Review

Electrochemical promotion of catalysis: the case of ethylene oxidation

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Abstract
The electrochemical promotion of catalysis (EPOC), also known as non-Faradaic electrochemical modification of catalytic activity (NEMCA), is a rather general phenomenon observed in about 30 years ago. This phenomenon has a strong impact on modern electrochemistry, heterogeneous catalysis and surface science. The EPOC effect can be achieved with porous thin film electrodes interfaced to solid electrolytes. A dramatic improvement in the catalytic activity has been obtained by polarization of the interface via an electrical current or potential application. It has been studied for more than 100 catalytic reactions, including oxidations, reductions and isomerisations and using a variety of metal or metal oxide catalysts, and different types of solid electrolytes. In this review paper the main features and mechanisms of the electrochemical promotion effect are summarized and discussed.

1. Introduction

Catalysis plays an important role in chemical industry. The first time a catalyst was used in chemical industry was in 1746 by J. Roebuck and S. Gardner in the manufacture of sulfuric acid in a lead chamber [1]. Nowadays heterogeneous catalysts are involved in at least one step in about 80% of the chemicals produced in chemical industry [2,3]. In addition, catalysts play a great importance in environmental chemistry, i.e. in removing pollutants by chemical reactions, e.g. by removing CO, NO and CHx emissions in automotive exhaust gas. For improving catalysts it is important that researchers from different fields work together. One of these fields is surface science. In surface science with a well-defined surface structure and chemical composition of a model catalyst and of elementary steps like adsorption,

desorption, and diffusion are studied under UHV (ultra high vacuum) conditions eemploying typically single crystals. The conditions and the samples in surface science are thus quite far away from the conditions of so-called real catalysis. This difference constitutes the famous "pressure gap" and "material gap" problem [4]. The pressure gap arises because surface model studies are usually conducted under low pressure conditions (p< 10^{-6} mbar), while industrial catalysis is performed at atmospheric or even higher pressure (p≈ 1-100 bar). Indeed, low pressure conditions provide a couple of advantages: a high level of purity can be realized, experiments are strictly isothermal due to low conversion rates, and, most of all, surface analytical techniques based on free electrons are available to characterize the catalyst surfaces [5]. Since the 1980s, many researchers have devoted their efforts to surface science studies in order to efficiently use the results to explain or even predict the catalytic activity of certain systems [6, 7]. The interfacing of electrochemistry and catalysis offers some exciting theoretical and technological possibilities. A dramatic improvement in the catalytic activity and selectivity of a composite catalyst metal/solid electrolyte (SE) has been achieved simply by polarization of the interface by application of an electrical current/potential. A solid electrolyte is highly efficient in order to improve the catalytic performance. Pioneered by Vayenas and his group in Patras, Greece found an efficient realization by depositing porous metal electrodes onto a solid electrolyte that electrochemical promotion of catalysis (EPOC) was

investigated systematically on a large scale [8]. However, the EPOC effect has been demonstrated already for more than 100 catalytic reactions, fundamental questions still remain unresolved in the postulated mechanism by Vayenas and co-workers. A brief overview of some EPOC studies, of different systems and using a varity of catalysts supported on different types of solid electrolytes, is then provided in Table 1.

2. Solid electrolytes

In solid-state ionics, solid electrolytes (SE's) are an unusual group of materials which have high ionic conductivity with negligible electronic conductivity. They conduct electrically not due to the transport of electrons, but via the movement of ions through vacancies (voids, or empty crystallographic positions) in their crystal structure. One component of the structure, the cation or anion, is essentially free to move throughout the structure, acting as charge carrier. SE's are intermediate in nature between crystalline solids which possess a regular structure with immobile ions, and liquid electrolytes which have no regular structure and fully mobile ions. The preparation and properties of SE's have been discussed in a number of books and reviews [27-32]. Solid electrolytes can be made from organic or inorganic materials, such as yttrium stabilized zirconia (YSZ) which is an O^{2-} ion conductor at temperature higher than 250 °C, β''-Al_2O_3 which is conductive for Na^+ ion at temperature between 180 and 300 °C, $CsHSO_4$ and Nafion, which are proton conductors at temperatures about 150 and 25 °C, respectively, CaF_2 which is an F^- ion conductor at temperature range between 550-700 °C, and mixed ionic-electronic conductors, e.g. TiO_2 and CeO_2.

Table 1: The electrochemical promotion studies of different systems over different catalysts supported on different types of solid electrolytes. SE= Solid electrolyte, I_{WC}= constant current applied between the working and the counter electrodes, V_{WR}= fixed voltage applied between the working and the reference electrodes, Λ= faradaic efficiency, ρ= rate enhancement ratio, YSZ= yttrium stabilized zirconia, BCN18= $Ba_3Ca_{1.18}Nb_{1.82}O_{9-\alpha}$, PVD= Physical Vapour Deposition technique, SZY= Strontia zirconia yttria perovskite ($SrZr_{0.95}Y_{0.05}O_{3-\alpha}$), T.D= Thermal decomposition process, CIZ= $CaIn_{0.1}Zr_{0.9}O_{3-\alpha}$, and NASICON= $Na_3Zr_2Si_2PO_{12}$.

System	Catalyst	SE	Applied I_{WC} or V_{WR}	Λ	ρ	Ref.
$C_3H_6 + O_2$	Pt paste	YSZ	-65 µA	-2648	3.5	9
$C_2H_4 + O_2$	Pt past	TiO_2	50 µA	1880-1974	11.3-21	10
$C_2H_4 + O_2$	Pt past	CeO2	-5 V	-5.2×10^4	3	11
$C_3H_6 + NO + O_2$	Rh paste	YSZ	60 µA	381	52	12
$C_2H_4 + O_2$	Pt paste	BCN18	-1 V	-1340	6.2	13
$CH_4 + O_2$	Pd PVD	YSZ	1 V	2.4-258	-	14
$H_2O + CO$	Pt paste	YSZ	-1.5 V/2.5 V	-30/-0.6	2.3/0.78	15
$H_2O + CO$	Pd paste	SZY	2.5 V	8	2	16
$C_7H_8 + O_2$	RuO_2 T.D	YSZ	-100 µA/100 µA	-5/12	4/8	17
$C_7H_8 + O_2$	Ag paste	YSZ	-4 µA/-1V	-9500/-10500	4.8/4.2	18
$CH_4 + O_2$	ePd pas	YSZ	1 V	153	68	19
$H_2 + N_2$	Fe paste	CIZ	-1 V	0.6	2	20
$C_2H_4 + O_2$	Pt past	CIZ	-3 µA	17740	2.87	21
$C_3H_8 + O_2$	Pt paste	YSZ	3.5 mA/5 mA	141/52	-	22,23
$C_2H_6 + O_2$	Pt paste	YSZ	220 µA	170	16.5	24
$C_2H_4 + O_2$	Pt past	NASICON	-7 µA	-	10	25
$CH_3OH + O_2$	Pt past	YSZ	10 µA	100	2	26

