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Electrochemical promotion of Rh catalyst in gas-phase reduction of NO by propylene

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Abstract

The concept of non-faradaic electrochemical modification of catalytic activity (NEMCA) has been applied for the *in situ* control of catalytic activity of a rhodium film deposited on YSZ (yttria stabilized zirconia) solid electrolyte towards reduction of 1000 ppm NO by 1000 ppm C_3H_6 in presence of excess (5000 ppm) O_2 at 300 °C. A temporary heating at this feed composition results in a long-lasting deactivation of the catalyst under open circuit conditions due to partial oxidation of the rhodium surface. Positive current application (5 μA) over both the active and the deactivated catalysts gives rise to an enhancement of N_2 and CO_2 production, the latter exceeding several hundred times the faradaic rate. While active rhodium exhibits a reversible behaviour, electrochemical promotion on the deactivated catalyst is composed of a reversible and an irreversible part. The reversible promotion results from the steady-state accumulation of current-generated active species at the gas exposed catalyst surface whereas the irreversible effect is due to the progressive reduction of the catalyst resulting in an increased recovery rate of lost catalytic activity. The results are encouraging with respect to application of rhodium for the catalytic removal of NO from auto-exhaust gases under lean-burn conditions.

1. Introduction

The reduction of NO, CO and hydrocarbon (CH) pollutants, emitted from vehicles, has become one of the greatest challenges in environmental protection. For this reason, the subject is being intensely studied by numerous groups from academic as well as industrial research laboratories [1, 2]. The objective is to transform, under excess oxygen conditions, the oxidizing pollutant (NO) and the two reducing pollutants (CO and CH) into harmless products such as N_2, CO_2 and H_2O. One meets two main problems with this respect: (i) the reduction of NO with CO or CH is not selective because, in addition to N_2, the byproduct N_2O is also generated; (ii) the excess of O_2 which is always present in the exhaust gases can prevent the reduction of NO by consuming the reducing partners (CO and CH) via direct oxidation.

There have been many reports and suggestions for the active catalysts to resolve this problem. In practice, for the last two decades the so-called three-way catalytic converters (TWC) have been used as auto-exhaust catalyst [3]. The name reflects the simultaneous catalytic treatment of the three pollutants, NO, CO and CH. Three-way catalysis is possible provided the fuel/air ratio, termed λ, in the gas mixture is stoichiometric. Hence, a special sensor and electronic control system has been developed so as to guarantee the desired gas composition. Indeed, the control system is more critical than the catalyst itself, which contains Rh and Pt key constituents [4].

The catalytic activity of metal [5, 6] and oxide [7, 8] catalysts deposited on solid electrolytes can be altered by applying potential or current to the catalyst. This phenomenon has been reported in the literature as non-faradaic electrochemical modification of catalytic activity (NEMCA) [9] or electrochemical promotion (EP) [10]. It has also been shown that the catalytic activity of catalyst films on YSZ solid electrolyte for the gas phase combustion of ethylene can be increased by electrochemical pretreatment [11].

In the present paper the electrochemical promotion of a YSZ supported rhodium catalyst is studied for the catalytic reduction of NO by propylene (C_3H_6, a model CH) in presence of oxygen. The aim of this work is to study the possibility of *in situ* modification of the catalytic activity by current application for auto-exhaust catalysts. Measurements were carried out at relatively low temperature (300 °C) providing moderate conversions and selectivity but allowing the study of the deactivation and the electrochemically assisted recovery of lost catalytic activity.

2. Experimental details

The electrochemical cell was constituted as follows (Figure 1(a)). A rhodium film was deposited on the internal surface of a cylindrical YSZ (ZrO_2 stabilized with 6% mol Y_2O_3) solid electrolyte monolith ring (Maret SA, 20 mm OD, 17 mm ID and 10 mm height) by sputter deposition technique. Rhodium sputtering was performed in Ar atmosphere (20 Pa) with a discharge of 700 V at room temperature for 4 h. A gold film electrode was then deposited on the outside jacket of the ring by thermal decomposition of a gold paste (Gwent Electronic Materials Ltd, C70219R4). The electrochemical cell was put in a plug flow reactor, both electrodes being exposed to the reacting gas mixture (Figure 1(b)).

