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ORIGINAL PAPER

Electrochemical promotion of Pt impregnated catalyst for the treatment of automotive exhaust emissions

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Abstract This study has shown that Pt/K-βAl_2O_3 electrochemical catalyst can reach high catalytic activity for the selective reduction of N_2O by C_3H_6. In addition it was also demonstrated that Electrochemical Promotion could be a solution to reduce the adverse effects of poisons (O_2 and H_2O) on the catalytic activity. For instance, in the presence of O_2 (1%) and H_2O (3%) in the reactive stream, electrochemical pumping of potassium ions to the Pt catalyst increased the N_2O reduction rate by a factor of 7.4 at 400 °C. We have also demonstrated that the wet impregnation procedure led to a very stable Pt film, with very good resistance to thermal sintering under real operation conditions. Therefore, the use of Pt impregnated films deposited on K-βAl_2O_3 solid electrolytes is a feasible solution for the treatment of automotive exhaust gases.

Keywords Selective catalytic reduction · N_2O · Electrochemical promotion · Pt impregnated catalyst · NEMCA effect

1 Introduction

The phenomenon of Electrochemical Promotion (NEMCA effect) was discovered more than 25 years ago by the group of Vayenas who reported [1] that solid electrolytes could be used as electro-active catalyst supports in order to alter the activity of catalyst electrode films in a very pronounced and controllable manner. This phenomenon is based on the control, by an applied potential, of the catalyst work function, due to electrochemical pumping of ions (promoters) from a solid electrolyte [2, 3]. This phenomenon has been applied to improve the behaviour of a wide variety of catalyst in a large number of important catalytic reactions [4]. Recently the NEMCA effect has been successfully applied in environmental catalysis such as in the combustion of hydrocarbons [5–10], the oxidation of CO [11, 12] and the selective reduction of NO [13–17]. However, apart from previous work of Marwood and Vayenas [18], there have been no further studies of electrochemical promotion on the reduction of nitrous oxide (N_2O).

N_2O has been long considered as a relatively harmless species and has not attracted the attention of scientists, engineers and politicians due to the underestimation and unawareness of its contribution to environmental problems. However, nitrous oxide has recently been recognized as an important greenhouse gas, the third one after CO_2 and CH_4. In addition, the harmful effect of N_2O in our environment is further aggravated by its indirect contribution to ozone layer depletion as the main precursor of stratospheric NO_x [19]. For these reasons, N_2O was included in the six-gas basket defined by the United Nations Framework Convention on Climate Change in Kyoto (1997) [20]. A major source of N_2O generation is agriculture, but these emissions are difficult to treat due to their nature. Anthropogenic activities, which are estimated to contribute 30–40% of total emissions, are found in industrial processes, mainly the production of adipic and nitric acid, and stationary combustion processes, where N_2O coexists with other components such as O_2, NO_x, hydrocarbons and water.

Recently [21], the selective catalytic reduction (SCR) of N_2O with light hydrocarbons has been proposed as a promising abatement alternative for the removal of this

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pollutant. However, previous studies have shown [22] that the presence of O_2 and H_2O in N_2O containing tail-gases causes adverse effects on the catalyst due to inhibition or poisoning effects, thus limiting its practical application.

The aim of this work was to asses whether Electrochemical Promotion could be a solution to reduce such adverse effects, by increasing the activity of the catalyst. Thus, we have investigated, the Selective Catalytic reduction of N_2O by hydrocarbons over an electrochemical catalyst. The selection of Pt as catalyst and K-βAl_2O_3 as solid electrolyte was based on previous studies which have shown the extraordinary behaviour of this catalyst for the removal of other pollutants such as C_3H_6 [6] and CO [11] which usually accompany N_2O in automotive exhaust emissions. For the case of C_3H_6 combustion [6], it was found that Pt/K-βAl_2O_3 can be strongly promoted at low temperature under both stoichiometric and oxygen rich conditions. For instance, under C_3H_6/O_2: 2000 ppm/7% at 200 °C, a rate enhancement ratio $\left(\rho_{CO_2}\right)$ of 7 was achieved under application of $V_{WR} = -2$ V, increasing propene conversion from 10 to 70%. For the CO oxidation reaction [11], the effect of catalyst polarization drastically increased the catalytic rate by more than 11 times by decreasing the light off temperature at approximately 40 °C.

