Catalysis Today 146 (2009) 330–335

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Pt/K–βAl_2O_3 solid electrolyte cell as a ‘‘smart electrochemical catalyst’’ for the effective removal of NO_x under wet reaction conditions

Antonio de Lucas-Consuegra *, Ángel Caravaca, Fernando Dorado, José L. Valverde

Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Avenida Camilo José Cela 10, 13005 Ciudad Real, Spain

ARTICLE INFO

Article history:
Available online 7 April 2009

Keywords:
Electrochemical promotion
NEMCA effect
Electrochemical catalyst
Electrochemical sensor
Selective catalytic reduction
SCR

ABSTRACT

This study has shown that the phenomenon of electrochemical promotion can be used to activate a metal catalyst for the selective catalytic reduction of nitrogen oxides (NO_x) in the presence of water in the feed. The application of different potentials optimized the catalytic performance of the Pt catalyst-working electrode at each reaction temperature range. In addition, the measurement of the open circuit voltage in the cell gave useful information on the competitive adsorption between the reactants. Thus, very interestingly, the combined use of the Pt/K–βAl_2O_3 cell as a sensor and as an electrochemical catalyst allows anticipating and optimizing the catalytic behaviour of the system under changing reaction conditions, such as those found in the exhaust of an engine. Finally, characterization of the cell by Cyclic Voltammetry along with NO_x analysis and XRD provided useful information about the nature of the promoter species under wet reaction conditions.

1. Introduction

The phenomenon of electrochemical promotion (EPOC) also called non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA effect) was discovered more than 25 years ago by the group of professor Vayenas, who reported [1] that solid electrolytes could be used as electro-active catalyst supports in order to alter the catalytic activity of catalyst electrode films. This phenomenon occurs when catalytic reactions take place on a variety of metal films in contact with a solid electrolyte, where this latter acts as a source of electrochemically controlled promoter ions that directly modify the behaviour of the catalyst film (working electrode) [2,3]. Thus, this new phenomenon enables to improve in a much pronounced and controlled manner the catalytic performance of metal catalyst, which allows reducing the energy requirements (working at lower temperatures) [4] or the amount of metal (using thin films) [5].

From the discovery of this phenomenon, it has been applied for over seventy catalytic reactions on a large number of catalyst electrodes interfaced to a variety of solid electrolytes and mixed electronic–ionic conductors [6]. Most of these studies deal with environmental catalysis, particularly in automotive pollution control, as it is an urgent need, especially due to the likely stricter future legislations. For instance, recent studies have explored the utility of electrochemical promotion to promote Pt catalytic activity and selectivity for the selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) under large excess of oxygen [7–15]. Some of these works have been focused on the practical application of the NEMCA effect for the abatement of NO_x emissions. For instance, Balomenou et al. [9] reported a novel monolithic electropromoted reactor based on a Pt–Rh catalyst which achieved a near complete fuel and NO conversion at 300 °C. Also, we have recently reported [7,11], following previous studies [16,17], a novel and simple method to prepare the Pt catalyst-working electrode by a wet impregnation procedure. This technique generates a catalyst film which could be electrochemically promoted at low temperatures and could be used for the deposition of catalyst films into the channels of typical industrial supports [16,17]. However, all these previous studies [7–15] have been carried out under dry reaction conditions which are not representative of the real exhaust emissions of a car engine.

The aim of this study was to apply the NEMCA effect to improve the catalytic performance of Pt for the SCR of NO_x in the presence of water steam in the feed, as a new approach for the practical application of the NEMCA effect on this kind of processes. In addition, the possibility of simultaneous use of the solid electrolyte cell as an electrochemical catalyst and as a sensor has been investigated for the further development of a ‘‘smart electrochemical catalyst’’, whose optimum working potential could be anticipated and applied in the own system.

---

* Corresponding author. Tel.: +34 926295300; fax: +34 926295318.
E-mail address: Antonio.Lconsuegra@uclm.es (A. de Lucas-Consuegra).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.02.043

