In Situ Controlled Promotion of Catalyst Surfaces Via Solid Electrolytes: The NEMCA Effect

Constantinos G. Vayenas, Ioannis V. Yentekakis, Symeon I. Bebelis, and Stylianos G. Neophytides

Department of Chemical Engineering, University of Patras, GR-26500 Patras, Griechenland

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The catalytic activity and selectivity of metal films interfaced with solid electrolytes can be varied in situ in a dramatic and reversible manner by applying currents or voltages (typically ±1–2 V) between the catalyst film and a counter electrode also deposited on the solid electrolyte. Catalytic rates can thus be varied by up to a factor of 200. The induced steady-state change in catalytic rate is up to five orders of magnitude larger than the steady-state rate of electrochemical supply of ionic species from the solid electrolyte onto the catalyst surface. This novel effect termed Non-Faradaic Electrochemical modification of catalytic activity (NEMCA) has been studied for over 40 catalytic reactions on Pt, Rh, Pd, Ag, Ni and IrO_2 catalysts using a variety of solid electrolytes (O^{2-}, F^-, Na^+, H^+ conductors) and also, more recently, in aqueous alkaline solutions. Besides potential technological applications, this new effect allows for a systematic study of the role of promoters in heterogeneous catalysis. In this paper the main features of in situ controlled promotion are reviewed and the origin of the effect is discussed on the basis of recent XPS, TPD and cyclic voltammetric investigations.

1. Introduction

Promoters play a key role in industrial heterogeneous catalysis, yet their exact role has been studied in detail and is reasonably well understood only for a limited number of model catalyst systems [1]. Most previous studies have addressed the role of promoters on the chemisorption of coadsorbed species under ultra high vacuum conditions without examining the effect of promoters on catalytic rates [1, 2]. This is primarily due to the difficulty of in situ supplying or removing promoters to or from catalyst surfaces under catalytic reaction conditions.

The use of electrochemistry to activate, promote and precisely tune heterogeneous catalytic processes is a new development [3 – 16] which emerged due to the existence of solid electrolytes. Depending on their composition, these specific anionic or cationic conductors exhibit ionic conductivity useful for catalytic applications ($>10^{-4}\,ohm^{-1}\,cm^{-1}$) at temperatures 25 ° to 1000 °C. Within this broad temperature range, which covers practically all heterogeneous catalytic reactions, solid electrolytes can be used as reversible in situ promoter donors, or poison acceptors, to affect the catalytic activity and product selectivity of metals deposited on solid electrolytes in a very pronounced, reversible and, to some extent, predictable manner [9]. This is accomplished by supplying the reactants (e.g. $C_2H_4+O_2$) over the metal catalyst film and using the latter both as a catalyst and also as the working electrode of the solid electrolyte cell:

gaseous reactants, catalyst working electrode |solid electrolyte|
(e.g. $C_2H_4+O_2$), (e.g. Pt, Rh, Ag) |(e.g. $ZrO_2-Y_2O_3$)|
counter, electrode, (e.g. Pt, Au), auxiliary gas (e.g. O_2)

The auxiliary gas may also be the reactive mixture itself in the so-called "single pellet" design [9, 17].

Upon varying the catalyst potential via a potentiostat it is found that not only the electrocatalytic (net charge-transfer) reaction rates are affected, but also the catalytic (no net charge-transfer) reaction rate changes in a dramatic, controlled and reversible manner. The steady state increase in catalytic reaction rate can be at least a factor of 100 higher than the open-circuit (unpromoted) catalytic rate and up to 3×10^5 times higher than the rate of ion supply to the catalyst via the solid electrolyte [4, 9, 16]. This is why this novel effect has been termed non-Faradaic electrochemical modification of catalytic activity (NEMCA effect [3 – 10, 13 – 16]). The terms electrochemical promotion [18] and in situ controlled promotion [11] have been also proposed for the NEMCA effect which has been studied already for more than 40 catalytic reactions and does not seem to be limited to any specific type of catalytic reaction, metal or solid electrolyte, particularly in view of the recent demonstrations of NEMCA with conducting metal oxide catalysts (IrO_2 [15]), mixed conducting TiO_2 supports used as the electrolyte [19] and aqueous electrolyte solutions [14].

