Catalysis Today 146 (2009) 293–298

Contents lists available at ScienceDirect

Catalysis Today

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

Use of potassium conductors in the electrochemical promotion of environmental catalysis

Antonio de Lucas-Consuegra [a,*], Fernando Dorado [a], Carmen Jiménez-Borja [a], Angel Caravaca [a], Philippe Vernoux [b], José L. Valverde [a]

[a] *Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Avenida Camilo José Cela 10, 13005 Ciudad Real, Spain*
[b] *Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, 2 avenue Albert Einstein, F-69626 Villeurbanne, France*

ARTICLE INFO

Article history:
Available online 17 May 2009

Keywords:
Electrochemical promotion
NEMCA effect
Potassium conductors
Environmental catalysis
NO_x storage/reduction

ABSTRACT

This study summarizes the effect of the electrochemical promotion of catalysis (EPOC) by using potassium conductors in environmental catalytic reactions applied to the removal of several automotive pollutants, such us CO, C_3H_6 and nitrogen oxides (N_2O and NO_x). It has been shown the extraordinarily potential of using Pt/K–βAl_2O_3 in a wide variety of environmental reactions (oxidation, reduction), activating the catalyst at lower reaction temperatures and decreasing the inhibitory effect of poisons such as water in the reaction atmosphere. In addition, a new application of potassium conductors-based electrochemical catalysts has been developed for the NO_x storage/reduction process (NSR). The idea of coupling catalysis and solid-state electrochemistry on this process would allow to improve and simplify the current NSR technology. Finally, the results have been obtained under reaction conditions compatible with the treatment of automotive exhaust emissions. This demonstrates the potential for the practical use of the phenomenon of electrochemical promotion by using potassium conductors on this kind of process.

1. Introduction

The non-Faradaic electrochemical modification of catalytic activity process (NEMCA effect) was discovered [1] and developed by Vayenas et al. [2,3]. This process is based on the modification of the chemisorption properties of the catalyst, by an applied potential, as a consequence of the electrochemical pumping of ions (promoters) from a solid electrolyte to the catalyst film [4,5]. This phenomenon allows improving the catalytic performance of a metal catalyst in a very pronounced and controlled way, which can lead to the reduction of the energy requirements (working at lower temperature) or the amount of metal (using thin films). From the discovery of the NEMCA effect, it has been successfully applied for more than 70 catalytic reactions on a large number of catalyst–electrodes interfaced to a variety of solid electrolytes and mixed electronic–ionic conductors [3]. Some of these studies deal with environmental catalysis, particularly in automotive pollution control, since it is an urgent need, especially due to likely more strict future legislations. The majority of these studies have been carried out by using O^{2-}-based conductors such as YSZ [6–10] and Na^+-based ones such as Na–βAl_2O_3 [11–13] and NASICON [14,15]. However to the best of our knowledge, apart from the two previous works [16,17], the NEMCA effect by using potassium conductors has not been applied in environmental catalysis. For instance, Lambert et al. [16] have shown that electropumping potassium ions to metal catalyst films can lead to very large and reversible changes in both catalytic activity and selectivity for a range of different reactions: the catalytic reduction of NO by CO and by propene over Pt, Rh and Cu, the combustion of propene over Pt, and the selective hydrogenation of acetylene over Pt. Also Goula et al. [17] have shown strong modification in both: catalytic activity and selectivity on the $C_3H_6 + NO + O_2$ reaction over potassium-modified Ir surfaces.

Potassium is known as a classical promoter [18] in heterogeneous catalysis and has been widely used in several catalytic reactions. For instance, potassium has been identified as one of the best promoter of Pt/Al_2O_3 catalysts for the oxidation of CO [19].

During the last 3 years our group in collaboration with the group of Vernoux have been working in the application of the NEMCA effect using potassium conductors to the removal of automotive exhaust pollutants by oxidation and reduction reactions [20–23]. In addition, we have recently developed a new application of cationic-based electrochemical catalysts in pollutant trapping processes [24]. Hence, electrochemical catalysts could be developed for new environmental reactions such as NO_x storage/reduction process (NSR) by using the ions electrochemi-

---

[*] Corresponding author. Tel.: +34 926295300; fax: +34 926295256.
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.2009.04.009

cally transferred from the support as a storage component (e.g., potassium ions).

This paper reviews the main achievements reached by our group with potassium conductors electrolytes. These studies have evidenced the interest of using Pt/K–βAl_2O_3 electrochemical catalyst in a wide range of environmental processes showing that the NEMCA effect is a general phenomenon not limited to some particular reactions. In addition, it has been shown that the use of Pt/K–βAl_2O_3 electrochemical catalyst allows to achieve high efficiencies for the removal of automotive exhaust pollutants under near-real Diesel exhaust working conditions, i.e., low temperatures, excess of O_2 in the reaction atmosphere and presence of water steam.