2 Experimental

2.1 Electrochemical catalyst preparation and characterization

The electrochemical catalyst consisted of a porous, continuous thin Pt film (geometric area 2.01 cm^2) deposited on one side of a 20 mm diameter and 1 mm thick 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 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 elsewhere [23], by successive steps of deposition and thermal decomposition (450 °C for 1 h) of a H_2PtCl_6 precursor solution, with a metal concentration of 0.1 M. The final Pt loading was 0.68 mg Pt cm^{-2}.

The resultant dispersion of the catalyst-electrode film (fraction of active sites) was determined by the electrochemical technique developed by Ladas et al. [24]. In addition, the Pt catalyst-working electrode was characterized before and after catalysis by X-ray diffraction (XRD) with a Philips PW 1710 instrument using Ni-filtered Cu Kα radiation. The electrical resistance of the Pt catalyst-working electrode film was also investigated before and after experiments with a digital multimeter UNI-T.

2.2 Catalytic activity measurements

Catalytic testing was performed at atmospheric pressure in a quartz reactor (single chamber) described previously [23]. The cell was placed on fritted quartz of 21 mm diameter, with the counter and reference electrode facing the fritted quartz. An inner quartz tube was pressed onto the Pt working electrode to ensure electrical contact. The temperature of the catalyst was measured with a K-type thermocouple (Thermocoax) placed inside the inner quartz tube. The entire reactor was placed in a furnace (JH HEE.CC4) equipped with a heat control system (Conatec 4801). Constant potentials or currents across the cell were measured and imposed using a potentiostat-galvanostat Voltalab 21 (Radiometer Analytical). The reaction gases were Praxair certified standards of 4% C_3H_6/He, 4% N_2O/He, O_2 (99.99% purity), and He (99.999% purity), which was used as the carrier 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 at 24 °C. The tubing down stream from the saturator was heated at 100 °C to prevent condensation. The reactants were introduced into the reactor with the following concentrations: N_2O (1000 ppm), C_3H_6 (2000 ppm), O_2 (0–1%), H_2O (0–3%) balanced with He. The overall gas flow rate was kept constant at 12 L h^{-1}. Reactants and products gases were analyzed with a micro gas-chromatograph (Varian CP-4900), and a chemiluminescence analyzer (Teledyne 9110 EH). Nitrogen was the only N-containing product since NO and NO_2 were never detected in this study. Before these analyses, the water was trapped by a condenser at −5 °C. 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 to 200 °C under He flow. The reactive mixture flow ($N_2O/C_3H_6/O_2$:1000 ppm/2000 ppm/1%) was switched into the reactor and the sample was heated to 600 °C at 5 °C min^{-1}. The catalyst was maintained at 600 °C for 12 h in order to stabilise its activity and to assess the catalyst durability and then, the temperature was decreased to 200 °C at 5 °C min^{-1}.

3 Results and discussion

3.1 Electrochemical catalyst characterization

The surface mol (number of active sites) of the catalyst-electrode film was determined by the electrochemical technique developed by Ladas et al. [24] carried out under He at 300 °C. The experimental procedure was as follows. Firstly, potassium ions were removed from the Pt surface by application of a positive potential of 2000 mV, until the current between the catalyst and counter electrode vanished. Then, the polarization was stopped until the voltage reached a constant value. Finally, a current of −30 µA was applied and the potential variation between the catalyst and the reference electrode (V_{WR}) was recorded (Fig. 1). The initial change in V_{WR} is given by Eq. 1:

$$\frac{e\,d(V_{WR})}{dt} = \frac{eP_0}{\varepsilon_0}\frac{dC_k}{dt} = \frac{P_0 I}{\varepsilon_0 A_c} \qquad (1)$$