C. Wagner was first to propose the use of solid electrolytes to measure in situ the thermodynamic activity of oxygen on metal catalysts [20]. This led to the technique of solid electrolyte potentiometry [21]. Huggins and Mason were first to use solid electrolyte cells to carry out electrocatalytic reactions such as NO decomposition [22]. The use of solid electrolyte cells for "chemical cogeneration", i.e. for the simultaneous production of electrical power and industrial chemicals was first demonstrated in 1980 [23]. The first non-Faradaic enhancement in heterogeneous catalysis was reported in 1981 for the epoxidation of ethylene [24] but it was only in 1988 that it was realized that electrochemical promotion is a general phenomenon [3]. In addition to the group which first described the electrochemical promotion effect [3 – 5, 7 – 9, 13 – 17], the groups of Sobyanin [6], Haller [10], Lambert [11, 12], Stoukides [25] and Comninellis [15] have also made significant contributions in this area. The importance of NEMCA in heterogeneous catalysis – surface science and electrochemistry has

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been discussed by Pritchard [18] and Bockris [26], respectively.

Detailed [9, 27, 28] and shorter [13, 29, 30] reviews of the electrochemical promotion literature have been published recently. In this paper the main features of electrochemical promotion are briefly surveyed and reviewed and the physical origin of the NEMCA effect is discussed on the basis of very recent XPS [31, 32], TPD [33, 34] and cyclic voltammetric [34, 35] investigations.

2. Experimental

The basic experimental setup is shown schematically in Fig. 1 a. The metal working catalyst electrode, usually in the form of a porous metal film 3 – 20 µm in thickness, is deposited on the surface of a ceramic solid electrolyte (e.g. Y_2O_3- stabilized-ZrO_2 (YSZ), an O^{2-} conductor, or β''-Al_2O_3, a Na^+ conductor). Catalyst, counter and reference electrode preparation and characterization details have been presented in detail elsewhere [4, 9, 11] together with the analytical system for on-line monitoring the rates of catalytic reactions by means of gas chromatography, mass spectrometry and IR-spectroscopy.

The superficial surface area of the metal working catalyst-electrode is typically 2 cm^2 and its true gas-exposed surface area is typically 5 – 10^3 cm^2 as measured via surface titration of oxygen and CO or C_2H_4 [7 – 13]. The catalyst electrode is exposed to the reactive gas mixture (e.g. $C_2H_4+O_2$) in a continuous flow gradientless reactor (CSTR). Under open-circuit conditions (I = 0) it acts as a regular catalyst for the catalytic reaction under study, e.g. C_2H_4 oxidation. The counter and reference electrodes are usually exposed to ambient air.

A galvanostat or potentiostat is used to apply constant currents between the catalyst and the counter electrode or constant potentials between the catalyst and reference electrodes. In this way ions (O^{2-} in the case of YSZ, Na^+ in the case of β''-Al_2O_3) are supplied from (or to) the solid electrolyte to (or form) the catalyst-electrode surface. The current is defined positive when anions are supplied to or cations removed from the catalyst electrode. There is compelling evidence [9, 31 – 35] that these ions (together with their compensating (screening) charge in the metal thus forming surface dipoles) migrate (spillover) onto the gas-exposed catalyst electrode surface [9]. Thus the solid electrolyte acts as an active catalyst support and establishes an effective electrochemical double layer on the gas-exposed, i.e. catalytically active, electrode surface [10, 27].

The (average) work function of the gas-exposed catalyst-electrode surface was measured in situ, i.e. during reaction at atmospheric pressure and temperatures up to 300 °C, by means of a Kelvin probe (vibrating condenser method) using a Besocke Delta-Phi Kelvin probe with a Au vibrating disc as described in detail elsewhere [7, 9].

