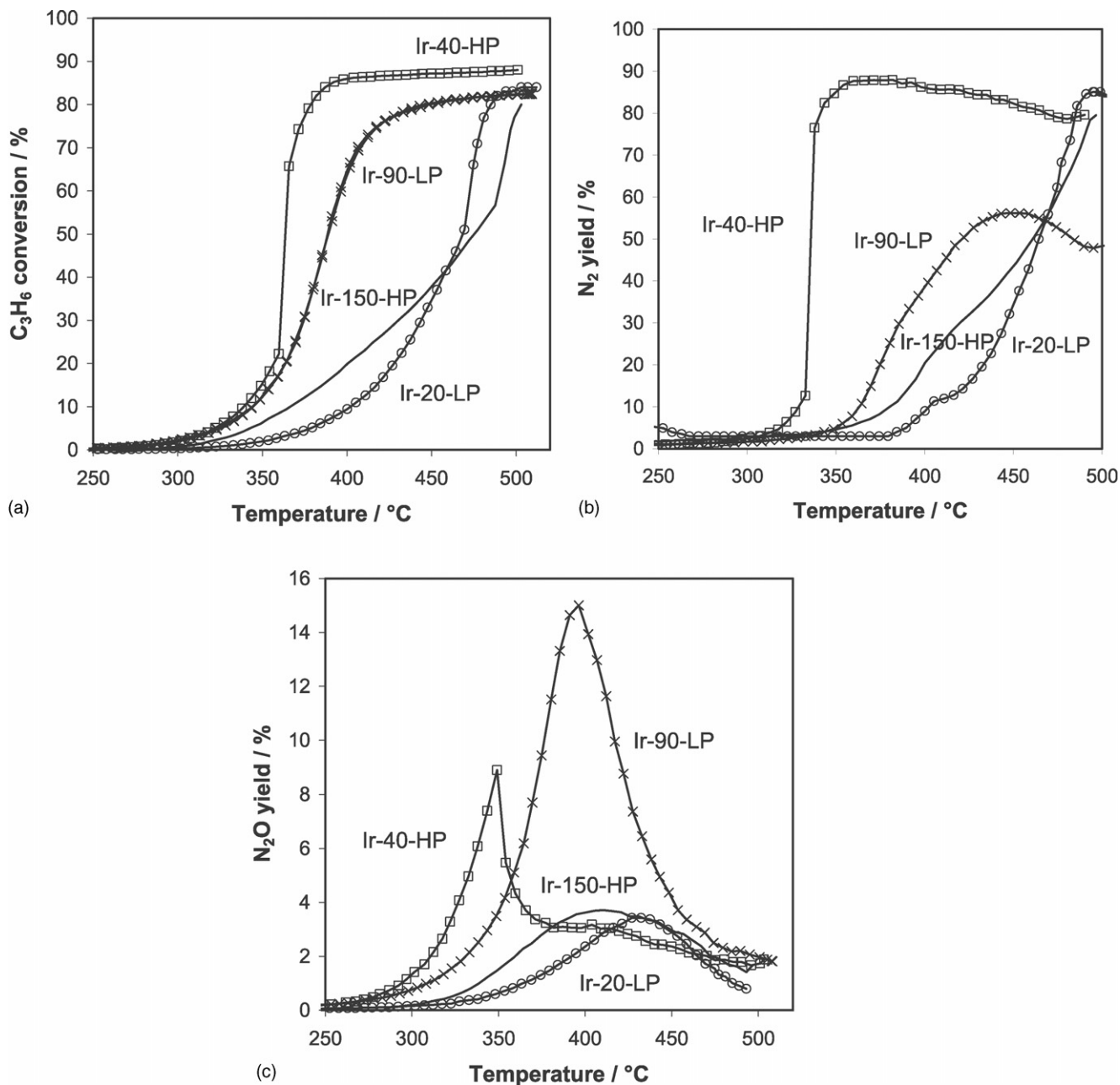


Fig. 9. (a) Propene conversion vs. temperature for catalysts Ir-150-HP, Ir-90-LP, Ir-40-HP and Ir-20-LP. Feed composition— $C_3H_6/NO/O_2$: 2000 ppm/2000 ppm/1%. (b) N_2 yield vs. temperature for catalysts Ir-150-HP, Ir-90-LP, Ir-40-HP and Ir-20-LP. Feed composition— $C_3H_6/NO/O_2$: 2000 ppm/2000 ppm/1%. (c) N_2O yield vs. temperature for catalysts Ir-150-HP, Ir-90-LP, Ir-40-HP and Ir-20-LP. Feed composition— $C_3H_6/NO/O_2$: 2000 ppm/2000 ppm/1%.

