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Milestones and perspectives in electrochemically promoted catalysis

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ABSTRACT

Electrochemical promotion of catalysis is a unique tool for the *in situ* tuning of catalytic activity of electronically conductive metals or metal oxides in contact with solid electrolytes. The importance of electrochemical promotion to heterogeneous catalysis, surface science and electrochemistry research for the investigation of spillover phenomena and metal–support interactions is well recognized. The unlimited applications of the phenomenon, in terms of catalysts, solid electrolytes or catalytic reactions selection, has been proven through numerous laboratory investigations. Though the molecular origin of electrochemical promotion has been revealed, using a variety of experimental techniques and theoretical calculations, there is still a shortage on the practical level. However, in the last decade, spectacular progress has been made in the development of effective, low cost electropromoted catalysts and reactors. The major technological advances and milestones towards the practical utilization of electrochemical promotion are surveyed in view of electrocatalysts development and system/reactor engineering.

1. Introduction

Since the discovery [1] of the effect of non-Faradaic electrochemical modification of catalytic activity (NEMCA effect) or electrochemical promotion of catalysis (EPOC) [2–8] as a tool for controlling the catalytic activity of a catalyst interfaced with a solid electrolyte via electrical current or potential application, EPOC has been observed and investigated for more than 70 catalytic reactions. It is now well established that EPOC is not limited to any particular class of conductive catalysts, solid electrolytes or catalytic reactions [2–4]. Regarding the mechanism of the phenomenon, it is also well established through numerous electrochemical and spectroscopic techniques that EPOC is due to potential-controlled transport of ionic species (e.g. O^{2-}, H^+, Na^+) through the solid electrolyte support and migration of the discharged species to the catalytically active metal/gas interface [2–4,9]. The current understanding of the physicochemical origin of this phenomenon, its limits and obstacles for practical utilization have been reviewed recently [4].

The possibility of application of the NEMCA effect in conventional flow reactors has already been recognized since 1994 [10], as this would foster the ultimate direct utilization of electrochemical promotion in commercial reactors, as those used in the chemical industry and in automotive exhaust catalysis. The latter depends on several technical and economical factors [11] which are intimately related to specific technical considerations and problems, among which two stand out:

1. Moving from low surface area, high materials cost, thick film catalyst structures (state-of-the-art in current laboratory experiments) to electrochemically promotable, nano-scale structures that are sufficiently active, robust and inexpensive so as to be deployed in practical reactors.
2. Devising configurations for thin film or nanoscopically patterned catalyst–electrode structures with efficient current collection and compact design.

These anticipated technical challenges have been the subject of sedulous research in this decade and the latest progress in modeling, materials development and reaction engineering has been impressive pointing out that the main obstacles for practical utilization can be overcome. At the same time, there is also a strong industrial interest and involvement aiming to EPOC commercialization.

The present review discusses a series of critical technological developments in electrochemical promotion studies towards its direct utilization in two areas:

(i) Electrocatalysts development.
(ii) System/reactor engineering.

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2. Results and discussion

2.1. Electrocatalysts development

2.1.1. Electrochemical promotion of classically promoted and commercial catalysts

Most electrochemical promotion studies employ model catalysts, usually noble metals, with low dispersion. Thus, although electropromotion in low activity catalysts is well established there was a concern whether an already active or even classically promoted catalyst could be further promoted electrochemically. In this direction the electropromotion of a "classically" promoted catalyst and of a commercial catalyst were explored.

In the former case, a Rh catalyst film deposited on YSZ electrolyte was classically promoted by depositing on its surface a NaOH solution followed by drying and thorough H_2O evaporation in a classical "dry impregnation" process [12]. The resulting promoted Rh film exhibited a dramatic enhancement in its catalytic performance, compared to the same unpromoted Rh/YSZ film for the reduction of NO by CO in presence of O_2 (Fig. 1). The promoting effect of sodium was an expected result evident from previous electrochemical promotion investigations on Rh films deposited on β''-Al_2O_3, an Na^+ conductor. The main reason is that Na further enhances NO dissociation. The question that arises now is: can one further enhance the performance of this "classically" promoted Rh catalysts by using electrochemical promotion? For that reason, the effect of application of external voltage and the concomitant supply (+1 V) or removal (−1 V) of O^{2-} to or from the promoted Rh surface was examined. The results showed an enhancement in catalytic performance (the light-off temperature is further decreased and the selectivity is further enhanced) under positive potentials and negligible effect under negative polarization (Fig. 1). So, the answer to the question is clear: *one can electrochemically promote an already classically promoted catalyst*. The fact that negative potentials fail to further enhance catalysts performance is not surprising since the effect of negative potentials is equivalent to alkali supply on the catalyst surface, in terms of decrease of catalysts work function. The Rh catalyst was already promoted by the alkali species (Na) and thus already having a low work function can only be marginally affected by negative potential application.