The most often used SE in EPOC experiments is yttrium stabilized zirconia (YSZ). Basically, it is a zirconium-oxide based ceramic, in which the particular crystal structure of zirconium oxide cubic fluorite structure stabilized at room temperature by the addition of yttrium oxide. These oxides are commonly called "zirconia" (ZrO_2) and "yttria" (Y_2O_3). The addition of yttria to pure zirconia replaces some of the Zr^{4+} ions in the zirconia lattice with Y^{3+} ions.

This produces oxygen vacancies to maintain charge neutrality in the lattice, as three O^{2-} ions replace four O^{2-} ions as shown in Fig. 1 [33, 34]. It also permits YSZ to conduct O^{2-} ions (and thus conduct an electrical current), provided there is sufficient vacancy site mobility, a property that increases with temperature. At elevated temperatures the oxygen vacancies are mobile, provided an increase of the ionic oxygen conductivity. In fact, more than 99% of the current through YSZ is carried by the oxide ions. The ionic conductivity of YSZ depends on the dopant Y_2O_3 concentration. According to the literatures the maximum ionic conductivity lies around 8-10 mol%

Y_2O_3 doping [35- 41]. Accordingly, the stability and the ability of YSZ to conduct O^{2-} ions makes it well suited to use for a variety of applications, e.g. as refractory ceramics, thermal-barrier coatings, ceramic glazes, insulators, electroceramics, oxygen sensors, solid oxide fuel cells, chemical and electrochemical reactors as well as abrasives, grinding media and machining tools [36-49].

3. Electrochemical activation of catalysis

One emerging application of SE cells is the electrochemical activation of catalytic reactions taking place on their gas-exposed electrode surfaces. In this review we select and discuss the ethylene oxidation reaction on Pt/YSZ as an example for the EPOC systems. The reason for this choice is due to the huge Λ–factor of 3×10^5 of this system which has been measured since 1989 and cited in several publications. However, for the same system and under the same conditions vastly differing values of 2.5-77, 188, 865, 975, 15000 and 3×10^5 were reported for different Pt/YSZ samples as given by Table 2.

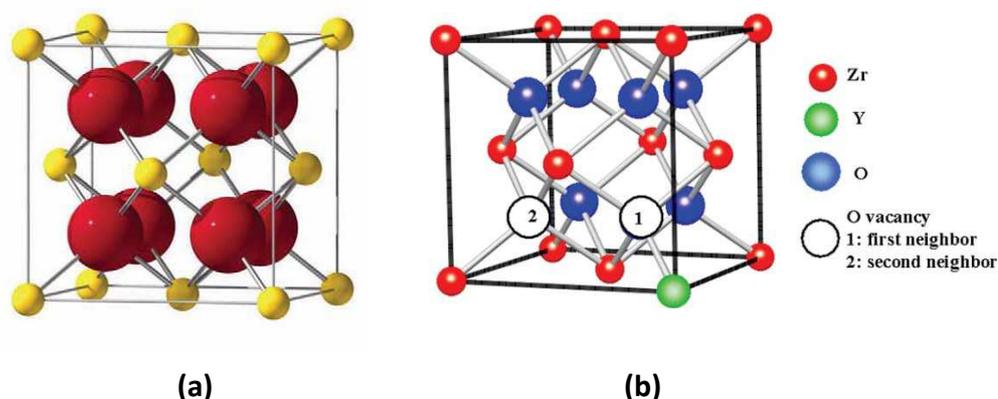**(a)**   **(b)**

Fig. 1: (a) Cubic fluorite type structures of: (a) Zirconia (ZrO_2) with the O ions shown in red circles and the smaller Zr ions shown in yellow, and (b) Yttrium stabilized zirconia (YSZ), adopted from references [33, 34].

Table 2: Electrochemical promotion studies of ethylene oxidation ($C_2H_4 + O_2$) over diffrent type of catalysts supported on YSZ. YSZ= yttrium stabilized zirconia, Λ= faradaic efficiency, ρ= rate enhancement ratio, PLD= Pulsed laser deposition, and T.D= Thermal decomposition process.

Catalyst	Applied I_{WC} or V_{WR}	Λ	ρ	Ref.
Pt paste	1 µA/1 V	$74000/3 \times 10^5$	26/55	50
Pt paste	300 mV	15000	10	51
Pt paste	2 V	975	95	52
Pt paste	1 V	865	-	53
Pt paste	270 µA	188	67	54
Pt paste & PLD	400 µA	2.5-77	1.14-2.2	55
Pt sputter	0.5 mA	370	4.2	56
Pt sputter	1 V	2.4	-	57,58
Pt-Ag sputter	2 V	2.18	1.2	59
Pt-Au paste	-20 µA	-704	3	60
Pd paste	11 µA	16000	1.7	61
Rh sputter	50 µA	1024	52	62
Rh paste	100 µA-400 µA	770-1620	3.5-88	63
RuO_2 T.D	200 µA	170	11	64

3.1 Phenomenology and basic definitions

Solid electrolytes interfaced with noble metal electrodes allow an EPOC effect simply by varying the electrode potential. The principle possibility of using solid electrolytes to control the chemical potential of a surface species has already been recognized by C. Wagner in 1970 [65]. He proposed the use of solid electrolyte potentiometry (SEP) for the measurement of oxygen activity simultaneously with reaction rate measurements during oxidation reactions. Vayenas and Saltsburg were the first to fellow reaction rates and oxygen activities during the oxidation of SO_2 on platinum, gold and silver [66]. In their pioneering work in the early 1980s

Vayenas et al. reported the control of catalytic reactions via electrochemical polarization of the metal/solid electrolyte interface. They found that the catalytic activity of a porous metal catalyst films could be dramatically increased in a controlled manner by polarization of the catalyst/solid electrolyte interface in an electrochemical cells of the type [26,67].