2. Experimental

Two kinds of electrochemical catalyst were prepared and tested. The first configuration used for the conventional NEMCA experiments (CO and C_3H_6 oxidation and selective catalytic reduction of N_2O) consisted of a porous and continuous thin Pt film deposited on one side of a K–βAl_2O_3 disk (Ionotec). The Pt film was deposited, as described in detail elsewhere [13], by successive steps of deposition and thermal decomposition of an H_2PtCl_6 precursor solution. Gold counter and reference electrodes were deposited on the opposite side of the disk by application and calcination of thin coatings of gold paste. On the other hand, a second configuration was used for the NO_x storage/reduction process. Due to the higher required surface areas for this kind of process, a tubular configuration was used. It consisted on a porous, continuous thin Pt film (geometric area of 45 cm^2) deposited inside a 18 mm in inner diameter, 40 mm in length and 1 mm in thickness of a K–βAl_2O_3 tube (Ionotec). A gold counter-electrode was deposited on the outer side of the solid electrolyte tube in order to perform polarizations. Both electrodes were prepared by using the corresponding metal pastes and annealed at 800 °C for 12 h in air. For both configurations, prior to the electrochemical promotion experiments, the catalysts were reduced in a stream of H_2 at high temperature for 1 h. Before the catalytic activity measurements, the electrochemical catalyst was firstly treated in each case under reaction conditions at high temperature for a long time, i.e., 600 °C for 12 h for the case of the N_2O reduction study. It allows to stabilise the catalyst film morphology and to probe catalyst durability required in commercial catalyst formulations against the thermal sintering.

The catalytic activity measurements were carried out within a specific quartz reactors, as described in previous studies at atmospheric pressure [10,13]. The reaction gases were Praxair certified standards of 1% CO/He, 4% C_3H_6/He, 4% N_2O/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). For the experiments carried out under wet conditions, 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), i.e., corresponding to 3 vol% of water in the stream. The tubing downstream from the saturator was heated to 100 °C to prevent condensation. Reactants and products were analyzed using an on-line micro-gas chromatograph (Varian CP-4900). For the CO and C_3H_6 combustion processes, CO_2 concentration in the effluent from the reactor was additionally monitored by an infrared (IR) analyzer (Horiba VA-3000) while the NO and NO_2 measurements in the NSR experiments were additionally analyzed by a chemiluminiscence analyzer (Teledyne 9110 EH). All electrodes, W (catalyst or working electrode), R (reference) and CE (counter-electrode) were connected to a potentiostat-galvanostat Voltalab (Radiometer Analytical). Reference and counter-electrode were made from gold, which was catalytically inert in the process.

The catalytic activity of the system was evaluated in terms of conversion. The magnitude of the phenomenon of electrochemical promotion was characterized by the measurements of the rate enhancement ratio (ρ), defined as in previous studies [13] by the following equation:

$$\rho = \frac{r}{r_0} \tag{1}$$

where "r_0" denotes the unpromoted reaction rate (without electrochemical promoter) under application of a high positive reference potential (2 V for the case of the removal of CO, C_3H_6 and N_2O and 3 V for the removal of NO_x by NSR) and "r" denotes the electrochemically promoted reaction rate under presence of the electrochemical promoter achieved at lower values of the previous reference potentials.

3. Results and discussion

3.1. CO oxidation

The catalytic activity for the CO oxidation reaction (CO/O_2: 5000 ppm/5000 ppm) was investigated through temperature-programmed reaction experiments (light-off measurements) under application of different polarizations (Fig. 1). In first place, it could be observed that CO oxidation was strongly temperature dependent, increasing conversion from 1 to 90% between 190 and 340 °C. Full conversion of CO was never achieved due to the cell configuration, which implies a bypass of the flow to the Pt film. Several studies have shown that the CO oxidation at low temperature is inhibited by the CO adsorption step [3,5,20,25,27]. Then, an increase in the reaction temperature implies the desorption of CO molecules and subsequently the dissociative adsorption of oxygen, leading to CO oxidation. The operating temperature window at which this activation takes place depends on several factors, e.g., type of metal catalyst, CO/O_2 ratio, total reactant flow.

Fig. 1 shows that for a given system, the phenomenon of electrochemical promotion could be used to decrease the activation temperature of the reaction. Thus, as the applied potential decreased (which involves a decrease in the catalyst work function [4]), the activation began at lower temperatures. This process took place due to the migration of potassium ions electrochemically transferred from the solid electrolyte to the

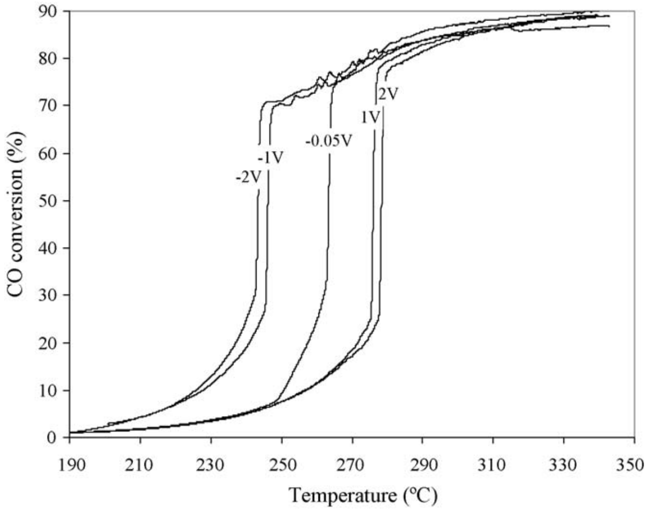


Fig. 1. Light-off curves of the electrochemical catalyst Pt/K–βAl_2O_3 under different catalyst potentials. Reaction conditions: CO = 5000 ppm, O_2 = 5000 ppm, He balance, total flow rate = 6.5 L/h.