more porous one (Table 1). Ir-20-LP and Ir-150-HP present important N_2 yields and C_3H_6 conversions only for temperatures higher than 400 °C. The electrochemical catalyst Ir-90-LP is the only one which does not reach high N_2 yield values at 500 °C. From these results, one can suggest that dense and thick films are more difficult to activate during the on-stream treatment at 500 °C.

Catalytic activity of Ir-40-HP was also carried out under lean-burn conditions with a feed composition containing 5% of O_2 . Before increasing the oxygen content, the sample was previously treated at 500 °C under the stoichiometric reactive mixture for 5 h. The partial pressure of oxygen was increased

from 1% to 5% at 400 °C. We observed a drop of the N_2 yield from 92% to 7.2%. At the same time, propene conversion decreases from 87% to 52%. The prevailing reaction becomes propene combustion. By increasing the temperature from 400 to 500 °C, the NO conversion enhances to reach significant values at 500 °C (Fig. 10). At this former temperature, the NO conversion is 55%. Furthermore, the N_2O yield is extremely low since N_2 selectivity is higher than 97%. The electrochemical catalyst Ir-40-HP exhibits stable and high NO conversion at 500 °C for a period of 60 h. Let us note that we observed the production of a low amount of CO, about 150 ppm, over the whole duration of the catalytic test at 500 °C.

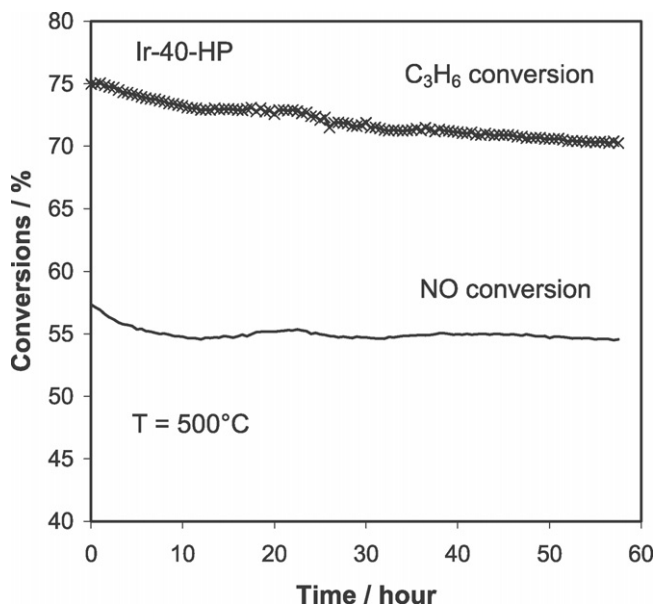


Fig. 10. Long-term stability of NO and C_3H_6 conversions at 500 °C on Ir-40-HP. Feed composition— $C_3H_6/NO/O_2$: 2000 ppm/2000 ppm/5%.

3.3. Catalytic activity measurements under closed-circuit

All Ir/YSZ electrochemical catalysts were pretreated at 500 °C for 5 h on stream and then cooled down. The effects of the polarisation on the catalytic activity were investigated at 400 °C during the second temperature increase. Both positive and negative overpotentials of ± 1 V were applied between the Ir film and the gold counter-electrode. Fig. 11a and b shows the effect of the overpotential on the catalytic activity of Ir-40-HP, the most effective electrochemical catalyst, which was exposed to the stoichiometric reactive mixture. Positive polarisation generates a strong enhancement of N_2 yield and propene conversion. By applying +1 V, N_2 yield drastically increases