Reactants were Carbagas certified standards of 1% C_3H_6/He, 1% NO/He and 20% O_2/He; the balance was pure He of 99.996%. Reactants and products were continuously monitored by using online infrared (NDIR) analysers (Siemens: Ultramat 5E-2R for C_3H_6 and CO_2; Ultramat 6 for NO and N_2O). Analysis of O_2 and N_2 was made by using an offline gas chromatograph (Shimadzu GC-8A, detector TCD, column Alltech S5 CTR packed with Chromosorb 107/molecular sieve 5A). The composition of the gas mixture in the feed was C_3H_6:NO:O_2/ 0.1:0.1:0.5 kPa. The gas flows were controlled by mass flow controllers (Bronkhorst, F-201C and E-5514-FA), the total flow rate was 200 ml min^{-1} in ambient conditions. The total pressure in the reactor was atmospheric. The reaction temperature, maintained in the range between 300 and 400 °C with a precision of ± 1 °C, was measured with a K-type (Ni/Cr–Ni/Al) thermocouple.

Electrochemical polarization was made in galvanostatic mode. A galvanostat–potentiostat (EG&G PAR model 362) was used to apply constant currents between the catalyst as anode and the gold counter-electrode as cathode, see Figure 1(a). The applied anodic current was low (5 μA) in order to induce small variations around the open circuit behavior. Under the used experimental conditions, this current corresponds to an electrochemical (faradaic) production of 0.06 ppm CO_2.

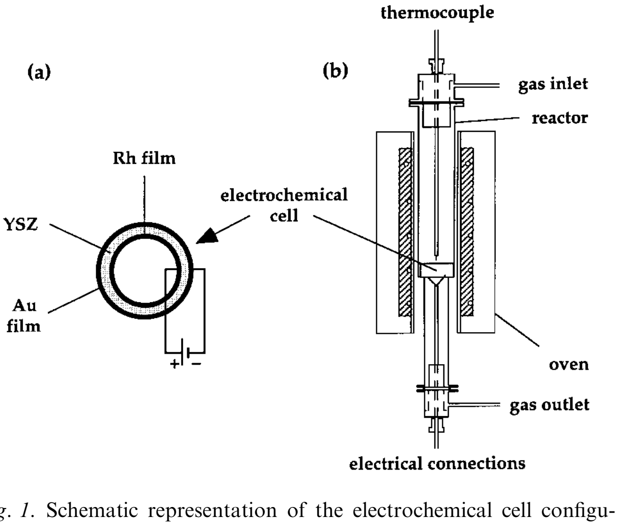

Fig. 1. Schematic representation of the electrochemical cell configuration (a) and of the plug flow reactor (b).

The following transients are given: the cell potential between working and counter electrode, V_{WC}/V, and the concentration of two main reaction products, P_{N_2}/ppm and P_{CO_2}/ppm. The transients of V_{WC} and P_{CO_2} are online monitored signals, whereas that of P_{N_2} is calculated from the online signals of P_{NO} and P_{N_2O} by excluding other nitrous products than N_2 and N_2O. This was confirmed by offline gas chromatographic measurements of N_2.

Measurements of catalytic activity were made over both the deactivated and the active rhodium catalysts. For the deactivation of the catalyst, the following procedure was used: under continuous feed with the reacting gas mixture, the reactor was heated to 400 °C for 1 h then cooled down to the temperature of the experiments (300 °C). The procedure of reactivation was as follows: the catalyst was polarized by an anodic current of 5 μA at 300 °C under continuous feed with the reacting gas mixture until the stabilization of the catalytic performance. Under these experimental conditions the activation procedure lasted several tens of hours when starting at the deactivated state. After current interruption, the catalytic activity rapidly stabilized at a somewhat lower level. The resulting high activity is well reproducible and it does not exhibit any significant decrease during use in open circuit conditions for days.

3. Results and discussion

The catalytic performance of the YSZ supported rhodium catalyst in the reduction of NO with C_3H_6 in presence of oxygen was investigated at 300 °C, both in open circuit and in electrochemically promoted conditions. In this system several electrochemical and catalytic reactions may take place.