Gaseous reactant, Metal catalyst (WE)│Solid electrolyte│Metal (CE), Auxiliary gas   (1)

where the metal catalyst film is the working electrode (WE) and a typically catalytically inert metal is the counter electrode (CE). The auxiliary gas can be ambient air when using the ''fuel cell'' type design (Fig. 2a) or the reactive gas mixture itself in the, so called, single

pellet design (Fig. 2b) [50,68]. This effect is so-called electrochemical promotion of catalysis (EPOC) or non-Faradaic electrochemical modification of catalytic activity (NEMCA).

In further studies the EPOC effect has been demonstrated for about 100 reaction systems utilizing a number of different solid electrolytes the most important ones being O^{2-} conducting yttrium stabilized

zirconia (YSZ) and Na^+ conducting β''-Al_2O_3 [8]. Nearly all of these studies have been conducted in the 10^{-2} mbar to atmospheric pressure range with structurally and chemically ill-defined metal electrodes prepared, for example, by depositing Pt paste with a brush onto YSZ followed by calcination. Surface science type studies of the EPOC effect were started about 15 years ago [48,59,69-71]. As was demonstrated with photoelectron spectroscopy and other methods, the physical basis of the EPOC effect is the electrochemically induced spillover of the transported ionic species onto the surface of the metal electrode after discharge at the three-phase-boundary (tpb), gas/metal/solid electrolyte.

3.2 Experimental results

The basic experimental setup used to observe the EPOC effect or the NEMCA effect on O^{2-}-conducting solid electrolytes is shown in Fig. 2a with a half-closed YSZ tube as catalytic reactor using the fuel-cell type. For the electrochemical measurements a standard three-electrode set-up displayed in Fig. 2b is used. In a typical NEMCA experiment, for example in the combustion of ethylene, the catalytic reaction takes place on the catalyst

surface of a conductive porous Pt film of roughly 1-10 μm thickness the Pt film also serves, at the same time, as the working electrode (WE) in a solid electrolytic cell: Gaseous reactant (e.g. C_2H_4 + O_2), Pt catalyst (WE)│YSZ│Pt (CE), auxiliary gas (e.g. air).

The porous Pt electrodes are prepared by simply depositing a Pt paste with a brush followed by calcination and sintering. Figure 3 shows a typical galvanostatic NEMCA experiment carried out in the setup of Fig. 2a [50]. The experiments are carried out with the partial pressures of the feed gases being in the 10^{-2} to mbar range but with He as carrier gas so that the total pressure is around 1 bar. Mass flow controllers are used to adjust the feed of the reactants. Under open- circuit (OC) conditions (I = 0, no electrochemical rate contribution) the catalytic (no net charge-transfer) reaction is given by the catalytic reaction:

$$C_2H_4 + 3O_2 \rightarrow 2H_2O + 2CO_2 \qquad (2)$$

For the non-electrochemist it is worth reminding that "a galvanostatic process" always fixes the current, I_{WC}, between the working electrode (WE) and the counter electrode (CE) at a desired constant value. Whereas "a potentiostatic process" always fixes the potential, V_{WR}, between the WE and the reference electrode (RE) at a certain constant value. Application of a constant electrical currents, I_{WC}, between the catalyst WE and the CE (galvanostatic operation) or a constant potentials, V_{WR}, between the catalyst WE and RE (potentiostatic operation) gives rise to very pronounced, non-Faradaic changes (i.e. $\Delta r \gg I/2F$) in the catalytic rate, r, and quite often in product selectivity [8].

The difference between Faradaic and non-Faradaic rate increase is explained as fellows. The electrocatalytic reaction taking place at the tpb, where the O^{2-} ions are discharged as follow:

$$C_2H_4 + 6O^{2-} \rightarrow 2H_2O + 2CO_2 + 6e^- \quad (3)$$
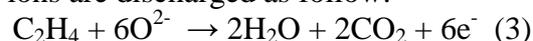
Supposing a current efficiency of 100%, the maximum possible electrochemical reaction rate, r_F, (mol O/ s), is calculated with Faraday's law:

