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Coupling catalysis to electrochemistry: a solution to selective reduction of nitrogen oxides in lean-burn engine exhausts?

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Abstract

The non-faradaic electrochemical modification of catalytic activity (NEMCA) was investigated in selective catalytic reduction (SCR) of NO by propene on Pt films deposited on NASICON, a Na^+ conducting solid electrolyte. This study was carried out under lean-burn conditions. In such a system, electrochemical promotion is shown to strongly enhance both the catalytic activity and the selectivity to N_2. Such an improvement can be obtained using low overpotentials, applying −100 mV to the Pt catalyst-electrode enhances the selectivity to N_2 from 41 to 61%. The use of NASICON allows work to be done at quite low temperatures (about 300 °C) compatible with the treatment of automotive exhausts.

Keywords: Selective catalytic reduction; SCR; NO_x; Propene; Platinum; NASICON; Electrochemical promotion; NEMCA

1. Introduction

Pollution from automotive traffic is an increasing problem, especially in urban areas. Nitrogen oxides (NO and NO_2) are among the main pollutants resulting from the internal combustion process. The catalytic posttreatment of emitted nitrogen oxides is efficient only in the case of gasoline vehicles which are operated near the stoichiometric air/fuel ratio. Classical three-way catalytic converters (TWC) are simultaneously able to reduce NO_x into nitrogen and to oxidize carbon monoxide and unburned hydrocarbons into CO_2. Under oxygen-rich conditions, such as those encountered in exhaust of diesel or lean-burn engines, NO_x reduction into nitrogen cannot be achieved by TWC since the reductants are primarily oxidized by O_2 in excess. However, future legislation, such as EURO 4 standards in Europe, that will be active from 2005, makes necessary the posttreatment of exhaust gases for NO_x abatement. The selective catalytic reduction (SCR) of NO_x by hydrocarbons seems to be a good candidate, especially when supported platinum is used as the catalyst. This catalyst allows high and durable NO_x conversion in real diesel exhaust, especially at low temperatures (between 200 and 350 °C) corresponding to those of such an engine working in an urban cycle [1–3]. Furthermore, supported platinum catalysts are resistant to poisoning by steam or SO_2 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 N_2O [1–3], a greenhouse effect gas, rather than being reduced to harmless N_2. The present work was initiated to determine if electrochemical promotion could be a solution to SCR of nitrogen oxides in lean-burn engine exhausts.

The non-faradaic electrochemical modification of catalytic activity (NEMCA) or electrochemical promotion of catalysis (EPOC), discovered and developed by Vayenas et al. [4–6], is an innovative concept which can be used to in situ control of the catalytic performances. 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, and Rh in contact with a solid electrolyte, which was generally either an O^{2-} conductor like YSZ (Y_2O_3-stabilized ZrO_2) [7–9] or a Na^+ conductor like β''-Al_2O_3 [10,11]. Various recent stud-

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ies [12–16] have explored the utility of EP 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''-Al_2O_3. These papers show 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 an excess of oxygen, the promotion efficiency drastically decreases. Moreover, by using β''-Al_2O_3 [14], negative overpotentials, i.e., pumping of Na^+ to the surface of the Rh film, result in a marked activity loss at 350 °C. The authors proposed that this deactivation may be attributed to three additional effects, including strong alkali-metal inhibition of propene adsorption, excessive formation of Na_2O, and essentially oxidation of Rh to Rh_2O_3. Using a Rh/YSZ system, Foti et al. [13] found that a simple heating from 300 to 400 °C under a reactive mixture containing 1000 ppm C_3H_6, 1000 ppm NO and 5000 ppm O_2 results in a drop of the catalytic activity due to oxidation of the Rh surface. Their results show that a positive current ($i = +5$ µA) enhances the catalytic activity but not the selectivity toward nitrogen at 300 °C. Williams et al. [16] have recently investigated a bimetallic Rh–Ag film deposited on YSZ under lean-burn conditions, i.e., $C_3H_6/NO/O_2$; 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 N_2 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 [15] have used EP to promote the reduction of NO by propene in the presence of oxygen over Pt deposited on YSZ. We found that, when using a stoichiometric mixture, i.e., $C_3H_6/NO/O_2$; 2000 ppm/2000 ppm/1%, a negative current significantly increases the NO and C_3H_6 conversions but not the selectivity to N_2. The promotional effect has been related to the propene oxidation and then occurs in a temperature domain ranging from the beginning of C_3H_6 oxidation to its total oxidation, i.e., between 310 and 370 °C. Under lean-burn conditions, we did not observe any electrochemical promotion.