2. Experimental

2.1. Catalytic activity measurements

The catalytic activity measurements were carried out in an experimental setup described in detail in a previous work [11]. The reaction gases were Praxair certified standards of 4% C_3H_6/He, 4% NO/He, O_2 (99.99% purity) and He (99.999% purity), which was used as the vector gas. The gas flow was controlled by a set of calibrated mass flowmeters (Brooks 5850 E and 5850 S) while water was introduced to the reacting stream by means of a saturator. The content of water in the reaction mixture was controlled by using the vapour pressure of H_2O at the temperature of the saturator (30 °C). The tubing down stream from the saturator was heated to 100 °C to prevent condensation. The reactants were introduced into the reactor with the following concentrations: NO (2000 ppm), C_3H_6 (2000 ppm), O_2 (5%), H_2O (5%) balanced with He. The overall gas flow rate was kept constant at 15 L h^{-1}. Reactant and product gases were analyzed with a micro-gas-chromatograph (Varian CP-4900), and a chemiluminescence analyzer (Teledyne 9110 EH). The catalytic activity of the electrochemical catalyst for NO_x removal was analyzed by two parameters: the NO_x conversion (which involves the overall NO_x conversion to N_2 and N_2O) and the N_2 selectivity. Constant voltages across the cell were imposed using a potentiostat–galvanostat (P/G) Voltalab 21 (Radiometer Analytical). All analyzers outputs, as well as the potentiostat–galvanostat outputs (current and potential) were continuously monitored and recorded.

2.2. Electrochemical catalyst preparation

The electrochemical catalyst consisted of a porous, continuous thin Pt film (geometric area of 2.01 cm^2) deposited on a side of a 20 mm in diameter and 1 mm in thickness K–βAl_2O_3 disk (Ionotec). Gold counter and reference electrodes were deposited on the other side. First, the Au counter and reference electrodes were deposited by the application of thin coatings of gold paste (Gwent Electronic Materials C1991025D2), followed by calcination at 800 °C for 2 h. Then, the Pt film was deposited, as described in detail elsewhere [11], by successive steps of deposition and thermal decomposition (650 °C for 1 h) of an H_2PtCl_6 precursor solution, with a metal concentration of 0.1 M. The final Pt loading was 1.63 mg Pt/cm^2. Prior to the catalytic activity measurements, the catalyst was reduced in a stream of H_2 at 450 °C for 1 h. After the reduction process, the sample was cooled down to 200 °C under He flow. The reactive mixture flow was switched into the reactor and the sample was heated to 450 °C at 5 °C min^{-1}. The catalyst was maintained at 450 °C for 12 h in order to stabilise its activity and probe the catalyst durability against the thermal sintering. Then, the temperature was finally decreased to 200 °C at 5 °C min^{-1} for the catalytic experiments. Initially, before the application of each potential, a positive potential of 3000 mV was applied between the Pt catalyst and the Au reference electrode until the current between the catalyst and the counter electrode vanished, in order to clean the catalyst surface from potassium and to define a reproducible state of the Pt catalyst surface.

2.3. Characterization measurements

The number of Pt active sites of the catalyst-electrode film was determined by the electrochemical technique developed by Ladas et al. [18]. It was found to be 5.65×10^{-7} mol Pt (222.5 cm^2), which led to a metal dispersion of 3.4%. Cyclic Voltammetry measurements in conjunction with NO_x analysis were also performed at a sweep rate of 2 mV/s with the potentiostat–galvanostat in order to investigate the formation and decomposition of the promoter species. The Pt catalyst-working electrode film supported on the K–βAl_2O_3 disk before (fresh sample) and after catalysis (used sample) was also investigated by X-ray diffraction (XRD) with a Philips PW 1710 instrument using Ni-filtered Cu K_α radiation. For the used sample, the electrochemical catalyst was kept before the analysis under wet reaction conditions at 400 °C for 2 h and with the application of a potential $V_{WR} = -2$ V, in order to favour the formation of the promoter species. The diffractograms were then compared with the JCPDS-ICDD references for identification purposes of the promoter phases.

3. Results and discussion

The catalytic activity of the Pt/K–βAl_2O_3 electrochemical catalyst was firstly investigated (Fig. 1) through temperature-programmed reaction experiments (light-off measurements) under application of four different catalyst potentials (V_{WR} = 3, 1, 0.5 and −1 V) and at open circuit (O.C.) conditions. Firstly, let us note that the application of different polarizations allows controlling the amount of potassium ions electrochemically transferred to the Pt catalyst. Thus, in agreement with previous studies [4,7,10,11] with cationic electrochemical catalyst, a high positive potential (e.g., 3 V) allows to keep a catalyst surface free of electropositive ions (unpromoted conditions). However, a decrease in the catalyst potential leads to a progressive increase on the promoter coverage, electropromoting the catalyst surface. On the other hand, it can be observed that propene oxidation (Fig. 1a) was