catalyst, which enhanced the CO oxidation rate by increasing the coverage of electron–acceptor species (O_2), at the expense of electron–donor (CO) [4,20]. Thus, the presence of electropositive potassium ions supplied to the Pt catalyst, strongly increased the catalytic activity by decreasing the light-off temperature (temperature corresponding to 50% of conversion) in 40 °C. Other important point is that the temperature corresponding to the beginning of the catalytic activity (5% of CO conversion) decreased from about 240 °C without promoters (+2 V) to 210 °C in the presence K^+ cations (−2 V). Such activation at lower temperatures implies an important improvement of the catalytic performance of the system since most of the pollutant exhaust emission in current catalytic converters, takes place during the first minutes of the working of the engine (cold-start conditions) when the exhaust gases temperature are not high enough [26]. In addition, these promotional effects are one of the highest that have ever been obtained for CO oxidation by electrochemical promotion. In addition, all these results have been obtained at a lower temperature range than previously reported [5,6,27–32] for CO oxidation with annealed pastes, which clearly demonstrate that the electrochemical cell based on Pt impregnated catalyst supported on $K–\beta Al_2O_3$ solid electrolyte presents a significant potential for the abatement of these kinds of pollutants.

3.2. Propene combustion

The catalytic activity of the $Pt/K–\beta Al_2O_3$ electrochemical catalyst was firstly investigated at 270 °C under near-stoichiometric oxygen conditions, C_3H_6/O_2: 2000 ppm/1%. Fig. 2 shows the steady-state effect of the applied potential (V_{WR}) on both propene conversion and propene oxidation rate (expressed as O consumption rate, in mol O/s). It can be observed that starting from a potassium clean surface ($V_{WR} = 2$ V), and then decreasing the catalyst potential, the catalytic performance of Pt is strongly improved, increasing propene conversion from 30 to 63%. It should be pointed out, that this was the first time that such large increase in the rate of propene combustion reaction was found below 300 °C [21]. As already mentioned, the variation of the catalyst work function upon polarization induced changes in the binding strength of chemisorbed species. When there is no promoter on the catalyst ($V_{WR} = 2$ V), the Pt surface is predominantly covered by propene or by propene-derived carbonaceous species [9,10]. Thus, a decrease of the catalyst potential to the Pt electrode enhanced propene oxidation rate by increasing the coverage of electron–acceptor species (O_2) at the expense of electron–donor (C_3H_6) [9,21], which led to the observed electrophilic NEMCA effect (the reaction rate increased as the catalyst potential decreased).

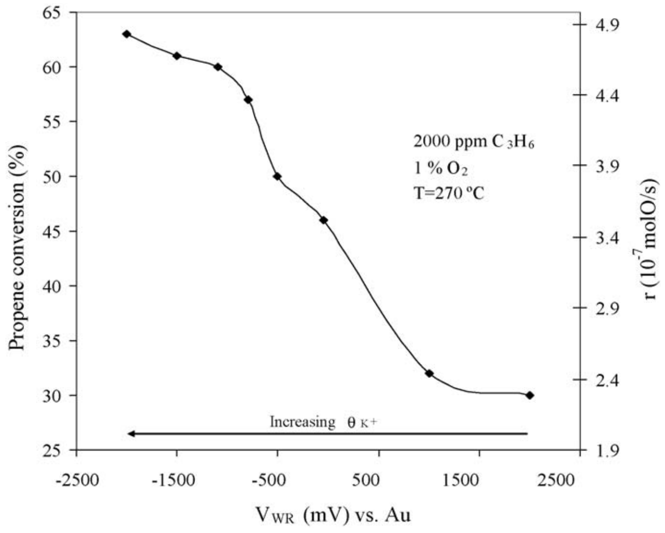


Fig. 2. Steady-state effect of applied catalyst potential (V_{WR}) on both: propene conversion and catalytic reaction rate (r) expressed in mol O/s. Total flow rate = 4 L/h.