from 38% to 64% while propene conversion rises from 47% to 60%. The N_2O yield is almost unchanged by decreasing from 7.2% to 6.8%. The catalytic activity remains very stable upon positive overpotential and very quickly recovers its initial value when the potential stops. The open-circuit voltage is the same before and after the positive polarisation, i.e. +58 mV. The faradaic efficiency (Λ) calculated from the change of oxygen consumption rate was found to be 382. This indicates that the observed increase of the catalytic rate is 382 times higher than that predicted by the Faraday law which gives the O^{2-} diffusion rate from the electrolyte onto the catalyst. The application of a negative overpotential of -1 V has a significant inhibiting effect on the catalytic activity. We observed a drop of N_2 and N_2O yields as well as the propene conversion. As soon as the negative overpotential is applied, catalytic activity drastically decreases. However, after about 30 min of polarisation, the activity slowly and gradually increases. For instance, propene conversion very rapidly drops from 48% to 28% after 30 min of polarisation and then reaches 33% after 150 min. The Λ value, calculated from the value of oxygen conversion at the end of the negative polarisation was found to be 570. When the negative polarisation stops, we observed a strong activation of the catalytic activity which achieves levels similar to those observed upon positive polarisation. One can suggest that the negative polarisation induces a modification of the physicochemical properties of the electrochemical catalyst. However, this former is reversible since N_2 yield and C_3H_6 conversion gradually decrease as well as N_2O yield slowly increases to reach their initial values. At the end of the negative polarisation, the open-circuit voltage is +8 mV. This value gradually increases with time to reach +58 mV, its initial level, after more than 5 h.

Similar effects of the polarisation on the catalytic activity were observed with all the samples. These results demonstrate that NO reduction into N_2 by propene can be electrochemically

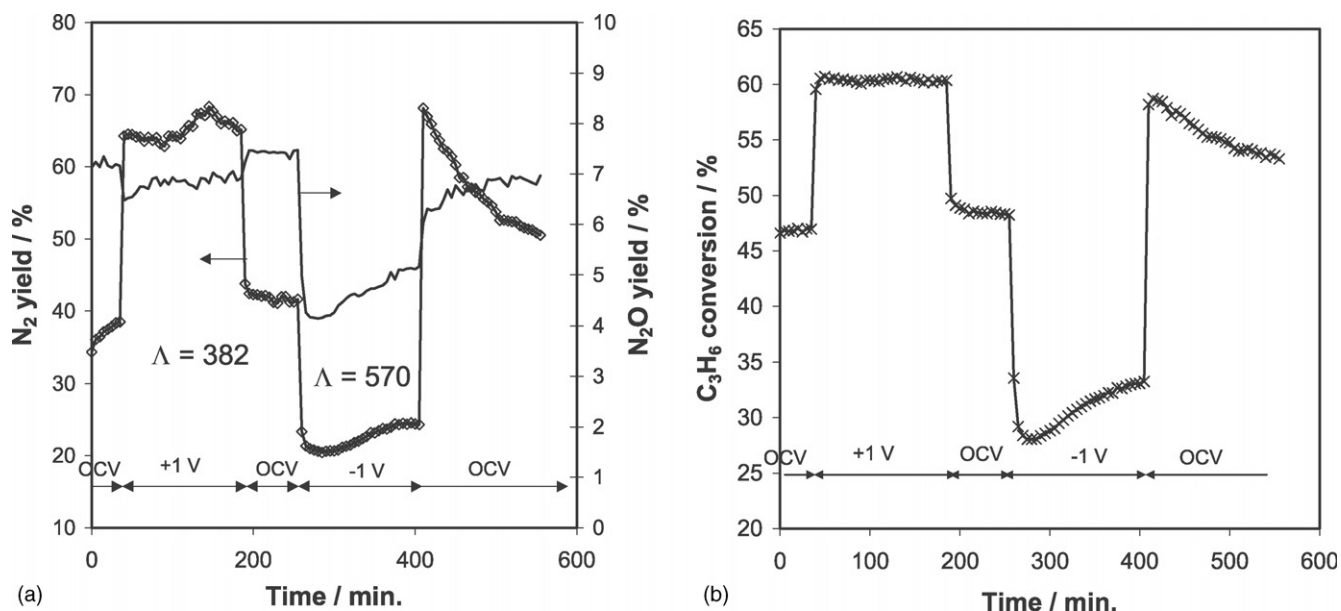


Fig. 11. (a) Effect of the overpotential on N_2 and N_2O yields for Ir-40-HP catalyst. Feed composition— $C_3H_6/NO/O_2$: 2000 ppm/2000 ppm/1%. $T = 400$ °C. (b) Effect of the overpotential on propene conversion for Ir-40-HP catalyst. Feed composition— $C_3H_6/NO/O_2$: 2000 ppm/2000 ppm/1%. $T = 400$ °C.