$$r_F = I/nF \quad (4)$$

with I represent the applied electric current, n the charge number of the transported ions (for O^{2-}, n = 2), and F the Faraday constant. If open-circuit and Faradaic reactions would be additive, Eq. 4 would give the maximum expected increase in reaction rate due to polarization. Figure 3 shows the evolution of the experimentally observed reaction rate, r, in a stepwise anodic polarization cycle, i.e. before, during, and after galvanostatic polarization of the catalyst/YSZ interface in the combustion of ethylene over a Pt/YSZ reported by Vayenas et al. [50]. As indicated by Fig. 3 under open-circuit (OC) conditions ($I = 0$, no electrochemical rate contribution) the catalytic reaction rate is equal, $r_0 = 1.5$ x 10^{-8} mol O/s. We now apply a positive constant current ($I_{WE} = 1$ μA) between the Pt WE catalyst and the counter electrode. In this way oxygen ions, O^{2-}, are supplied to the catalyst at a rate I/2F = 5.2 x 10^{-12} mol O/s, according to Faraday's law. The catalytic rate starts increasing and within 25 min gradually reaches a value r = 4 x 10^{-7} mol O/s which is 26 times larger than the initial value r_0. Since positive current or potential causes O^{2-} ions to be drawn to the WE, the measured increase in catalytic C_2H_4 combustion seems simply to be caused by the additional oxygen supply.
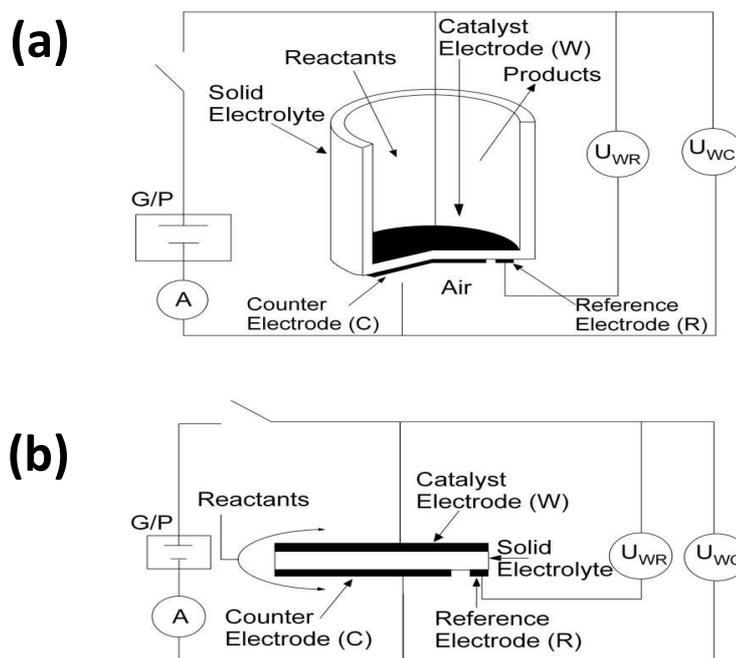

Fig. 2: Typical experimental set-up for EPOC experiments using the fuel-cell type (a) and single-pellet type (b) configurations; G/P. galvanostat / potentiostat controls the electric current / the electric potential. Using a half-closed YSZ tube a reactor the reactants are fed inside the tube where they react at the surface of the Pt working electrode (WE) whereas the reference electrode (RE) outside the tube is held in ambient air thus fixing the potential of the RE [68]. Reprinted with permission from Elsevier.

Unexpectedly, the rate increase is strongly non-Faradaic by a factor of 74000! This means the increase in the catalytic rate is 74000 times larger than the Faradaic rate I/2F. Thus each O^{2-} ions supplied to the Pt catalyst causes at steady-state 74000 oxygen atoms, chemisorbed on the Pt surface, to react with C_2H_4 and to form CO_2 and H_2O.

Vayenas et al. introduced the term Faradaic efficiency or Λ-factor which is the electrochemically induced rate increase divided by the Faradaic rate. In Fig. 3 Λ has a value of 74000. The highest Λ–factor is reported with Λ = $3x10^5$ for the same reaction (i.e. ethylene oxidation over Pt/YSZ), but under application of a constant potential V_{WR} = +1 V to the Pt WE with respect to the RE, meaning that each transported O^{2-} ion catalyzes the oxidation of about $1x10^5 C_2H_4$ molecules to CO_2 [50]. Also Λ-values are possible to be negative values depending on whether a positive or negative applied electric potential or current causes a promotion effect (i.e. depend on the polarity of the WE). When Λ = 1 means Faradaic reaction. If Λ is smaller than 1, then instead of promotion are has a poisoning effect. The measured Λ-values range from $3x10^5$ down to $-5x10^4$ [8]. In EPOC experiments two parameters are commonly used to quantify the magnitude of the phenomenon, defined as [8]:

(a) The faradaic efficiency, Λ, is defined as the ratio of the observed rate increase to the highest possible electrochemical rate:

$$\Lambda = \Delta r/ I/2F \qquad (5)$$

where $\Delta r = r - r_0$ is the change in the catalytic rate caused by the current or potential application and I/2F is the rate of supply (I > 0) or removal (I < 0) of O^{2-} to or from the catalyst. The applied current is given as I and F is the Faraday's constant. When │Λ│>1 the changes in the catalytic rate are non-Faradaic and the reaction exhibits NEMCA behavior. When Λ>1 the reaction is termed electrophobic and when Λ< -1 the reaction is termed electrophilic. Pure electrocatalysis dominates when Λ=1 and the reaction then exhibits regular Faradaic behavior, i.e. the increase in the reaction rate, Δr, equals the rate of ion transport through the electrolyte I/2F.

(b) The rate enhancement ratio, ρ, defined as:

$$\rho = r/ r_0 \qquad (6)$$

where r is the electropromoted catalytic rate observed under polarization by an applied current or potential and r_0 is the regular (i.e. open-circuit) catalytic rate. For the experiment of Fig. 3, the maximum ρ value is 26; ρ values up to 150 or even higher and down to 0 have been obtained [8].

