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Electrochemical promotion of toluene combustion on an inexpensive metallic catalyst

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ABSTRACT

Electrochemical promotion of the complete catalytic oxidation of toluene at 310 °C is reported, using a Ag/YSZ/Ag two electrode system where Ag films were deposited on YSZ from $AgNO_3$ aqueous solution followed by reduction in H_2. After on-stream activation, a non-negligible conversion (about 30%) at OCV is reached and then the rate of the catalytic toluene conversion into CO_2 and H_2O can be multiplied by a factor higher than 1.5, by application of a small negative current (about−4 μA cm^{-2}). The associated Faradaic efficiency is very high and may exceed −13,000.

1. Introduction

From the end of the 20th century, the removal of volatile organic compounds (VOCs) emitted from industrial and domestic processes has drawn a lot of attention. An efficient solution is their catalytic oxidation to H_2O and CO_2 [1]. Supported Pt and Pd are well-established catalysts for this purpose but the quest for cheaper and more available materials is of ever-increasing importance for tomorrow's applications. Such materials are much less active than Pt or Pd but their performance can be improved by using electrochemical promotion of catalysis (NEMCA or EPOC) [2,3]. During the past years, most of the work on EPOC for hydrocarbon combustion focused on lower molecular weight alkanes or alkenes, such as methane, ethylene, propane, propylene, etc. However, for environment protection purpose, the abatement of aromatic organic compounds is still much more important, because they can be far more harmful. Among these aromatic VOCs, toluene is a very important one because it is mainly released into the atmosphere from industrial (benzene fabrication...) and consumer (evaporation from gasoline...) uses and it can cause central nervous system problems for regular exposure to 100 ppm levels. Studies of EPOC applied to toluene combustion are very scarce. The pioneering one was carried out using RuO_2/YSZ operated at 400–500 °C [4]. Promotional and non-Faradaic effects were found for both anodic (1.5 V) and cathodic (−1.5 V) polarizations, enhancing the rate of toluene oxidation by factors of 8 and 4, respectively. In a more recent work [5], we explored the EPOC performance of an Ag/YSZ system and found a significant NEMCA effect when applying negative potential or current at a temperature much lower (300 °C) but still compatible with a sufficient oxygen ions conductivity of YSZ. These results were obtained using an Ag paint as the thin film precursor but such a method also suffers from some drawbacks: (i) the composition of the commercial Ag paste is usually unknown and some organic additives, binders or impurities may lead to catalyst poisoning and (ii) the metallic films prepared by this method need to be pre-treated at high temperatures in air or pure oxygen for the decomposition of the organic compounds. In the specific case of Ag, such a high temperature treatment would lead to a loss of metal by reactive thermal evaporation of the silver oxide (AgO) in a background of molecular oxygen [6]. From a practical point of view, it is necessary to find a simple, efficient and cost-effective way to prepare catalytic films, very similar to the techniques used to obtain DSA® coatings [7,8], although such apparently simple techniques may suffer from some difficulties [9]. RuO_2 deposits on YSZ obtained by the thermal decomposition of $RuCl_3$ precursor [4] or Pt films prepared by impregnation on Na(or K)-β-Al_2O_3 [10,11] are good examples of the application of such simple and efficient methods in EPOC studies.

2. Experimental

2.1. Catalyst preparation

The electrochemical catalyst consisted of a thin Ag film (working electrode (WE), geometric area of ca. 2 cm^2) deposited on one side of a 17 mm diameter and 1 mm thick Y_2O_3 stabilized ZrO_2 electrolyte disk (YSZ, 8 mol% Y_2O_3), with Ag counter

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electrodes (CE) on the other side. No reference electrode was added.

To obtain the Ag film, we adapted a deposition/reduction method similar to the one proposed by Vannice and coworkers [12] to prepare various supported Ag catalysts. As the first step, the Ag film was deposited on the one side of YSZ pellets by direct deposit of 500 μL of a $AgNO_3$ (Alfa Aesar # 043087, purity 99.995%) aqueous solution. Such a volume allowed a complete wetting of the pellet surface. A solution at 26.5 g $AgNO_3$ L^{-1} was used in order to aim at about 4 μm thick films (thickness is reported to a compact Ag film, considering 10.5 kg L^{-1} for Ag density [13]). The disk was then dried in flowing air at 140 °C for 2 h. Then, 500 μL of the $AgNO_3$ aqueous solution was deposited onto the second face of the YSZ pellet, in order to obtain the counter-electrode. The disk was dried again at 140 °C, then reduced in H_2 at 300 °C for 2 h (heating ramp: 2 °C min^{-1}) in a quartz reactor and then cooled down to room temperature. After that, the complete system was checked for electrodes electronic conductivity at room temperature and assembly ionic conductivity at 300 °C. The thickness of the Ag film was estimated as 3.3 μm, from the weight increase of the pellet after impregnation and after reduction, assuming the density of metallic Ag.