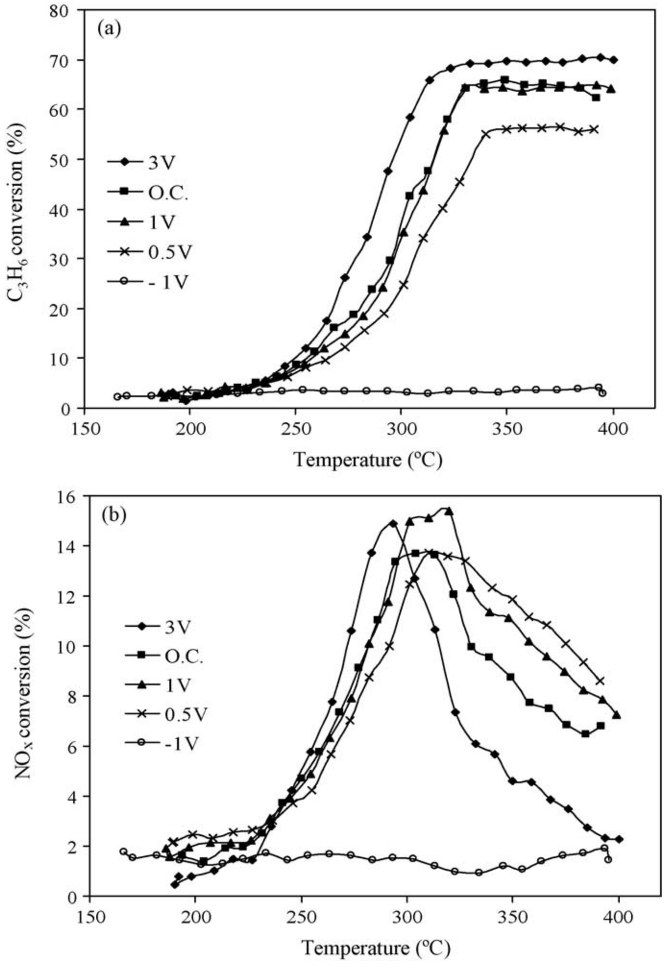

Fig. 1. C_3H_6 (a) and NO_x (b) conversion vs. reaction temperature at different catalyst potentials and at open circuit (O.C.) potential. Conditions: $C_3H_6/NO_x/O_2/H_2O$: 2000 ppm/2000 ppm/5%/5%.

strongly temperature dependent for $V_{WR} > -1$ V, with an increasing conversion from 250 to 310 °C. Full conversion of propene was never reached because of the geometry of the cell, which implies that a small part of the flow bypasses the Pt film. It can also be observed that a decrease in the applied catalyst potential decreased the propene oxidation rate in the whole temperature range. This behaviour, already observed in a previous study for the SCR of NO_x by C_3H_6 under large excess of O_2 on the feed, was attributed to a strong inhibition of propene adsorption and a relative increase of the oxygen coverage under negative polarization [11]. On the other hand, NO_x conversion (Fig. 1b) increased with temperature to get a maximum which depended on the applied catalyst potential. Thus, a positive potential of 3 V increased the NO_x reduction rate at low temperatures (below 290 °C), while a decrease in the catalyst potential to 0.5 V increased NO_x reduction rate at higher reaction temperatures. It can also be observed that the application of much negative potentials led to a strong decrease in the catalytic activity, due to blocking of Pt active sites by promoter compounds, as already observed in previous studies with sodium conductor based electrochemical catalysts [7,11]. It is also interesting to note that the catalytic performance of the system at open circuit (O.C.) conditions was located between 3 and 1 V, due to the thermal migration of potassium promoter ions from the electrolyte to the Pt catalyst film.

According to the current theory of electrochemical promotion, one may rationalize the promotional phenomenon on the basis of the electrode work function modification upon applied potential [19]. The variation of the Pt work function would alter the strength of the chemical bonds between metal and adsorbates, and then would modify the competitive adsorption of the reactants. A decrease in the catalyst potential, and therefore, in the catalyst work function, leads to an increase in the electronic density of Pt, with a concomitant spillover of K^+ ions from the electrolyte onto the Pt surface. It weakens the Pt chemical bond with electron donor adsorbates, such as C_3H_6 and H_2O, and strengthens those with electron acceptors such as O_2 and NO [19,20]. Furthermore, the electronic effect of the potassium promoters strengthens the metal–N bond (increasing NO coverage) and weakens the N–O bond (facilitating NO dissociation), which explains the observed increase in N_2 selectivity as the catalyst potential decreased (Fig. 2).