where I is the current, P_0 is the initial dipole moment of K on Pt ($P_0 = 3.95 \times 10^{-29}$ C m), C_K is the numbers of atoms of potassium per square meter, A_c is the catalyst surface area in m^2, $e = 1.6 \times 10^{-19}$ C atom^{-1} and $\varepsilon_0 = 8.85 \times 10^{-12}$ C^2 J^{-1} m^{-1} Thus, from the initial slope of the V_{WR} variation vs. time (inset Fig. 1), the surface area of the catalyst-electrode was computed via Eq. 1. The number of active Pt sites was found to be 4.14×10^{-7} mol Pt (163 cm^2), which led to a metal dispersion of 6%. This value of dispersion was very close to that recently published (5%) in a previous study [6] for a similar catalyst-working electrode using the technique of surface titration. This demonstrates the good qualitative agreement between these two techniques (galvanostatic transient and surface titration) commonly used for the characterization of catalyst-electrode films used in NEMCA experiments. The catalyst working electrode was also characterized by XRD and electrical resistance measurements before and after the catalytic experiments. The Pt particle size was estimated by the Scherrer equation [25] from the analysis of the shape of the peak (111) obtained in the XRD spectra, as described in previous work [6]. As the catalyst geometry and homogeneity of the coating may influence the electrical resistance, measurements of this parameter were done taking as a reference different points of the catalyst film, with a fixed distance of 8 mm. Table 1 shows the measured properties of the catalyst electrode film for the fresh (before catalysis) and used (after catalysis) catalyst. Peak assignments for Pt based on JCPDS standards are consistent with a Pt face-centred cubic structure (FCC). No patterns of platinum oxides appeared in the aged sample, demonstrating that the Pt film maintained its chemical nature during the catalytic experiments. A slight increase in Pt particle size was observed in the sample after catalysis. However, this sintering was limited since the size of the Pt particles only increased from 35 nm in the fresh sample to 42 nm in that after catalysis. As expected, an increase in the electrical resistance of the Pt film was observed due to sintering of the Pt particles. However, good electrical conductivity of the catalyst-working electrode was verified in the sample after catalysis, demonstrating that the whole surface was polarized during the NEMCA experiments. All these facts confirm that the Pt film prepared by thermal decomposition of a precursor solution is stable and shows an good resistance to thermal sintering, even after long time working in the reactor under wet reaction conditions (during stabilization and catalytic experiments). The resistance against water is an important factor for any catalyst with potential for nitrogen oxide removal.

Table 1 Properties of the Pt catalyst-electrode film before (fresh catalyst) and after (used catalyst) catalytic experiments

Phase (Structure)	Fresh catalyst Pt (FCC)	Used catalyst Pt (FCC)
Pt particle size (nm)	35	42
Electrical resistance (Ω)	11.5	22.8

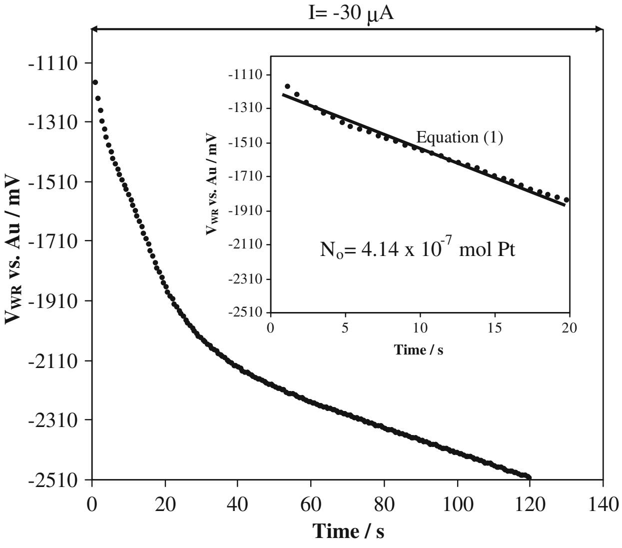

Fig. 1 Transient effect of constant applied current (I = −30 µA) on catalyst potential (V_{WR}) under He atmosphere at T = 300 °C. Inset: initial slope of the V_{WR} variation vs. time