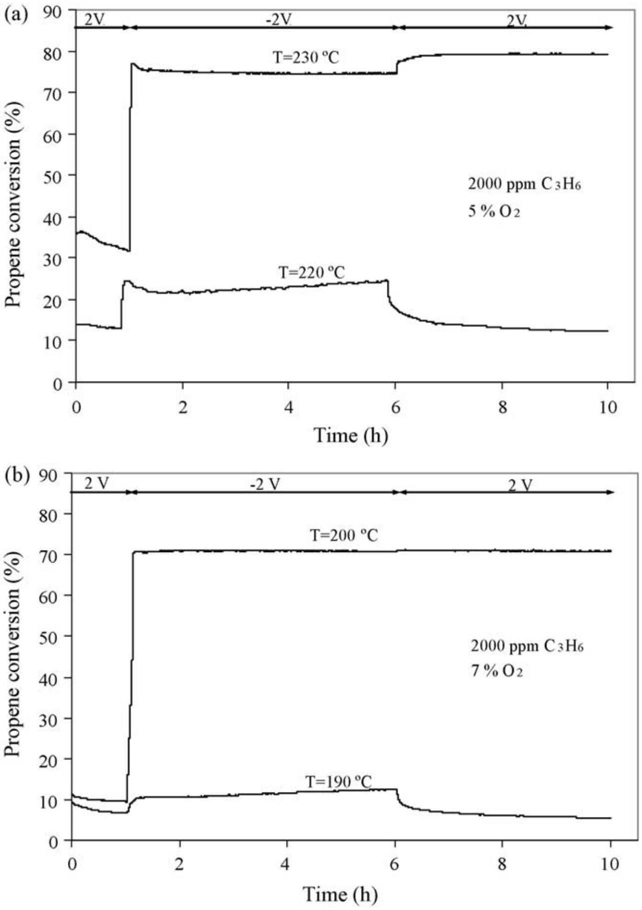


Fig. 3. Propene conversion response to step changes in applied catalyst potential vs. time at different reaction temperatures and oxygen concentrations: (a) 5% O_2, (b) 7% O_2. Total flow rate = 4 L/h.

Fig. 3 shows the response of propene conversion vs. time to step changes in the applied catalyst potential under different oxygen-rich concentrations (2000 ppm C_3H_6, 5–7% O_2) and reaction temperatures. It can be observed that the catalytic activity can be strongly promoted under large excess of oxygen in the reaction atmosphere. For instance, under C_3H_6/O_2: 2000 ppm/7%, at 200 °C (Fig. 3(b)), propene conversion was strongly increased by application of $V_{WR} = -2$ V. Even though the temperature was quite low, a very high conversion (70%) was obtained together with an increased in more than seven times ($\rho = 7.1$) of the reaction rate. It should also be mentioned that this was the first time that such large promotional phenomenon was found for propene combustion under excess of oxygen using Pt-based electrochemical catalyst. For instance, previous works have found that electro-pumping Na^+ ions from $Na–\beta Al_2O_3$ [11] or NASICON [14] can activate Pt catalysts for propene oxidation under fuel-rich conditions as in Fig. 2. Nevertheless, under oxygen-rich conditions, as in the real Diesel exhaust gases, the electrochemical supply of Na^+ ions decreased the catalytic activity. Therefore the use of $Pt/K–\beta Al_2O_3$ electrochemical catalyst shows potential for the practical application of EPOC for the removal of VOCs, since the system could be electrochemically promoted under excess of oxygen and at very low temperatures; e.g., at 200 °C under 7% O_2. On the other hand, it is also interesting to note that an irreversible promotional behaviour appeared under certain reaction conditions. For instance, under 7% O_2 at 200 °C, the initial unpromoted catalytic rate was not achieved even after applying V_{WR} = 2 V for 4 h. Therefore, at this temperature, there is a "permanent NEMCA effect" [33]. The permanent NEMCA effect is one of the most interesting and potentially important characteristics of the electrochemical promotion from a practical viewpoint [3]. For instance, the permanent NEMCA effect would reduce the electrical energy requirements (polarizing the catalyst only for a short time), and could lead to the practical application of NEMCA during the catalyst preparation. Further investigations of this phenomenon in a previous study [21] by a variety of in situ (cyclic voltammetry, FTIR) and ex situ techniques (SEM-EDX) have shown strong evidences that the permanent NEMCA effect was due to the electrochemical creation and stabilization of promoter oxides and superoxides on the catalyst surface such as potassium oxides and peroxides. These kind of species are formed on the catalyst surface during the negative polarization but could not been totally removed during the positive one which led to the observed permanent effect. Thus according to our previous work [21], the formation of different kinds of promoter phases on the catalyst surface during the negative polarization could explain the different behaviours observed in Fig. 3. The formation of carbonates species of low stability led to the reversible NEMCA effect while the formation of more stable promoting phases, i.e., potassium oxides or superoxides at certain oxygen coverages (at higher temperatures or under higher oxygen amount) led to the observed irreversible effect. Even, when both kinds of promoter phases coexist on the catalyst surface, the removal of the less stable one (also probed of lower promotional effect [21]) led to a slight increase in the reaction rate during the last transient at 2 V (Fig. 3(a) at 230 °C).