In the present paper, the electrochemical promotion of a NASICON-supported platinum is studied for the SCR of NO by propene under lean-burn conditions. NASICON (NA Super Ionic CONductor), i.e., $Na_3Zr_2Si_2PO_{12}$, is a Na^+ conducting electrolyte. This compound is a promising material for applications of electrochemical promotion because it exhibits a better thermal stability and resistance to H_2O than β''-Al_2O_3, a high ionic conductivity, even at low temperatures, and a three-dimensional mobility of Na^+ ions in the structure. Petrolekas et al. [17] have shown that NASICON was more efficient than β''-Al_2O_3 for electrochemical promotion of ethylene oxidation on Pt. The aim of this work was to study the possibility of in situ modification of the catalytic activity and selectivity to N_2 by overpotential application. Measurements were carried out under a gaseous mixture, which simulates the exhaust of a lean-burn engine and at a relatively low temperature (295 °C). Furthermore, we used low values of overpotentials in order to preserve the operation life of the electrolytic cell.

2. Experimental

2.1. Materials

The $Na_3Zr_2Si_2PO_{12}$ solid electrolyte was prepared by the sol-gel method [18]. The precursors were tetraethoxysilane (Ventron, 99%) and zirconium (IV) butoxide (Aldrich, 80 wt% solution in 1-butanol) mixed in butanol (Aldrich, 99%), NaOH (Fluka, 98%), and $NH_4H_2PO_4$ (Fluka, > 99%) mixed in water. Samples of high density were obtained by isostatic pressing and sintering at 1000 °C for 8 h. A Pt catalyst porous film was deposited from a paste (Engelhard-Clal 6926) in order to fully cover one side of the NASICON pellet (17 mm in diameter and 1.1 mm thick). After annealing at 820 °C, the Pt film contained 3 mg Pt/cm^2 for a thickness of 3 µm. Gold counter and reference electrodes were deposited onto the opposite side of the electrolyte disc.

2.2. Catalytic activity measurements

The catalytic activity measurements of Pt film deposited on NASICON were carried out within a specific quartz reactor, as described in a previous study [19]. The reaction gases were mixtures of C_3H_6 (Air Liquide, 7710 ± 230 ppm C_3H_6 in He), O_2 (Air Liquide, 99.99% purity), NO (Air Liquide, 7970 ± 160 ppm NO in He), and helium (Air Liquide, 99.999% purity) which was used as the vector gas. The gas composition was controlled by mass flow controllers (Brooks, with accuracy better than 1%). In the following, the gas composition will be expressed in parts per million or percentages. The reactive mixture contains 2000 ppm of NO, 2000 ppm of propene, and 5% of oxygen. The overall gas flow rate was kept constant at 10 L h^{-1} (±0.1 L h^{-1}). Gas analysis was performed by two chromatographs, one (Intersmat, IGC 120 MB) equipped with a thermal conductivity detector (TCD) and the other (Intersmat, IGC 120 FL) with a flame ionization detector (FID). The nitrogen oxides (NO and NO_2) were analyzed by an on-line chemiluminescence NO_x analyzer (Cosma, TOPAZE 3000). Prior to the catalytic activity measurements, the sample was pretreated in H_2 at 300 °C for 1 h in order to reduce platinum and to obtain a reference state.

The main overall reactions which can take place are the following:

$$C_3H_6 + \tfrac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O, \tag{1}$$

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

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

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2. \tag{4}$$

The C_3H_6 conversion was calculated as

$$C_3H_6 \text{ conversion} = 100P_{CO_2}/(P_{CO_2} + 3P_{C_3H_6}), \qquad (5)$$

where P_{CO_2} and $P_{C_3H_6}$ are the partial pressure of CO_2 and C_3H_6 in the outlet gas, respectively. The NO conversion is defined as the percentage conversion of NO to N_2 and N_2O on a N-atom basis. We also calculate the production of N_2, N_2O, and NO_2, which is defined as the percentage of NO converted to these products. The selectivity to N_2 is defined as