A step forward for the electropromotion of promoted catalysts was realized by Yiokari et al. [13] who attempted to electropromote a commercial catalyst for the NH_3 synthesis. The catalytic synthesis of ammonia from its elements via the Haber–Bosch process is of major industrial importance and the high pressure synthesis is catalyzed by Fe promoted with K_2O, CaO and Al_2O_3. In that study, a commercial fully promoted Fe-based catalyst (supplied by BASF) was used, deposited on $CaZr_{0.9}In_{0.1}O_{3-\alpha}$, a proton conducting solid electrolyte. The catalyst was milled and deposited via a slurry. Since the commercial Fe-based catalyst is electronically conducting, as it is not supported on an insulating support (e.g. SiO_2, Al_2O_3), it was found that this catalyst film deposited on the H^+ conductor had sufficient conductivity to also act as an electrode of the solid electrolyte cell. The reaction was carried out in a high pressure (50 atm) reactor incorporating 24 $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ cell-pellets, electrically connected in parallel (Fig. 2) [13].

The rate of ammonia production was enhanced by more than 1100% in the nitrogen rich regime (Fig. 3), upon potential application of −1 V between the working electrode and the Ag reference electrode. The extent of the NEMCA effect depends strongly on the kinetic regime of the reaction. Very pronounced non-Faradaic behavior is observed in the regime $0.33 \le H_2/N_2 \le 0.67$ where ρ values of 12 or more were obtained. The enhancement in the catalytic activity is due to the electrochemical supply of H^+ to the catalyst which decreases the catalyst work function and thus strengthens the chemisorptive bond of electron acceptor N while at the same time weakening the bonds of electron donor H and NH_3. Thus, it was once again confirmed that a promoted, already active, catalyst can be further enhanced by electrochemical promotion.

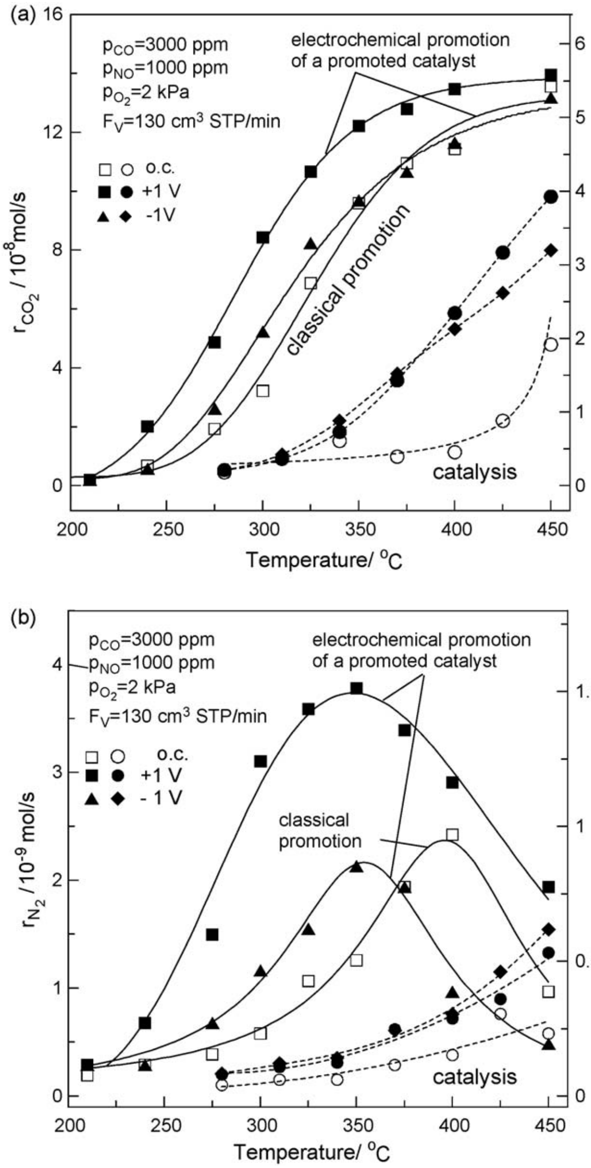

Fig. 1. Catalysis (○), classical promotion (□), electrochemical promotion (●, ◆) and electrochemical promotion of a classically promoted (sodium doped) (■, ▲) Rh catalyst deposited on YSZ during NO reduction by CO in presence of gaseous O_2 [12]. The figure shows the temperature dependence of the catalytic rates and turnover frequencies of CO_2 (a) and N_2 (b) formation under open-circuit (o.c.) conditions and upon application (via a potentiostat) of catalyst potential values, U_{WR}, of +1 and −1 V [12].

2.1.2. Electrochemical promotion with highly dispersed catalysts and sputtered films

A major drawback of typical electrochemical promotion catalysts was the use of thick catalyst films (0.1–5 μm thick) mostly made via paste deposition, leading to poor material utilization (metal dispersion below 0.01%). Practical applications would require the use of thin (on the order of few nm thick) catalyst electrodes or dispersed catalysts.