3.3 EPOC mechanism

In order to explain the measured non-Faradaicity of such a reaction system, e.g. the huge Λ-factor of $3x10^5$ in case of the ethylene oxidation reaction on Pt/YSZ [50]. Vayenas and co-workers proposed "sacrificial promoter" mechanism. The mechanism of the EPOC effect developed for the O^{2-} conducting Pt/YSZ system was based on the existence of two different oxygen species, regular chemisorbed oxygen and a special spillover species which acts as "sacrificial promoter".
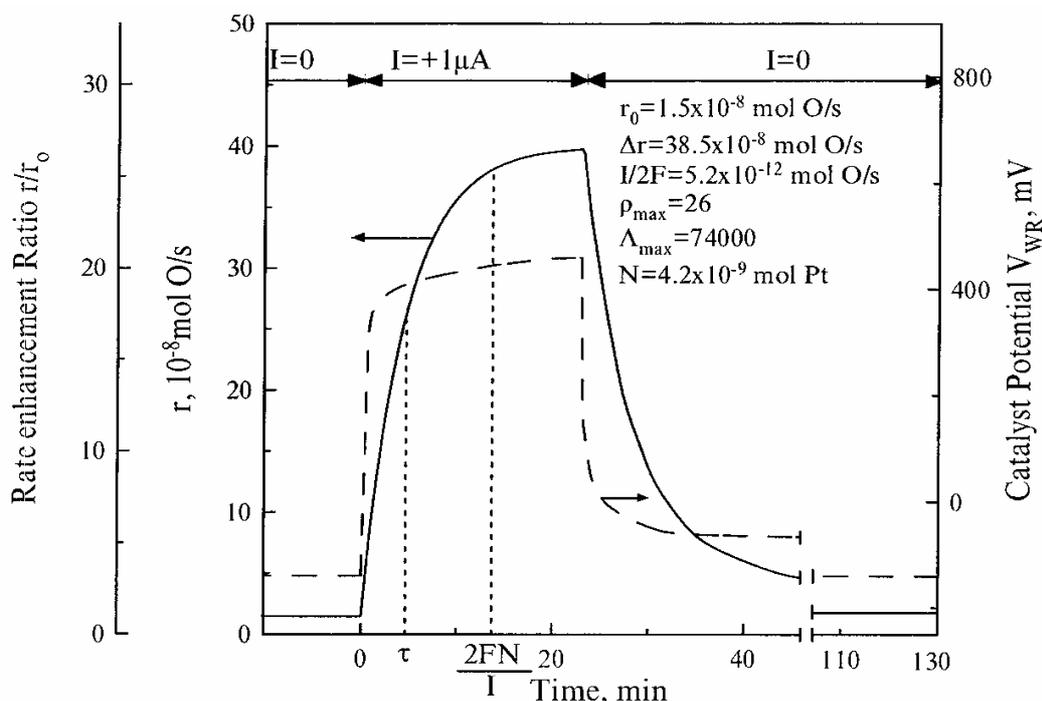
Fig. 3: A typical galvanostatic NEMCA experiment of ethylene oxidation at a Pt/YSZ catalyst. The experimental (τ) and computed (2FN/I) rate relaxation time constants are indicated on the figure. The parameter (2FN/I) is the number of active sites of the Pt catalyst (N is the Pt/gas interface surface area in mol Pt). The dashed line represents the catalyst WE electrode potential, V_{WR}, response with respect to the reference electrode. Experimental conditions: T= 643 K, $p(O_2)$= 4.6 x 10^{-2} mbar, $p(C_2H_4)$= 3.6 x 10^{-3} mbar [50]. Note the experiment carried out in the setup of Fig. 2a. Reprinted with permission from Elsevier.
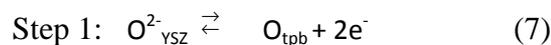
This "sacrificial promoter" mechanism which involves two oxygen species has been advocated in numerous papers, reviews and monographs by Vayenas and co workers [8,72-78].

They proposed an oxygen spillover species which (i) should be strongly polar, i. e. have a charge $O^{\delta-}$ with δ being close to two and (ii) should be bonded more strongly to platinum than chemisorbed oxygen, and (iii) should have a reduced reactivity as compared to chemisorbed oxygen. Owing to the high polarity of the spillover adsorbate complex the spillover oxygen should modify the binding strength of coadsorbed species thus causing a variation of the activation barriers of surface reactions. Since this special spillover species is less reactive than

chemisorbed oxygen it can influence the surface reaction of many coadsorbed molecules while being very slowly consumed itself. This special spillover species thus acts very similar to a classic electronic promoter with the non-Faradaicity being a natural consequence of the reduced reactivity. The existence of a special oxygen spillover species proposed by Vayenas and co workers based on a single old XPS (X-ray photoelectron spectroscopy) measurement [79]. As indicated by Fig. 4 upon applying a positive potential to the catalyst WE electrode the O1s spectrum shifts to lower binding energies (BE) developing a new special spillover oxygen species has BE of 528.8 eV (versus 530.4 eV for regular chemisorbed oxygen on Pt).

In contrast, using a microstructured Pt/YSZ sample XPS under low pressure conditions ($p < 10^{-6}$ mbar) showed that the spillover species is identical to chemisorbed oxygen from the gas phase as shown in Fig. 5 [80]. The regular chemisorbed oxygen has a binding energy (BE) with an O1s of 530.4 eV. This result is in agreement with physical intuition because oxygen spilling over from the tpb onto the surface of the metal electrode the oxygen should lose its memory of where it came from originally. The electrochemically induced spillover of oxygen ions onto the surface of the metal electrode is shown in Fig. 6. The oxygen ions which are transported through the YSZ solid electrolyte are discharged at the tpb and then the discharged oxygen generated at the tpb

(O_{tpb}) spills over the electrode surface forming a layer of chemisorbed oxygen (O_{ad}). One can thus formulate the following steps:

Step 1: $\quad O^{2-}_{YSZ} \overset{\rightarrow}{\rightleftarrows} \quad O_{tpb} + 2e^{-}$ $\qquad$ (7)

Step 2: $\qquad O_{tpb} \overset{\rightarrow}{\rightleftarrows} \quad O_{ad}$ $\qquad$ (8)

Therefore the net charge transfer (electrocatalytic) reaction at the tpb is:

$\qquad O^{2-}_{YSZ} \overset{\rightarrow}{\rightleftarrows} \quad O_{ad} + 2e^{-}$ $\qquad$ (9)