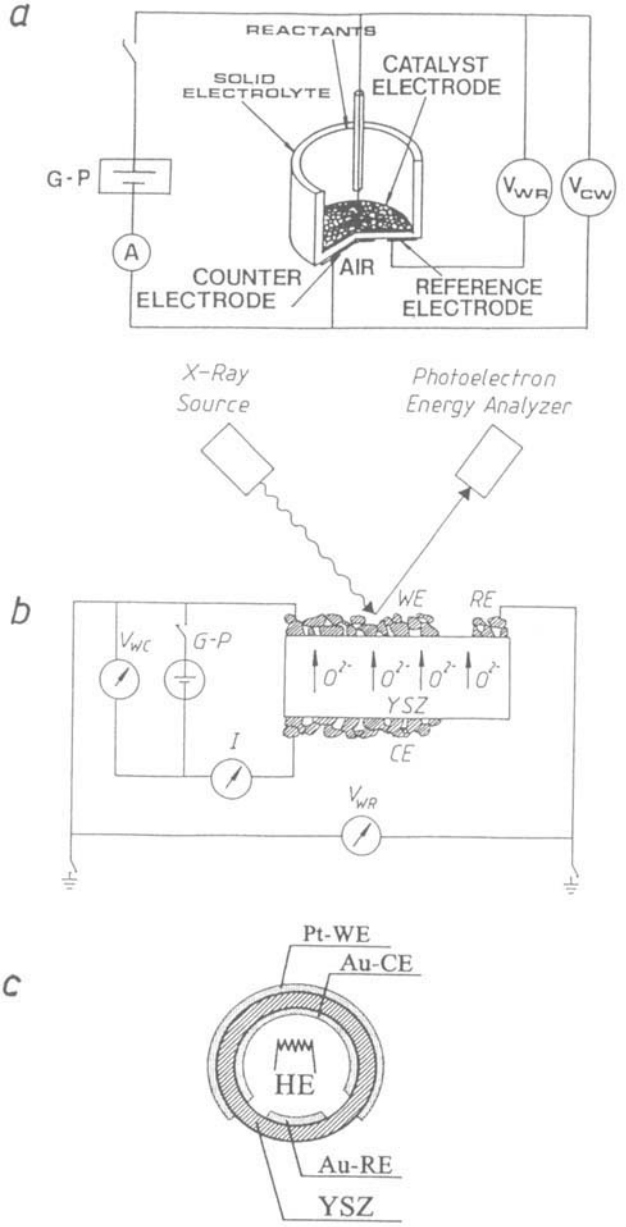

Fig. 1
Schematic of the experimental setup for NEMCA studies (a), and for using XPS (b) and for TPD studies (c); G-P: Galvanostat-Potentiostat; WE: Working Electrode, RE: Reference Electrode; CE: Counter Electrode; HE: Heating Element

The experimental setup for using XPS to investigate metal electrode surfaces under conditions of electrochemical O^{2-} pumping is shown schematically in Fig. 1 b. A 2-mm thick YSZ slab (10 mm × 13 mm) with a Pt catalyst electrode film, a Pt reference electrode and a Ag counter electrode was mounted on a resistively heated Mo holder in an ultra-high-vacuum (UHV) chamber (base pressure 5×10^{-10} Torr) and the catalyst-electrode film (9 mm × 9 mm) was examined at temperatures 25 ° to 525 °C by XPS using a Leybold HS-12 analyzer operated at constant ΔE mode with 100-eV pass energy and a sampling area of 5 mm × 3 mm. Electron binding energies were referenced to the metallic Pt $4f_{7/2}$ peak of the grounded catalyst electrode at 71.1 eV, which always remained unchanged with no trace of an oxidic component. Further experimental details can be found in Ref. [31].

Fig. 1c shows the experimental setup used for the recent TPD and cyclic voltammetric investigations of the origin of NEMCA [33, 34]. The experiments were carried out in an UHV chamber (base pressure 10^{-9} Torr) equipped with a quadrupole mass spectrometer (Balzers QMG 420). The Pt film was deposited in the form of a half-ring on the outer surface of a tubular YSZ specimen (O.D. 19 mm, thickness 2 mm, length 30 mm). Pt and Au counter and reference electrode preparation and characterization details are given elsewhere [9, 33, 34]. Three modes of oxygen adsorption of the Pt film (true surface area 80 cm^2) were used at temperatures 600 to 670 K:

a) Gaseous oxygen adsorption by exposure to $P_{O_2} = 4 \cdot 10^{-6}$ Torr for various exposure times t_{O_2}, corresponding to several kL (1 L = 10^{-6} Torr·s).

b) Electrochemical oxygen supply at a rate $I/2F$ for various times, t_I, of positive current I application between the Pt catalyst and Au counter electrode.

c) Mixed gaseous and electrochemical adsorption. In this mode the film is first exposed to $P_{O_2} = 4 \cdot 10^{-6}$ Torr for a time t_{O_2}, followed by electrochemical supply of oxygen for a time t_I.

After oxygen adsorption the sample was cooled rapidly to 570 K, followed by a linear increase in temperature at a heating rate β (K/s) to obtain the TPD spectra.