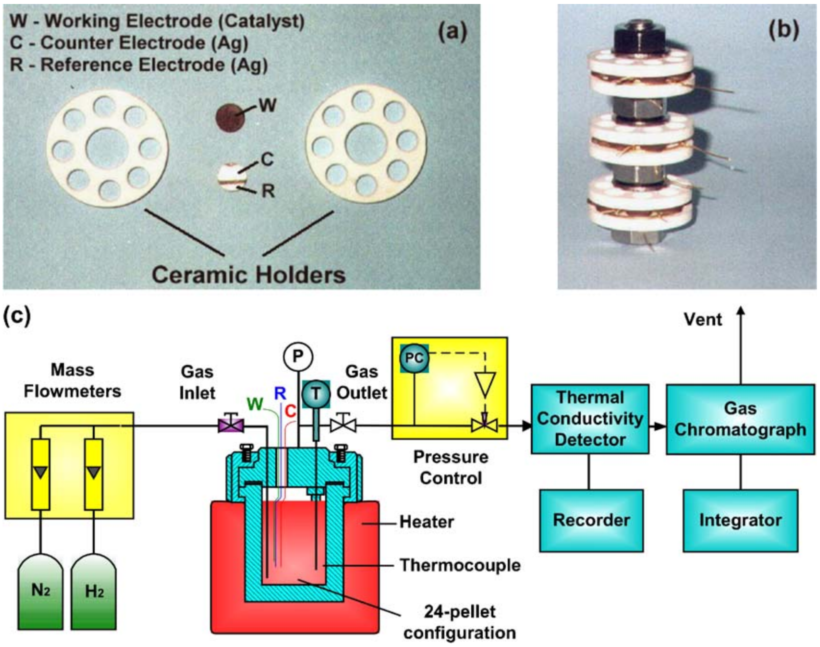

Fig. 2. Experimental set-up: (a) machinable ceramic holders and two proton conducting pellets showing the location of catalyst, counter and reference electrodes. (b) Twenty-four pellet unit. (c) High-pressure reactor, gas feed and analysis unit [13].

The first attempt to achieve a highly dispersed electropromoted catalyst was realized [14] by dispersing the active catalyst phase (Pt) on an electronically conductive support (Au) in contact with the electrolyte. In a first step the porous Au film was deposited on YSZ, using typical paste deposition method, and subsequently the film was impregnated with an aqueous H_2PtCl_6 solution followed by drying, calcinations and reduction with H_2. The resulting finely distributed Pt catalyst particles in the Au current collector was found to be 20–100% dispersed. As shown in Fig. 4, this finely dispersed Pt catalyst could be electrochemically promoted with ρ values on the order of 3 and Λ values on the order of 10^3. The implication is that oxide ions, O^{2-}, generated or consumed via polarization at the Au/YSZ/gas three-phase-boundaries migrate (backspillover or spillover) on the gas exposed Au electrode surface and reach the finely dispersed Pt catalyst thereby promoting its catalytic activity. Although obviously less expensive electron conducting catalyst supports have to be sought for practical applications, this study has clearly established the technical feasibility of inducing NEMCA on finely dispersed noble metal catalysts. The latter was realized in the electrochemical promotion of H_2 oxidation at room temperature using aqueous alkaline solutions and finely dispersed Pt/graphite electrodes [15,16] as

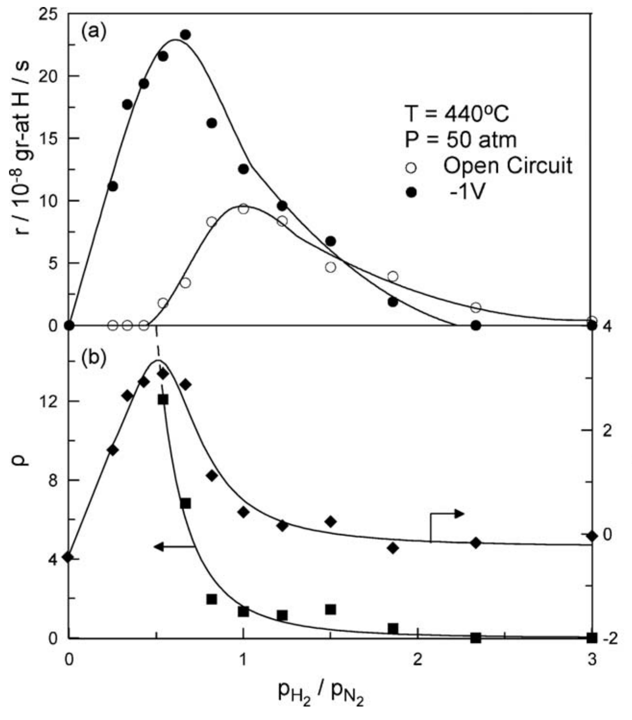

Fig. 3. (a) Effect of inlet H_2/N_2 ratio on the rate of NH_3 synthesis over promoted $Fe/CaZr_{0.9}In_{0.1}O_{3-\alpha}$ under open-circuit (○) and for $U_{WR} = -1.0$ V (●). (b) Corresponding ρ (r/r_0) (■) and Λ $(=\Delta r_H/(-I/F))$ (◆) values [13].