Recently, Imbihl conclude that the O1s BE at 528.8 eV which often cited as evidence for $O^{\delta-}$ with ($\delta \approx 2$) stems from oxygen of YSZ which floats with the applied potential due to not all parts of the metal catalyst WE electrode may be in electrical contact with each other [81-83].
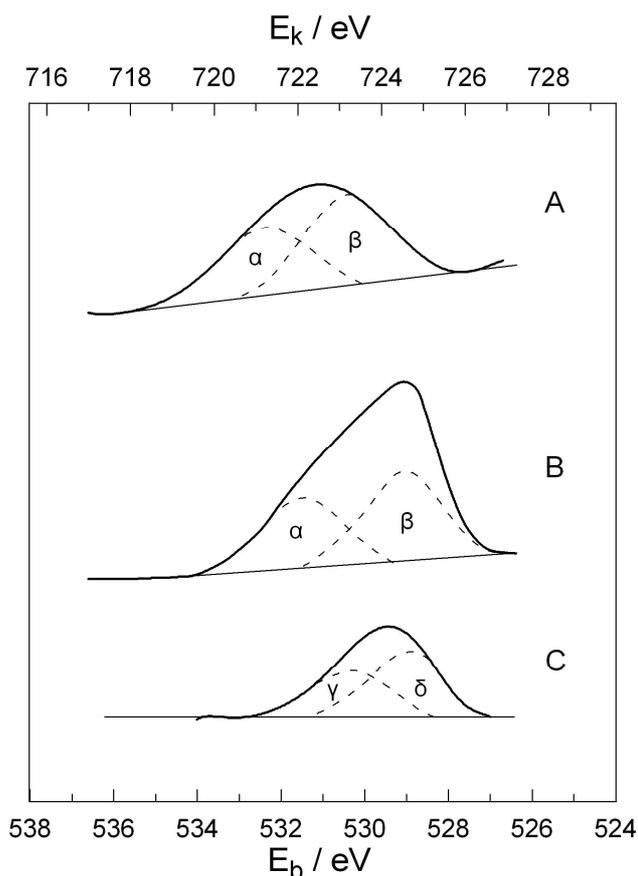

Fig. 4: Photoelectron spectra of the O 1s region of a porous Pt/YSZ catalyst demonstrating the effect of electrochemical pumping at 673 K. (A) Open-Circuit conditions, (B) $V_{WR} = +1.2$ V and (C) Difference spectrum of A and B, From ref. [79].

Noteworthy, the proposal of a special oxygen spillover species in Pt/YSZ was not only based on XPS alone but also on the appearance of an additional peak in CV (cyclic voltammetry) and in TPD (temperature-programmed desorption). CV of the system Pt/YSZ gives rise to a number of peaks reflecting the oxidation or reduction of the oxygen species in this system as shown in Fig. 7 [84]. In contrast, the peak assigned in cyclic voltametry by Vayenas et al. [53,84] to the special spillover species was shown to be caused by Si contamination, for other detailed investigations by Janek et al. as shown in Fig. 8 [85]. In TPD after prolonged electrochemical pumping via positive current or potential application causes significant oxygen spillover from the solid electrolyte YSZ to the catalyst surface and causes oxygen to adsorb in two distinct adsorption states, a strongly bonded "special spillover" ionic oxygen and a weakly bonded atomic oxygen state with a temperature of 50 K lower than that of normally chemisorbed oxygen [86,87]. But then again isotopic O^{16}/O^{18} exchange experiments with Pt/YSZ conducted by Sobyanin et al. demonstrated that an electrochemical polarization of the Pt/YSZ interface does not lead to an enhanced binding strength of oxygen on Pt [88]. They also suggested that an electrochemically initiated chain mechanism might be responsible for the non-Faradaic rate increase [89-91]. A third possibility has been introduced recently by Toghan et al. who suggested that ignition mechanism [48,49,57-59,92]. The ignition mechanism does not require a special oxygen spillover species and instead assigns the spillover species the role of triggering the reactive removal of an inhibitory adlayer. Using ethylene oxidation on Pt/YSZ as example, the basic idea is that ethylene decomposition on Pt produces a carbonaceous CH_x film which inhibits O_2 adsorption and hence protects the carbonaceous layer against reactive removal by O_2. However, in the presence of an excess of O_2 in the gas phase the CH_x layer is only metastable. Upon application of a positive potential spillover oxygen is created which eats holes in the CH_x layer as schematically depicted in Fig. 9.

To sum up, strictly speaking, the absence of a valid proof does not mean that this species does not exist. One should therefore leave the possibility open that in the future some further experiments will be able to demonstrate that at high coverage/high pressure such a special spillover species exists or not. So far there is a quite agreement as the identity of chemisorbed oxygen and the spillover species at low coverage/low pressure is accepted by Vayenas and Imbihl, i. e. under these conditions only one oxygen species exists [81,92].
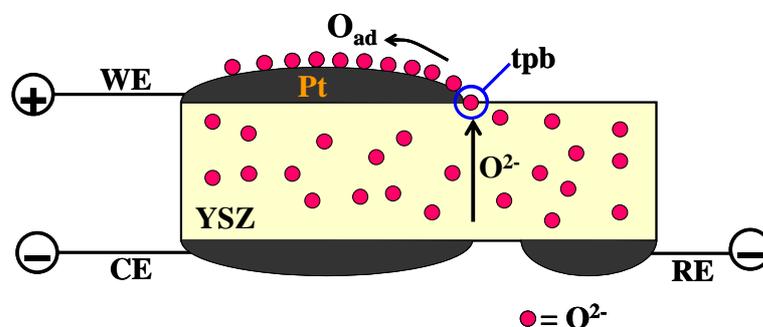