Thus, taking into account the recent identified rules of chemical/electrochemical promotion [6,21], depending on the nature of the species more strongly adsorbed on the catalyst surface (unpromoted reaction kinetic), a positive or negative potential should be applied in order to improve the reaction rate. Let us note that this is one of the main advantages of the phenomenon of electrochemical promotion vs. the use of a heterogeneous catalyst classically promoted (chemical promotion), as there is the possibility to in situ control (under working reaction conditions) of the optimum promoter coverage which maximizes the reaction rate (as it can be drawn from Fig. 1). This point is even more important for automotive applied catalysis, where the operating conditions of the process are continuously changing depending on the working regime of the engine.

The effect of catalyst polarization on the catalytic activity was also investigated by potentiostatic experiments carried out at different reaction temperatures (Fig. 3). In good qualitative agreement with Figs. 1 and 2, a decrease in the catalyst potential always led to a large N_2 selectivity increase, while the effect on the NO_x conversion depended on the reaction temperature. Below 300 °C, there was a decrease of the NO_x reduction rate when the catalyst potential decreased (electrophobic NEMCA behaviour [6]), while at 350 °C, the system exhibited a maximum for NO_x reduction rate at $V_{WR} = 0.5$ V (volcano NEMCA behaviour [6]).

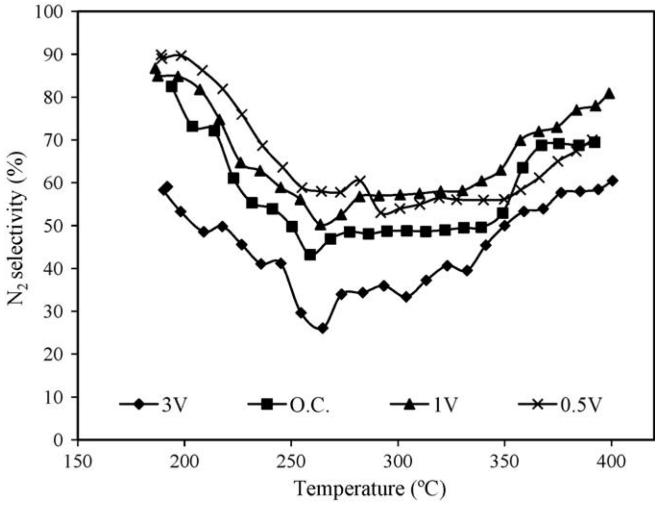

Fig. 2. N_2 selectivity vs. reaction temperature at different catalyst potentials and at open circuit (O.C.) potential. Conditions: $C_3H_6/NO_x/O_2/H_2O$: 2000 ppm/2000 ppm/5%/5%.

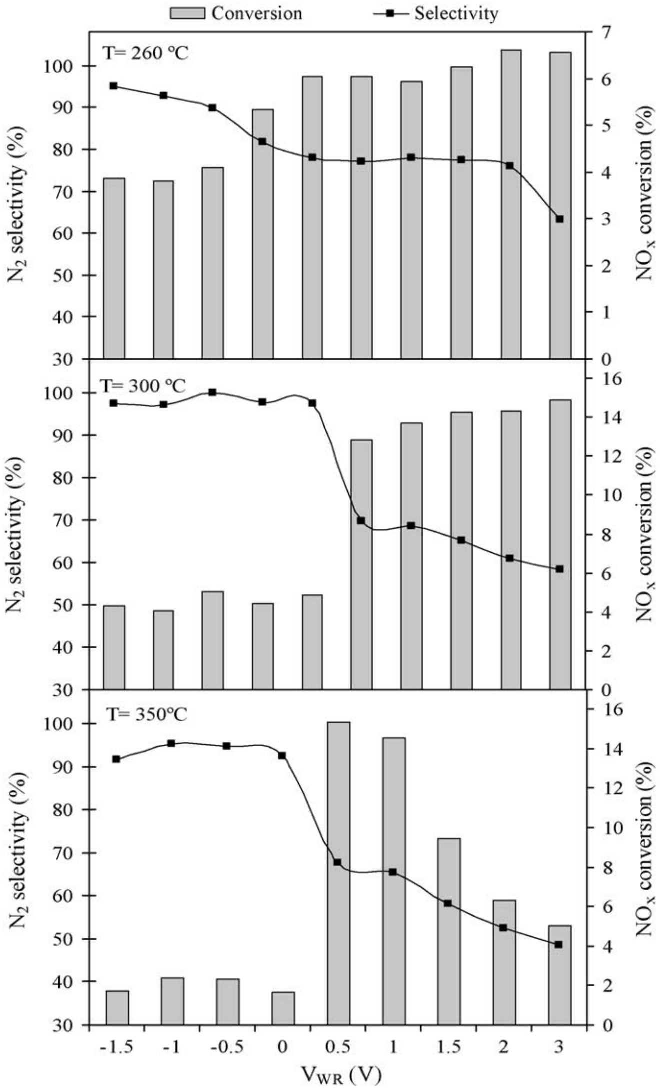

Fig. 3. Influence of the reaction temperature on the steady state potentiostatic variation of N_2 selectivity and NO_x conversion. Conditions: $C_3H_6/NO_x/O_2/H_2O$: 2000 ppm/2000 ppm/5%/5%.