(a) Possible anodic reactions at the tertiary phase boundary (TPB) of the catalyst:

$$O^{2-} \rightarrow \tfrac{1}{2}O_2 + 2\,e^- \tag{1}$$

$$C_3H_6 + 9\,O^{2-} \rightarrow 3\,CO_2 + 3\,H_2O + 18\,e^- \tag{2}$$

$$2\,Rh + 3\,O^{2-} \rightarrow Rh_2O_3 + 6\,e^- \tag{3}$$

$$Rh + 2\,O^{2-} \rightarrow RhO_2 + 4\,e^- \tag{4}$$

(b) Possible catalytic reactions at the gas exposed surface of the rhodium catalyst:

$$C_3H_6 + 9\,NO \rightarrow 3\,CO_2 + \tfrac{9}{2}\,N_2 + 3\,H_2O \tag{5}$$

$$C_3H_6 + 18\,NO \rightarrow 3\,CO_2 + 9\,N_2O + 3\,H_2O \tag{6}$$

$$C_3H_6 + \tfrac{9}{2}O_2 \rightarrow 3\,CO_2 + 3\,H_2O \tag{7}$$

$$2\,Rh + \tfrac{3}{2}O_2 \rightleftharpoons Rh_2O_3 \tag{8}$$

$$Rh + O_2 \rightleftharpoons RhO_2 \tag{9}$$

The composition of the gas mixture (C_3H_6:NO:O_2/ 0.1:0.1:0.5 kPa) in the feed was slightly oxidizing with respect to the stoichiometric composition. It has been found that, under these conditions, a simple heating from 300 to 400 °C results in a drop of catalytic activity. Figure 2 shows the variation of V_{WC}, P_{N_2} and P_{CO_2} as a function of time during the deactivation procedure. Due to the large heat capacity of the oven, the temperature did not reach the set value before about 20 min. It is seen that the procedure results in an important loss of catalytic activity: the production of N_2 and CO_2 at 300 °C become 7 to 11 times lower. At this temperature and without the assistance of an electric current, no spontaneous reactivation of the catalyst occurs. In fact, in open circuit conditions, all signals remained unchanged for many hours.

Figure 3 shows typical galvanostatic transients on both deactivated (curves *d*) and active (curves *a*) catalysts. The polarization cycles were identical consisting of an anodic current application step (5 μA; 90 min) followed by a current interruption of 90 min. It is seen that anodic polarization considerably enhances the rates of N_2 and CO_2 production (Reactions 5–7) in all cases. The promotion achieved is highly nonfaradaic: the enhancement factors of CO_2 production, Λ_{CO_2},

$$\Lambda_{CO_2} = \Delta r_{CO_2} \times \left(\frac{zF}{i}\right) \tag{10}$$

defined as the ratio between the increase in CO_2 production rate, Δr_{CO_2} (mol s^{-1}), and the faradaic rate of electrochemical CO_2 production ($z = 6$, see Equation 2), are obtained in the range between 300 and 700. On the other hand, the nitrogen selectivity, S_{N_2}, defined as the fraction of the total NO consumption (via Reactions 5 and 6) converted to N_2 (via Equation 5), and calculated with production rates, r (mol s^{-1}), as

$$S_{N_2} = \frac{r_{N_2}}{r_{N_2} + r_{N_2O}} \tag{11}$$

is moderate: an average value of 0.50 ± 0.03% was obtained independently of the current application and also of the activation state of the catalyst.

Beside their actual level of catalytic performance, the deactivated and the active rhodium catalysts exhibit a different reversibility of the polarization cycles, as also seen in Figure 3. On the deactivated catalyst (curves *d*), the production rates are still increasing after 90 min of current application. After current interruption, the catalytic activity rapidly drops but remains at a significantly higher lever than before polarization. Two different effects of polarization on catalytic performance may be distinguished: a reversible electrochemical promotion, EP_r, and an irreversible effect persisting after current interruption, EP_i. The extent of the two effects are comparable. Over the active catalyst (curves *a* in Figure 3), no irreversible effect is observed, the system exhibits a perfectly reversible behaviour.