2.2. Characterization techniques

2.2.1. XRD

XRD patterns of the pellet samples were obtained on a Bruker D8 Advance, using the Cu Kα line (0.15418 nm). The angular scan was performed from 10° to 70° (2θ), with 0.02° steps. The average crystallite size was estimated using the Scherrer equation:

$$D = \frac{0.90\lambda}{\beta \cos\theta}$$

where D is the average crystallite size (nm), λ the incident wavelength (nm), β the corrected full width at half maximum (radian) and θ the Bragg angle.

2.2.2. SEM

The Ag/YSZ samples were investigated by SEM using a Jeol JSM-5800LV scanning electron microscope, operated at 20 kV and 75 μA and controlled by SPIRIT (Princeton Gamma Tech) software.

2.2.3. TPD, TPO and TPR

For flow TPD experiments, solids were placed on a quartz wool bed in a U-shaped quartz reactor, positioned vertically in a programmable tube furnace. Temperature was measured by two K-type thermocouples contacting the outer part of the reactor. The TPD experiments were performed in He at a flow 30 mL min^{-1} monitored by a Brooks mass flow controller. A part of the gas exiting the reactor (about 14 mL min^{-1}) was sampled by a heated capillary and analyzed by an Inficon Transpector 2 quadrupole mass spectrometer. Signals at m/e = 2, 16, 17, 18, 28, 30, 32, 44 amu, corresponding, respectively to H^+, O^+, OH^+, H_2O^+, N_2^+ or CO^+, NO^+, O_2^+ and CO_2^+ ions, were recorded. For TPO and TPR experiments, 1% O_2/He and 1% H_2/He mixtures were used, respectively (flow rates: 30 mL min^{-1}).

2.3. Catalytic tests

The catalytic reaction was carried out using a specific electrochemical glass reactor operating under atmospheric pressure. A schematic drawing of the reactor is shown in Fig. 1. The Ag/YSZ/Ag pellet was deposited on a glass frit with catalyst-working electrode facing downward. A metallic rod allowed: (i) to press the pellet against the frit, (ii) to decrease the dead volume of the reactor and (iii) to establish the electrical contact with the counter-electrode. The rod was made of aluminum, submitted to a previous treatment

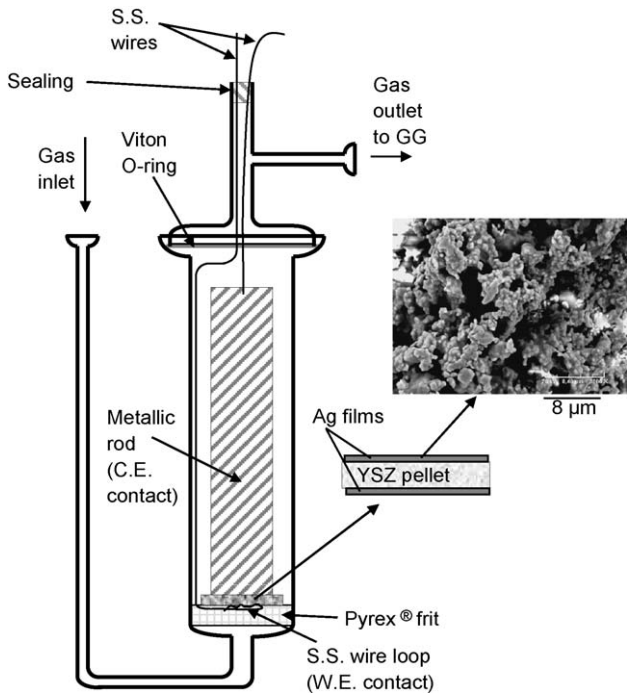

Fig. 1. Schematic drawing of the reactor and sample. SEM micrograph of Ag film.

in air at 300 °C in order to form a stable alumina layer, not too porous and not too resistive. Electrical contact with the working electrode was made by a loop of stainless steel wire. Therefore, this system is absolutely expensive metal-free provided that neither Au nor Pt was used for the electrodes or for the electrical contacts. A typical SEM micrograph of the Ag film is shown in the inset. As reported in a previous paper [14] the film appeared very porous. XRD and EPMA indicated that it is made of metallic silver. For activity evaluation, a mixture of O_2, toluene and He (1% O_2, 500 ppm toluene, He as the balance, total flow rate, 100 mL min^{-1}) was fed into the reactor. The reactants and products were analyzed by a PerkinElmer Clarus 500 gas chromatograph with a TCD detector. As the major product of the reaction, the yield of CO_2 was generally used to evaluate the toluene conversion. The CO concentration was always below our detection limit.

