REVIEW

Bridging electrochemistry and heterogeneous catalysis

Costas G. Vayenas

Abstract The discovery of the effect of the electrochemical promotion of catalysis (EPOC) or non-Faradaic electrochemical modification of catalytic activity (NEMCA effect) is described together with the key steps of its exploration at high pressure and high vacuum and its rationalization via electrochemical and surface science techniques. Recent attempts for its practical utilization are also surveyed.

C. G. Vayenas
Department of Chemical Engineering, University of Patras,
Caratheodory 1 St,
Patras 26504, Greece

C. G. Vayenas (✉)
Academy of Athens,
Panepistimiou 28 Ave,
Athens 10679, Greece
e-mail: cgvayenas@upatras.gr

Introduction

Although electrochemistry and heterogeneous catalysis are both branches of Physical Chemistry and share several common features, e.g., they utilize similar isotherms to describe adsorption phenomena, there had been very little interaction between the two scientific communities before 1970. Names like Frumkin, Bockris, or Conway meant little to catalysis researchers, and names like Bodenstein, Wolkenstein, or Schwab meant little to electrochemists. The need to develop efficient electrodes for fuel cells has brought the catalytic and electrochemical communities much closer together in recent years [1] as the similarities between heterogeneous catalysis (no net charge transfer reactions) [2] and electrocatalysis (net charge transfer reactions) [3] have been recognized, particularly at the nanoparticle limit [4].

Furthermore, it has been found that not only catalysis can benefit electrocatalysis (e.g., via the steam reforming of hydrocarbons on Ni at the anodes of solid oxide fuel cells [1, 4]) but also that electrocatalysis can affect and activate heterogeneous catalysis in a very pronounced manner via the effect of electrochemical promotion of catalysis (EPOC) or non-Faradaic electrochemical modification of catalytic activity (NEMCA effect) [5]. In this paper, we present the key events which led to the discovery of this effect and to its detailed study for more than a hundred catalytic reactions until today.

Electrochemical activation of catalysis

Catalysts and electrodes

It was Carl Wagner who first proposed in a seminal paper [6] the study of metal heterogeneous catalysts by using them

simultaneously as electrodes in solid electrolyte cells based on electrolytes such as 8 mol% Y_2O_3-stabilized ZrO_2 (YSZ), an O^{2-} conductor. The use of the same piece of metal simultaneously as a catalyst and as an electrode looks like a very simple idea today but was a nontrivial step at the time. Wagner had proposed the measurement of the chemical potential of oxygen on metal catalyst surface this way. This led a few years later to the technique of solid electrolyte potentiometry (SEP) [7]. He had also suggested that the measurement of catalytic rates could be accomplished by measuring the current in such galvanic cells, i.e., he had predicted a Faradaic behavior of catalytic rates with varying potential [6].

What Wagner had not proposed was the use of gas chromatography or mass spectrometry to measure directly catalytic rates and any non-Faradaic effect which the cell current or potential could have on them [6]. Very few electrochemical laboratories were using instruments such as a gas chromatograph or a mass spectrometer these days (before 1980 or so), in the same way that no catalytic laboratory was using any galvanostat or potentiostat.

The present author was very lucky that his PhD Thesis adviser at the University of Rochester, Howard Saltsburg, had read Wagner's paper [6], had understood its potential importance, and asked him to do his thesis in this area working on the oxidation of SO_2.

The passive potentiometric measurements proposed by Wagner and performed during my thesis with Saltsburg led to some useful mechanistic information of SO_2 oxidation on different metals [7], and the technique was coined a few years later SEP [8, 9].

However, my attempts with Professor Saltsburg to affect the catalytic rate via electrical current application failed totally, not too surprising today, since we used a 12-V battery for that purpose instead of a galvanostat or potentiostat. I had hardly heard the names of such instruments at the time; they were not to be found in catalytic or surface science laboratories those days. With the invaluable help of Professor Bockris' classical book on Electrochemistry with Reddy [10], Howard Saltsburg and I were trying hard to learn as much electrochemistry as we could, even creating a reading graduate course which also involved my thesis coadviser Professor W. David Smith. But we were not fast enough to understand the need for a galvanostat or potentiostat for our exploratory experiments at Rochester which ended in 1976 as H. Saltsburg left for a sabbatical at Julich and I left as an Assistant Professor for Yale and a year later for MIT.

A gas chromatograph and a galvanostat

It may sound unbelievable today, but I think that the simple apparatus I built with the help of my student Mike

Stoukides in the Chemical Engineering Department at MIT in 1979 to explore the effect of current or potential application on a catalyst (Ag) interfaced with a solid electrolyte (YSZ) was the first apparatus combining a galvanostat–potentiostat (for imposing fixed currents or potentials) with a gas chromatograph (for measuring the catalytic rate of C_2H_4 epoxidation on Ag). In fact, we had the luxury of having in the apparatus also an IR analyzer for monitoring continuously the concentration of CO_2 in the continuous flow reactor products. This simple but powerful combination of electrochemical and gas analysis instruments was soon to lead to very interesting results.

Oxygen activity, Fermi level, and work function

A few weeks before the first critical experiment with Mike Stoukides in February 1980, we had a visit in our Chemical Engineering at MIT by Professor Vladimir Ponec from Prague, one of the internationally leading catalysis researchers at that time. As a young Assistant Professor, I explained to him the experiment I had in mind (Fig. 1) "Upon applying a potential (e.g. 1 V) between our Ag ethylene epoxidation catalyst and the Ag counter electrode we are going to change the chemical potential of oxygen on our Ag catalyst and also the work function of the Ag catalyst. We are thus very eager to see what effect this will have on catalytic activity and selectivity" I said. "You are going to change the Fermi level of your catalyst, not its work function" he responded calmly and authoritatively. "Yes I see" I responded smoothly. After a few minutes, we said good bye, and he wished me good luck. Very little did I know then about the differences between changes in Fermi level and changes in work function, Φ, and it was going to take me some 10 years before I knew enough.

Ponec was of course right to say that upon applying a potential of 1 V between our catalyst electrode and a
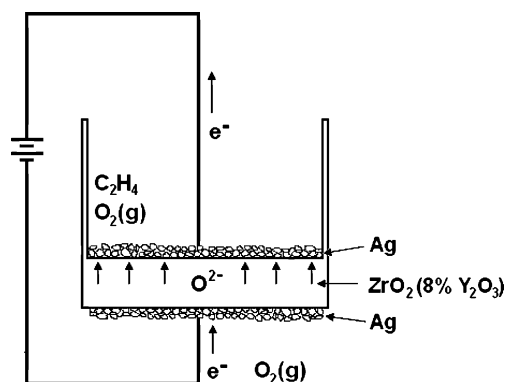
Fig. 1 Reactor design for the first NEMCA experiments [19, 20]. The Ag catalyst-electrode film is exposed to the C_2H_4–O_2 mixture, and the counter electrode is exposed to ambient air

reference electrode, we are changing the Fermi level (or equivalently the electrochemical potential, $\bar{\mu}$, of electrons) in our catalyst by 1 eV. But for any electrode surface, it is [3–5]:

$$-\bar{\mu} = \Phi + e\Psi \tag{1}$$

where Ψ, the Volta potential, is just the electrical potential a few micrometers outside the electrode surface (so that any image forces are negligible) [3]. Thus, upon applying a potential ΔU, it is:

$$e\Delta U = \Delta(-\bar{\mu}) = \Delta\Phi + e\Delta\Psi \tag{2}$$

If there is no change induced in the coverages of species adsorbed at the catalyst/gas interface, then from the Helmholz equation, it follows that $\Delta\Phi=0$ and thus the electrode surface is just being charged, i.e., $\Delta\Psi = \Delta U$. But if an overall neutral double layer is always present at the metal–gas interface, then it is always $\Psi=0$ and $\Delta\Psi=0$ [5]. Under these conditions, Eq. (2) dictates that:

$$e\Delta U = \Delta\Phi \tag{3}$$

which implies that the surface coverages and thus the density of the double layer must have changed in such a way as to satisfy Eq. (3).