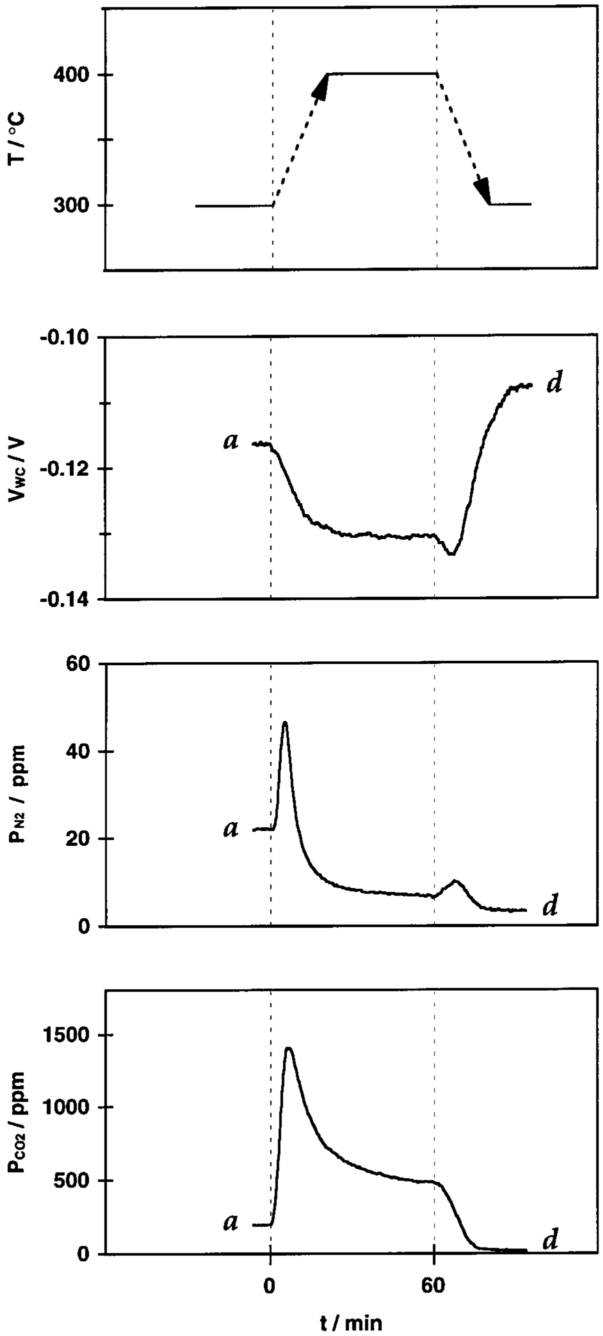

Fig. 2. Transients of temperature (*T*), cell potential (V_{WC}), N_2 production (P_{N_2}) and CO_2 production (P_{CO_2}) during deactivation of the Rh/YSZ film catalyst by heat treatment. *a*: active state, *d*: deactivated state. Feed composition: C_3H_6 (0.1 kPa):NO (0.1 kPa) : O_2 (0.5 kPa).

Over the deactivated rhodium catalyst, the effect of the time of polarization was also investigated. Three polarization cycles were performed by varying the time of current application (60, 90 and 120 min), each cycle being started over the deactivated catalyst of similar activity (produced P_{N_2} and P_{CO_2} were 3 ± 0.6 and 18 ± 3 ppm, respectively). The recorded galvanostatic transients are seen in Figure 4(a) and (b) where, instead of the absolute values, the enhancements of N_2 and CO_2 production have been plotted in order to make the