$$\text{Selectivity to } N_2 = 100P_{N_2}/(P_{N_2} + P_{N_2O}), \qquad (6)$$

where P_{N_2} and P_{N_2O} are the partial pressure of N_2 and N_2O in the outlet gas, respectively. The three electrodes, W (catalyst electrode or working electrode), R (reference), and CE (counterelectrode) were connected to a potentiostat-galvanostat Voltalab 80 (Radiometer Analytical). The catalyst potential V_{WR} was measured between the working electrode (Pt) and an Au electrode which 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. The overpotential ΔV_{WR} was defined as the difference between V_{WR} and the open-circuit voltage (OCV), then $\Delta V_{WR} = V_{WR} - \text{OCV}$. Hence, upon applying a negative (positive) overpotential, the Na^+ cations are supplied (removed) to (from) the Pt catalyst surface. Polarization effect on the catalytic reaction rate is characterized by the rate enhancement ratio (ρ) defined by $\rho = r/r_o$, where r_o (in mol/s) is the catalytic rate at OCV and r the catalytic rate under polarization. The magnitude of the electrochemical promotion effect is described by the faradaic efficiency, Λ, defined by $\Lambda = \Delta r/(I/F)$, where $\Delta r = r - r_o$ is the electrochemically induced change in catalytic rate, I the current, and F the Faraday constant.

3. Results

3.1. Catalytic activity measurements under open-circuit conditions

The catalytic behaviors of the platinum film deposited on NASICON are plotted in Fig. 1. The propene oxidation (1) is strongly temperature dependent increasing from 10 to 80% between 286 and 330 °C. The overall NO conversion versus temperature passes through a maximum of 18% at 319 °C. The production of N_2 (2) reaches 6.4% at 302 °C, while that of N_2O (3) is 13.5% at 319 °C. The operating temperature window, defined as the full-width at half-maximum (FWHM) of the NO conversion, of the Pt/NASICON system can be estimated to 60 °C, in the range 290–350 °C. This domain corresponds to that of the strong increase of the hydrocarbon oxidation rate. The production of NO_2 (4) starts when the N_2O production begins to decrease and the propene conversion reaches its maximum. In the operating temperature window, the selectivity to N_2 drops from 41 to 20–25% after the temperature of the maximal N_2 production, i.e., 302 °C. At 319 °C, temperature of the maximum NO conversion, the selectivity to N_2 is only 24%. This catalytic behavior is similar to that reported in the literature for platinum coated on YSZ [15] with a shift of 30 °C down to lower temperatures for the activation of propene and a more extended operating temperature window. Let us note that, even at 400 °C, the propene conversion is not total. This is certainly due to the specific geometry of the cell which implies that a small part of the reactive mixture is not in contact with platinum. In addition, compared to a powdered catalyst [1–3], the reactive mixture did not flow through the catalyst bed but just licked the Pt film.

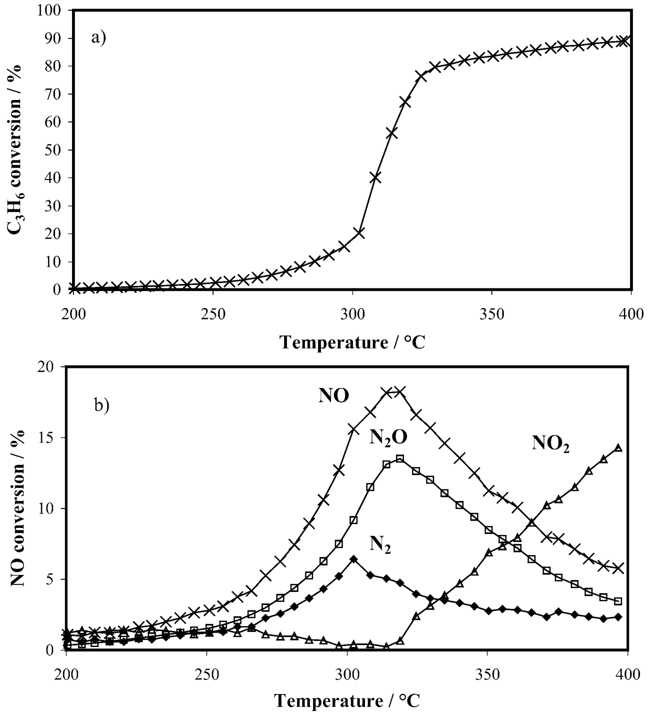

Fig. 1. Propene conversion (a) and overall NO conversion and conversions of NO into N_2, N_2O, and NO_2 (b) as a function of temperature for Pt/NASICON system at OCV.