A Voltalab® system (Radiometer Analytical PGP 201) was used for constant current application and for open voltage measurement.

Two classical parameters were used to describe the magnitude of electrochemical promotion:

(1) The apparent Faradaic efficiency, Λ, defined from: $\wedge = \frac{r-r_o}{I/nF} = \frac{\Delta r}{I/nF}$ where r_o, in mol O/s (case of an O^{2-} conductor), is the catalytic rate at OCV; r is the catalytic rate under polarization; n is the number of exchanged electrons during the electrode reaction (n = 2 with an O^{2-} conductor) and Δr is the catalytic reaction rate change associated with the current I. A catalytic reaction exhibits the NEMCA effect when $|\Lambda| > 1$. A reaction, which is accelerated by a negative current or overpotential (oxygen removed from the catalyst surface in the present case) with a value of Λ lower than -1 exhibits an electrophilic NEMCA behavior. Conversely, when the catalytic reaction is promoted by a positive current or overpotential (here oxygen supplied to the catalyst surface) with $\Lambda > 1$, its NEMCA behavior is called electrophobic.

(2) The rate enhancement, ρ, defined from: $\rho = \frac{r}{r_o}$

where r is the electro-promoted catalytic rate and r_o is the unpromoted (open-circuit) catalytic rate.

3. Results and discussion

3.1. Ag films elaboration and characterization

As reported in the literature, since the pioneering works of Le Chatelier [15] metallic silver can be obtained by direct decomposition of silver oxide [6,16]. Vannice and coworkers [12] also reported the preparation of supported Ag catalysts by deposition of $AgNO_3$ solution followed by drying and reduction. We first investigated the decomposition of bulk $AgNO_3$. A small amount (8.7 mg) of $AgNO_3$ was placed onto quartz wool and introduced into a U-shaped quartz tube. Then TPD experiment was carried out under He flow using a heating rate of 5 °C min^{-1}. The TPD profiles are shown in Fig. 2(a) for signals at m/e = 18, 30, 32 and 44 amu. Peaks corresponding to simultaneous O_2 and NO evolution are detected within the temperature range from about 400 to 500 °C. Such profiles and intensity ratio are characteristic of nitrate decomposition [17,18]. Using FTIR spectroscopy, these concomitant desorption peaks were attributed to the decomposition of unidentate or bidentate nitrates [19]. After cooling down to room temperature, TPR run was carried out in 1% H_2/He flow using a heating rate of 20 °C min^{-1}. Quantitative approach for H_2 was made possible by calibrating the MS with pure He and 1 vol.% H_2/He using a reactor by-pass and checking for MS linearity in this range. Profiles at m/e = 2 and 18 amu during the TPR run are shown in Fig. 2(b). They clearly demonstrate a reduction occurring within a wide range of temperature (from about 200 to 550 °C). This confirmed by the lower-than-expected amount of H_2 consumed during the TPR, shows that silver oxide was formed but also that a large part of the initial material was lost by vaporization and condensation on the cold spots of the tubing, as previously reported [6]. Therefore, we investigated the possibility to simultaneously decompose and reduce $AgNO_3$ by treating it in a