Thus, under wet reaction conditions, the catalytic reaction rate was optimized with an electrochemically clean potassium surface (V_{WR} = 3 V, unpromoted conditions) for a temperature lower than 300 °C, while a certain coverage of potassium promoter (V_{WR} = 1 and 0.5 V) increased NO_x reduction rate above 300 °C.

Thus, in order to explain the observed promotional effect and to monitor the surface activity of adsorbed species, open circuit potential measurements were carried out under reaction conditions. Thus, Fig. 4 shows the variation of the open circuit potential ($V°_{WR}$) and the Optimal Applied Catalyst Potential ($V_{WR\ opt}$) vs. the reaction temperature under wet reaction conditions. The Optimal Applied Catalyst Potential was defined as the applied potential which maximized the NO_x conversion at each temperature range in Fig. 1b. Firstly, a good qualitative agreement in the tendency of both curves can be clearly observed. Below 290 °C, a high value of the open circuit potential was measured between working and reference electrodes, suggesting that at this temperature range the Pt active sites are predominantly covered by electron acceptor species: NO and O_2. Let us remark that this point clearly diverge with the behaviour under dry reaction conditions observed in a previous study on NO_x SCR by C_3H_6 [7]. In this previous work, lower values of $V°_{WR}$ were measured at low temperatures in comparison with higher temperatures. Under dry reaction conditions, as long as C_3H_6 is not completely oxidized (low temperature), the Pt active sites are predominantly covered by the hydrocarbon, while NO and O coverage remains low [22], which causes a low value for $V°_{WR}$. However, as reported in a previous study for Pt based catalyst [23], at low temperature some water vapour (below 5%) has a positive effect on the NO_x reduction rate. This effect has been attributed to the removal of carbonaceous species which block Pt active sites on which NO dissociates. After removing the deposits, more active sites can play a role in NO and O_2 adsorption and dissociation. Hence, the conversion of NO_x is improved [24]. Thus, at low temperature under unpromoted wet reaction conditions, the Pt active sites are predominantly covered by electron acceptor species (NO and O instead of C_3H_6) which causes the observed high $V°_{WR}$ values. Therefore, under these conditions, a positive potential should be applied in order to keep certain coverage of the reductant on the catalyst surface and thus improving the NO_x reduction rate, as observed in Figs. 1 and 3. However, as the reaction temperature increases, and hence the propene oxidation, is likely that water molecules start to adsorb competitively with NO_x. It would explain the typical inhibiting effect of water for the SCR process at high temperatures (in contrast with the promoter effect observed at low temperatures), as described in previous studies [24]. Moreover, water is well known to be an electron donor species and therefore to decrease the catalyst potential [20]. It would cause the decrease in the $V°_{WR}$ with the reaction temperature and the abrupt change observed above 320 °C, temperature at which most of C_3H_6 has been oxidized. Under these conditions, a decrease in the applied catalyst potential increases the NO_x reduction rate as the coverage of water molecules strongly decreases by the presence of the electrochemical promoter, as already observed for SCR of N_2O under similar conditions [20]. Then, from Fig. 4, it is clear that the measurement of the open circuit potential allowed predicting the optimum applied potential, which optimized the behaviour of the system for the removal of NO_x. This latter parameter is quite important, not only for the operation of the electrochemical catalyst at varying reaction conditions, but also for understanding the previously mentioned promotional effect at each temperature range.

Fig. 5 compares the potentiostatic behaviour of the electrochemical catalyst at 350 °C under dry (0% H_2O) and wet (5% H_2O) reaction conditions. Thus, it shows the influence of the applied catalyst potential (V_{WR}) on the variation of the N_2 rate enhancement ratio (ρ_{N_2}), where this latter was defined by the following equation:

$$\rho_{N_2} = \frac{r}{r_0} \quad (1)$$

where r_0 is the N_2 production rate under unpromoted conditions (V_{WR} = 3 V), and r is the N_2 production rate under electrochemically promoted ones ($V_{WR} < 3$ V). In addition, the inset in the figure shows the variation of the open circuit potential ($V°_{WR}$) under dry and wet reaction conditions at 350 °C. In agreement with previous studies [7], under dry reaction conditions and high reaction temperatures, a typical electrophobic NEMCA behaviour was observed (a decrease in the catalyst potential decreased the reaction rate). However, there is a different behaviour under wet conditions which shows that at this temperature water steam is adsorbed competitively with the other reactants [24]. This assumption can be further confirmed by the observed decrease in the value of the open circuit potential ($V°_{WR}$), which evidences again that under the explored conditions water acts as an electron donor adsorbate. Under these conditions, as already mentioned, a decrease in the catalyst potential and therefore an increase in the electropositive promoter coverage increases the NO_x reduction rate by decreasing the adsorption of water steam (electron donor) and increasing the NO_x chemisorption (electron acceptor). These