Fig. 6: Scheme showing the electrochemically induced spillover of oxygen ions onto the surface of the metal electrode. Oxygen ions are transported through the YSZ solid electrolyte during the anodic (positive) polarization of the metal catalyst (working electrode) and are discharged at the tpb and the discharged oxygen species then migrate onto the surface of the Pt electrode.
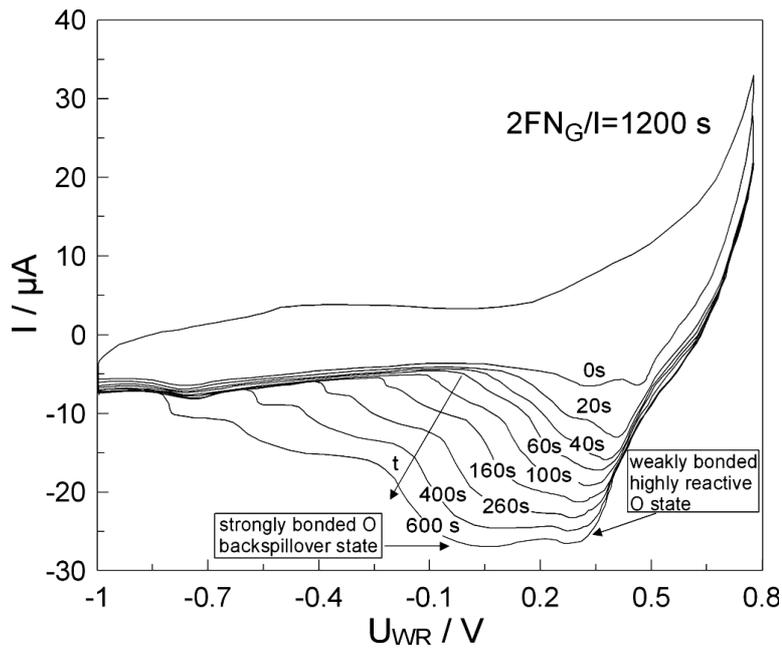
Fig. 7: Cyclic voltammograms (CV) of the Pt/YSZ catalyst electrode for various holing time at 673 K under UHV conditions, from ref. [84]. The Pt film was deposited on the surface of YSZ specimen using a thin coating of Pt paste followed by drying and calcination in air.
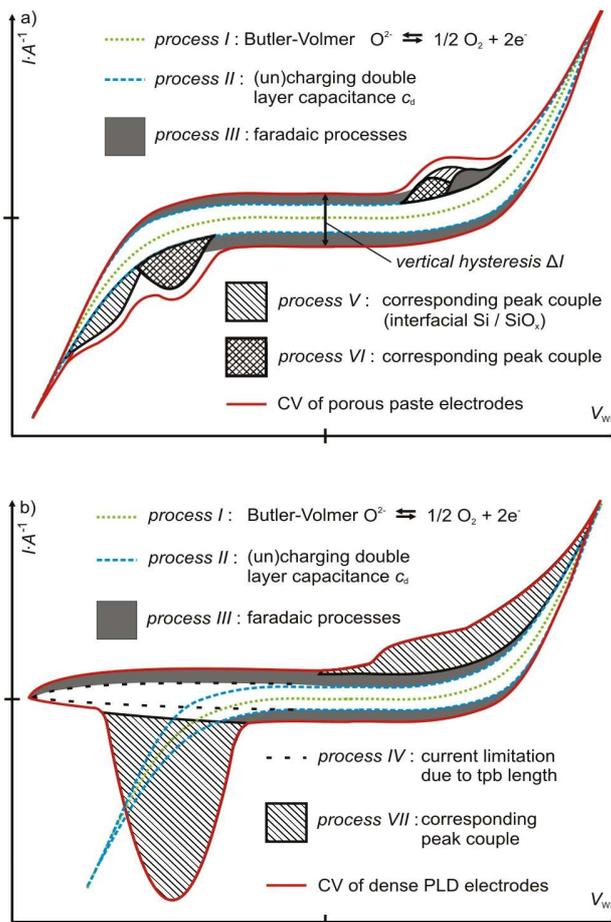

Fig. 8: Interpretation of CV peaks using different Pt/YSZ electrodes: (a) porous Pt film, and (b) dense Pt(111) film produced by pulsed laser deposition (PLD), according to ref. [85].
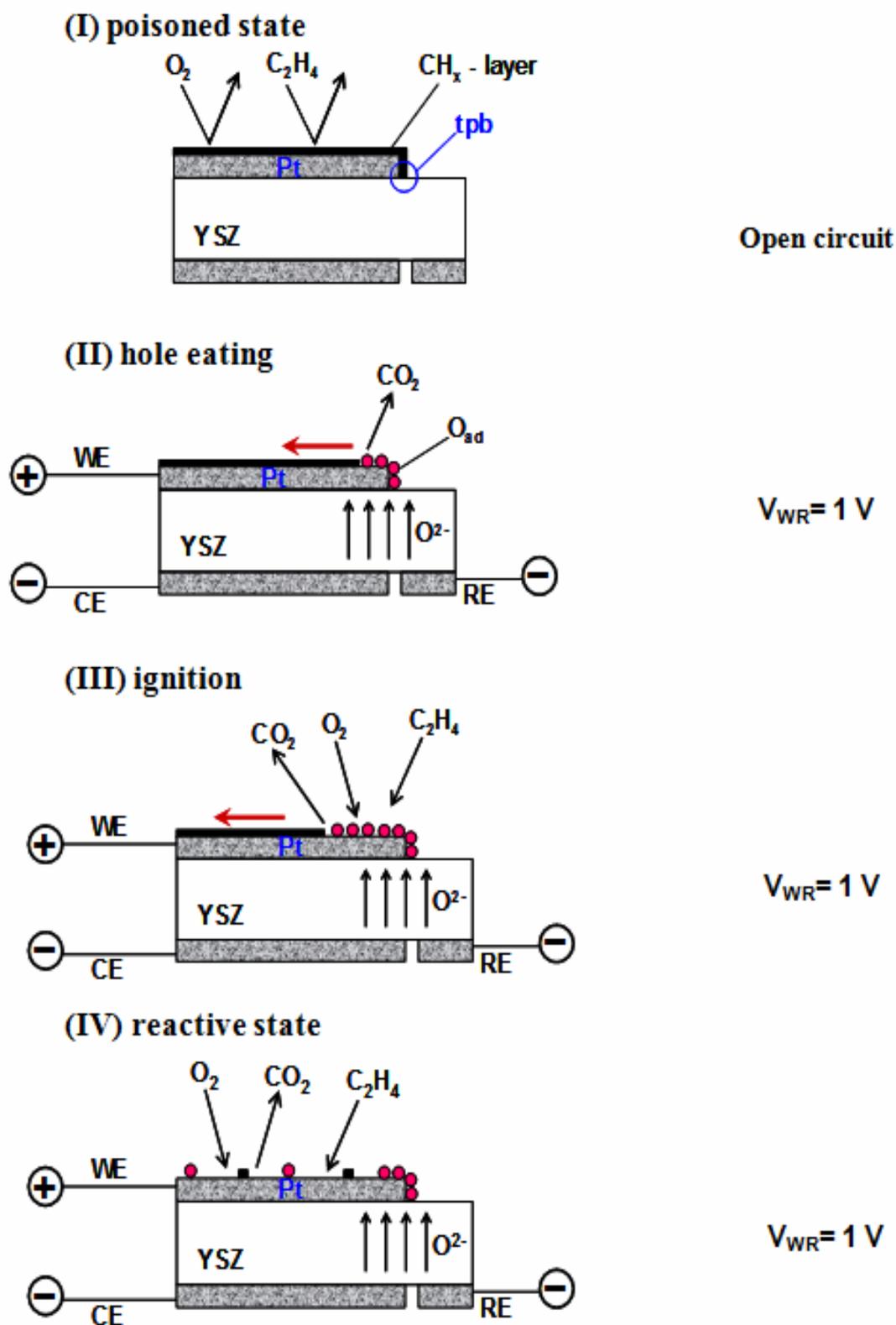
Fig. 9: Schematic drawing of the ignition mechanism as proposed by Toghan et al. for the electrochemical activation of catalytic ethylene oxidation on Pt/YSZ under UHV conditions. YSZ = yttria-stabilized zirconia, tpb = three-phase-boundary (solid electrolyte/metal/gas), WE = working electrode, CE = counter electrode and RE = reference electrode, from [92].