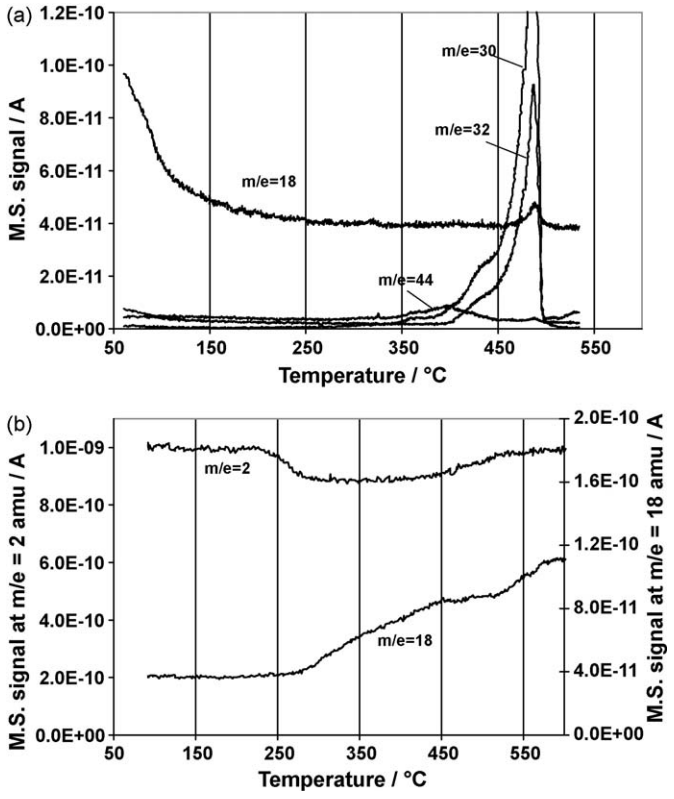

Fig. 2. TPD experiment on $AgNO_3$ sample (heating rate: 5 °C min^{-1}, He flow: 30 mL min^{-1}) followed by TPR (heating rate: 20 °C min^{-1}, 1% H_2–He flow: 30 mL min^{-1}).

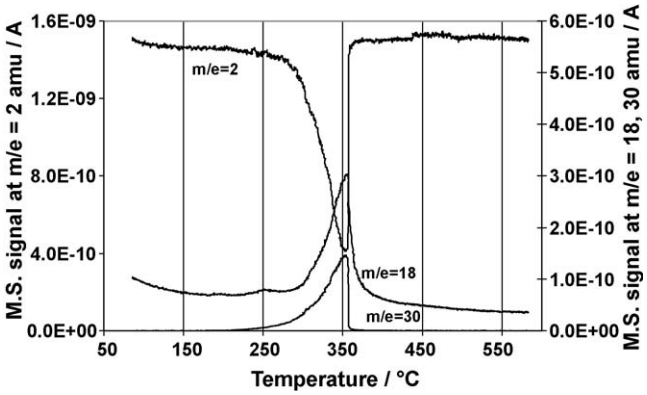

Fig. 3. TPR of $AgNO_3$ sample (heating rate: 5 °C min^{-1}, 1% H_2–He flow: 30 mL min^{-1}).

H_2-containing flow. The corresponding TPR profiles at m/e = 2, 18 and 30 amu are reported in Fig. 3 (8.3 mg sample) and they clearly show a simultaneous decomposition/reduction of $AgNO_3$ starting from about 200 °C and briskly stopping at 370 °C. Quantitative approach (after MS standardization using pure He, 1 vol.% H_2/He, and 1 vol.% O_2/He mixture) and further TPO/TPR runs showed that $AgNO_3$ transformation to metallic Ag was complete and that no significant amount of metallic material was lost during the process. In order to simulate what occurs during the processing of a real sample, where $AgNO_3$ is deposited on a YSZ pellet from an aqueous solution, 500 μL of a solution containing 26.5 g $AgNO_3$ L^{-1} were deposited on both the faces of a YSZ pellet, as described above. After drying at 140 °C, the pellet was deposited on a quartz frit in a specially adapted reactor and was submitted to: (i) heating at 5 °C/min under He flow (30 mL min^{-1}) up to 140 °C and (ii) heating at 5 °C/min under 1% H_2–He flow (30 mL min^{-1}) up to 300 °C with a 30 min plateau at this temperature. These conditions were a bit different from those employed during the real process (heating rate: 2 °C/min and pure H_2) because we needed to cope with the requirements of continuous MS analysis. Plots of temperature and signals at m/e = 2, 18 and 30 amu with respect to treatment time are shown in Fig. 4. One can note that temperature profile is not really satisfying, due to regulation parameters not very adapted to isothermal maintains at quite low temperatures. Nevertheless, it clearly appears that total decomposition/reduction of $AgNO_3$ to metallic Ag is performed under these conditions for temperatures not exceeding 300 °C. After removal of the sample, the deposited film exhibited a very good electrical conductivity.