3.2. Catalytic activity measurements under closed–circuit conditions

At 295 °C, the conversions of NO and C_3H_6 are 11 and 13%, respectively, and the selectivity to N_2 is 41%. Fig. 2 shows the variation of the steady-state rate enhancement ratios for reaction products (CO_2, N_2, and N_2O) with respect to the overpotential ΔV_{WR} at 295 °C. Each point was obtained by fixing the potential until the current vanished and stabilized to a value lower than 1 µA. The application of low overpotentials (either positive or negative) does considerably modify the catalytic properties of Pt. The propene conversion can be lowered by a factor of 3 by positive overpotentials and increased by 1.7 by negative

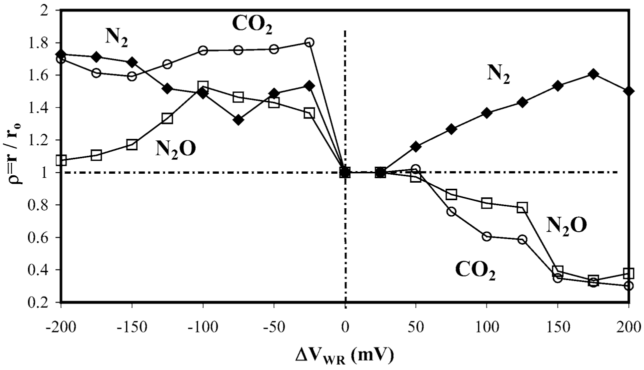

Fig. 2. Variation of the rate enhancement ratio ρ for reaction products versus the overpotential ΔV_{WR}. (○) CO_2, (◆) N_2, and (□) N_2O. $T = 295\,^\circ C$.

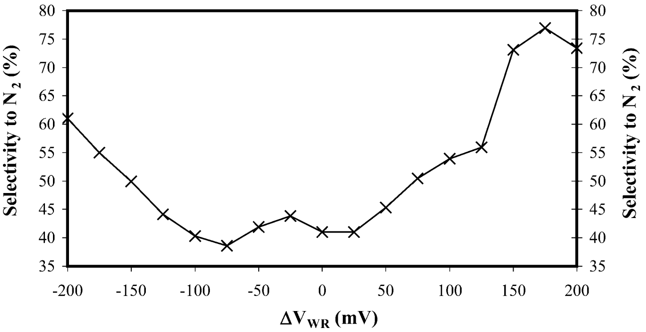

Fig. 3. Variation of the selectivity to N_2 versus the overpotential ΔV_{WR}. $T = 295\,^\circ C$.

ones. Simultaneously, negative overpotentials significantly increase the rate of NO removal whereas negative ones decrease it. The reaction rate is significantly controlled via voltage application. The most important point is that applying a low overpotential through the Pt/NASICON interface allows considerable improvement in the selectivity toward nitrogen (Fig. 3). Negative overpotentials, below −100 mV, enhance the selectivity to N_2 from 41 to 61% by promoting the N_2 production. Surprisingly, application of positive overpotentials in the range from +50 to +200 mV, thus decreasing the sodium coverage, strongly decreases the N_2O production and simultaneously increases that of N_2. At 295 °C, potential of −200 mV drastically enhances the selectivity to N_2 from 41 to 73%. In the same time the propene conversion drops from 13 to 3%.

We have also investigated the promotional effect at 320 °C, a temperature corresponding to the maximal NO conversion, i.e., 17% and to high C_3H_6 conversions ($> 70\%$). Whatever the direction of the applied polarization, the propene conversion does not vary while the NO conversion and the selectivity to N_2 are considerably modified. The important point is that a negative polarization increases the selectivity to N_2 from 24 to 55% while the NO conversion reaches 20.5%. The high faradaic efficiency (Λ) values obtained clearly show that the process is non-faradaic, but this parameter must be considered with caution using a Na^+ conductor, because Na is neither a reactant nor a product, conversely to what is observed with O^{2-} ions conductors such as YSZ.