3.4 NEMCA time constant (τ)

Setting the potential V_{WR} back to zero in an EPOC experiment, such as the one depicted in Fig. 3, the rate returns to its initial value within a few minutes, i.e. in this case EPOC is reversible reaction. As indicated by Fig. 3, τ is of the order of 2FN/I and this turns out to be a general observation in NEMCA studies with O^{2-} conductors is that the magnitude of τ can be predicted by [8]:

$$\tau \approx 2FN/I \qquad (10)$$

with N (mol) represents the number of adsorption sites on the electrode surface and I is the ionic current. The parameter 2FN/I denotes the time, τ, required to form a monolayer of O_{ad} on the metal surface, i.e. to fill the electrode surface with ions discharged at the tpb. This necessarily requires the spillover of ions discharged at the tpb onto the surface of the metal electrode.

3.5 Permanent EPOC (P-EPOC)

Electrochemical promotion is called "permanent" if the reaction rate under open-circuit conditions after current or potential interruption remains different from the value before current or potential application. As shown in Fig. 10 the EPOC effect is generally completely reversible, whereas irreversible "permanent" EPOC has been observed under certain conditions. Experimentally, the first observation of P-EPOC made by Comninellis et al. for C_2H_4 oxidation on IrO_2 as an electrode on a YSZ solid electrolyte cell [93]. An electrochemical promotion leading to an enhanced activity which persist after switching off the electric potential and has been summarized under "permanent EPOC" or "permanent NEMCA effect" [53, 93-96]. The activation of the catalyst is explained through the formation of a higher oxide, $IrO_{2+\delta}$. In the light of the experiments with ethylene oxidation over Pt/YSZ, it is very likely that often a restructuring of the catalyst is behind this so-called "permanent EPOC" effect [57,58].

In order to quantify the irreversible character of the promotion a "permanent" rate enhancement ratio, γ, Comninellis and co-workers used:

$$\gamma = r_{per}/r_0 \qquad (11)$$

where r_0 and r_{per} denote the open-circuit catalytic rate before and after the polarization pulse, respectively.
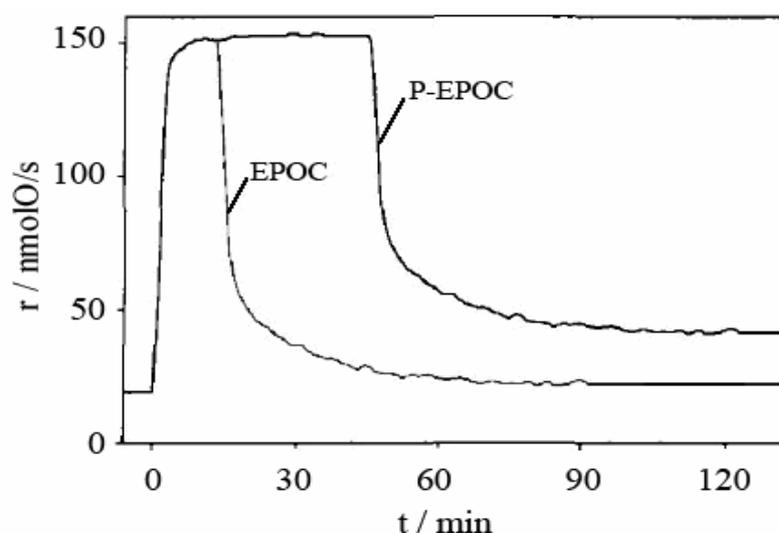
Fig. 10: A typical galvanostatic NEMCA experiment of ethylene oxidation at IrO_2/YSZ catalyst due to current application (300 µA) for two different polarization times: (a) short polarization to give reversible EPOC and (b) long polarization to give P-EPOC [93]. Experimental conditions: T= 380 °C, p(O_2)= 17 kPa, p(C_2H_4)= 140 Pa, reproduced with permission from Springer.

4. Summary and open question

An electrochemical promotion of heterogeneously catalyzed reactions (EPOC) can be achieved with porous thin film electrodes interfaced to a solid electrolyte. Upon application of an electric current or potential to the WE electrodes a reaction which is catalyzed by the metal may be strongly enhanced. Pioneered by Vayenas et al. the EPOC effect has been demonstrated for about 100 reaction systems comprising a vast range of different reactions, catalytic metals and different solid electrolytes. Typically, the electrochemically induced rate increase is non-Faradaic with respect to the ionic current. Mechanistically, the electrochemical promotion effect could be traced back to the spillover of the transported ionic species from the tpb where it is discharged onto the surface of the metal electrode. A "sacrificial promoter mechanism" based on the existence of a special spillover oxygen species was postulated by Vayenas et al. in order to explain the EPOC effect. In fact, despite a large body of experimental studies fundamental questions still remain unresolved. There is a quite agreement as the identity of chemisorbed oxygen and the spillover species at low coverage/low pressure (under these conditions only one oxygen species exists), it remains open whether or not such a special spillover species develops at higher pressure. This will be achieved only experimentally by using in situ XPS studies at higher pressure in order to provide useful information about the nature of the spillover species.

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