The quantification of superficial metallic Ag (Ag^0) sites is of great important to assess the performance of the catalyst. For this purpose, Vannice and coworkers [20,21] suggested to use O_2

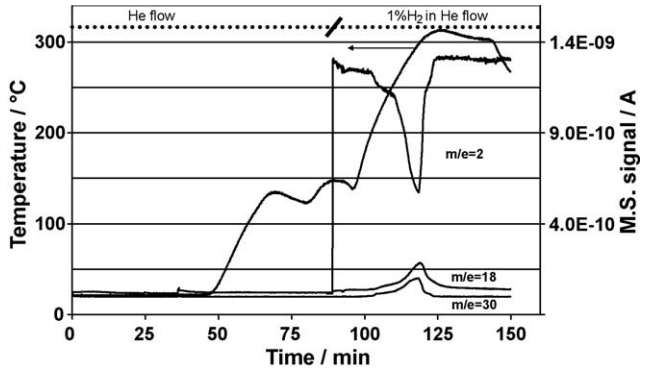

Fig. 4. Processing of $AgNO_3$ deposited (from aqueous solution) onto YSZ pellet followed by M.S.

chemisorption at 170 °C followed by titration by H_2 of the adsorbed oxygen species. As underlined by Bianchi and coworkers [22], the adsorption temperature T_a = 170 °C seems to be the best compromise between the fact that O_2 adsorption on Ag is an activated process and that bulk Ag_2O is likely to be formed at higher T_a. According to the Vannice group, the stoichiometry of O_2 adsorption is:

$$2Ag^0 + O_2 \rightarrow 2AgO_{ads} \quad (1)$$

and titration of the O_{ads} species performs according to:

$$AgO_{ads} + H_2 \rightarrow Ag^0 + H_2O \quad (2)$$

Repetitive cycles of successive O_2 adsorption and titration by H_2 were performed and analysis carried out by MS, according to a procedure previously described [23]. As the number of Ag^0 sites is expected to be very low, we had to use a reactor with a very small dead volume (about 0.2 mL) to increase sensitivity. Then the silver films had to be scratched from the YSZ pellet (including a part of the support) and put in this reactor between to pieces of quartz wool. For the same reason, the experiment was repeated six times. A typical adsorption/reduction cycle is shown in Fig. 5. First, the O_2/He mixture flow (30.1 mL min^{-1} corresponding to 0.2052 μmol O_2 s^{-1}) was established, by-passing the reactor, and was analyzed by the mass spectrometer in order to provide reference signal level for quantitative oxygen analysis. During this time, the reactor was flushed with pure He. Then, the mixture was passed through the reactor (shown by a "A" mark in Fig. 5) and the amount of oxygen both adsorbed (irreversibly and reversibly) and necessary to fill the reactor volume was determined by integration of peak O_1. Then the reactor was by-passed again (shown by a "B" mark in Fig. 5) and purged by He during a time sufficient to remove all O_2 not irreversibly adsorbed. The mixture was passed again through the reactor (shown by a second "A" mark in Fig. 5) and the amount of oxygen both reversibly adsorbed and necessary to fill the reactor volume was determined by integration of peak O_2. The peak area difference $AO_1 - AO_2$ directly gives the O_2 amount irreversibly adsorbed at 170 °C and consequently the value of Ag^0 using Eq. (1). In a similar way, using a H_2/He mixture (27.3 mL min^{-1} corresponding to 0.1859 μmol H_2 s^{-1}), the peak area difference $AH_1 - AH_2$ gives the H_2 amount necessary to titrate the adsorbed oxygen species, according to Eq. (2). In the present case, we can only obtain by this method a rough determination of the number of Ag^0 sites, because of the detection limits of the MS and possible material loss when recovering the Ag films and transferring them to the reactor. Nevertheless, average values $AO_1 - AO_2$ = 1.5 ± 0.5 μmol O_2 and $AH_1 - AH_2$ = 2.6 ± 0.3 μmol H_2 were obtained. If we consider 2.6 μmol H_2 as the most accurate value, as it is justified by the stoichiometries considered above, and if we admit that we recovered twice 7.8×10^{-5} mol Ag from the surface films (determined from the volume of $AgNO_3$ solution initially deposited on each face and confirmed by mass increase), this leads to a dispersion value of about 1.5–2%. This value corresponds to particles about 70 nm in diameter, very compatible with results obtained from XRD [14] and with some results of Vannice and coworkers on Ag/SiO_2 systems [20] using specific reduction conditions.