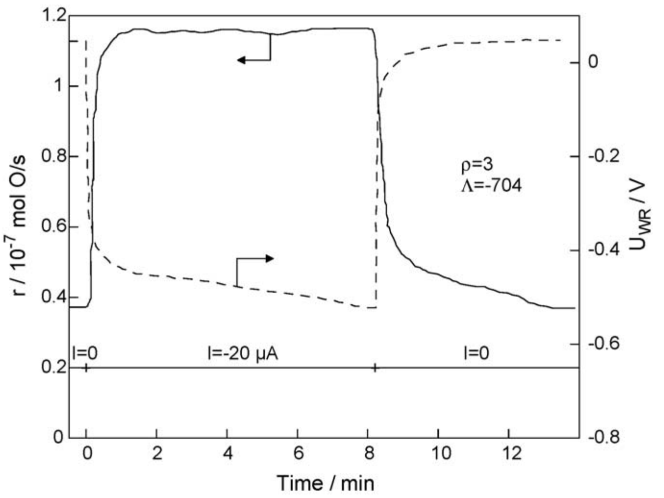

Fig. 4. Transient effect of an applied negative current ($I = -20$ mA) on the reaction rate r of C_2H_4 oxidation on Pt finely dispersed on Au supported on YSZ (solid curve) and on the catalyst potential U_{WR} (dashed curve). Conditions: $T = 421$ °C, $p_{O_2} = 14.8$ kPa, $p_{C_2H_4} = 0.1$ kPa, flow = 411 ml/min, open circuit rate: $r_o = 0.037 \times 10^{-6}$ mol/s [14].

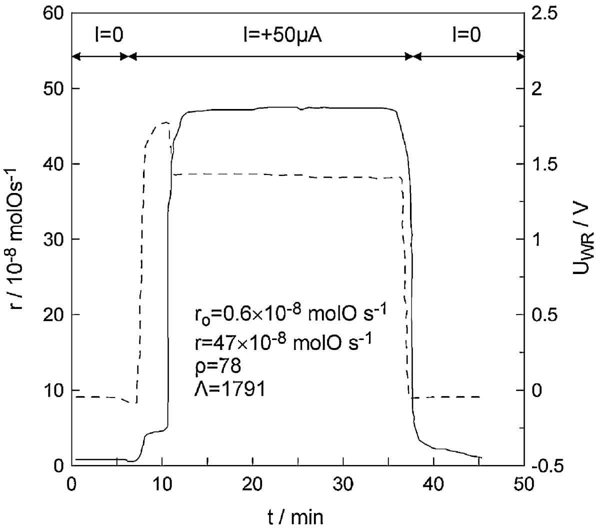

Fig. 5. Rate (solid line) and catalyst potential (dotted curve) responses of a Rh/TiO_2/YSZ catalyst–electrode to a step change in applied current of +50 μA [20].

well as in the electropromotion of H_2 oxidation [17] and 1-butene isomerization to 2-butene (cis- and trans-) [18,19] using Nafion as the solid electrolyte and finely dispersed Pt and Pd deposited on carbon as the electrode, respectively.

Very recently electropromotion studies have been extended to thin sputter coated porous amorphous metal catalysts [20]. Ethylene oxidation was used as a model catalytic oxidation system for the electrochemical promotion of sputtered Rh films deposited on YSZ. The thus prepared film had a thickness of 40 nm and the metal dispersion was of the order of 10%, i.e. 10% of the porous film metal atoms were surface atoms, which is comparable to that of state-of-the-art conventional supported catalysts. It was found [20] that the catalytic activity of Rh for C_2H_4 oxidation can be reversibly enhanced via anodic current or potential application by up to a factor of 80 and that the increase in the oxidation rate is up to 2000 times larger than the rate of supply of O^{2-} to the Rh catalyst–electrode (Fig. 5). Smaller anodic currents caused periodic catalytic rate and potential oscillations. The observed pronounced electrophobic electrochemical promotion of C_2H_4 oxidation on Rh is qualitatively identical to that observed with thick paste Rh films. The performance of these films is remarkable not only in terms of electrochemical promotion efficiency but also in reference to long term stability and endurance. Pt and Rh films prepared with the same deposition method were employed in a monolithic electro-promoted reactor (MEPR) both for ethylene oxidation and NO reduction by C_2H_4 in the presence of oxygen; this will be discussed in the following sections.

Furthermore, it was recently shown [21] that the turnover frequencies (reaction rate per surface atoms) on electropromoted Pt or Rh films are a factor of 5–10 higher for C_2H_4 oxidation or NO reduction than on commercial supported catalysts under identical gas composition and temperature conditions. Thus, electrochemical promotion of such thin films leads to better noble metal utilization than that obtained with state-of-the art commercial nanodispersed catalysts.