3.2 Catalytic activity measurements

The catalytic activity of the Pt/K-βAl_2O_3 material was firstly investigated by several potentiostatic transients under dry reaction conditions. Figure 2 depicts the response of the N_2O conversion vs. time to step changes in the applied catalyst potential (V_{WR}) at different reaction temperatures with a fixed gas composition of $C_3H_6/N_2O/O_2$: 2000/1000/2000 ppm. The inset in Fig. 2 depicts the current vs. time variation during the negative imposition of $V_{WR} = -1$ V. Consecutive steps of positive (2 V) and negative (−0.5 and −1 V) polarizations were applied for 2 and 4 h respectively in order to study the behaviour of the catalyst during long term polarization stages. Under all explored reaction temperatures and starting from an electrochemically clean potassium surface (2 V) the application of negative polarization (electrochemical pumping of potassium ions to the Pt surface) led to a very strong increase in the N_2O reaction rate. However, subsequent applications of positive polarizations

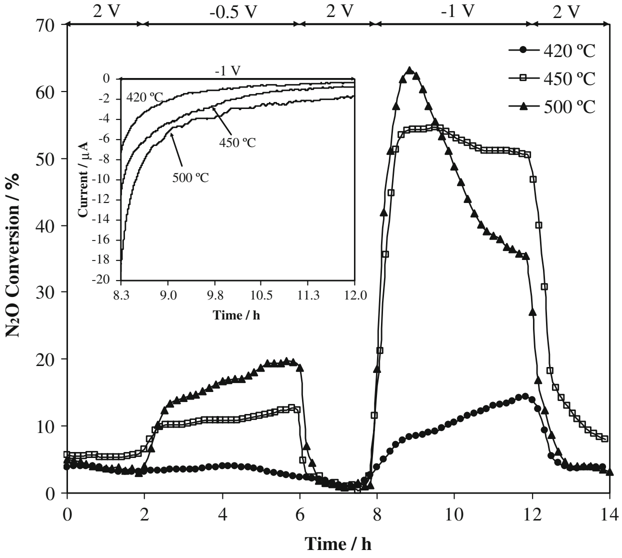

Fig. 2 Transient effect of step changes in applied potential on N_2O conversion at different reaction temperatures. Inset: current vs. time variation during the negative imposition of $V_{WR} = -1V$. Conditions: $C_3H_6/N_2O/O_2$: 2000 ppm/1000 ppm/2000 ppm, He balance, total flow rate = 12 L h^{-1}