Table 2

Open-circuit voltage and faradaic efficiency values recorded at 400 °C upon ± 1 V with corresponding currents at the Ir/YSZ interface

Samples	V_{WRO} (mV) vs. Au	i (μ A) (+1 V)	Λ (+1 V)	i (μ A) (-1 V)	Λ (-1 V)
Ir-20-LP	+68	+180	14	-388	3
Ir-40-HP	+58	+172	382	-197	570
Ir-90-LP	+103	+33	54	-117	77
Ir-150-HP	+99	+269	26	-210	32

promoted on Ir/YSZ electrochemical catalysts. This promotion exhibits an electrophobic NEMCA effect, the reaction rate increasing much more than predictable from the Faraday law when a positive polarisation is applied. Table 2 summarises faradaic efficiency values recorded at 400 °C upon ± 1 V with corresponding currents at the Ir/YSZ interface. Under similar operating conditions [23], Pt/YSZ electrochemical catalysts exhibited opposite NEMCA behaviours, i.e. electrophilic ones, since NO reduction by propene is electropromoted by applying a negative overpotential. The microstructure of the Ir/YSZ electrochemical catalyst has a strong effect on the value of the faradaic efficiency. The most suitable microstructure for the electrochemical promotion seems to be that of Ir-40-HP which is porous and thin (about 40 nm). Furthermore, currents induced by the polarisation of the thick and dense sample (Ir-90-LP) are lower than those recorded for porous or thin films.

Fig. 12 presents the effect of a positive current on the catalytic activity of Ir-40-HP under lean-burn conditions at 400 °C. The open-circuit voltage was +110 mV instead of +58 mV under stoichiometric conditions. We also observed an electrophobic NEMCA effect with a faradaic efficiency of 166. Catalytic activity abruptly increases when a positive current of -100μ A is applied, reaches a steady state and instantaneously recovers its initial value when the polarisation stops. This result demonstrates

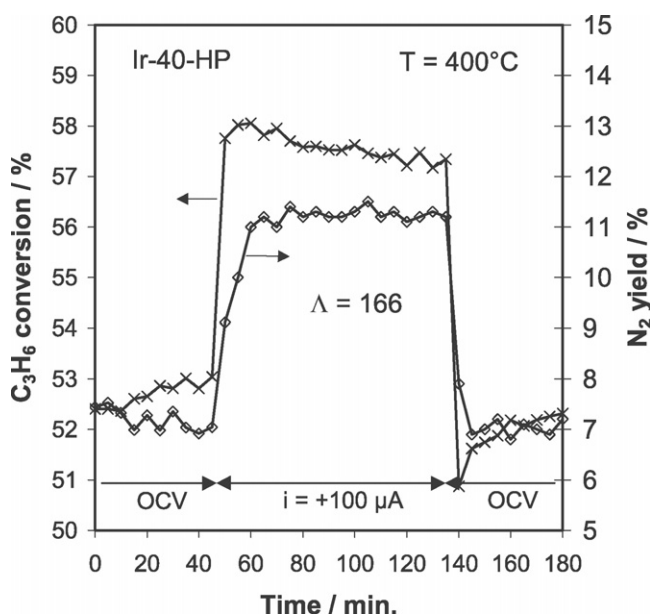


Fig. 12. Effect of a positive current on propene conversion and N_2 yield for catalyst Ir-40-HP under lean-burn conditions at 400 °C. Feed composition— $C_3H_6/NO/O_2$: 2000 ppm/2000 ppm/5%.

that NO reduction by C_3H_6 into N_2 on Ir/YSZ electrochemical catalysts can be electropromoted even under lean-burn conditions. This promotion effect was not evidenced by using a Pt/YSZ electrochemical catalyst. Nevertheless, the enhancement of propene conversion and N_2 yield is less pronounced than under stoichiometric conditions. We did not observe any modification of the N_2O yield with the polarisation. As expected, a negative polarisation also generates a decrease of the catalytic activity. The effect of the film microstructure on their ability to be electropromoted seems to be more pronounced than under stoichiometric conditions. For instance, with Ir-150-HP, a positive overpotential of +1 V promotes the propene conversion from 29% to 40.5% whereas the N_2 yield is almost unchanged. With this kind of microstructure, propene combustion is much more electropromoted than NO reduction by propene.