2.2. *System/reactor engineering*

A major issue related to practical utilization of electrochemical promotion is that of efficient electrical current collection, ideally with only two electrical leads entering the reactor and without an excessive number of interconnects, as in fuel cells. Two strategies have been used to tackle this issue: the "wireless" NEMCA design and the bipolar configuration.

2.2.1. *Bipolar electrochemical promotion*

The pioneer work of Marwood and Vayenas has demonstrated that direct electrical contact, via a metal wire, to the catalyst–electrode is not necessary to induce the effect of electrochemical promotion [22]. It was found that it suffices to apply the potential, or current, between two terminal electrodes which may, or may not, be catalytically active. This experimental set-up comprises the bipolar or "wireless" NEMCA design concept [22–25]. The concept appears to be very similar with that of the "bipolar" design used now routinely in aqueous electrochemistry. The implications of this discovery for electrochemical promotion are quite significant since it shows that, at least in principle, the design of an electrochemically promoted reactor can become much simpler than that of a fuel cell.

The first attempt to impose NEMCA in a bipolar configuration was realized by utilizing multi-stripe and multi-dot [24] Pt catalysts placed between two Au terminal electrodes on YSZ for the C_2H_4 oxidation reaction (Fig. 6, inset). In this case, large terminal voltages (of the order of 30 V) are applied between the two Au

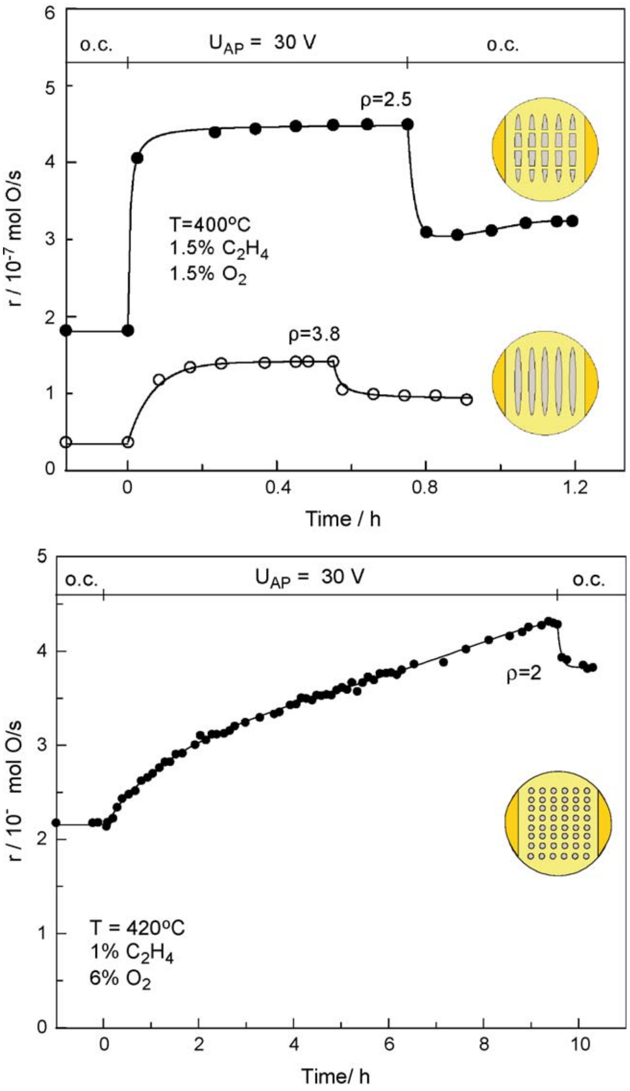

Fig. 6. Transient effect of an applied potential, U_{AP}, between the two terminal gold electrodes (30 V) on the catalytic rate of ethylene oxidation (expressed in mol O/s) for (a) dotted (filled circles) and multi-striped (open circles) platinum configuration (b) for a multi-dotted platinum configuration [24].

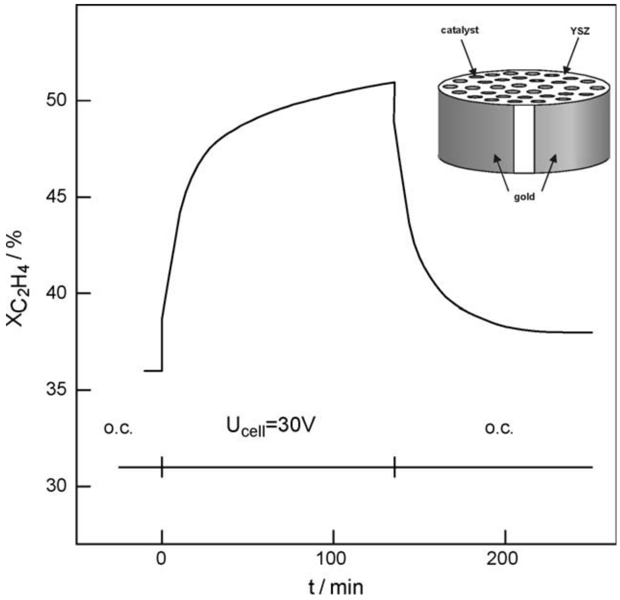

Fig. 7. Temporal evolution of the ethylene conversion in the multiple-channel RuO_2/YSZ cell during a potentiostatic step of U_{cell} = 30 V. OC: open-circuit. Feed composition: C_2H_4:O_2/0.2:12 kPa, F_V = 175 cm^3 STP/min, T = 360 °C; (inset) channel electrochemical cell termed bipolar configuration of second generation [23].