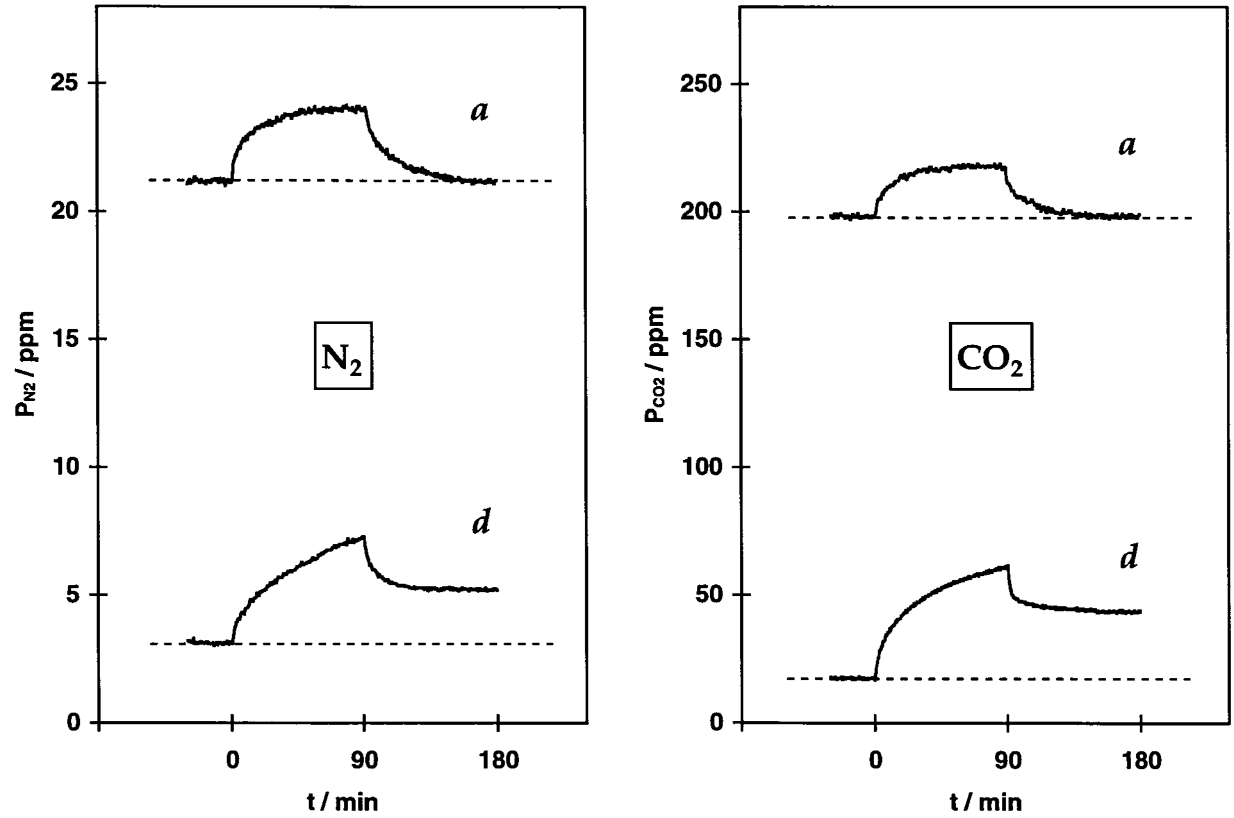

Fig. 3. Transients of N_2 and CO_2 production over the active (*a*) and the deactivated (*d*) Rh/YSZ film catalyst during a galvanostatic polarization cycle. Anodic current application (+5 μA) at t = 0 min; current interruption at t = 90 min. Feed composition: C_3H_6 (0.1 kPa):NO (0.1 kPa):O_2 (0.5 kPa); T = 300 °C.

comparison easier. It is seen that the irreversible effect of anodic polarization, EP_i, increases with increasing polarization time whereas the reversible effect of current application, EP_r, is independent of it; see also Table 1. One may conclude that reactivation at low temperature (300 °C) of a deactivated rhodium catalyst may be efficiently assisted by anodic polarization. Beside a temporary nonfaradaic promotion due to current application, a permanent reactivation of the catalyst occurs. The achieved recovery of catalytic activity is proportional to the time of polarization.