From these results, one can conclude that the promotion efficiency is structure sensitive. The most suitable microstructure of the catalytic film seems to be a high porosity associated with a low thickness.

4. Discussion

This study has shown that Ir/YSZ electrochemical catalysts can reach high catalytic activity for the SCR of NO by propene in the presence of oxygen. Under stoichiometric conditions, porous and thin (about 40 nm) Ir film achieves N_2 yield higher than 80% between 350 and 500 °C. Under lean-burn conditions, the same sample presents high and durable NO conversion at 500 °C. Ir thin films are very selective and mainly produce harmless N_2 . The production of NO_2 was found to be extremely low and the N_2O yield never exceeds 15%. Furthermore, the Ir loading used for catalytic activity measurements was extremely low, i.e. about 0.16 mg for the most efficient Ir film. Studies on supported Ir catalysts commonly used more than 1 mg of Ir [9,10,14]. This confirms that magnetron sputtering is a suitable technique for synthesis of effective thin catalytic films. Furthermore, this process generates reproducible coatings with a controlled microstructure according to the operating conditions selected during the sputtering.

The effect of the Ir films microstructure on their catalytic activity was investigated for the SCR of NO by propene. Experiments have clearly demonstrated that this former reaction is structure sensitive on Ir films. By using Ir black and Ir-H-ZSM5 catalysts, Wögerbauer et al. [14] have shown that NO reduction was strongly influenced by Ir crystallite size. Furthermore, according to recent studies [8–10] on nanodispersed Ir catalysts, we found that iridium films require special pretreatment conditions to develop their catalytic efficiency. The production of N_2 on Ir/YSZ electrochemical catalysts drastically improved during an on-stream treatment at 500 °C for 5 h. During this activation procedure, Ir particles size increases as checked by XRD measurements. Large Ir particles, of the order of 25 nm, seem to be the most effective for the NO reduction by propene. From Wögerbauer et al. [14], with increasing crystallite size, the number of sites effective for NO adsorption significantly increases leading to a drop of oxygen coverage. The variation of the open-circuit voltage during the

on-stream treatment at 500 °C confirms this assumption. Indeed, we observed a decrease of the potential which corresponds to a decrease of the oxygen thermodynamic activity on Ir. The enhancement of the N₂ yield also seems to be associated to the establishment of an optimal Ir⁰/IrO₂ ratio. Both XRD and XPS measurements have identified the presence of IrO₂ on the Ir films after the on-stream treatment, in good agreement with studies of Wögerbauer et al. [14]. This result, as well as the positive values of the open-circuit voltage, suggests that oxygen is predominantly adsorbed on Ir in competition with propene and nitric oxide, in our operating conditions. Wögerbauer et al. [14] have shown that the lower the IrO₂ amount, the higher the NO reduction activity. One can suggest that there is a direct link between the oxygen coverage and the amount of IrO₂. By considering that large Ir particles are less easily oxidized than smaller ones, the growing of Ir particles during the on-stream treatment could limit the IrO₂ formation and consequently could inhibit oxygen adsorption.

By using samples previously activated on-stream at 500 °C, the catalytic activity during the second temperature increase was found to be significantly lower than during the decrease. These experiments suggest that the treatment on stream at high temperatures is necessary to reach best catalytic performances. Furthermore, we have measured a small production of CO, about 100 ppm. Nawdali et al. [10] have found that the presence of CO is necessary to activate Ir/Al₂O₃ catalyst for the SCR. CO adsorption should favour the formation and the stabilization of the reduced or partially reduced active Ir sites possibly located onto IrO₂ particles.

Another important result of this study is that NO reduction by propene into N₂ can be electrochemically promoted on Ir/YSZ electrochemical catalysts. This promotion exhibits an electrophobic NEMCA effect, the reaction rate increasing when a positive polarisation is applied. On the opposite, the N₂ yield was found to drastically decrease upon negative polarisations. Effects of the polarisation followed similar trends whatever the microstructure of the Ir film and the partial pressure of oxygen. Therefore, Ir/YSZ electrochemical catalysts exhibit NEMCA behaviours opposite to those observed on Pt/YSZ under similar operating conditions [23]. Referring to assumptions on the origins of the NEMCA effect, the change in the electrode overpotential ΔV_{WR} results in a modification of the work function $e\Phi$ of the gas-exposed electrode surface of the porous catalyst film:

$$\Delta(e\Phi) = e\Delta V_{WR} \quad (3)$$

The theoretical validity of this equation has been discussed in the literature [31–36] and it seems restricted to the cases where outer potential ($\Delta\psi$) variations can be neglected. This implies the following conditions:

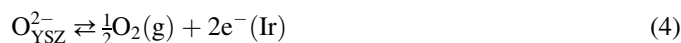
- application of moderate overpotentials;
- low lateral interactions between surface ions;
- fast surface diffusion of ionic species.