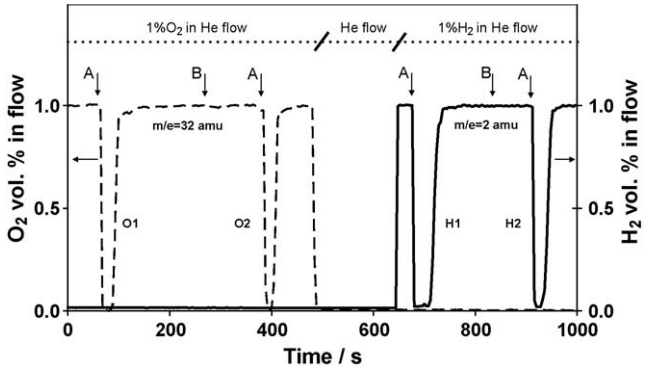

Fig. 5. O_2 chemisorption on Ag^0 sites followed by H_2 titration of adsorbed oxygen species (Ag films deposited on YSZ were scratched for this purpose). A: gas mixture sent toward reactor and B: gas mixture sent toward by-pass and reactor purged under pure helium flow.

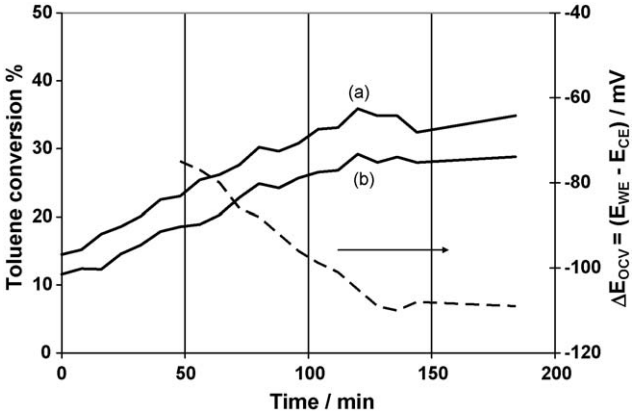

Fig. 6. Toluene conversion (calculated from (a) CO_2 production and (b) toluene consumption) and potential difference change during the early stage of the catalytic test at 310 °C (1% O_2, 500 ppm toluene, He as the balance, total flow rate, 100 mL min^{-1}).

3.2. Catalytic performances

As a preliminary work, we investigated the activity of the empty reactor for toluene combustion. Conversely to what we observed in previous studies [14,5] using a different reactor [24] a noticeable toluene conversion was detected from 290 °C and reached about 8% at 310 °C. Blank experiments were performed with and without the aluminum rod to check that no additional toluene conversion could be attributable to the metal itself. Then the reactor was loaded with a Ag/YSZ/Ag pellet. The thickness of the catalyst-electrode film was 3.3 μm as determined by weighting (for 4.0 μm expected) and thickness of the counter-electrode film was 3.6 μm (for 4.0 expected). The sample was heated at 5 °C min^{-1} up to 310 °C in He flow (100 mL min^{-1}) and then the reactive mixture was admitted to the reactor. In Fig. 6 is plotted toluene conversion, calculated from both CO_2 production (a) and toluene consumption (b). We observe a discrepancy according to the calculation method used. If some parallel reaction was taking place, or if toluene condensation occurred between the reactor and the gas chromatograph, the conversion calculated from toluene consumption would be higher than those calculated using the CO_2 production. Moreover, it is worth noting that both traces vary in very parallel ways and that the values obtained from toluene consumption just appear as shifted by −5% conversion or so. This also rules out any significant parallel reaction and toluene adsorption or desorption from walls and tubing during the catalytic test. The explanation for this observation is that the signal considered as a reference for 500 ppm toluene was obtained at the very beginning of the experiment, by-passing the reactor, with tubing and walls not saturated. Therefore, the actual concentration taken as reference was lower-than-expected (maybe 400 ppm or so) and subsequent values obtained during the catalytic test overestimate the toluene concentration and then underestimate the conversion values.