3. Results and Discussion

Catalytic Rate Modification

Fig. 2 shows a typical NEMCA experiment carried out in the setup depicted on Fig. 1a. The catalytic reaction under study is the complete oxidation of C_2H_4 on Pt [4]:

$$CH_2 = CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O \qquad (1)$$

The figure shows a typical galvanostatic transient, i.e., it depicts the transient effect of a constant applied current on the rate of C_2H_4 oxidation (expressed in moles of atomic oxygen per second, mol O/s).

The Pt catalyst film with a surface area corresponding to $N = 4.2 \cdot 10^{-9}$ mol Pt, as measured by surface titration techniques [4, 9], is deposited on Y_2O_3-doped ZrO_2 and is exposed to $P_{O_2} = 4.6$ kPa, $P_{C_2H_4} = 0.36$ kPa in the CSTR-type flow reactor depicted schematically on Fig. 1a. Initially ($t < 0$) the circuit is open ($I = 0$) and the open-circuit catalytic rate r_o is $1.5 \cdot 10^{-8}$ mol O/s. The corresponding turnover frequency (TOF), i.e., oxygen atoms reacting per site per s is $3.57\,\mathrm{s}^{-1}$.

Then at $t = 0$ a galvanostat is used to apply a constant current of +1 μA between the catalyst and the counter electrode (Fig. 1). Now oxygen ions O^{2-} are supplied to the

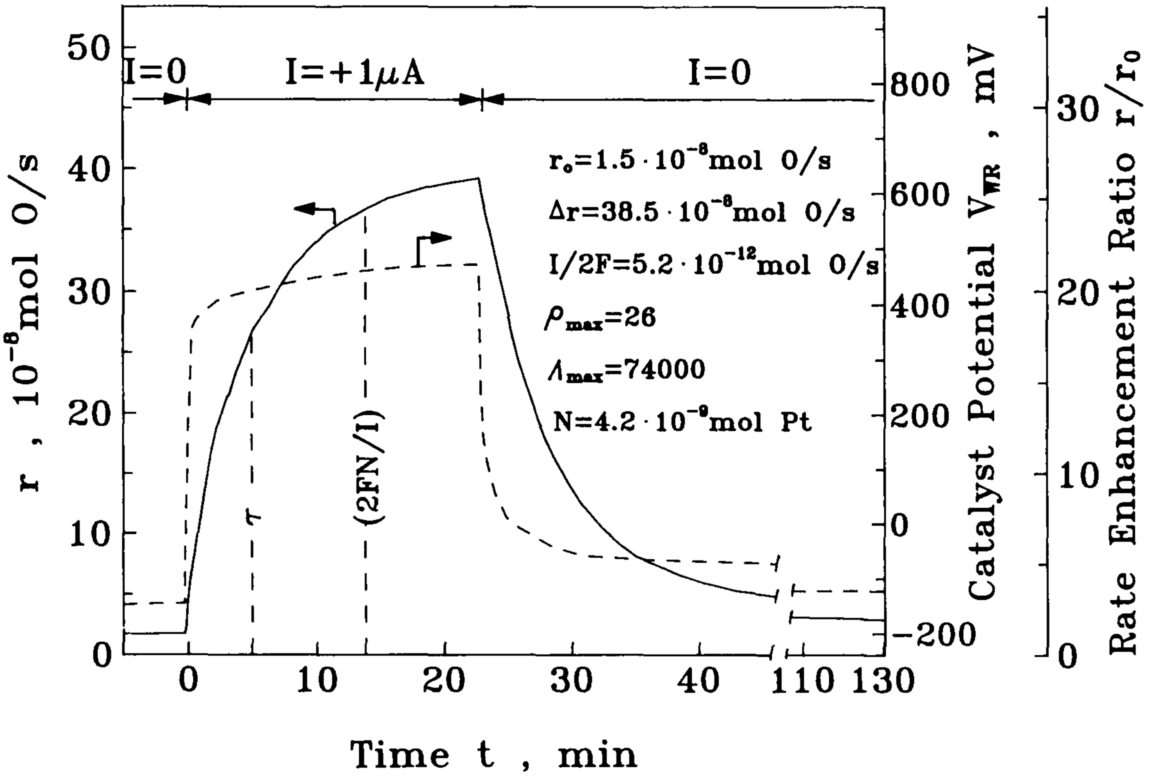

Fig. 2
Rate and catalyst potential response to step changes in applied current during C_2H_4 oxidation on Pt; $T = 370\,°C$, $P_{O_2} = 4.6$ kPa, $P_{C_2H_4} = 0.36$ kPa. The steady-state rate increase Δr is 74000 times higher than the steady-state rate of supply of O^{2-} to the catalyst ($\Lambda = 74000$) (Ref. 4)