Variations of the catalyst work function (WF) modify the ability of catalyst electrons to participate into a chemical bond,

according to the nature of the adsorbate. When WF increases (decreases), energy required for extracting an electron increases (decreases) and, consequently, the chemical bond with an electron-donor adsorbate is strengthened (weakened) whereas that with an electron acceptor is weakened (strengthened). According to the classification of Vayenas [37], propene is considered as an electron donor whereas oxygen and nitric oxide as an electron acceptor. Applying positive (negative) overpotentials increase (decrease) WF and then Ir–C₃H₆ bond is strengthened (weakened) whereas both Ir–O and Ir–NO are weakened (strengthened). Therefore, by considering that oxygen is predominantly adsorbed on Ir surface, positive polarisation promotes the catalytic activity because it decreases the oxygen coverage. One can conclude that the effect of the positive polarisation is similar to that of the Ir particles growing observed during the on-stream treatment, i.e. decreasing the oxygen coverage in order to favour NO and C₃H₆ adsorption. As expected, negative overpotential strengthens the Ir–O bond and then leads to an increase of the oxygen coverage and to a concomitant significant deterioration of the catalytic activity. However, when the negative polarisation stops, we observed a strong activation of the catalytic activity which achieves levels similar to those observed upon positive polarisation and then gradually decreases to its initial value at OCV. One can suggest that a cathodic polarisation can gradually reduce a part of IrO₂. Therefore, when the inhibiting effect of the negative polarisation stops, the amount of IrO₂ and most probably of the oxygen coverage were lower, leading to high catalytic activity. The low value of the open-circuit voltage, i.e. +8 mV instead of +58 mV before the polarisation, confirms this assumption. Thus, the same promoting effect as observed upon positive polarisations was observed. Finally, Ir⁰ is gradually oxidized under the reactive mixture to reach the same Ir⁰/IrO₂ ratio as before the polarisation. Then, OCV and the catalytic activity recover their initial values.

In previous studies [23,25], we have shown that, under similar operating conditions, propene is strongly adsorbed on Pt films. Contrary to Ir, oxygen coverage is low on Pt films under NO/C₃H₆/O₂ reactive mixture. This explains the opposite NEMCA behaviours observed between Ir and Pt for the NO reduction by propene in the presence of oxygen.

The electropromotion efficiency was found to be structure sensitive. Experiments have shown that the most suitable microstructure of Ir/YSZ electrochemical catalysts was a high porosity and a very low thickness in the range of 20–40 nm. One can suggest that a low thickness decreases the diffusion length of ions coming from the electrolyte. A high porosity of the film leads to extend the triple-phase boundaries between the solid electrolyte, the catalyst and the gas phase. This could improve the rate of the electrode reaction (4) and then the promotion efficiency:



Current values recorded during positive polarisations of +1 V, which are directly linked to the kinetic of the electrochemical reaction (4), confirm this assumption since lower currents were achieved for dense and thick films.

5. Conclusions

Ir/YSZ electrochemical catalysts can reach a high catalytic activity for the SCR of NO by propene in the presence of oxygen. These results confirm that magnetron sputtering is a suitable technique for synthesis of effective thin catalytic films. Iridium films require on-stream treatment at 500 °C in order to develop their catalytic efficiency by increasing Ir particles size and establishing an ideal Ir⁰/IrO₂ ratio. Experiments seem to indicate that the NO reduction by C₃H₆ could be structure sensitive. The most suitable Ir film contains large Ir particles, of the order of 20 nm, and presents a high porosity and very low thickness (20–40 nm). Catalytic activity of Ir films can be electrochemically promoted. This promotion exhibits an electrophobic NEMCA effect, the reaction rate increasing when a positive polarisation is applied. The promotion efficiency was also found to be structure sensitive.

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