of $V_{WR} = 2$ V gradually decreased the N_2O reduction rate leading to reversible NEMCA effects. The observed promotional effect with a Pt/K-βAl_2O_3 electrochemical catalyst may be explained on the basis of the binding strength modification upon applied catalyst potential [6, 11]. It is well known that under hydrocarbon and nitrogen oxide mixtures, as long as the hydrocarbon conversion is low, the Pt surface is mainly covered by the hydrocarbon species which are strongly adsorbed on the active sites [13, 23]. However, a decrease in catalyst potential enhances the activity of the catalyst by increasing the coverage of electron acceptor species (O_2 and N_2O) at the expense of electron-donor ones (C_3H_6) [4, 6, 14], which leads to the observed electrophilic NEMCA effect (the reaction rate increased upon negative polarization). Although the bigger effect of the applied negative potential was attained in the first moments after polarization, the catalyst behaviour was not stable during the long term potentiostatic steps. This dynamic catalytic performance can be explained following the variation of the current vs. time curves (inset) during the negative imposition of $V_{WR} = -1$ V, which displays the rate of ion supply to the Pt catalyst-working electrode. Thus, from Fig. 2 it is clear that, although most of the potassium ions migrate to the catalyst in the first moments after polarization (causing the most pronounced effect), the rate of potassium ion migration decreased very slowly (leading to a long term dynamic response on the catalytic rate). However, at the end of each potentiostatic transient (at t = 4 h) under negative polarization, the activity of the catalyst was almost stable as the rate of ion supply tends to cero. On the other hand, during the application of a catalyst potential of $V_{WR} = -1$ V, N_2O conversion showed a maximum at temperatures above 420 °C, indicating the existence of an optimum potassium coverage that maximized the N_2O reduction rate. Hence, the catalytic activity increased strongly in the initial stages after polarization but decreased after a certain time. This decrease in the level of promotion may be attributed to excessive coverage of potassium promoter on the catalyst surface (the ionic conductivity increases with reaction temperature). For instance, at 450 °C under application of $V_{WR} = -1$ V, Faraday's law gives a potassium promoter coverage $\theta_k = 1$. This amount of potassium promoter coverage leads to a relative increase in surface coverage of adsorbed oxygen atoms at the expense of C_3H_6 and N_2O molecules [13]. It is well known [13, 26], that under a reaction atmosphere of propene, nitrogen oxides and oxygen, the oxygen coverage on the catalyst increases with reaction temperature and, therefore, with propene conversion. In addition, as reported in previous studies [27], electropositive promoters enhance oxygen adsorption more strongly than that of nitrogen oxides. As a consequence, an increase in reaction temperature (above 450 °C) under high promoter coverage ($V_{WR} = -1$ V) resulted in a relative increase in surface coverage of oxygen adsorbed atoms at the expense of C_3H_6 and N_2O molecules, thus causing a decrease in the level of promotion. This explanation could be further confirmed considering that, above certain reaction temperatures (above 420 °C), the decrease in N_2O conversion during the potentiostatic imposition of $V_{WR} = -1$ V was more pronounced and began at a smaller time.

The efficiency of Electrochemical Promotion to improve the behaviour of the Pt catalyst for the removal of N_2O was also investigated under real exhaust reaction conditions (large oxygen concentration and water in the feed). Figure 3 shows the influence of reaction temperature on the steady state potentiostatic variation of the N_2O rate enhancement ratio (ρ) under a fixed composition of $C_3H_6/N_2O/O_2/H_2O$: 2000 ppm/1000 ppm/1%/3%. Initially, before the application of each potential, a positive polarization of 2 V was applied until the current between the catalyst and the counter electrode vanished. This experimental procedure allowed the catalyst surface to be cleaned from promoter ions so that a reference state was defined. According to previous studies of electrochemical promotion with cationic conductors [6, 11, 13, 28], the rate enhancement ratio was defined by the Eq. 2:

$$\rho = r/r_0 \qquad (2)$$

where r_0 is the catalytic reaction rate under unpromoted conditions ($V_{WR} = 2$ V), and r is the rate under promotion ($V_{WR} < 2$ V). 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

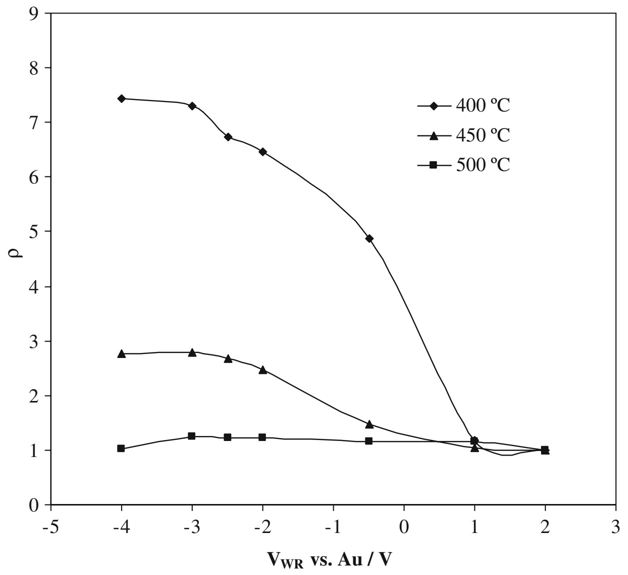

Fig. 3 Influence of the reaction temperature on the steady state potentiostatic variation of the N_2O rate enhancement ratio (ρ) under real conditions. Conditions: $C_3H_6/N_2O/O_2/H_2O$: 2000 ppm/1000 ppm/1%/3%, He balanced, total flow rate = 12 L h^{-1}