catalyst-gas-solid electrolyte three-phase boundaries (tpb) at a rate $G_O = I/2F = 5.2 \cdot 10^{-12}$ mol O/s. The catalytic rate starts increasing (Fig. 2) and within 25 min gradually reaches a value $r = 40.0 \cdot 10^{-8}$ mol O/s, which is 26 times larger than r_0. The new TOF is $95.2\,s^{-1}$. The increase in catalytic rate $\Delta r = r - r_0 = 38.5 \cdot 10^{-8}$ mol O/s is 74000 times larger than $I/2F$. This means that each O^{2-} supplied to the Pt catalyst causes at steady-state 74000 additional chemisorbed oxygen atoms to react with C_2H_4 to form CO_2 and H_2O. This is why this novel effect has been termed Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA).

There is an important observation to be made regarding the time required for the rate to approach its steady-state value. Since catalytic rate transients obtained during galvanostatic (i.e. constant current) operation are found in NEMCA studies to be usually, but not always [9], of the type:

$$\Delta r = \Delta r_{max}[1 - \exp(-t/\tau)] \qquad (2)$$

i.e., similar to the response of a first order system with a characteristic time constant τ, one can define the NEMCA time constant τ as the time required for Δr to reach 63% of its maximum, i.e., steady-state value. As shown on Fig. 2, τ is of the order of $2FN/I$ and this turns out to be a general observation in NEMCA studies utilizing doped ZrO_2, i.e.:

$$\tau \approx 2FN/I \qquad (3)$$

What this observation shows is that NEMCA is a catalytic effect, i.e., it takes place over the entire gas-exposed catalyst surface and is not an electrocatalytic effect localized at the three-phase-boundaries (tpb) metal-solid electrolyte-gas. This is because $2FN/I$ is the time required to form a monolayer of an oxygen species on a surface with N sites when it is supplied at a rate $I/2F$. The fact that τ is found to be shorter than $2FN/I$, but of the same order of magnitude, shows that only a fraction of the surface is occupied by oxygen spillover species, as discussed in detail elsewhere [9]. It is worth noting that if NEMCA were restricted to the tpb, i.e., if the observed rate increase were due to an electrocatalytic reaction, then τ would be practically zero during galvanostatic transients.

As shown on Fig. 2 NEMCA is reversible, i.e., upon current interruption the catalytic rate returns to its initial value within roughly 100 min. The rate relaxation curve upon current interruption conveys valuable information on the kinetics of reaction and desorption of the promoting oxygen species as discussed in detail elsewhere [36]. Negative current application has practically no effect on the rate of this particular reaction.

Effect of Gaseous Composition on Regular (Open-Circuit) and NEMCA-Induced Reaction Rate

Fig. 3 shows the effect of O_2 to C_2H_4 ratio on the regular (open-circuit) steady-state rate of C_2H_4 oxidation on Pt and on the NEMCA-induced rate when the same catalyst film is maintained at a potential of +1 V (V_{WR} = +1 V) with respect to the reference Pt/air electrode (Fig. 1a). It can be seen that the effect is much more pronounced at high $P_{O_2}/P_{C_2H_4}$ ratios, where the NEMCA-induced reaction rate or TOF values are a factor of sixty higher than the corresponding open-circuit rate. A quantitative description and explanation of the NEMCA behaviour of C_2H_4 oxidation on Pt can be found elsewhere [4, 9].