Such an observation highlights the difficulty to carry out toluene calibration at such low concentrations and it is the reason why, for the following of this paper, conversion and reaction rate

are calculated from the CO_2 signal, which gives more accurate values. After admitting the reactive mixture to the reactor and waiting for stream stabilization, the conversion is measured ($t = 0$). The corresponding toluene conversion value (about 15%) is slightly above the one recorded with empty reactor, showing a moderate activity of the silver film. Along the time, the conversion value regularly increases to reach about 30% after 2 h on stream and then stabilizes. Such a behavior was reported by many authors on silver catalysts, for example concerning CO oxidation [22], CH_4 deep oxidation [25] or hydrogen dissociation [26] and was attributed to structure and grain size changes of the silver surface. Although we did not use a conventional three-electrode electrochemical system and no real reference electrode, it is interesting to consider the potential difference (ΔE_{OCV}) between the catalyst-electrode (WE, pressed against the frit) and the counter-electrode (CE, pressed against the metallic rod). As the two electrodes are of the same material and of similar thicknesses, ΔE_{OCV} is expected to be constant and near-zero. Nevertheless, ΔE_{OCV} value was quite unstable around −50 mV at the beginning of the experiment and after that continuously decreases when toluene conversion increases and then stabilizes at about −110 mV when toluene conversion stabilizes. This behavior is very consistent with what we observed with a Ag/YSZ/Au system [14] and indicates that the two electrodes are not equivalent with respect to the catalytic reaction and that WE activates on stream and is likely to be responsible for the main part of the catalytic process. This is fully justified by the cell geometry and stream accessibility to each electrode. As the counter-electrode is pressed against the metallic rod and faces a very confined volume, it is likely that almost the totality of toluene conversion is insured by the working electrode, which faces the incoming gas stream. Therefore free potential change and stabilization may be considered as a good qualitative indicator of WE on-stream activation and conversion stabilization. As shown later in the text, the absence of promotional effect when positive currents are used also indicates that the counter-electrode participation to overall toluene conversion is not significant.

As shown in Fig. 7, applying a negative small current (−2 μA) to the catalyst-electrode significantly increases the toluene conversion. Over it, toluene conversion increases from about 34% to reach about 55% after 25 min and then remains quite stable. The corresponding value $\rho = 1.6$ could seem quite low, but it is noteworthy to recall that initial OCV conversion was quite high. After the stabilization of activity, the calculated Faradaic efficiency Λ was about −13,000, which means that the promotion is strongly non-Faradaic. It is worthy mentioning that such a Faradaic efficiency is similar to the values we reported for paste-made Ag film catalyst (Λ ranging from −2100 to −39,700) [5]. The toluene conversion value is shown to recover quite quickly its initial value upon turning the electrical current off. This experiment can be totally repeated and similar results were obtained when the current is turned on again, indicating it is a repeatable, reversible and non-permanent effect. Applying positive currents (+2, +10 and +20 μA) to the catalyst-electrode does not increase nor decrease significantly the value of toluene conversion. This proves that the enhancement occurs when oxygen ions species are drawn from the catalyst surface, as reported previously with non-symmetrical Ag/YSZ/Au systems with Ag films obtained either by a paste [5] or by decomposition/reduction of $AgNO_3$ [14]. As electro-promotion appears only for negative currents, one could expect a promotional effect from the counter-electrode when positive current is applied. As no promotional effect is observed in this case, it proves that CE faces a very confined volume and that the participation of the counter-electrode is negligible as also suggested by results reported in Fig. 6. According to the rules of EPOC established by Vayenas and coworkers [27], the promotion of toluene catalytic combustion over Ag film catalyst follows an electrophilic NEMCA behavior which can be observed when the electron-donor reactant is more strongly adsorbed on the catalyst surface than the electron-acceptor reactant. These results can be explained by the fact that toluene is a non-saturated hydrocarbon and has π-electrons in its structure, which make it strongly adsorbed on the surface of Ag as an electron-donor therefore hindering the adsorption of O_2 (an electron-acceptor). The application of a negative potential or current leads to the migration (by electrochemical pumping) of O^{2-} from the surface of Ag catalyst, thus changes the work function and favours the adsorption of oxygen.

The results reported in Fig. 8 show the effect of various values of the negative current applied to the catalyst-electrode: −2, −4, −10, −20 and −40 μA. With respect to toluene conversion, the three intermediate experiments (−4, −10, and −20 μA) do not exhibit much difference. Conversely to what is often observed, the value of imposed current does not influence much the time necessary to reach the maximal conversion. This can be attributable to the very porous nature of the film and the necessary time to reach a steady state once the current is established. This chemical phenomenon is more likely to be rate determinant than the electrical one. We did not report on the figures the values of ΔE_{WE-CE}, the potential difference between WE and CE, because it is mainly governed by the ohmic drop within the YSZ pellet, the resistance of which is very high for such low temperatures. Typically, ΔE_{WE-CE} reached its maximal value in less than 1 min after applying the current. Recorded ΔE_{WE-CE} values were repeatable for each current (within ±5%): −680 mV for −4 μA, −890 mV for −10 μA, −1800 mV for −20 μA, and −2400 mV for −40 μA. After turning off the current, ΔE_{WE-CE} values