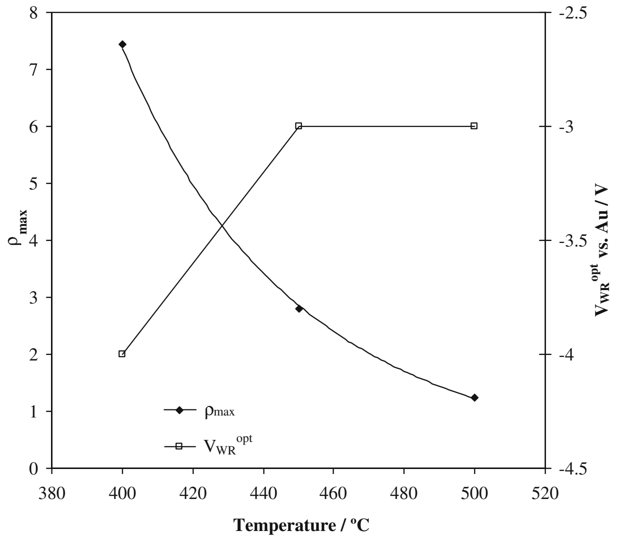

Fig. 4 Influence of reaction temperature on maximum value of the rate enhancement ratio (ρ_{max}) and on the optimum applied catalyst potential (V_{WR}^{opt}). Conditions: $C_3H_6/N_2O/O_2/H_2O$: 2000 ppm/1000 ppm/1%/3%, He balanced, total flow rate = 12 L h^{-1}

catalyst potential, the catalytic performance improved. For instance, at 400 °C the application of $V_{WR} = -4$ V increased the N_2O reduction rate by a factor of 7.4. However, as the reaction temperature increased, the efficiency of electrochemical promotion to improve the catalytic activity decreased. This progressive decrease in promotion level with reaction temperature can be clearly observed on Fig. 4, which depicts the variation of both the maximum value for the rate enhancement ratio (ρ_{max}) and the optimum potential at which such a maximum effect was attained (V_{WR}^{opt}) vs. the reaction temperature. The decrease in the level of promotion with reaction temperature was consistent with the second negative transient shown in Fig. 2 under dry reaction conditions above 420 °C. In addition, in good agreement with Fig. 2, the value of the V_{WR}^{opt} increased from -4 V to -3 V above 400 °C. Therefore, under wet reaction conditions, the behaviour of the electrochemical catalyst with reaction temperature was very similar to that observed under dry reaction conditions at high reaction temperatures above 450 °C and low values of catalyst potential $V_{WR} = -1$ V. In fact, two common trends can be drawn for both reaction conditions as the reaction temperature increases:

(1) A decrease in the efficiency of electrochemical promotion.
(2) A decrease in the potassium coverage which maximizes the N_2O reduction rate.

A similar decrease in the level of promotion has already been observed in a previous study of SCR of NO by C_3H_6 [13]. As mentioned above, this is easy to understand in terms of alkali metal enhanced adsorption of O_2 at the expense of other reactants. However, very interestingly the system could be electrochemically promoted under wet reaction conditions. Thus, in order to explain the origin of the observed promotional effect and to characterize the nature of the different adsorbates that participate in the reaction, the variation of the open circuit potential (V_{WR}°) vs. time was measured under a changing gas atmosphere (Fig. 5). The measured voltage represented the open circuit potential difference between the catalyst potential and that of the gold reference electrode, both exposed to the gas atmosphere. As observed in Fig. 5, the presence of different adsorbed species on the catalyst surface strongly modified the value of the open circuit potential. According to the current theory of electrochemical promotion [4], depending on the change that chemisorbed species induce on the open circuit potential and, consequently, on the catalyst work function ($e\Delta V_{WR} = \Delta\phi$) of the Pt catalyst surface, a major distinction can be made between electropositive (electron donor) and electronegative (electron acceptor) adsorbates. From Fig. 5, it can be clearly observed that while O_2 and N_2O maintained a high positive open circuit potential (electronegative adsorbates), C_3H_6 and H_2O strongly decreased it (electropositive adsorbates). Thus, taking into account the competitive adsorption between all the reactants on the Pt surface, looking at the value of the open circuit potential under reaction conditions, one could envisage the electronic nature of the species which are more strongly adsorbed on the Pt catalyst surface. As already shown in previous work [13, 26] one could anticipate qualitatively the NEMCA behaviour