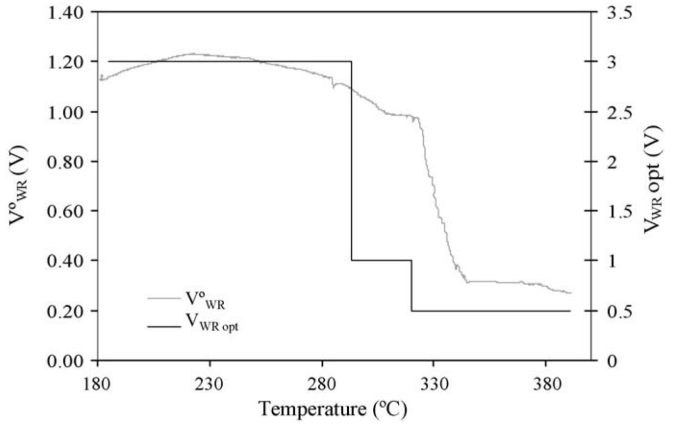

Fig. 4. Influence of the reaction temperature on the open circuit potential ($V°_{WR}$) and the Optimum Applied Catalyst Potential ($V_{WR\ opt}$). Conditions: $C_3H_6/NO_x/O_2/H_2O$: 2000 ppm/2000 ppm/5%/5%.

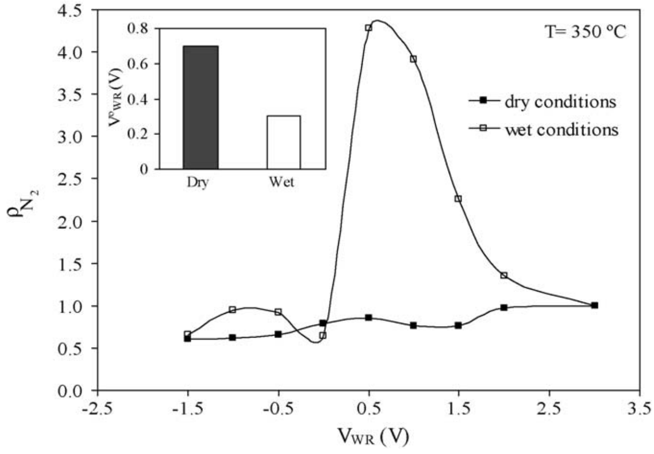

Fig. 5. Influence of the presence of water (5%) on the steady state potentiostatic variation of the N_2 rate enhancement ratio (ρ_{N_2}) and on the value of the open circuit potential ($V°_{WR}$, inset). Conditions: $C_3H_6/NO_x/O_2/H_2O$: 2000 ppm/2000 ppm/5%/0–5%, T = 350 °C.

results demonstrate again that the measurement of the open circuit potential allows to anticipate the NEMCA behaviour of the system [25], and therefore the possible development of these cells as “smart electrochemical catalyst” for continuously changing condition processes.