3.3. Selective catalytic reduction (SCR) of N_2O by propene

The catalytic activity of the Pt/K–βAl_2O_3 electrochemical catalyst was also investigated for the removal of N_2O. In first place the electropromotion effect was investigated ($C_3H_6/N_2O/O_2$: 2000 ppm/1000 ppm/2000 ppm) by consecutive steps of positive (V_{WR} = 2 V) and negative polarizations (V_{WR} = −0.5 and −1 V) applied for 2 and 4 h respectively at 450 °C (Fig. 4). The variation of the current vs. time curves during the potentiostatic steps displays the rate of formation and decomposition of the promoter phases during different polarization steps. Under negative polarization, the promoter ions were electrochemically transferred from the solid electrolyte to the catalyst, leading to a cathodic electron charge transfer reaction between the ions and the different species adsorbed on the catalyst surface (negative current). However, under positive polarization, the promoter ions returned to the solid electrolyte, leading to the anodic charge transfer reaction (positive current). Concerning the variation of the catalytic activity, it can be observed that starting from an electrochemically clean potassium surface (V_{WR} = 2 V), the application of negative polarizations always increased both the N_2O and C_3H_6 reaction rates. For instance, the application of V_{WR} = −1 V increased the N_2O conversion from 1.3 to 50% (ρ = 38.46) while the C_3H_6 conversion increased from 27 to 33% (ρ = 1.22). It is apparent that K acted as a strong promoter for the reduction of N_2O, which could be explained again taking into account an increase in the chemisorption of N_2O (electron–acceptor molecule) at the expense of C_3H_6 (electron–donor one) this latter being strongly adsorbed on the catalyst surface under unpromoted conditions [22].

The efficiency of electrochemical promotion for the removal of N_2O was also investigated under near-real Diesel exhaust reaction conditions, excess of oxygen and water on the feed ($C_3H_6/N_2O/O_2/H_2O$: 2000 ppm/1000 ppm/1%/3%). Fig. 5 shows the influence of the reaction temperature on the steady-state potentiostatic variation of the N_2O rate enhancement ratio (ρ) defined by Eq. (1). It can be observed that under all the explored reaction temperatures, starting from a potassium clean Pt surface (V_{WR} = 2 V), and then decreasing the catalyst potential, the catalytic performance of Pt improved. For instance, at 400 °C the application of a catalyst potential of V_{WR} = −4 V increased the N_2O reduction rate by a factor of 7.4. The origin of the observed promotional result under wet conditions has been attributed to a decrease in the chemisorption of H_2O induced by the electropositive promoter. As already reported in previous studies [34] water molecules are usually strongly adsorbed on Pt active sites inhibiting the chemisorption of the other reactants and therefore hindering the catalytic activity. However, water has been identified as an electron donor adsorbate [22,23] and therefore its adsorption decreased on the active sites under presence of the electropositive promoter facilitating the chemisorption of the other reactants and leading to the observed increase in the catalytic activity. This promotional effect is in good agreement with the recent identified rules of chemical/electrochemical

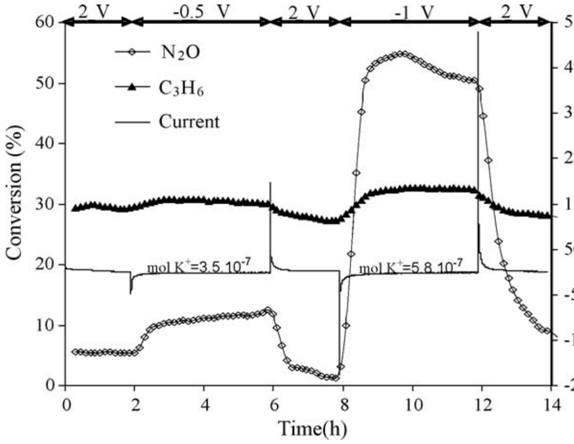


Fig. 4. Transient effect of step changes in applied potential on N_2O and C_3H_6 conversion and on the corresponding current. Conditions: T = 450 °C, $C_3H_6/N_2O/O_2$: 2000 ppm/1000 ppm/2000 ppm, He balance, total flow rate = 12 L/h.

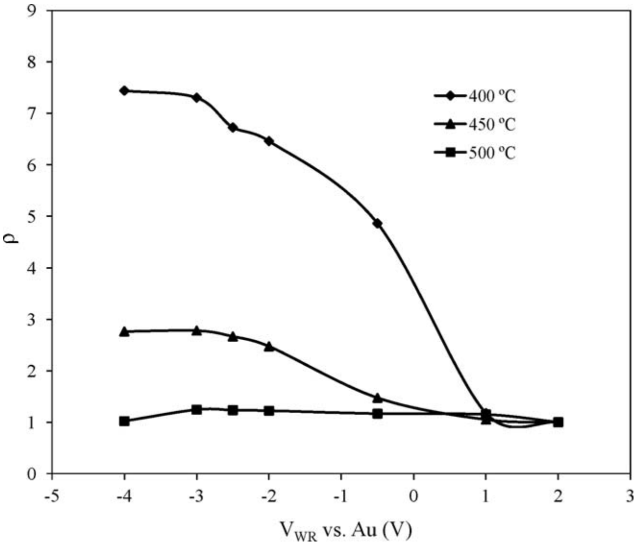


Fig. 5. Influence of the reaction temperature on the steady-state potenciostatic variation of the N_2O rate enhancement ratio (ρ) under wet reaction conditions. Conditions: $C_3H_6/N_2O/O_2/H_2O$: 2000 ppm/1000 ppm/1%/3%, He balance, total flow rate = 12 L/h.