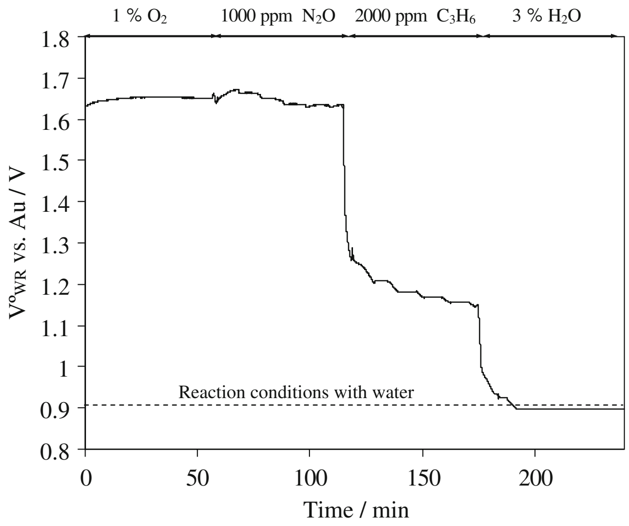

Fig. 5 Influence of reaction atmosphere on open circuit potential (V°_{WR}) at 400 °C. Reaction conditions with water denotes: T = 400 °C, $C_3H_6/N_2O/O_2/H_2O$: 2000 ppm/1000 ppm/1%/3%, He balanced, total flow rate = 12 L h^{-1}

(electrophilic or electrophobic) by measuring the open circuit potential. Thus, from Fig. 5, the value of the open circuit potential under reaction conditions is very low, suggesting that electron donor species are mainly adsorbed on the Pt catalyst surface. In addition, the measured value of the open circuit potential in the presence of all the reactants is very similar to that of the open circuit potential in the exclusive presence of water. This suggests, as already reported in previous studies with powdered catalyst [29], that under wet reaction conditions, water is strongly adsorbed on the Pt catalyst active sites. This strong adsorption of water decreases the adsorption of the other reactants strongly causing an inhibiting effect (as checked experimentally by a decrease in the N_2O conversion). Thus, the origin of the observed promotional effect under wet reaction conditions (Figs. 3 and 4) may be attributed to a decrease in H_2O coverage (electron donor species, which is initially strongly adsorbed on the catalyst surface), since as already mentioned, a decrease in catalyst potential to the Pt electrode increased the coverage of electron acceptor species (O_2 and N_2O) at the expense of electron-donor species (C_3H_6, H_2O) [4, 6, 14]. This promotional effect is in good agreement with the recently identified rules of chemical and electrochemical promotion [4, 30], as the effect of addition of a promoter on the catalytic activity depends on the initial coverage of the different molecules that participate in the reaction. The observed promotional effect under wet reaction conditions opens a new alternative to decreasing the adverse effect of poisons on the behaviour of a catalyst under real exhaust emissions.

4 Conclusions

Electrochemical promotion by potassium ions of Pt impregnated catalyst is a promising solution to the treatment of automotive exhaust emissions. The use of the wet impregnation procedure for the preparation of the catalyst-working electrode led to a stable Pt film with very good resistance to thermal sintering under real operation conditions (presence of O_2 and H_2O in the feed). In addition, the resultant Pt/K-βAl_2O_3 electrochemical catalyst reaches high catalytic activity for the SCR of N_2O by propene, decreasing the adverse effect of poisons such as O_2 and H_2O. Nevertheless, the efficiency of electrochemical promotion decreased at high reaction temperatures; this is attributable to a relative increase in O_2 coverage at the expense of N_2O and C_3H_6.

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