electrodes, so that the potential difference in each individual cell formed between the Pt stripes or dots is of the order of 1 V. Each isolated Pt film becomes a "bipolar" electrode as half of it is polarized anodically while the other half is polarized cathodically. This synergy at anodic and cathodic polarization can easily explain the overall smaller ρ values obtained as compared with those in classical electrochemical promotion experiments (Fig. 6).

A brilliant demonstration of the bipolar design concept came from the group of Comninellis at EPFL (Fig. 7) [23]. A monolith was made from YSZ and the surface of the monolith channels was covered with a RuO_2 catalyst (Fig. 7, inset). Two terminal Au electrodes were deposited on the outside surface of the monolith. Potential application between the two terminal Au electrodes was found to induce NEMCA on the RuO_2 catalyst which is not in electrical contact with any metal wire [23]. The Faradaic efficiency Λ values for C_2H_4 oxidation are on the order of 10^3 while C_2H_4 conversion could be enhanced from 35% to 50% (Fig. 7) [23].

Recently, a novel configuration using a mixed ionic–electronic conducting (MIEC) support has been developed by Poulidi et al. for use in electrochemical promotion experiments [26–28]. The mixed conductivity of the support eliminates the need for an external circuit. In this system polarization is achieved by the use of an appropriate sweep gas that creates a chemical potential difference across the membrane. In analogy with classic EPOC experiment where the promoter is driven by the application of an overpotential across the membrane-support, the principle of operation of this wireless configuration lies on the use of oxygen sweep on one side of the reactor which creates the necessary oxygen chemical potential difference that drives oxygen ion promoters across the membrane and ensure the supply of these promoters to the catalyst. Initial results on mixed oxide-ion–electronic and protonic–electronic conductors have shown the feasibility of the wireless configuration of EPOC experiments, while significant rate changes were obtained [26–28].

2.2.2. Monolithic electrochemically promoted reactor (MEPR)

Since the actual competitor of an electrochemically promoted chemical reactor is a chemical reactor itself (fixed bed, monolithic, fluidized bed) it follows that efficient, compact and intelligent reactor designs must be realized to make an electrochemically promoted reactor commercially attractive.

The recently developed MEP reactor [29] provides a practical structured electrochemically promoted reactor which allows, in principle, the transition from laboratory studies to practical applications. The MEP reactor can be considered as a hybrid between a classical monolithic honeycomb reactor and a planar solid oxide fuel cell [30]. The core of the MEPR is a ceramic casing, made of machinable glass ceramic (Macor®). The internal faces of the two opposing reactor walls have appropriately machined parallel grooves where a number of solid electrolyte plates are inserted. These surfaces are also used to create the two necessary current collectors, one establishing electrical contact with all catalyst films deposited on the top side of the plates, while the other current collector establishes electrical contact with all catalyst films deposited on the bottom side of the plates. In this way, a significant practical simplification is realized as both the top and bottom catalyst films can be electrochemically promoted (with reverse polarity) via only two external connecting wires. The reactor is enclosed in a suitable metal casing of stainless steel with a baffling system at the gas entrance aiming to achieve as uniform a gas flow distribution as possible at the gas entrance. A schematic of the assembled MEPR is shown in Fig. 8.

The MEP reactor is a simple device that permits easy practical utilization of electrochemical promotion. It accomplishes an efficient and compact reactor design, which can be assembled and dismantled at will, has only two external connecting wires and its catalytic plates can be replaced whenever necessary. It exhibits excellent mechanical and thermal stability enabling its use under harsh environments, such as in a car engine exhaust. Furthermore it is possible to use one of the plates as a gas sensor element and utilize the potential signal generated by this element to dynamically control the current or potential applied to the electropromoted catalytic plates.

The electropromoted reactor has already been evaluated successfully for hydrocarbon oxidation and NO reduction by C_2H_4 in the presence of O_2 using both conventional thick films and