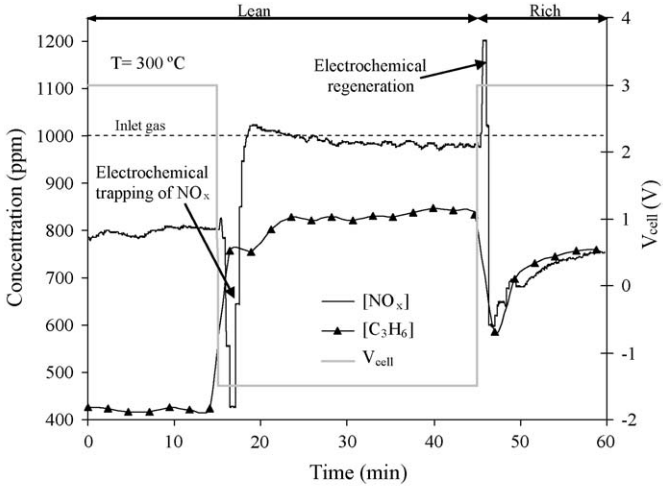


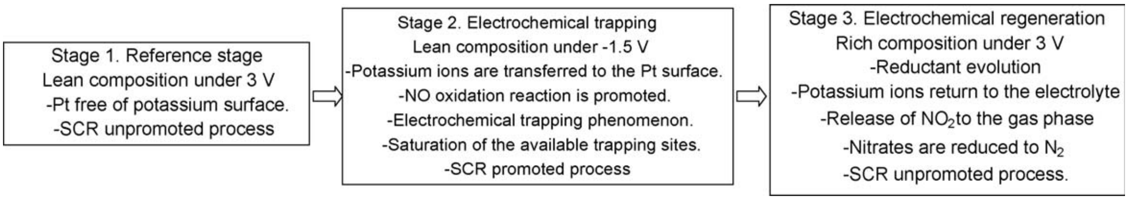
Fig. 6. NO_x and C_3H_6 outlet concentration profiles vs. time during NO_x storage/reduction experiments at 300 °C. Lean phase ($NO/C_3H_6/O_2$: 1000 ppm/1000 ppm/5% O_2, He balance), $V_{cell} = -1.5$ V, 30 min of duration. Rich phase ($NO/C_3H_6/O_2$: 1000 ppm/1000 ppm/0.5% O_2, He balance), $V_{cell} = 3$ V, 15 min of duration. Total flow rate = 15 L/h.

promotion [3,35] and evidences that effect of addition of a promoter on the catalytic activity depends on the initial coverage of the different molecules that participate in the reaction. On the other hand it can be observed a decreased in the rate enhancement ratio as the reaction temperature increased. This fact could be attributed in first place to the increase in the reaction rate under unpromoted conditions with the reaction temperature that obviously decrease the value of the rate enhancement ratio according to Eq. (1). But in addition we can also address a decrease in the level of promotion at higher temperatures due to a relative increase in surface coverage of oxygen adsorbed atoms at the expense of C_3H_6 and N_2O molecules [22,23].

Finally, it should be mentioned that the catalyst durability was also confirmed by a long-term deactivation experiment carried out under wet condition (not shown here) showing the high stability of the system for long time working under real conditions [22].

3.4. Electrochemical assisted NO_x storage/reduction process

Fig. 6 displays a typical NO_x storage reduction process which has been schematized in Fig. 7. Fig. 6 shows the outlet NO_x and C_3H_6 concentrations profile vs. time during the transient from lean ($NO/C_3H_6/O_2$: 1000 ppm/1000 ppm/5%) to rich conditions ($NO/C_3H_6/O_2$: 1000 ppm/1000 ppm/0.5%), at a constant temperature of 300 °C. At $t = 0$ min (Stage 1 in Fig. 7), the gas was switched to the lean composition, and a potential of 3 V was applied (unpromoted conditions). Under these conditions, the outlet NO_x concentration was approximately 800 ppm, due to the SCR (selective catalytic reduction of NO_x by propene) activity of the Pt film free of alkali ions [13], while the C_3H_6 concentration was much lower (400 ppm) due to its additional combustion with O_2. Subsequent application at $t = 15$ min of a constant potential of −1.5 V under lean atmosphere (Stage 2 in Fig. 7), resulted in a significant decrease of the NO_x concentration while the C_3H_6 concentration was strongly increased. In addition, there was a continuous increase in the NO_2 concentration at the expenses of a decrease in the NO one (not shown here), which evidences that the presence of potassium ions promotes the NO oxidation reaction [36]. The origin of the observed NO_x concentration sharp drop was attributed to the ability of the electrochemical catalyst to temporary storage NO_x in the form of potassium nitrates, as already observed with powdered catalyst [37]. The increase in the NO oxidation reaction rate initiated the NO_x storage process, which evidences, in good agreement with previous studies [37], that the initial step of NO oxidation into NO_2 was the rate limiting one for the NSR process. Thus, potassium ions electrochemically pumped to the Pt film simultaneously acted as storage components and trap part of the NO and NO_2 in the form of nitrites and nitrates [24]. This storage can occur during 210 s which is compatible with real Diesel applications since the lean phase duration of conventional NSR catalysts is around few minutes. During the electrochemical trapping of NO_x in the lean phase, the NO_x concentration decreased to a minimum value of around 450 ppm at $t = 17$ min. Due to the configuration of the tubular electrochemical catalyst, a bypass could occur and therefore a non-negligible part of the reactive gas could be not in contact with the Pt catalytic film. This could explain why the NO_x level did not drop to zero upon negative polarizations. The amount of NO_x stored during this phase was estimated to be 10.2 μmol. After this storage phase, NO_x concentration began to increase until it matched the inlet value, indicating that the available trapping sites were saturated. From this time, the NO_x trap, the NO oxidation and the SCR processes were negligible because K–compounds, mainly nitrates, covered the surface of the active Pt film. Let us mention that the C_3H_6 level did not return to its inlet value maybe because propene combustion could occur in gas phase in the dead volume of the tubular electrochemical reactor. At $t = 45$ min, the inlet gas was switched to the rich mixture (Stage 3 in Fig. 7) and a catalyst potential of 3 V was applied for other 15 min. Under such conditions, a fast increase in the outlet NO_x concentration was observed for the first seconds, which corresponds with a net increase in NO_2 concentration. This may have happened because the stored NO_x were released from the catalyst under positive polarization. Under these conditions, potassium ions returned to the solid electrolyte and part of the previously stored NO_x were reduced by C_3H_6 to N_2 (SCR process), regenerating the Pt catalyst surface for a new cycle. The integral amount of NO_x released was 0.95 μmol, and therefore 90% of stored NO_x was reduced to N_2. In agreement with previous studies of Pt-based NO_x trap catalyst [38], no trace of N_2O was observed during the reduction of stored nitrates. In addition, it could be observed that during the rich period, NO_x and C_3H_6 concentrations achieved a minimum value. We suggest that during the positive polarization, an optimum potassium coverage was attained for the SCR and hydrocarbon combustion process [13]. At $t = 60$ min, a steady-state value of NO_x concentration was achieved of around 750 ppm, indicating a quite higher SCR activity of the clean Pt catalyst (3 V) under rich atmosphere (0.5% O_2), in comparison with the previous lean one (5% O_2). However, the C_3H_6 concentration