Therefore, whenever one observes experimentally that Eq. (3) is satisfied [11], then this simply implies that an overall neutral double layer is present at the metal/gas interfaces of the catalyst and of the reference electrode [5]. Things are as simple as this, and we only confuse the issue by introducing quantities which are not measurable and whose sum or difference equals the measurables $\bar{\mu}$, Φ, and $e\Psi$. Such quantities are the Galvani potential, φ, the chemical potential of electrons, μ, the surface potential, χ, etc. [3, 5] (Fig. 2). Contrary to $\bar{\mu}$, Φ, and Ψ, the absolute values of φ, μ, and χ are not measurable [3, 5]. For surface scientists, it is also useful to mention that $e\Psi$ is just equal to the vacuum level. And for aqueous electrochemists, it is useful to mention that Eq. (3) is also valid for emersed electrodes in aqueous electrochemistry [12].

All this is in retrospect quite simple but can still be confusing and not so easy to grasp at the first moment. Fortunately, a good understanding of Eqs. (2) and (3) is not needed to carry out the experiment Mike Stoukides and I were ready to do. Vladimir Ponec was right of course about changing the Fermi level, and I, accidentally, was also right about changing simultaneously the work function. The latter, fortunately, turns out to be true due to the spillover of ions from the solid electrolyte to the metal/gas interface. I am very thankful to V. Ponec for the brief discussion in 1980 and even more thankful to Professors D. Kolb, S. Trasatti, and R. Parsons for some longer and sometimes
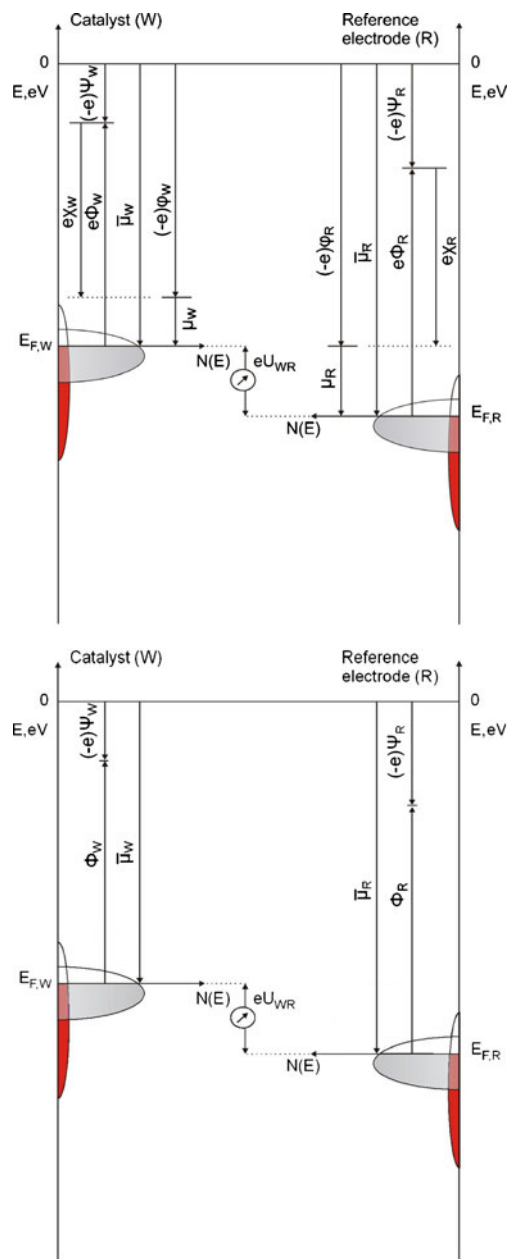
Fig. 2 *Top* Schematic representation of the density of states $N(E)$ in the conduction band of two transition metal electrodes (W and R) and of the definitions of work function Φ, chemical potential of electrons μ, electrochemical potential of electrons or Fermi level $\bar{\mu}$, surface potential χ, Galvani (or inner) potential φ and Volta (or outer) potential Ψ for the catalyst (W) and for the reference electrode (R). The measured potential difference U_{WR} is by definition the difference in $\bar{\mu}$; φ, μ, and $\bar{\mu}$ are spatially uniform; Φ and Ψ can vary locally on the metal surfaces; the Ψ terms are equal for the case of fast spillover, in which case they also vanish for an overall neutral cell. *Bottom* Same as top but showing only the measurable and essential $\bar{\mu}$, Φ, and Ψ. Reprinted with permission from the Electrochemical Society [17]

more animated discussions at the turn of the century [13, 14] which helped me to complete conceptually the picture shown in Fig. 2 and to utilize the concept of absolute potential [15, 16] in solid state electrochemistry [5, 17, 18].

The first transient

Mike Stoukides was only 5 years younger than me and had ranked second among some 60 PhD candidates at the MIT qualifier exams that year. I still remember with very vivid and nostalgic feelings this sunny morning of February 13, 1980 when we were ready for the first experiments.

For the previous 2 weeks, Mike struggling alone as I was writing proposals had not been successful to affect the catalytic rate via potential application. But when we checked and corrected all the electrical connections together and pressed the galvanostat button, then in a few seconds, the red pen recording the IR CO_2 signal in a strip chart recorder started moving upward slowly until the signal had increased by 20% or so. In retrospect, this was a very small effect in comparison to what was to be found in years to come, but we could both understand that this was just a beginning. We looked at each other with great joy and relief. We stopped the current. The CO_2 signal returned to its initial value. We applied a negative current. The CO_2 signal went down (Fig. 3). We were very happy and everybody in the lab was happy too: Jim Michaels, Marc Manton, Pablo Debenedetti, Catherine Teague, Wu Cheng Cheng, Bowei Lee, Roger Farr, and Dave Ortman; they were all excited with this first success, we had a great team, and I am truly thankful to all of them.