4. Discussion

Our results emphasize that the application of negative overpotentials through the Pt/NASICON interface leads to a significant enhancement of the selectivity toward nitrogen. Furthermore, the rates of NO reduction and hydrocarbon oxidation considerably increase. These results have been obtained under a gaseous mixture, which simulates the exhaust of a lean-burn engine and at a relatively low temperature. Furthermore, the necessary low values of the applied potentials preserve the operation life of the electrolytic cell. Such results, leading to high selectivity to N_2 in O_2-rich conditions, were never reported in the literature by using a Na^+ conducting electrolyte. With a $Rh/\beta''\text{-}Al_2O_3$ system, Williams et al. [14] observe similar promotional effects on the catalyst activity and selectivity upon negative polarizations, but, when increasing the oxygen amount ($C_3H_6/NO/O_2$, 1/1/2%), the promotion efficiency drastically decreases. According to the authors, this is mainly due to the oxidation of Rh into Rh_2O_3 which is not catalytically active. From this specific point of view, the advantage of Pt is that the formation of such a bulky noncatalytically active oxide can be ruled out [20]. Williams et al. [16] have recently investigated a Ag-doped Rh film in order to improve resistance to oxidation of the rhodium. Deposited on YSZ, under lean-burn conditions, an applied overpotential of +100 mV can enhance the selectivity to N_2 from 28 to 55% at 386 °C. When using platinum deposited on YSZ [15], we did not observe any electrochemical promotion under lean-burn conditions. However, Pt is active at lower temperatures than Rh for the SCR of NO by propene [21]. Deposited on an alumina powdered support, Pt is active between 250 and 300 °C instead of the range 320–400 °C for Rh. At 300 °C, the ionic conductivity of YSZ could be not sufficient and the O^{2-} spillover between YSZ and Pt too slow. In the present study, the ionic conductivity of NASICON is larger than that of YSZ. Moreover, we observe a promotional effect on the NO conversion even when the C_3H_6 conversion is maximal and does not vary upon polarization. On the contrary, with the Pt/YSZ system, the electrochemical promotion has been related to the propene activation. One can think that the nature of ionic species has a great importance.

In order to explain the electrochemically induced modifications in activity and selectivity of Pt, it is necessary to consider the competitive adsorption between the three reactants. In $C_3H_6/NO/O_2$ reactive mixture, several studies [22–25] have suggested that, as long as C_3H_6 is not completely oxidized, the Pt surface is predominantly covered by propene or propene-derived carbonaceous species while the oxygen coverage remains low. Concerning the NO reduction, the initiating step is the NO adsorption and dissociation on Pt sites, followed by the combination of adsorbed NO and N to form either N_2 or N_2O. Burch and Watling [23] showed that the presence of O_2 is necessary to create propene-free sites on Pt where NO can be adsorbed.

We may rationalize the promotional phenomena observed with a Pt/NASICON system on the basis of the electrode work function modification upon applied overpotentials. Studies of Vayenas et al. [5,6] have established that a change in the electrode overpotential ΔV_{WR} results in a modification of the work function $e\Phi$ of the gas-exposed surface of the porous catalyst-electrode film:

$$\Delta(e\Phi) = e\Delta V_{\mathrm{WR}}. \tag{7}$$

The theoretical validity of the Eq. (7) has been discussed in the literature and confirmed by experimental results [26–30]. This relationship suffers from some deviations and seems restricted to the cases where outer potential $(\Delta\Psi)$ variations can be neglected. This is generally agreed to be achieved when moderate overpotentials are applied, low lateral interactions exist between surface ions, and surface diffusion of ionic species is fast. The variation of the Pt work function (WF) alters the strength of the chemical bonds between the metal and the adsorbates and then modifies the competitive adsorptions between the reactants.

A decrease of the Pt WF induced by a negative polarization increases the electronic density of Pt and there is a concomitant spillover of Na^+ ions from the electrolyte onto the Pt surface. The WF decrease weakens the Pt chemical bonds with electron-donor adsorbates, such as C_3H_6, and strengthens those with electron-acceptor ones, such as O_2 and NO [31]. This leads to an increase of oxygen and nitric oxide coverages. Taking into account that the Pt surface is poisoned by propene, the effect of the polarization is to promote C_3H_6 oxidation and NO reduction, as observed experimentally. The presence of Na on Pt acts the same way since it is known to enhance the NO and O adsorption on Pt [32,33]. Furthermore, it promotes the NO dissociation [11,34] which is necessary to increase the selectivity to N_2. Our experiments have shown that the selectivity to N_2 increases from a negative potential of -100 mV.