Fig. 4 shows the effect of C_2H_4 partial pressure at constant P_{O_2} on the rate of C_2H_4 oxidation on Rh at various

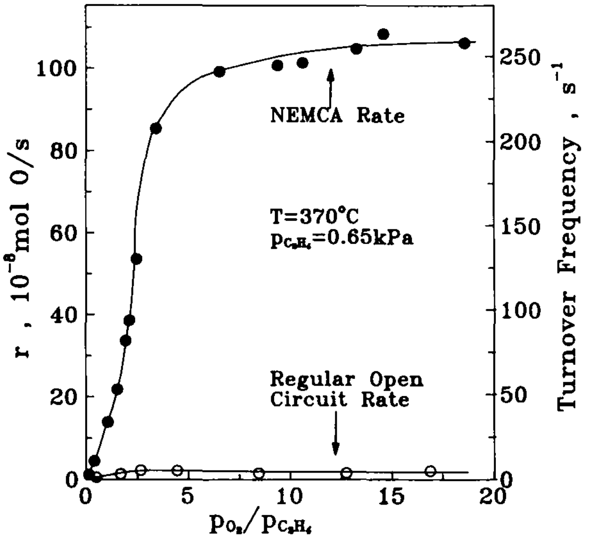

Fig. 3
Effect of gaseous composition on the regular (open-circuit) steady-state rate of C_2H_4 oxidation on Pt and on NEMCA-induced catalytic rate when the catalyst film is maintained at V_{WR} = 1 V (Ref. 4)

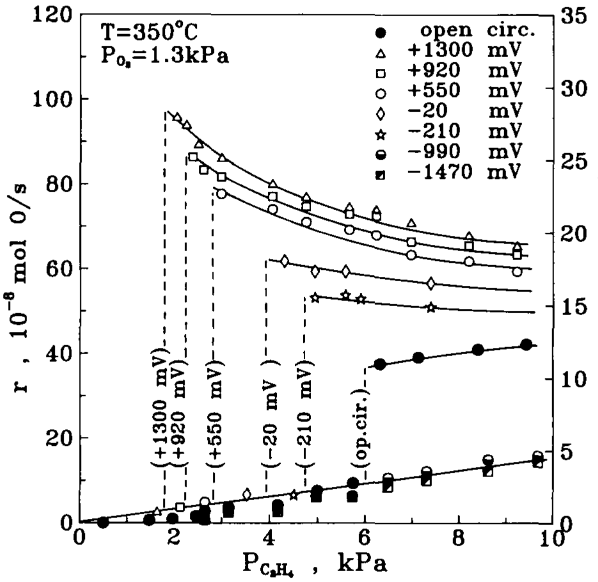

Fig. 4
Effect of gaseous composition and catalyst potential V_{WR} on the steady-state rate of C_2H_4 oxidation on Rh (Ref. 16)

imposed values of V_{WR} [16]. Increasing V_{WR} causes up to 90-fold (9000%) rate enhancement relative to the open-circuit rate value. The dramatic rate enhancement with increasing V_{WR} depicted in Figs. 3 and 4 is due to the weakening of the metal-covalently chemisorbed oxygen chemisorptive bond, cleavage of which is rate limiting, as discussed in detail elsewhere [4, 9, 16].

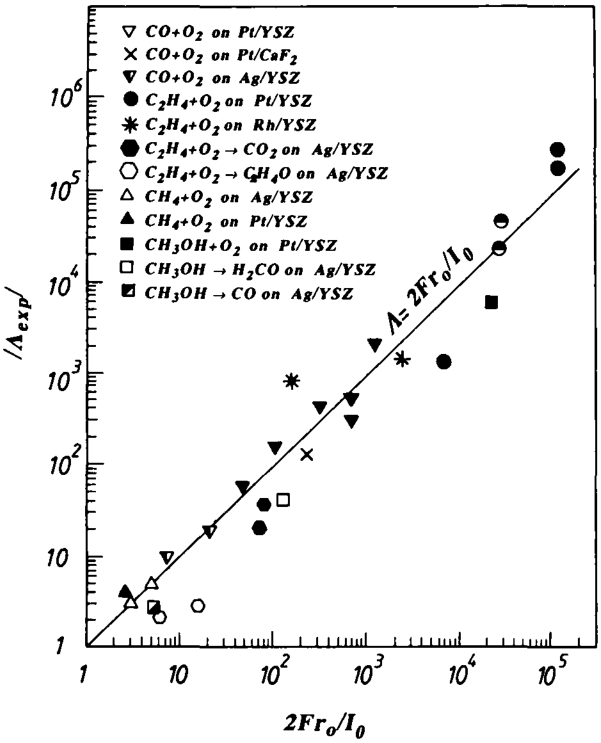

Fig. 5
Comparison of predicted and measured enhancement factor Λ values for the first twelve catalytic reactions found to exhibit the NEMCA effect

Definitions and the Role of the Exchange Current I_0

The NEMCA effect has been already studied for some forty catalytic reactions on Pt, Rh, Pd, Ag, Ni and Au surfaces and using O^{2-}, Na^+, H^+ and, very recently, F^--conducting solid electrolytes. Lists of these reactions are given in Refs. [9] and [27–29].