Our excitement grew bigger when we realized the same day that the selectivity to ethylene oxide was also significantly affected by potential (Fig. 4) and furthermore that the observed increase in the rates of ethylene oxide and CO_2 production were typically a factor 300 larger than that anticipated from Faraday's law (Fig. 5). So, we had a totally new and exciting phenomenon to describe, rationalize, and perhaps exploit [19, 20].
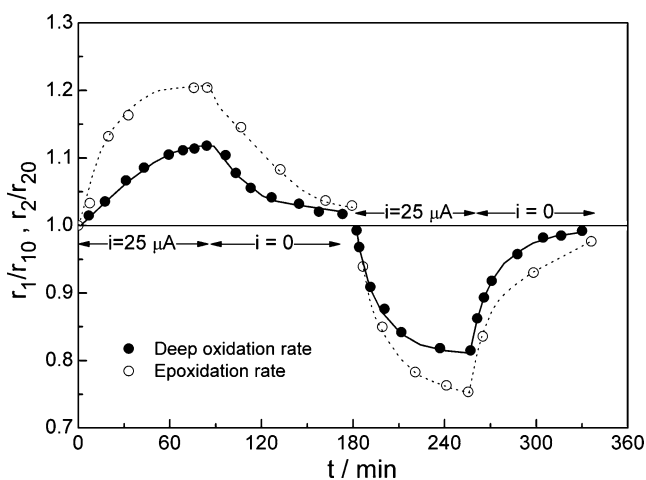
Fig. 3 Transient effect of electrochemical oxygen pumping during C_2H_4 epoxidation on Ag [20]; r_1 is the rate of epoxidation, and r_2 is the rate of CO_2 formation. Conditions: catalyst sample RC 2, $P_{ET} = 1.6 \times 10^{-2}$ bar, $P_{O2} = 9.5 \times 10^{-2}$ bar, and 400 °C [20]. Reprinted with permission from ACS
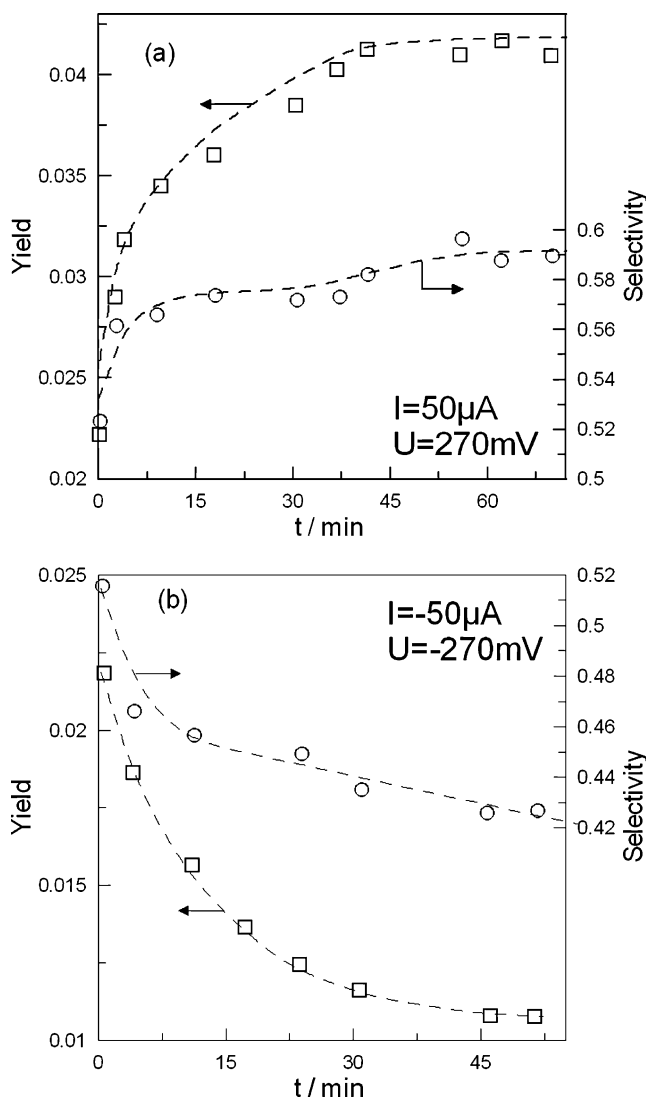
Fig. 4 Transient effect of electrochemical O^{2-} pumping to (a) and from (b) an Ag catalyst film on selectivity and yield to ethylene oxide [19]. Current applied at $t=0$; $p_{C2H4}=1.5$ kPa, $P_{O2}=10$ kPa; $T=400$ °C. U is the steady-state potential difference between the catalyst and the counter electrode. Reprinted with permission from Academic Press

Mike Stoukides was a very diligent graduate student, and by experimenting with no less than eleven YSZ tubular reactors over a period of a few months, he found that the relaxation time constant, τ for the catalytic rate transient upon current application, was described quite well by a simple expression:

$$\tau \approx 2FN_G/I \tag{4}$$

where F is Faraday's constant, I is the applied anodic current, and N_G is the independently measured reactive oxygen uptake of the catalyst electrode which, assuming a 1:1 adsorption stoichiometry, also expresses the gas exposed surface area of the catalyst electrode, expressed in mol metal. Thus, N_G is a measure of the surface area of
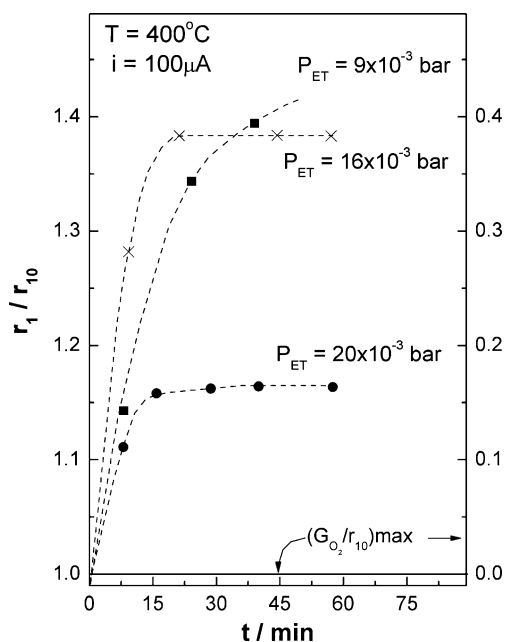
Fig. 5 Transient behavior of the rate of ethylene epoxidation r_1 when a constant current $i=100$ μA is applied at $t=0$. The P_{O2} values were 13.5×10^{-2}, 10×10^{-2}, and $6.\times10^{-2}$ bar for P_{ET} equal to $9.\times10^{-3}$, $16.\times10^{-3}$, and $20.\times10^{-3}$ bar, respectively [19]; G_{O2} is the rate, $I/4F$, of electrochemical O_2 supply to the catalyst. Reprinted with permission from Academic Press

the metal–gas interface where catalysis is taking place (Fig. 6, where the symbol Q had been used for $N_G/2$ [20]).