The promotional phenomenon under wet conditions was also investigated in a dynamic way by Cyclic Voltammetry along with NO_x analysis at 350 °C as shown in Fig. 6. It can be observed that starting from a potassium-free Pt surface ($V_{WR} = 3$ V) and then decreasing the catalyst potential (cathodic polarization), there was a continuous decrease in the NO_x concentration, achieving a minimum at $V_{WR} = 0.5$ V. At this point the optimal potassium coverage on the catalyst was achieved for the explored temperature, in good agreement with Figs. 1 and 3. An additional decrease of the catalyst potential led to a decrease in the catalytic performance due to an excessive formation of promoter phases that blocked the Pt active sites. The formation of such promoter phases was confirmed by the appearance of two different cathodic peaks (at $V_{WR} = -0.4$ and -2 V) as a result of the backspillover of K^+ ions and the subsequent formation of potassium compounds with different adsorbates located on the catalyst surface [26]. The decomposition of such promoter phases during the reverse cycle (anodic polarization) led to an increase in the NO_x reduction rate since Pt-free active sites were liberated for the catalytic process. It is interesting to note that, overlapping with the 3 anodic peaks, other 3 peaks for the NO_x concentration were clearly observed. It seems to indicate that, under wet reaction conditions, the promoter ions probably form a Pt surface compound with chemisorbed NO_x, as already observed in a previous study with Pt/Na–βAl_2O_3 electrochemical catalyst under dry conditions [11]. In order to confirm this assumption, the Pt catalyst-working electrode film of fresh and used samples was characterized by X-ray diffraction (XRD) (Fig. 7). For both samples, the peak assignments based on JCPDS were consistent with a Pt face-centred cubic (FCC) structure [27]. However, two new diffraction peaks appeared in the used sample which corresponded to the presence of potassium nitrate on the Pt surface. This observation supports the Cyclic Voltammetry results and evidences that the nature of the promoter phase under wet reaction conditions mainly consists of a based nitrate, in agreement with previous studies with sodium conductor based electrochemical catalysts under dry conditions [11,28,29]. In addition, from the high intensity of the KNO_3 diffraction peaks, one may suggest that the Pt/K–βAl_2O_3 electrochemical catalyst has a strong ability to trap NO_x from the gas phase to form KNO_3, which also opens a new application of these systems for trapping pollutant processes [30].

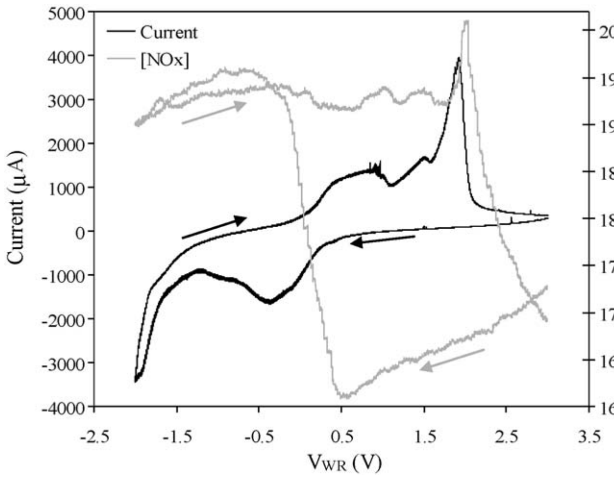

Fig. 6. Current and NO_x concentration vs. catalyst potential during Cyclic Voltammetry at 350 °C under wet reaction conditions ($C_3H_6/NO_x/O_2/H_2O$: 2000 ppm/2000 ppm/5%/5%). Scan rate 2 mV/s.

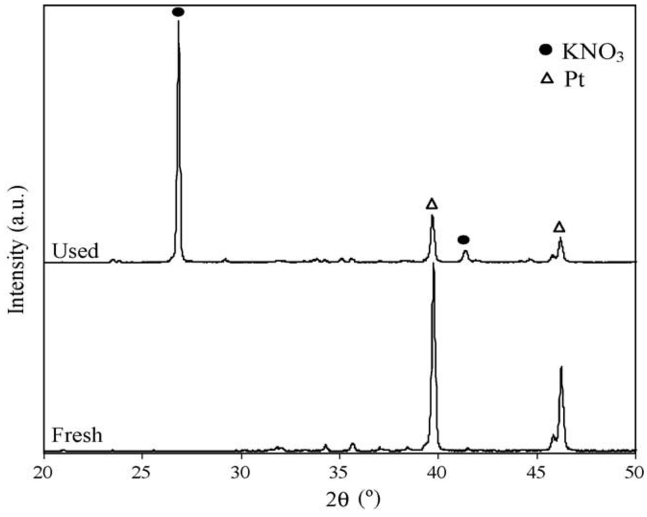

Fig. 7. XRD patterns of the Pt catalyst-working electrode film before catalysis (fresh) and after catalysis (used).

4. Conclusions

The present results clearly showed for the first time in literature that the phenomenon of electrochemical promotion could be used to improve the SCR of NO_x under wet reaction conditions. This phenomenon could be practically used to decrease the inhibitory effect of poisons in the reaction atmosphere, e.g., water steam. The combined use of Pt/K–βAl_2O_3 cell as sensor and as an electrochemical catalyst allows anticipating and optimizing the catalytic behaviour of the system, under changing reaction conditions, such as those expected for the exhaust of an engine. Additional characterization of the cell by Cyclic Voltammetry along with NO_x analysis and XRD revealed that the electrochemical promoter phase under wet conditions is in the form of potassium nitrates.