The observed deactivation of the catalyst might be explained either by poisoning, via chemisorption or physical deposition of reaction products, or by oxidation of the rhodium surface itself (Reactions 8 and 9). In practice, the above described deactivation/activation cycle may be repeated as many times as wished, resulting in a reproducible catalytic activity at the active state. On the one hand, this high reversibility and the observed long-term stability of the catalytic performance in both limiting states suggests that poisoning is not the principal cause of deactivation. On the other hand, it is known that the catalytic activity of rhodium strongly depends on the oxidation state of the active sites giving the best catalytic performance over the fully reduced metal [12]. In our experiments, the rhodium catalyst was probably never fully metallic due to its permanent contact with the oxidative gas mixture. The average surface oxidation state providing the highest activity at this feed composition at 300 °C was shortly called 'active' state. The N_2 and CO_2 production over the active rhodium catalyst were 21 ± 1 and 197 ± 5 ppm, respectively. These productions correspond to an NO conversion of 8.4% and to a C_3H_6 conversion of 6.6%. During the deactivation process, a progressive oxidation of the surface (Equations 8 and 9) takes place due the temperature rising up to 400 °C. Cooling down to 300 °C partly preserves this higher oxidation state because the kinetics of spontaneous surface reduction is considerably slown down. The rhodium surface obtained by the standard deactivation process and having such a higher average oxidation state was

Table 1. Reversible (EP_r) and irreversible (EP_i) electrochemical promotion of N_2 and CO_2 production over a deactivated Rh/YSZ catalyst at 300 °C by anodic current application (5 μA) with different polarization times, t_{pol}

t_{pol}/min	ΔP_{N_2}/ppm		ΔP_{CO_2}/ppm	
	EP_r	EP_i	EP_r	EP_i
60	2.06	1.45	17.9	22.2
90	2.03	2.06	16.9	26.6
120	2.01	2.49	17.4	30.4
Error/ppm	±0.05		±0.8	