The Pt WF may be increased by applying anodic overpotentials which induce a positive charge on the metal. This positive charge is compensated by electropumping Na^+ ions away from Pt. The decrease of the Pt electronic density weakens the Pt–O and Pt–NO bonds and strengthens the Pt–C_3H_6 one. Then, the oxygen coverage on Pt, which was initially low, becomes negligible. The Pt surface is nearly fully occupied by propene-derived species and NO. This surface state is similar to that in the absence of gaseous O_2. This leads to the significant decrease of C_3H_6 and NO conversions that we observed in this study. If one consider that adsorbed NO, NO(a), is in equilibrium with adsorbed O(a) and N(a) (8) resulting from the NO dissociation, then the low oxygen coverage induced by positive polarizations, enhances NO dissociation and consequently the selectivity to N_2,

$$\mathrm{NO(a)} \rightleftarrows \mathrm{N(a)} + \mathrm{O(a)}. \tag{8}$$

Some interesting results have been reported in the literature by adding alkalis to conventional highly dispersed platinum on γ-Al_2O_3. Most of these studies have been carried out with low concentrations of oxygen, near to the stoichiometric point [35], or in absence of oxygen [25,33]. Konsolakis et al. [35] have shown that the catalytic activity and selectivity of alumina-supported catalysts for the reduction of NO by propene were strongly promoted by alkali metals. At the stoichiometric point, the addition of Na significantly increases the selectivity to N_2. Under lean-burn conditions, Tanaka et al. [36] have shown that the addition of small amounts of Na (0.1 wt%) did not change the catalytic properties of Pt-supported SiO_2 catalysts. Under lean-burn conditions, Burch and Watling [37] have shown that the addition of K (2.42 wt%), Cs (7.25 wt%), and Ba (7.93 wt%) to Pt/Al_2O_3 catalysts (1 wt% of Pt) did not improve the catalytic performance as the selectivity to N_2, and even decreased the NO_x conversion. These studies seem to indicate that the dissociation of NO is not enhanced under lean-burn conditions to the same extent as reported by Konsolakis et al. [35] at the stoichiometric point. Electrochemical promotion (EP) provides an in situ control of the promoter concentration at the surface of the working electrode–metal catalyst by varying the applied potential. One may control reversibly the metal coverage by alkali ions. Furthermore, the total amount of sodium, which is pumped out from the electrolyte structure, interacts with the catalyst. An electrochemical double layer between $Na^{\delta+}$ species and $Pt^{\delta-}$ is established over the whole gas-exposed catalyst surface. The amount of Na^+ ions supplied to the Pt catalyst is controlled by the Faraday law. On the contrary, in the case of highly dispersed metal catalysts on an oxide support such as alumina or silica, a large part of chemically added sodium is in contact with the support only and not to the catalytically active phase. In addition, Na^+ ions can move easily in the 3 dimensions in the structure of NASICON. Moreover, the chemical addition of alkalis to a well-dispersed Pt-supported catalyst can decrease the Pt dispersion by decreasing the number of exchange sites during the procedure of Pt impregnation. This decrease of the Pt dispersion could explain the decrease of the NO_x conversion observed in the Ref. [37]. In our study, the amount of electrochemically provided Na^+ is low since we applied low values of potentials and currents. Based on the Faraday law, one can estimate the molar ratio of Pt to Na of 100:1 despite 1:10 in the Ref. [37].

5. Conclusions

This study clearly demonstrates that electrochemical promotion can strongly enhance the catalytic activity and the selectivity to N_2 of Pt interfaced with NASICON for the NO reduction by propene under lean-burn conditions. Negative overpotentials, below -100 mV, which lead to a Na supply to Pt surface, enhance the selectivity to N_2 from 41 to 61%. These results have been obtained below 300 °C, a relatively low temperature compatible with the treatment of automotive exhausts. Furthermore, the necessarily low values of the applied potentials preserve the operation life of the electrolytic cell and are compatible with an use in personal vehicles. Finally, coupling catalysis to electrochemistry by using the Pt/NASICON system could be an efficient solution for the selective catalytic reduction of nitrogen oxides in lean-burn engine exhausts, even if additional research is necessary.

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