Acknowledgments

Financial support by the Ministerio de Educación y Ciencia of Spain (Project CTQ2007-62512/PPQ) and the European Marie-Curie EFEPOC project (MSCF-CT-2006-046201) is gratefully acknowledged.

References

[1] M. Stoukides, C.G. Vayenas, J. Catal. 70 (1981) 137.
[2] C.G. Vayenas, S. Bebelis, I.V. Yentekakis, H.-G. Lintz, Catal. Today 11 (1992) 303.
[3] I.V. Yentekakis, G. Moggridge, C.G. Vayenas, R.M. Lambert, J. Catal. 146 (1994) 292.
[4] A. de Lucas-Consuegra, F. Dorado, J.L. Valverde, R. Karoum, P. Vernoux, Catal. Commun. 9 (2008) 17.
[5] P. Vernoux, F. Gaillard, R. Karoum, A. Billard, Appl. Catal. B 73 (2007) 73.
[6] C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, D. Tsiplakides, Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal–Support Interactions, Kluwer Academic/Plenum, New York, 2001.
[7] F. Dorado, A. de Lucas-Consuegra, C. Jiménez, J.L. Valverde, Appl. Catal. A 321 (2007) 86.
[8] S. Souentie, A. Hammad, S. Brosda, G. Foti, C.G. Vayenas, J. Appl. Electrochem. 38 (2008) 1159.
[9] S. Balomenou, D. Tsiplakides, A. Katsaounis, S. Thiemann-Handler, B. Cramer, G. Foti, Ch. Comninellis, C.G. Vayenas, Appl. Catal. B 52 (2004) 181.
[10] P. Vernoux, F. Gaillard, C. Lopez, E. Siebert, J. Catal. 217 (2003) 203.
[11] F. Dorado, A. de Lucas-Consuegra, P. Vernoux, J.L. Valverde, Appl. Catal. B 73 (2007) 42.
[12] A. Lintanf, E. Djurado, P. Vernoux, Solid State Ionics 178 (2008) 1998.
[13] B. Beguin, F. Gaillard, M. Primet, P. Vernoux, L. Bultel, M. Henault, C. Roux, E. Siebert, Ionics 8 (2002) 128.

[14] C. Kotsounis, A. Hammad, M. Lepage, Y. Sakamoto, G. Fóti, C.G. Vayenas, Top. Catal. 50 (2008) 192.
[15] S.P. Balomenou, D. Tsiplakides, C.G. Vayenas, S. Poulston, V. Houel, P. Collier, A.G. Konstandopoulos, C. Agrafiotis, Top. Catal. 44 (2007) 481.
[16] G. Fóti, I. Bolzonella, J. Eaves, Ch. Comninellis, Chimia 56 (2002) 137.
[17] E.A. Baranova, G. Fóti, Ch. Comninellis, Electrochem. Commun. 6 (2004) 389.
[18] S. Ladas, S. Bebelis, C.G. Vayenas, Surf. Sci. 251 (1991) 1062.
[19] C.G. Vayenas, S. Brosda, C. Pliangos, J. Catal. 203 (2001) 329.
[20] A. de Lucas-Consuegra, F. Dorado, C. Jimenez-Borja, J.L. Valverde, Appl. Catal. B 78 (2007) 222.
[21] S. Brosda, C.G. Vayenas, J. Wei, Appl. Catal. B 68 (2006) 109.
[22] R. Burch, T.C. Watling, Catal. Lett. 43 (1997) 19.
[23] M. Haneda, Y. Kintaichi, N. Bion, H. Hamada, Appl. Catal. B 42 (2003) 57.
[24] J.Y. Jeon, H.Y. Kim, S.I. Woo, Appl. Catal. B 44 (2003) 311.
[25] X. Li, F. Gaillard, P. Vernoux, Ionics 11 (2005) 103.
[26] P. Vernoux, F. Gaillard, C. Lopez, E. Siebert, Solid State Ionics 175 (2004) 609.
[27] A. de Lucas-Consuegra, F. Dorado, J.L. Valverde, R. Karoum, P. Vernoux, J. Catal. 251 (2007) 474.
[28] F.J. Williams, M.S. Tikhov, A. Palermo, N. Macleod, R.M. Lambert, J. Phys. Chem. B 105 (2001) 2800.
[29] I.V. Yentekakis, A. Palermo, N.C. Filkin, M.S. Tikhov, R.M. Lambert, J. Phys. Chem. B 101 (1997) 3759–3768.
[30] A. de Lucas-Consuegra, A. Caravaca, P. Sánchez, F. Dorado, J.L. Valverde, J. Catal. 259 (2008) 54.