In order to describe the new phenomenon, two new parameters were introduced [15–21], i.e., the rate enhancement ratio, ρ, defined from:

$$\rho = r/r_o \tag{5}$$
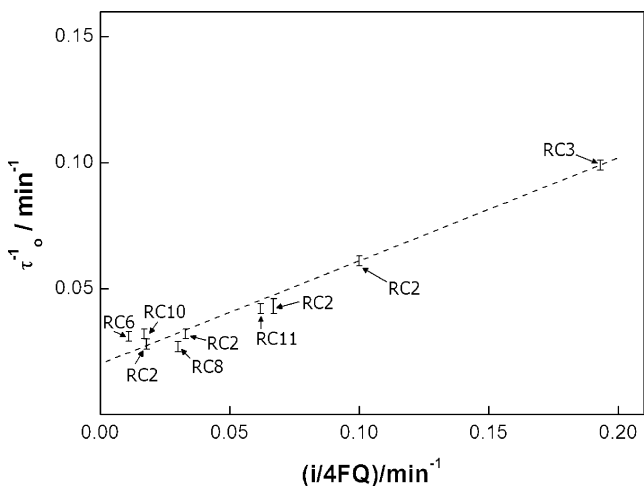
Fig. 6 Effect of Ag catalyst–electrode surface area Q (nowadays [5] symbol $N_G/2$) on the cell relaxation time constant. Conditions: 400 °C, $P_{O2}/P_{ET} \simeq 7$ [20]

where r_o is the open-circuit, i.e., unpromoted, rate and the Faradaic efficiency, Λ, defined from:

$$\Lambda = \frac{r - r_o}{(I/2F)} \tag{6}$$

Both r and r_o are expressed in mol O/s.

This first study of ethylene epoxidation led to ρ values up to 3 and Λ values up to 300. The latter implies that each O^{2-} ion supplied to the catalyst electrode causes on the average 300 chemisorbed oxygen atoms to react forming ethylene oxide and CO_2. Little did we suspect at that time that ρ values exceeding 100 (10,000% rate increase) and Λ values exceeding 10^5 would be found in a few years. And that eventually, Professor Bockris, one of the two or three leading electrochemists of the twentieth century, would call EPOC "one of the most remarkable advances in electrochemistry since 1950" [21, 22].

The exchange current and the name of the NEMCA effect

Seven years later, nostalgia had brought me back to the Ionian Sea at the University of Patras in Greece, and Symeon Bebelis, a PhD student of the caliber of Mike Stoukides, was trying as a starting point in his thesis to reproduce Mike's data. While the values of ρ were comparable, the values of Λ were much smaller, not even reaching unity. It took 3 months of utmost frustration to resolve this problem. Mike had been sintering his Ag catalysts at 650 °C and Symeon at 450 °C. As a result, the exchange current, I_0, of Symeon's Ag films was a factor of
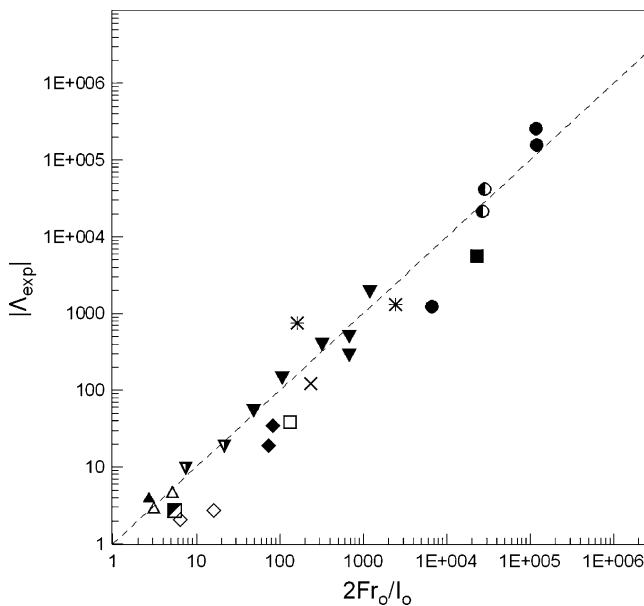
Fig. 7 Comparison of predicted from Eq. (7) and measured Faradaic efficiency, Λ, values for some of the early studies of catalytic reactions found to exhibit the NEMCA effect. Reprinted with permission from Elsevier Science [5]

at least 300 larger than the I_0 of Mike's films due to higher porosity of the catalyst film. This means that reaching the same overpotential (e.g., 1 V) required 300 times larger currents than with Mike's catalysts. In view of Eq. (6), this implies 300 times smaller Λ values. As soon as Symeon's catalysts had been sintered at 650 °C, then, thanks God, Mike's results could be exactly reproduced. Starting from this, we made the observation that the magnitude of Λ could be approximated for any EPOC study involving YSZ from:

$$|\Lambda| \approx 2Fr_o/I_0 \tag{7}$$

where I_0 is the exchange current of the electrode–electrolyte interface extracted from common Tafel plots [5] (Fig. 7).

This year, 1988, was quite important for electrochemical promotion. Three of my PhD students, Ioannis Yentekakis, Symeon Bebelis, and Stelios Neophytides, found Λ values well in excess of unity (in the range 100 to $3\cdot10^5$) for several different reactions on Pt and on Ag [23–26]. An example is shown in Fig. 8.

The work of S. Bebelis [23, 25] and S. Neophytides [23, 26] in particular showed that the catalytic rate, r, depended exponentially on catalyst potential, i.e.,

$$\ln(r/r_o) = \frac{\alpha F \Delta U}{RT} \tag{8}$$

where α is a constant characteristic of the reaction under study. Typically, $|\alpha|$ was found to be in the 0.2–1 range. When $\alpha > 0$, we termed the reaction electrophobic, and when $\alpha < 0$, we termed the reaction electrophilic.

We also introduced the term "Non-Faradaic Electrochemical modification of Catalytic Activity" (acronym NEMCA) to describe the new phenomenon [23–26].

The work function Φ and the exponential dependence of catalytic rates on Φ

The year 1990 was quite important for NEMCA for two reasons. First because Eq. (3) was first confirmed experimentally using a Kelvin probe [11] and second because two other research groups, involving Nikola Anastasijevic [27] and Vladimir Sobyanin [28, 29] started producing NEMCA papers.

The importance of the confirmation of Eq. (3), i.e., $e\Delta U = \Delta\Phi$, was significant, because now Eq. (8) could be written as:
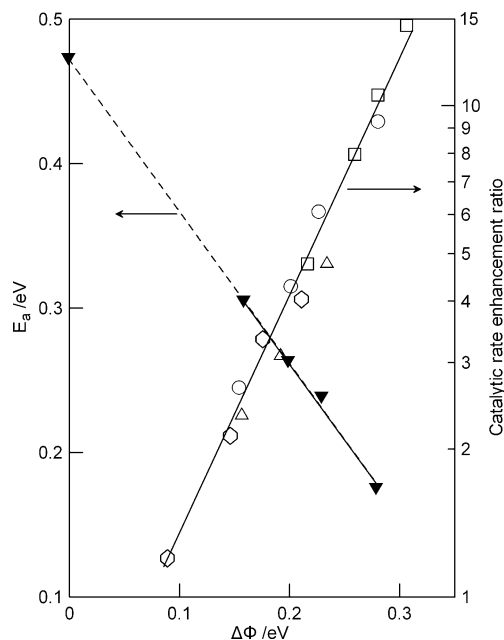
$$\ln(r/r_o) = \frac{\alpha\Delta\Phi}{k_b T} \tag{9}$$

with the same parameter α (Fig. 9). Not only this paper was published in Nature [11], but J. Pritchard wrote also in Nature an enthusiastic editorial about it and proposed the term "Electrochemical Promotion" [30].

The loneliness of NEMCA had disappeared by the end of 1990 with the involvement of the group of Gary Haller at Yale with his excellent student Carlos Cavalca [31].