Stage 1. Reference stage
Lean composition under 3 V
-Pt free of potassium surface.
-SCR unpromoted process

Stage 2. Electrochemical trapping
Lean composition under -1.5 V
-Potassium ions are transferred to the Pt surface.
-NO oxidation reaction is promoted.
-Electrochemical trapping phenomenon.
-Saturation of the available trapping sites.
-SCR promoted process

Stage 3. Electrochemical regeneration
Rich composition under 3 V
-Reductant evolution
-Potassium ions return to the electrolyte
-Release of NO_2 to the gas phase
-Nitrates are reduced to N_2
-SCR unpromoted process.

Fig. 7. Schematic representation of the main stages involved during an electrochemical assisted NO_x storage/reduction experiment.

achieved a higher value in comparison with the lean conditions, due to the higher tendency of the hydrocarbon to react with O_2. These results demonstrated that the solid-state electrochemistry could be used to electrochemically trap and regenerate a Pt catalyst for the effective removal of NO_x under lean burn reaction conditions [24]. In addition, the variation of the current vs. time curves (not shown here) followed exactly the same trend as the NO_x storage–reduction process. It allowed to monitor the time at which the catalyst was totally saturated in the lean period and the time at which was totally regenerated in the rich one. In a previous study, Li and Vernoux [39] used a similar configuration of Pt–Ba/YSZ, where the measurement of the catalyst potential allowed to follow the NO_x storage–reduction process on the chemically added Ba sites. However, an additional sight of the present configuration, where the trapping sites are in situ electrochemically supplied or removed vs. the previous one [39], is that it allowed not only to follow but also to control the trapping and the regeneration processes. However, in any of the two cases, the ability of the system to optimize the lean and rich sequences duration, just measuring the potential or the current, implies an important advance for the technological application of this NSR process. It means a new improvement of catalysis by solid-state electrochemistry not possible with a convectional catalyst, where a NO_x detector is required. In addition, this new application of a cationic-based electrochemical catalyst shows potential for the abatement of NO_x and opens a new range of alternatives not only for fundamental studies, but also for technological advancement of the NSR process.

4. Conclusion

This study clearly demonstrated that electrochemical promotion by potassium is a suitable technique to improve the efficiency of Pt catalysts in a wide variety of environmental reactions for the removal of: CO, C_3H_6, N_2O and NO_x. The presented results have been obtained under conditions compatible with the treatment of automotive exhaust emissions, activating the catalyst at lower temperatures and decreasing the inhibiting effect of poisons such as water on the reaction atmosphere. In addition, a new application of cationic-based electrochemical catalyst has been addressed for the effective removal of NO_x under lean burn reaction conditions by NO_x storage/reduction processes.

Acknowledgments

Financial support by the Ministerio de Educación y Ciencia of Spain (projects: CTQ2004-07350-C02-01/PQ and CTQ2007-62512/PPQ) and the European Marie-Curie EFEPOC project (MSCF-CT-2006-046201) are gratefully acknowledged.