In order to compare different catalytic reactions, it is useful to define three dimensionless parameters, i.e., the enhancement factor or Faradaic efficiency Λ, the rate enhancement ratio ρ and the promotion index P_i [9, 11]. The first parameter is defined from:

$$\Lambda = \Delta r/(I/2F) \ , \qquad (4)$$

where the change in catalytic rate Δr is expressed in terms of mol oxygen consumed or produced. More generally Λ can be defined from

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

where r' is expressed in g-equivalent/s.

A catalytic reaction is said to exhibit NEMCA when $|\Lambda| > 1$. When $\Lambda > 1$ as, e.g. in the case of C_2H_4 oxidation on Pt, the reaction is said to exhibit positive or electrophobic NEMCA behaviour. When $\Lambda < -1$ then the reaction is said to exhibit electrophilic behaviour.

The rate enhancement ratio ρ is defined from:

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

In the C_2H_4 oxidation example presented on Fig. 2 and discussed above the Λ and r values at steady-state are Λ = 74000 and $\rho = 26$.

As it turns out experimentally (Fig. 5) and can be explained theoretically [9] one can estimate the order of magnitude of the absolute value $|\Lambda|$ of the enhancement factor Λ for any given reaction, catalyst and catalyst-solid electrolyte interface from:

$$|\Lambda| \approx 2Fr_0/I_0 \ , \qquad (7)$$

where I_0 is the exchange current of the metal-solid electrolyte interface.

The parameter I_0 can be easily determined from standard $\ln I$ vs η (Tafel) plots [4, 9]. The overpotential η is defined from:

$$\eta = V_{WR} - V_{WR}^0 \ , \qquad (8)$$

where V_{WR} is the catalyst (working electrode, W) potential with respect to a reference (R) electrode. The overpotential η is related to current I via the classical Butler-Volmer equation:

$$(I/I_0) = \exp(\alpha_a F\eta/RT) - \exp(-\alpha_c F\eta/RT) \ , \qquad (9)$$

where α_a and α_c are the anodic and cathodic transfer coefficients, respectively. Thus by measuring η as a function of I one can extract I_0, α_a and α_c. Physically I_0 expresses the (equal under open-circuit conditions) rates of the electronation and deelectronation reaction at the tpb, e.g.:

$$O^{2-} \rightleftharpoons O(a) + 2e^- \ , \qquad (10)$$

where O(a) stands for oxygen adsorbed on the metal catalyst in the vicinity of the tpb. Thus, the exchange current I_0 is a measure of the non-polarizability of the metal-solid electrolyte interface.

As shown on Fig. 5, Eq. (7) is in very good agreement with experiment for all catalytic reactions studied so far. The agreement extends for more than five orders of magnitude. Thus, contrary to fuel cell applications where non-polarizable, i.e., high I_0 electrode-electrolyte interfaces are desirable to minimize activation overpotential losses, exactly the opposite is true for catalytic applications, i.e., I_0 must be low in order to obtain high Λ values, i.e., a strong Non-Faradaic rate enhancement.

Although Λ is an important parameter for determining whether a reaction exhibits NEMCA, it is not a fundamental one. The reason is that for the same catalytic reaction on the same catalyst material one can obtain significantly different $|\Lambda|$ values by varying I_0 (Eq. 7). The parameter I_0 is proportional to the tpb length [9] and can be controlled during catalyst film preparation by varying the sintering temperature and thus metal crystallite size and tpb length [9].

From a catalytic viewpoint an important parameter for quantifying NEMCA but also, more generally, the role of promoters is the promoter index P_i [11] defined from:

$$P_i = \frac{\Delta r/r_o}{\Delta\theta_i}\,, \tag{11}$$

where θ_i is the coverage of the promoting species i (e.g. $O^{\delta-}$, $Na^{\delta+}$) on the catalyst surface. When $P_i>0$ the species under consideration acts as promoter, while when $P_i<0$ it acts as a poison. For a species which just blocks catalytic sites it is $P_i=-1$; P_{Na} values up to 250 [11] and $P_{O\delta}$-values up to 100 have been measured [16] implying strong electronic interactions between the promoting species and the adsorbed reactants and intermediates. An example is shown on Fig. 6 where a Na coverage of 0.03 causes a 6-fold enhancement in the rate of CO oxidation on Pt deposited on β''-Al_2O_3, a Na^+ conductor ($P_{Na}\approx 200$). Even higher P_{Na} and ρ values have been recently measured for the NO reduction by C_2H_4 on Pt/β''-Al_2O_3 [12].