Alkali conductors

It was in a trip to Sofia that I met Professor G. Budevski, a very polite man and international expert on β''-Al_2O_3

Fig. 8 A NEMCA transient [25]: rate and catalyst potential response to step changes in applied current during C_2H_4 oxidation on Pt; $T=$ 370 °C, $p_{O2}=4.6$ kPa, $p_{C2H4}=0.36$ kPa. The experimental (τ) and computed ($2FN_G/I$) rate relaxation time constants are indicated on the figure. See text for discussion. $r_0=1.5\cdot10^{-8}$ mol O/s, $\Delta r=$ $38.5\cdot10^{-8}$ mol O/s, $I/2F=5.2\cdot10^{-12}$ mol O/s, $\rho_{max}=26$, $\Lambda_{max}=74{,}000$, $N_G=4.2\cdot10^{-9}$ mol Pt. Reprinted with permission from Academic Press

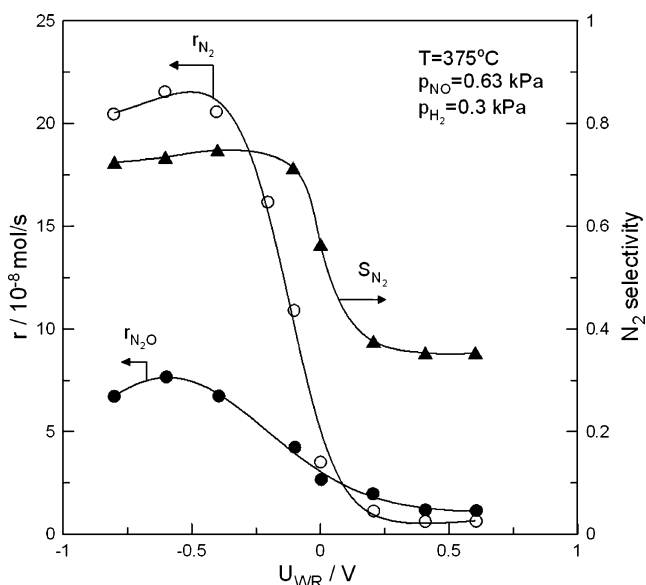Fig. 9 Effect of catalyst work function at constant gaseous reactant pressures on the activation energy E_a and catalytic rate enhancement ratio r/r_o of C_2H_4 oxidation on Pt; $P_{C2H4}=0.4$ kPa, $P_{O2}=4.8$ kPa, hexagons $T=399$ °C, $r_o=2.3$ s^{-1}; triangles $T=360$ °C, $r_o=1.7$ s^{-1}; circles $T=$ 324 °C, $r_o=1.0$ s^{-1}; squares $T=296$ °C, $r_o=0.6$ s^{-1}. The slope of the line for the activation energy is −1, and the slope of the line for the catalytic rate is $0.6/k_b T$ [11]. Reprinted from Macmillan Publishers Ltd

and other alkali conductors. He gave me our first β″-Al$_2$O$_3$ samples which I transferred to Patras by car with great care and excitement. A few days later, we had found EPOC for C$_2$H$_4$ oxidation on Pt/β″-Al$_2$O$_3$ with my coworkers Symeon Bebelis and Marina Despotopoulou [32]. So, NEMCA was not limited to the use of O^{2-} conductors only.
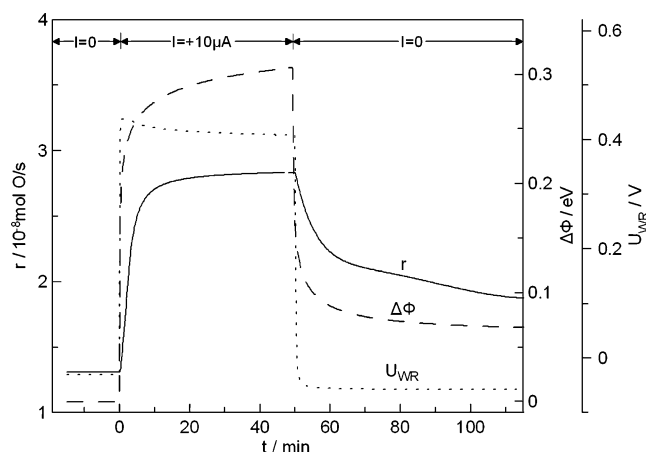
But the real breakthrough with alkali conductor EPOC came at the Schwab Conference in Berlin when Richard Lambert from Cambridge got interested in EPOC. We met for the first time personally, late in the evening, in front of my humble poster, and this was the beginning of a great collaboration and friendship (Fig. 10). Richard utilized efficiently his surface science arsenal to fully elucidate EPOC with alkali conductors [33–35]. He also introduced several other innovative ideas and electropromoted even the Fischer–Tropsch synthesis reaction [35].

Permanent NEMCA

An equally important thrust to EPOC came when Christos Comninellis, a very prominent electrochemist born in cosmopolitan Alexandria and living in Lausanne, joined the small but growing NEMCA community. He invited me for a few months at EPFL, and this was the beginning of another lifelong collaboration and friendship [36]. Christos, together with his excellent coworker for many years, György Fóti, started an impressive NEMCA activity at the EPFL and discovered, among other things, the permanent
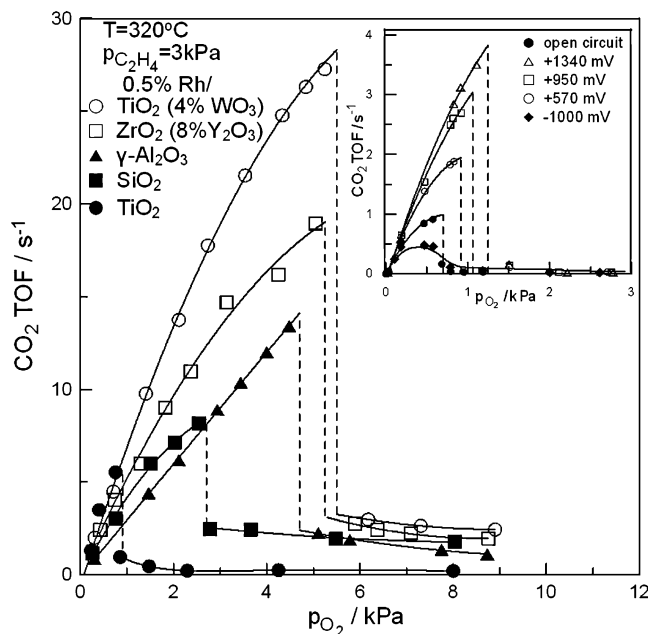

Fig. 11 Transient effect of constant applied current (I=+10 μA) on the rate (r) of C$_2$H$_4$ oxidation on IrO$_2$/YSZ, on catalyst work function change ($\Delta\Phi$) and on catalyst potential (U_{WR}). Conditions: T=380 °C, p_{O2}=15 kPa, and p_{C2H4}=0.05 kPa [38]. Reprinted with permission of the Electrochemical Society