References

[1] M. Stoukides, C.G. Vayenas, J. Catal. 70 (1981) 137.
[2] C.G. Vayenas, S. Bebelis, S. Ladas, Nature (London) 343 (1990) 625.
[3] 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.
[4] C.G. Vayenas, S. Bebelis, I.V. Yentekakis, H.-G. Lintz, Catal. Today 11 (1992) 303.
[5] I.V. Yentekakis, G. Moggridge, C.G. Vayenas, R.M. Lambert, J. Catal. 146 (1994) 292.
[6] J. Poppe, S. Volkening, A. Schaak, E. Schutz, J. Janek, R. Imbihl, Phys. Chem. 1 (1999) 5241.
[7] B. Beguin, F. Gaillard, M. Primet, P. Vernoux, L. Bultel, M. Henault, C. Roux, E. Siebert, Ionics 8 (2002) 128.
[8] S. Balomenou, D. Tsiplakides, A. Katsaounis, S. Thiemann-Handler, B. Cramer, G. Foti, Ch. Comninellis, C.G. Vayenas, Appl. Catal. B 52 (2004) 181.
[9] A. Kaloyannis, C.G. Vayenas, J. Catal. 182 (1999) 37.
[10] P. Vernoux, F. Gaillard, L. Bultel, E. Siebert, M. Primet, J. Catal. 208 (2002) 412.
[11] N.C. Filkin, M.S. Tikhov, A. Palermo, R.M. Lambert, J. Phys. Chem. A 103 (1999) 2680.
[12] F.J. Williams, M.S. Tikhov, A. Palermo, N. Macleod, R.M. Lambert, J. Phys. Chem. B 105 (2001) 2800.
[13] F. Dorado, A. de Lucas-Consuegra, P. Vernoux, J.L. Valverde, Appl. Catal. B 73 (2007) 42.
[14] P. Vernoux, F. Gaillard, C. Lopez, E. Siebert, Solid State Ionics 175 (2004) 609.
[15] P. Vernoux, F. Gaillard, C. Lopez, E. Siebert, J. Catal. 217 (2003) 203.
[16] R.M. Lambert, A. Palermo, F.J. Williams, M.S. Tikhov, Solid State Ionics 136 (2000) 677.
[17] G. Goula, P. Katzourakis, N. Vakakis, T. Papadam, M. Konsolakis, M. Tikhov, I.V. Yentekakis, Catal. Today 127 (2007) 199.
[18] I.M. Campbell, Catalysis at Surfaces, Chapman & Hall, New York, 1988.
[19] Y. Minemura, M. Kuriyama, S. Ito, K. Tomishige, K. Kunimori, Catal. Commun. 7 (2006) 623.
[20] A. de Lucas-Consuegra, F. Dorado, J.L. Valverde, R. Karoum, P. Vernoux, Catal. Commun. 9 (2008) 17.
[21] A. de Lucas-Consuegra, F. Dorado, J.L. Valverde, R. Karoum, P. Vernoux, J. Catal. 251 (2007) 474.
[22] A. de Lucas-Consuegra, F. Dorado, C. Jimenez-Borja, J.L. Valverde, Appl. Catal. B 78 (2008) 222.
[23] A. de Lucas-Consuegra, F. Dorado, C. Jimenez-Borja, J.L. Valverde, J. Appl. Electrochem. 38 (2008) 1151.
[24] A. de Lucas-Consuegra, A. Caravaca, P. Sánchez, F. Dorado, J.L. Valverde, J. Catal. 259 (2008) 54.
[25] A. Törncrona, M. Skoglundh, P. Thormählen, E. Fridell, E. Jobson, Appl. Catal. B 14 (1997) 131.
[26] M. Skoglundh, E. Fridell, Top. Catal. 28 (2004) 79.
[27] I.V. Yentekakis, C.G. Vayenas, J. Catal. 111 (1988) 170.
[28] C.G. Vayenas, S. Neophytides, R. Soc. Chem. Camb. 12 (1996) 199.
[29] C. Karavasilis, S. Bebelis, C.G. Vayenas, Mater. Sci. Forum 76 (1991) 175.
[30] T.I. Politova, G.G. Gal'vita, V.D. Belyaev, V.A. Sobyanin, Catal. Lett. 44 (1997) 75.
[31] O.A. Marina, V.A. Sobyanin, Catal. Lett. 13 (1992) 67.
[32] I.V. Yentekakis, C.G. Vayenas, J. Catal. 149 (1994) 238.
[33] E. Varkaraki, J. Nicole, E. Plattner, Ch. Comninellis, J. Appl. Electrochem. 25 (1995) 978.
[34] S.-C. Shen, S. Kawi, Appl. Catal. B 45 (2003) 63.
[35] S. Brosda, C.G. Vayenas, J. Wei, Appl. Catal. B 68 (2006) 109.
[36] S.S. Mulla, N. Chen, L. Cumaranatunge, W.N. Delgass, W.S. Epling, F.H. Ribeiro, Catal. Today 114 (2006) 57.
[37] T.J. Toops, D.B. Smith, W.P. Partridge, Appl. Catal. B 58 (2005) 245.
[38] S. Hammache, L.R. Evans, E.N. Coker, J.E. Miller, Appl. Catal. B 78 (2008) 315.
[39] X. Li, P. Vernoux, Appl. Catal. B 61 (2005) 267.