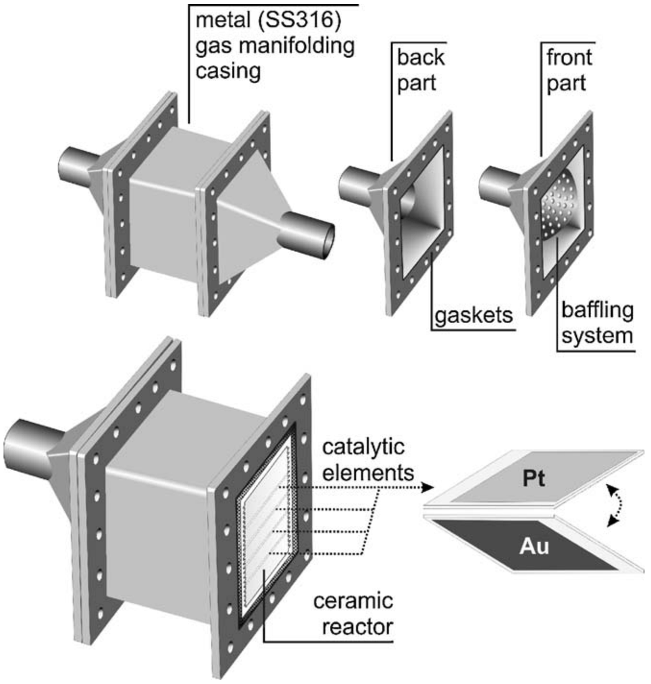

Fig. 8. Schematic of the assembled monolithic electropromoted reactor (MEPR) [29].

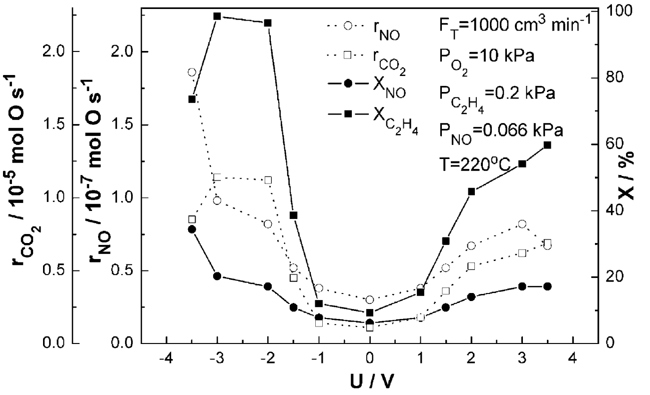

Fig. 9. Steady state effect of the applied potential on the NO conversion rate (r_{NO}), on the CO_2 formation rate (r_{CO2}) and on the conversion of NO and C_2H_4 (x_{NO}, $x_{C_2H_4}$) at $T = 220\,^{\circ}C$, and highly oxidizing conditions [34]. MEP reactor loaded with 22 Rh/YSZ/Pt plates (Rh films are the working electrode and the Pt films are the counter electrode).

thin sputtered noble metal electrodes [29,31–34]. Specifically, the MEPR with 22 Rh/YSZ/Pt parallel plate elements was found to promote selective catalytic reduction (SCR) of NO by 450% with near 100% selectivity to N_2, even in high excess of O_2 (10%) at temperatures 200–300 °C (Fig. 9) [34]. The corresponding Λ_{NO} and Λ_{CO_2} values were up to 2.4 and 350, respectively, and the rate enhancement ratio of complete C_2H_4 oxidation was up to 900% (Fig. 10) [34].

The monolithic electropromoted reactor was also tested under real conditions for the treatment of automotive exhaust gas of a diesel engine [32] demonstrating excellent mechanical and thermal stability after prolonged operation at flow rates as high as 56 L min^{-1} (mean gas residence times of 0.34 s and reactor space velocities up to $2.7 \times 10^4\,h^{-1}$). The MEP reactor can, conceptually, be scaled-up (or scaled-down) following a stack design and can, in principle, be used for many practical applications in exhaust treatment units and in chemical destruction or synthesis processes.

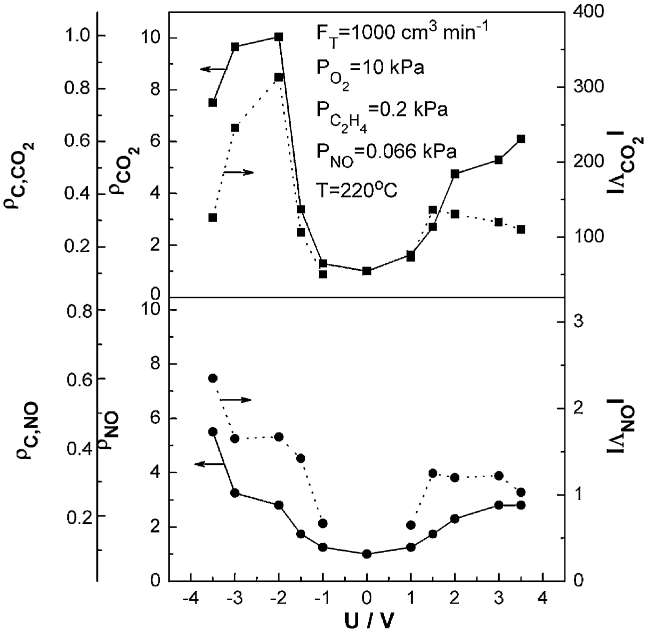

Fig. 10. Steady state effect of the applied potential on the rate enhancement ratio (ρ), on the effective enhancement ratio (ρ_c) and on the apparent Faradaic efficiency (Λ) for CO_2 formation and NO conversion at $T = 220\,^{\circ}C$, and highly oxidizing conditions [34]. MEP reactor loaded with 22 Rh/YSZ/Pt plates (Rh films are the working electrode and the Pt films are the counter electrode).