NEMCA (Fig. 11) [37, 38]. We were really blessed in Patras to host three of their outstanding PhD students at the time (Michel Marwood, Jacques Nicole, and Stefan Wodiunig) for periods of 3 to 6 months. These young and enthusiastic scientists contributed some really outstanding work in broadening the scope of EPOC from an electrochemical viewpoint [39, 40].
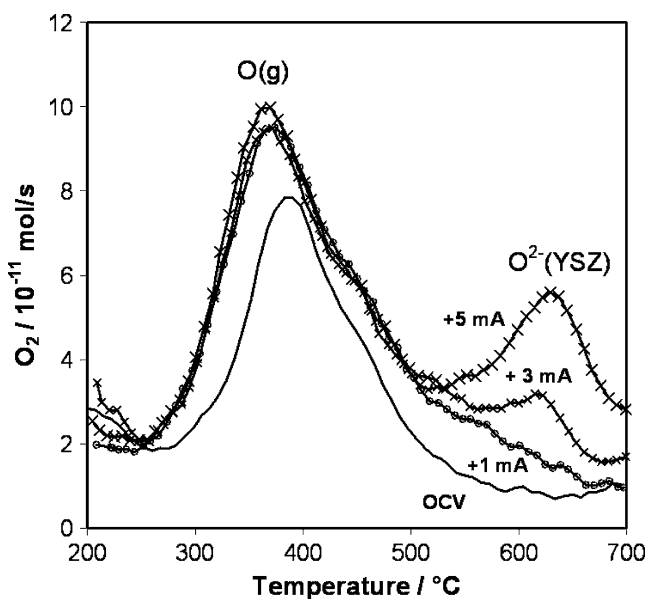

Fig. 10 Electrochemical promotion of NO reduction by H$_2$ on Pt/β″-Al$_2$O$_3$. Effect of catalyst potential on the rates of formation of N$_2$ and N$_2$O and on the selectivity to N$_2$ [34]. Reprinted with permission from Academic Press

Fig. 12 Effect of p_{O2} on the rate (*TOF*) of C$_2$H$_4$ oxidation to CO$_2$ on Rh supported on five supports of increasing Φ. Catalyst loading 0.5 wt.% [5, 40]. *Inset* Electrochemical promotion of a Rh catalyst film deposited on YSZ: effect of potentiostatically imposed catalyst potential U_{WR} on the rate and TOF dependence on p_{O2} at fixed p_{C2H4} [5, 40]. Reprinted with permission from Springer [5]

The search for the origin of NEMCA and its relation to promotion and metal-support interactions

The collaboration with Christos Comninellis at the EPFL and my colleague Xenophon Verykios in Patras was quite fruitful in identifying the basic common features between EPOC and metal-support interactions with ionically conducting supports [40] (Fig. 12). Xenophon, internationally renowned for his metal-support interactions work [41] and great proponent of the electronic theory of Catalysis, understood from the beginning the importance of NEMCA and provided invaluable support and advice to our team for many years.

Very useful was also the collaboration with Spyros Ladas in Patras which resulted in the first XPS investigation of EPOC [42] and also the work with Stelios Neophytides which resulted in the first high vacuum TPD work related with EPOC [43]. On the theoretical side, we were extremely fortunate to have Gianfranco Pacchioni and Fransesco Illas carrying out ab initio quantum mechanical cluster calculations [44] and finding good qualitative agreement with several key experimental findings of EPOC.

It was a very important breakthrough for EPOC when Philippe Vernoux [45, 46] and Jose Luis Valverde [47, 48] entered this area with their powerful teams and ingenious ideas [45–48]. The TPD work of Philippe, for example, showed the validity of the sacrificial promoter mechanism of EPOC under atmospheric pressure, which was a great step forward in EPOC-related research [46] (Fig. 13).
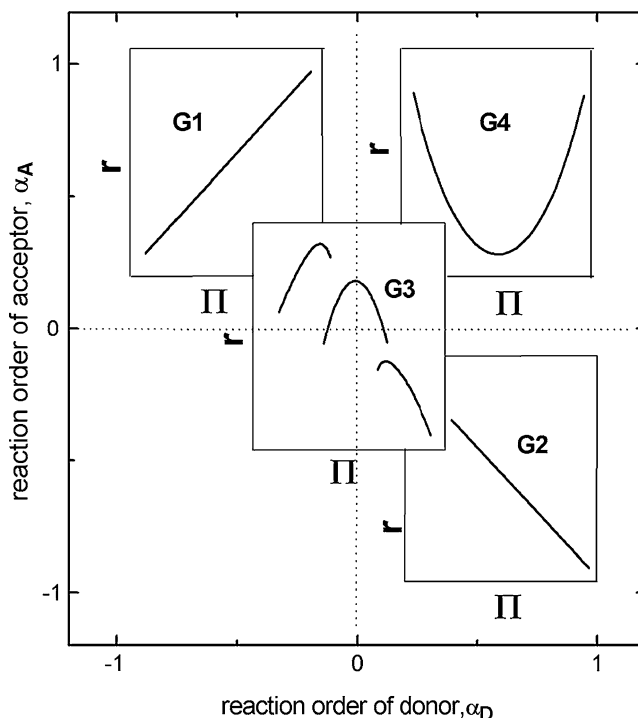
The rules of chemical and electrochemical promotion in a matrix

Writing a book on EPOC [5] forced me and my coauthors, Costas Pliangos and Susanne Brosda in particular, to search for common features and generalizations, and this led to the rules of electrochemical promotion [5, 49, 50]. Given the open-circuit kinetics of a catalytic reaction, one could now predict the nature of EPOC behavior to be observed, i.e., electrophobic, electrophilic, volcano, or inverted volcano [49, 50]. A few years earlier, this looked as a very distant dream. As I was giving a talk about EPOC and these rules in a conference up in the Rocky Mountains, I was very lucky to have Jimmy Wei, my former chairman at MIT, in the audience. Right after my talk, he said: "Let us have lunch together, you need a matrix to present the rules, otherwise nobody will remember them". During lunch, he drew on a napkin his matrix (Fig. 14). This led to a joint

Fig. 13 Atmospheric pressure O_2-TPD spectra after oxygen adsorption at 400 °C for 1 h under anodic polarization with different positive currents. +1 mA, +3 mA, and +5 mA. Operating conditions during oxygen adsorption: reactive mixture: O_2 1% in He, overall flow rate: 10 Lh^{-1}, temperature=400 °C [45]. Reprinted with permission from Springer Science

Fig. 14 Effect of reaction orders α_A and α_D with respect to the electron acceptor (A) and electron donor (D) reactant on the observed rate dependence on changing dimensionless catalyst work function Π (electrophobic (/), electrophilic (\), volcano (∪) and inverted volcano (∩)), and range of validity of the corresponding four promotional rules G1, G2, G3, and G4. These rules predict the rate vs Π behavior on the basis of the reaction kinetics, i.e., in terms of α_A and α_D [51], reprinted with permission from Elsevier

paper which extended these rules to chemical promotion as well [51].