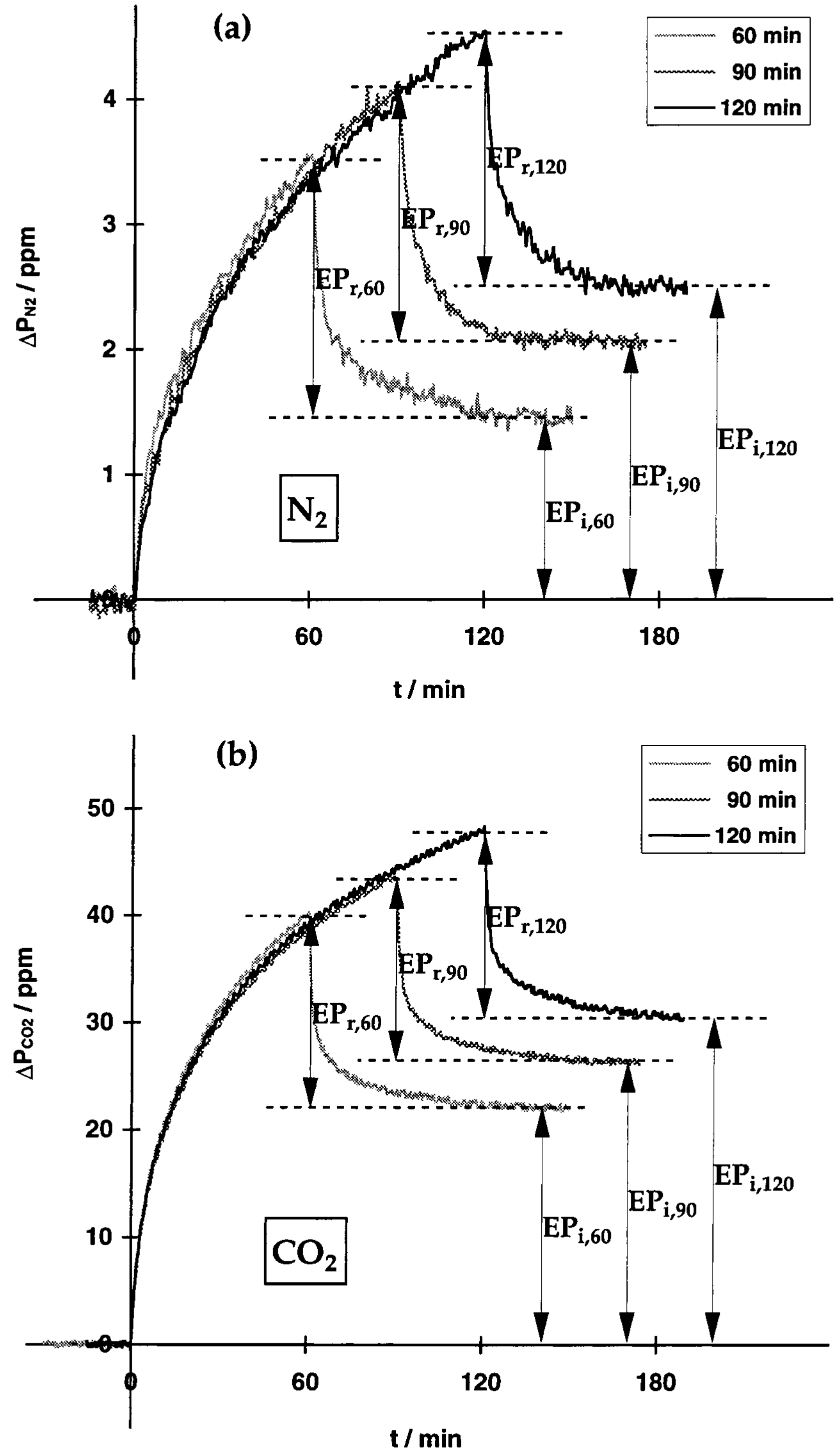

Fig. 4. Transients of N_2 production (a) and CO_2 production (b) over the deactivated Rh/YSZ film catalyst during galvanostatic cycles of different polarization times. Anodic current application (+5 μA) at $t = 0$ min; current interruption at $t = 60$, 90 or 120 min. Feed composition: C_3H_6 (0.1 kPa):NO (0.1 kPa):O_2 (0.5 kPa); $T = 300$ °C. Reversible electrochemical promotion: EP_r ; irreversible electrochemical promotion: EP_i.

considered as 'deactivated' catalyst. The catalytic activity over deactivated rhodium was low but still measurable with sufficient reproducibility; the N_2 and CO_2 production were around 3 and 18 ppm, respectively (1.2% NO conversion and 0.6% C_3H_6 conversion). Although the deactivated catalyst is overoxidized with respect to the gas mixture at 300 °C, its low catalytic activity is stable in time because of the very slow kinetics of spontaneous (open circuit) surface reduction at this temperature. Anodic current application was shown to efficiently enhance the catalytic activity giving rise to two effects. The reversible electrochemical promotion, EP_r, vanishing after current interruption is due to the steady-state accumulation of electrochemically generated active species at the gas exposed catalyst surface [6]. The irreversible electrochemical promotion, EP_i, persisting after current interruption is caused by the progressive reduction of the catalyst surface assisted by positive current application via weakening the Rh–O bond similarly to as observed on platinum oxides [13]. Obviously, the recovery of catalytic performance lost during deactivation is a function of the time of current application.

The observed behaviour of the active rhodium catalyst is in good agreement with this interpretation. Over the active catalyst the irreversible effect, EP_i, vanishes and the polarization cycles become perfectly reversible, as seen before. In the active state, in fact, the catalyst has the right average surface oxidation state corresponding to the composition of the reacting gas mixture at the given temperature. No further open circuit activation is possible since the lost activity has been fully recovered.

4. Conclusion

Gas-phase reduction of NO by propylene in the presence of excess oxygen over a rhodium film catalyst deposited on an YSZ solid electrolyte was studied. A temporary shift towards more oxidative feed compositions or a short temperature jump may cause a drop in the catalytic activity of rhodium via partial oxidation of the catalyst surface. At low working temperatures the spontaneous recovery of such an activity loss is very slow but it may be efficiently assisted by electrochemical polarization with insignificant power consumption. The electrochemical promotion obtained over a deactivated catalyst is composed of two parts: a reversible and an irreversible effect. Once the lost activity is recovered, the irreversible effect vanishes and a fully reversible behaviour is observed. It is believed that reversible promotion is due to the steady-state accumulation of electrochemically generated active species at the gas exposed catalyst surface whereas irreversible promotion, depending on both the activation state of the catalyst and the duration of the current application, results from the progressive modification of the catalyst surface itself.

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