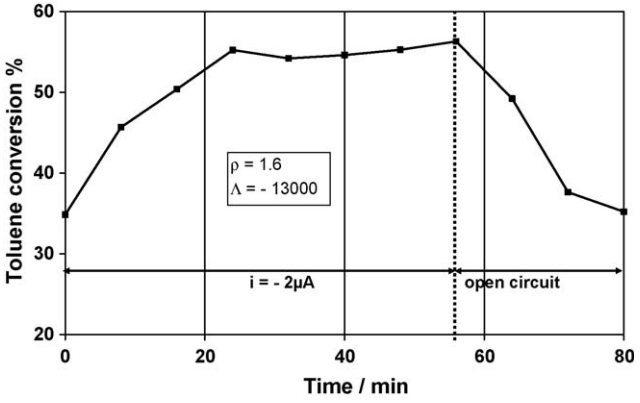

Fig. 7. Effect of −2 μA on the activity of Ag film catalyst deposited on YSZ pellet. Reaction condition: 1% O_2, 500 ppm toluene, He balance; total flow rate, 100 mL min^{-1}, 310 °C.

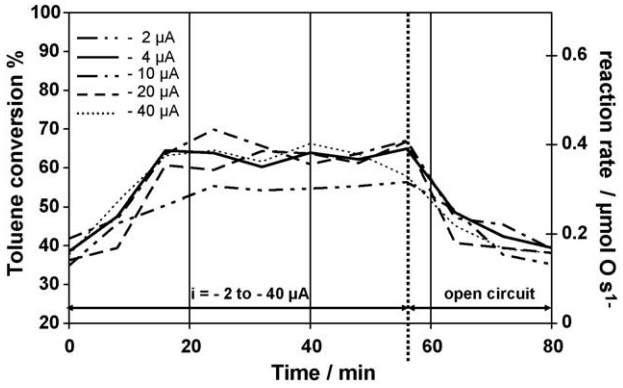

Fig. 8. Effect of various negative currents on the activity of Ag film catalyst deposited on YSZ pellet. Reaction condition: 1% O_2, 500 ppm toluene, He balance; total flow rate, 100 mL min^{-1}, 310 °C.

Table 1
Maximal toluene conversion, rate enhancement (ρ) and Faradaic efficiency (Λ) values from results of Fig. 8.

Current (μA)	Max. toluene conversion (%)	ρ	Λ
−2	55	1.6	−13,000
−4	64	1.7	−8,200
−10	66	1.6	−3,100
−20	64	1.8	−1,800
−40	65	1.7	−900

sharply decreased in some seconds and then free potential recovered its initial value after 15–20 min, according to a curve similar to conversion *vs* time. Obviously, using −2 μA is not enough under those initial activity and high ghsv ($7.5 \times 10^6\ h^{-1}$ referred to the volume of the active phase) conditions to reach an optimal promotion. For the highest current value (−40 μA) toluene conversion starts decreasing before current is turned off. This current value seems too high, but no explanation can be given for this phenomenon since no reversible damage to the system was observed. Corresponding rate enhancement (ρ) and Faradaic efficiency (Λ) values are gathered in Table 1. Obviously, maximal toluene conversion is limited by a non-catalytic phenomenon, probably the fact that catalyst surface is only "licked" by the reactant stream and that a non-negligible part of it can by-pass the catalyst. Therefore, the apparent value of Λ is the highest for the lowest currents. Nevertheless, the use of a −4 μA current seems to be a good practical choice under such experimental conditions allowing long time operation (4 h tests were ran) with neither toluene conversion decrease nor permanent promotional effect when current is turned off.

4. Conclusion

A significant NEMCA effect was achieved over a silver catalyst-electrode deposited onto YSZ from a $AgNO_3$ aqueous solution followed by H_2 reduction. After applying negative potential, prominent rate enhancement and high Faradaic efficiency up to −13,000 can be reached. This Faradaic efficiency value is comparable to what we reported for Ag/YSZ/Au systems where Ad was deposited either from a paste [5] or by a deposition/reduction technique [14]. Taking into account the simple manipulation and cost-efficiency of the deposition/reduction technique, and the ability to work with a system which does not contain any expensive metal, we think it is a method to be considered to elaborate EPOC systems used for the environmentally important application of the total oxidation of aromatic VOC's as toluene.

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