3. Perspectives

In parallel to the technological progress of EPOC in terms of electrocatalysts development and reactor/system engineering, a niche market for the implementation of EPOC concept should be identified in order to attract industrial interest. Environmental applications, both for pollutants destruction and for the production of clean energy carriers, is an area with great potential and thus has been the subject of a number of EPOC studies. Besides the NOx selective catalytic reduction in a MEP reactor, the production of clean transportation fuels, the NOx trapping and the CO selective oxidation in a hydrogen stream for use PEM fuel cells have been considered.

While electrochemical promotion has mostly applied to oxidation reactions, there is a plethora of studies on hydrogenation and de-hydrogenation reactions [2,35–38]. Among these studies, CO_2 and CO hydrogenation for the production of alcohols and other oxygenated products appear to be of considerable technological interest. Due to the constantly increasing atmospheric levels of CO_2, resulting from the combustion of fossil fuels, and the concomitant alarming environmental effects, the one-step hydrogenation of CO_2 to clean transportation fuels is currently one of the major technological challenges of heterogeneous catalysis. However so far no catalytic systems have been identified for the efficient one-step conversion of CO_2 to hydrocarbons. Preliminary results [2,38] indicate that there is significant promise in the selective electropromotion of CO_2 hydrogenation. The successful implementation of electrochemical promotion and EPOC-based catalytic units for the CO_2 hydrogenation are expected to be highly active, selective and durable and hopefully will thus improve the prospects of recycling CO_2 as a C-source for chemicals and fuels using renewable sources of energy.

The electrochemically assisted NOx storage/reduction (NSR) on a Pt–KβAl_2O_3 catalyst that can operate over a range of reaction conditions has recently been presented to be effective for the removal of NOx [39]. Under negative polarization, NOx is stored on the catalyst surface in form of potassium nitrates while, under positive polarization, the catalyst is regenerated, with N_2 being the only product of this process. The variation of the current under the applied polarizations allows monitoring the progress of both the storing and the regeneration phases, and thus optimisation of the duration of both sequences in a technically feasible manner. In addition, as the catalyst is regenerated electrochemically, it can operate continuously under a fixed lean gas composition, which implies an important technological advance for the NSR process.

Hydrogen fueled PEM fuel cells are considered as one of the most promising means of producing energy in the future. One of the major issues in PEM fuel cell market penetration is related to hydrogen production. For the short and medium term, hydrogen production from hydrocarbons or alcohol seems to be the most feasible alternative. However, during hydrogen production from these sources, carbon monoxide is formed as well. Even after thorough treatment of the thus produced hydrogen, small traces of CO (in ppm levels) remain in the hydrogen stream which adsorb on the anode and lead to CO-poisoning, thus impairing significantly the cell performance. Electrochemical promotion may offer an alternative tool for the purification of H_2 streams for use in PEM fuel cells through the electropromotion of water–gas-shift reaction or through EP enhancement of the selectivity of preferential oxidation of CO. Recent studies have proven that this possibility is viable [40].

Fuel cell applications extend beyond power generation and the introduction of electrochemically promoted organic isomerization reactions at PEFC cathodes by Smotkin and co-workers, extended NEMCA to non-redox reactions [18,19,41]. More recently the same group [42] presented the concept of "chemical transistors" based on spillover protons delivered as a base current to the effective double layer of Nafion encased Pd catalysts, creating a new prospect for the development of an area of synthetic chemistry that uses Nafion "wired" spillover protons for catalyzed organic transformations.

Electrochemical promotion of catalysis set a fine example of scientific evolution of an experimental observation to the discovery of a unique phenomenon and the establishment of a whole new research field. This was accomplished only through the involvement of several groups with different background and expertise and the adoption of a multidisciplinary approach. The EPOC community faces now a new challenge: the practical utilization of the phenomenon and the development of EPOC assisted processes. The major barriers for industrial applicability of EPOC have been identified and the first concepts to come through them have already been verified, as reviewed above. However, there is still a very long distance to cover in order to meet these ambitious expectations. Although this task calls for different skills, technological rather than scientific ones, the thus far success story suggests that a similar methodology should be embraced, that is a collaborative and open, to new ideas and disciplines, approach.

4. Conclusions

The recent scientific and technological advances on electrochemical promotion of catalysis manifest that the main obstacles for its practical limitations may be overcome. Although the fundamental understanding of EPOC phenomenon is well established, there are several issues mostly related to engineering aspects, such as durability, useful lifetime, electrolyte and stack cost minimization, scale-up and scale-down of electropromoted reactors that have not yet been addressed in any detail. However, there is already strong industrial interest and involvement and the next years are likely to lead to commercialization of some electropromoted units and processes. The demonstration of EPOC impact in a realistic target application would definitely open new perspectives towards its practical utilization.

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