### High vacuum EPOC and the sacrificial promoter mechanism

Since the early days of EPOC and the TPD work of Stelios Neophytides [43], the sacrificial promoter mechanism of EPOC [5] had been reasonably well established by several techniques. However, direct confirmation of this mechanism came only after the high vacuum TPD and TPR (temperature programmed reaction) work of Alexandros Katsaounis [52, 53] who used gas-supplied $^{18}O_2$ and studied both O_2 desorption from Pt/YSZ and CO oxidation

on the same catalyst. His results showed very clearly that YSZ lattice ^{16}O migrates via spillover to the Pt surface and acts there as a sacrificial promoter [52, 53].

The road to applications: high pressure operation and multipellet–multiplate reactors

During a trip to California and a talk at EPRI, Fritz Kalhammer, vice-President of EPRI and former student of Georg Maria Schwab in Munich in the late forties, became an EPOC enthusiast, and EPRI funded the first EPOC high pressure study (70 bar) for NH_3 synthesis involving 24 catalyst pellets [54]. This was a very demanding task for an academic laboratory.

Fig. 15 **a** Schematic of the monolithic electropromoted reactor (MEPR) [55]; reprinted with permission from Elsevier. **b** Transient effect of a constant applied current (+30 mA) on the catalytic rate of NO reduction (r_{NO}) and CO_2 formation (r_{CO2}), on the NO, C_2H_4, and O_2 conversion (X_{NO}, X_{C2H4}, X_{O2}) and on the Rh–Pt potential difference (U) during NO reduction by C_2H_4 using Rh and Pt catalyst-electrodes. $T=280$ °C [58]. Reprinted with permission from Springer
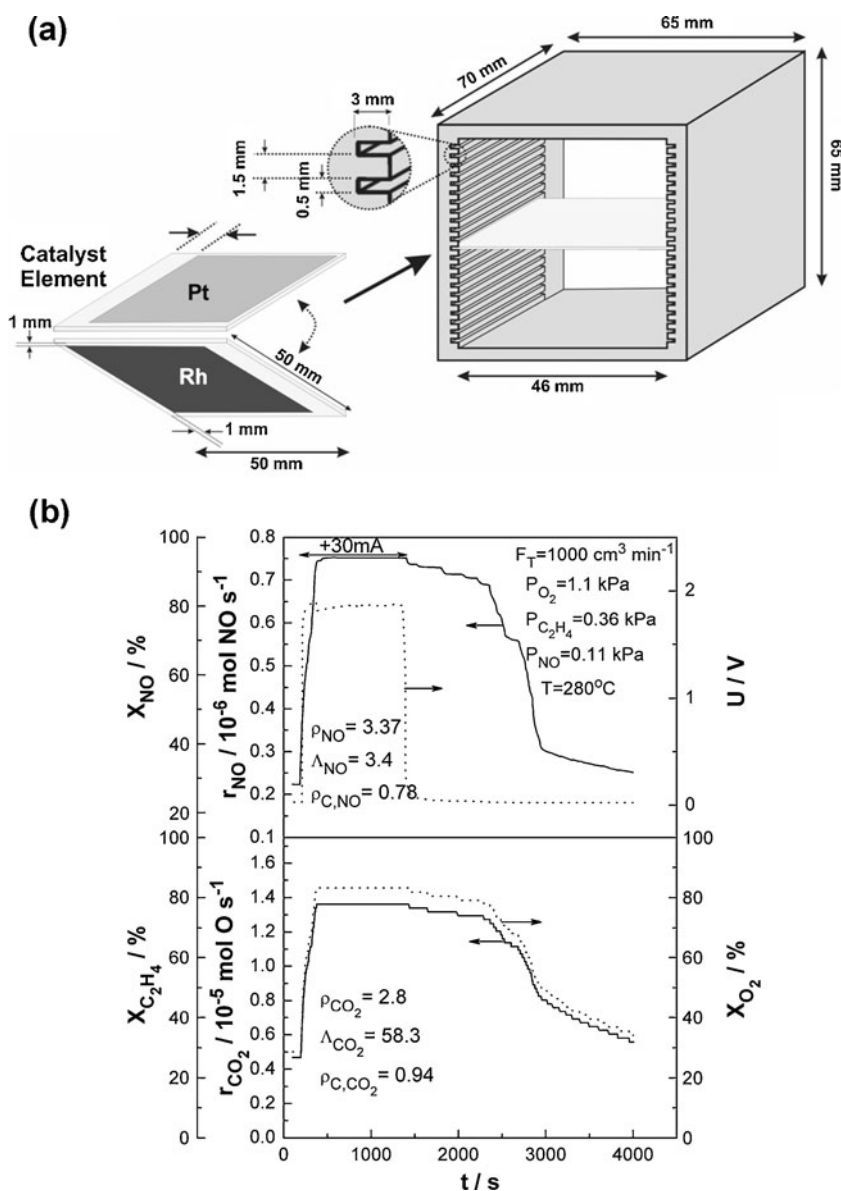
Our worries about safety and the very long EPOC transients (several hours) forced my coworkers (Constantina Yokari, Dimitrios Polydoros, and Alexandros Katsaounis) to work around the clock for at least 3 days. Alexandros in particular seemed to enjoy this enormously, wearing his pajamas in the lab and taking an occasional nap near our high pressure apparatus. The results were truly exciting [54] and showed the potential of EPOC for practical applications.

A big step in this direction was also the design, construction, and testing of the first monolithic electro-promoted reactors (MEPRs) [55–58] (Fig. 15). This was the result of a fruitful collaboration between BASF, EPFL, and Patras in which my coworkers Stella Balomenou and Dimitris Tsiplakides played a crucial role in the assembly and testing of the first MEPR units [55–58]. The road for practical applications in automotive exhaust treatment looks quite open after this work.

Summary and open questions

When looking back in the story of the discovery of EPOC, I first realize how incredibly lucky I have been with the quality and enthusiasm of my students, coworkers, and colleagues. I am truly indebted to them; we had and we are still having a great scientific and personal time.

I also realize how lucky we were with some choices we made and with some materials we used. Let me explain some of the lucky coincidences we had:

a. The amount of Engelhard Pt paste (a few milligrams) we were depositing using a brush on the inside bottom of YSZ tubes led after firing to 850 °C to a *porous* Pt film (roughly 1 to 3 μm thick) which provided sufficient but not too high conversion and catalytic rate ($\sim 10^{-7}$ mol/s or a few ccSTP/min) which could be measured accurately by a GC or IR CO_2 analyzer.

b. This moderate reactant conversion, typically 1–15%, allowed for detailed kinetic investigations of all the electropromoted reactions studied, and this was crucial for discovering eventually the promotional rules [49–51].

c. The reaction rate was not fast enough to cause internal or external mass transfer limitations in the temperature range (>300 °C) necessary to obtain sufficient ionic conductivity in the YSZ and thus permitting the supply of currents of the order 10–100 μA to the catalyst electrode.

d. The YSZ itself emits during firing of the metal catalyst paste films enormous amounts of nonstoichiometric oxygen [52]. This greatly enhances the cleanliness of the resulting Pt or other noble metal films by minimizing via combustion the amount of carbon deposition on the film [5].

All this was in retrospect very good luck indeed. But good luck usually comes with enthusiasm, curiosity, and persistence, and we had plenty of that in our lab for many years. This gave us all the joy of discovery.

Time will show if EPOC will find practical applications in exhaust treatment or in chemical synthesis. Nikola Anastasijevic has recently analyzed the current situation, the prospectives, and the actions to be taken [59].

References

1. Vielstich W, Lamm A, Gasteiger H (2003) Handbook of fuel cells. Fundamentals technology and applications. Wiley, New York
2. Ertl G, Knötzinger H, Weitcamp J (eds) (1997) Handbook of catalysis. VCH Publishers, Weinheim
3. Bockris JO'M, Reddy AKM, Gamboa-Aldeco M (2000) Modern electrochemistry. Kluwer Academic/Plenum Publishers
4. Wieckowski A, Savinova E, Vayenas CG (eds) (2003) Catalysis and electrocatalysis at nanoparticles surfaces. Marcel Dekker, New York-Basel
5. Vayenas CG, Bebelis S, Pliangos C, Brosda S, Tsiplakides D (2001) Electrochemical activation of catalysis: promotion, electrochemical promotion and metal-support interactions. Kluwer/Plenum Press, New York
6. Wagner C (1970) Adv Catal 21:323–381
7. Vayenas CG, Saltsburg HM (1979) J Catal 57:296–314
8. Vayenas CG, Georgakis C, Michaels J, Tormo J (1981) J Catal 67:348–361
9. Lintz HG, Vayenas CG (1989) Angew Chem 101(6):725–732
10. Bockris JM, Reddy AKN (1970) Modern electrochemistry. Plenum Press, New York
11. Vayenas CG, Bebelis S, Ladas S (1990) Nature 343:625–627

12. Rath DL, Kolb DM (1981) Surf Sci 109:641–647
13. Vayenas CG (2000) J Electroanal Chem 486:85–90
14. Vayenas CG, Tsiplakides D (2000) Surf Sci 467:23–34
15. Frumkin A, Damaskin B (1977) J Electroanal Chem 79:259–266
16. Trasatti S (1990) Electrochim Acta 35:269–271
17. Tsiplakides D, Vayenas CG (2001) J Electrochem Soc 148(5): E189–E202
18. Tsiplakides D, Vayenas CG (2002) Solid State Ionics 152–153:625–639
19. Stoukides M, Vayenas CG (1981) J Catal 70:137–146
20. Stoukides M, Vayenas CG (1982) ACS Symp Series 178:181–208
21. Vayenas CG, Jaksic MM, Bebelis S, Neophytides SG (1996) The electrochemical activation of catalysis. In: JO'M B, Conway BE, White RE (eds) Modern aspects of electrochemistry. Kluwer Academic/Plenum Publishers, New York, pp 57–202
22. Bockris JO'M, Minevski ZS (1994) Electrochim Acta 39(11/12):1471–1479
23. Vayenas CG, Bebelis S, Neophytides S (1988) J Phys Chem 92:5083–5085
24. Yentekakis IV, Vayenas CG (1988) J Catal 111:170–188
25. Bebelis S, Vayenas CG (1989) J Catal 118:125–146
26. Neophytides S, Vayenas CG (1989) J Catal 118:147–163
27. Baltruschat H, Anastasijevic NA, Beltowska-Brzezinska M, Hambitzer G, Heitbaum J (1990) Ber Buns Phys Chem 94:996–1000
28. Politova TI, Sobyanin VA, Belyaev VD (1990) React Kinet Catal Lett 41(2):321–326
29. Mar'ina OA, Sobyanin VA (1992) Catal Lett 13:61–70
30. Pritchard J (1990) Nature 343:592–593
31. Cavalca C, Larsen G, Vayenas CG, Haller G (1993) J Phys Chem 97:6115–6119
32. Vayenas CG, Bebelis S, Despotopoulou S (1991) J Catal 128:415–435
33. Harkness I, Lambert RM (1995) J Catal 152:211–214
34. Mar'ina OA, Yentekakis IV, Vayenas CG, Palermo A, Lambert RM (1997) J Catal 166:218–228
35. Lambert R (2003) Electrochemical and chemical promotion by alkalis with metal films and nanoparticles. In: Wieckowski A, Savinova E, Vayenas CG (eds) Catalysis and electrocatalysis at nanoparticles. Marcel Dekker, Inc, New York, pp 583–611
36. Varkaraki E, Nicole J, Plattner E, Comninellis C, Vayenas CG (1995) J Appl Electrochem 25:978–981
37. Nicole J, Comninellis C (1998) J Appl Electrochem 28:223–226
38. Tsiplakides D, Nicole J, Vayenas CG, Comninellis C (1998) J Electrochem Soc 145(3):905–908
39. Marwood M, Vayenas CG (1997) J Catal 168:538–542
40. Nicole J, Tsiplakides D, Pliangos C, Verykios XE, Comninellis Ch, Vayenas CG (2001) J Catal 204:23–34
41. Verykios X (2003) Support effects on catalytic performance of nanoparticles. In: Wieckowski A, Savinova E, Vayenas CG (eds) Catalysis and electrocatalysis at nanoparticles. Marcel Dekker, Inc, New York, pp 745–783
42. Ladas S, Kennou S, Bebelis S, Vayenas CG (1993) J Phys Chem 97:8845–8847
43. Neophytides SG, Vayenas CG (1995) J Phys Chem 99:17063–17067
44. Pacchioni G, Illas F, Neophytides S, Vayenas CG (1996) J Phys Chem 100:16653–16661
45. Li X, Gaillard F, Vernoux P (2007) Top Catal 44(3):391–398
46. Vernoux P, Gaillard F, Karoum R, Billard A (2007) Appl Catal B Environ 731(2):73
47. Dorado F, de Lucas-Consuegra A, Vernoux P, Valverde JL (2007) Appl Catal B Environ 73:42
48. de Lucas-Consuegra A, Dorado F, Valverde JL, Karoum R, Vernoux P (2008) Catal Comm 9(1):17
49. Vayenas CG, Brosda S, Pliangos C (2001) J Catal 203:329–350
50. Brosda S, Vayenas CG (2002) J Catal 208:38–53
51. Brosda S, Vayenas CG, Wei J (2006) Appl Catal B Environ 68:109–124
52. Katsaounis A, Nikopoulou Z, Verykios XE, Vayenas CG (2004) J Catal 222(1):192–206
53. Katsaounis A, Nikopoulou Z, Verykios XE, Vayenas CG (2004) J Catal 226(1):197–209
54. Yiokari CG, Pitselis GE, Polydoros DG, Katsaounis AD, Vayenas CG (2000) J Phys Chem 104:10600–10602
55. Balomenou S, Tsiplakides D, Katsaounis A, Thiemann-Handler S, Cramer B, Foti G, Comninellis Ch, Vayenas CG (2004) Appl Catal B Environ 52:181–196
56. Tsiplakides D, Balomenou S, Katsaounis A, Archonta D, Koutsodontis C, Vayenas CG (2005) Catal Today 100:133–144
57. Balomenou SP, Tsiplakides D, Katsaounis A, Brosda S, Fóti G, Comninellis Ch, Thiemann-Handler S, Cramer B, Vayenas CG (2006) Solid State Ionics 177:2201–2204
58. Souentie S, Hammad A, Brosda S, Foti G, Vayenas CG (2008) J Appl Electrochem 38:1159–1170
59. Anastasijevic NA (2009) Catal Today 146:308–311