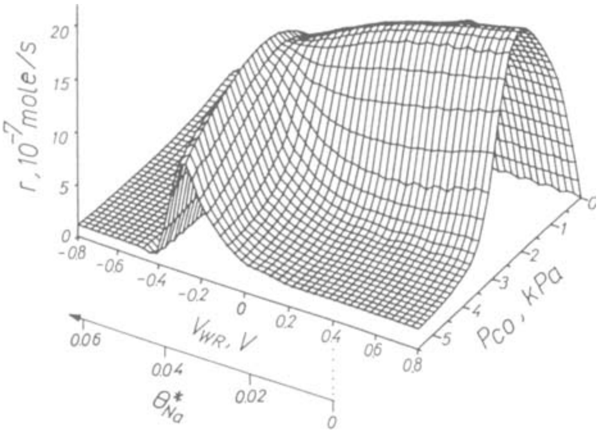

Fig. 6
Three-dimensional presentation of the effect of P_{CO}, catalyst potential and corresponding linearized sodium coverage on the rate of CO oxidation. Conditions: $T=350\,°C$, $P_{O_2}=6$ kPa (Ref. 11)

Selectivity Modification

One of the most promising applications of NEMCA is in product selectivity modification. An example is shown on Fig. 7 for the case of C_2H_4 epoxidation on Ag deposited on β''−Al_2O_3 [36]. The figure shows the effect of varying catalyst potential V_{WR} on the selectivity to ethylene oxide at various levels of addition of gas-phase chlorinated hydrocarbon "moderators". Combination of NEMCA and $C_2H_4Cl_2$ addition gives selectivities up to 88% which is one of the highest values reported so far for ethylene epoxidation.

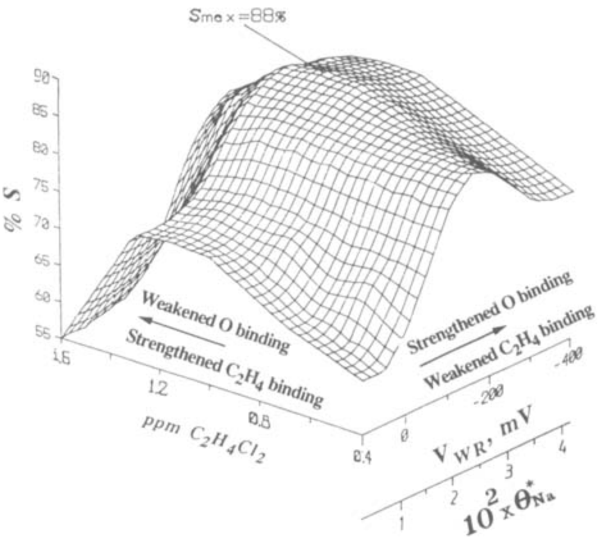

Fig. 7
Steady state effect of dichloroethane concentration, catalyst potential and corresponding linearized Na coverage on the selectivity to ethylene oxide during ethylene epoxidation on Ag/β''-Al_2O_3; $T=260\,°C$, $P_{O_2}=20$ kPa, $P_{C_2H_4}=65$ kPa (Ref. 36)

Work Function Measurements: An Additional Meaning of the EMF of Solid Electrolyte Cells with Metal Electrodes

One of the key steps in understanding the origin of NEMCA was the realization that solid electrolyte cells can be used both to monitor and to control the work function of the gas-exposed surfaces of their electrodes [7, 9]. It was shown both theoretically [4, 9] and experimentally [5, 7] that:

$$eV^0_{WR} = e\Phi_W - e\Phi_R \tag{12}$$

and

$$e\Delta V_{WR} = \Delta(e\Phi_W) \tag{13}$$

where $e\Phi_W$ is the catalyst surface work function and $e\Phi_R$ is the work function of the reference electrode surface. The reference electrode must be of the same material as the catalyst for Eq. (12) to hold, but Eq. (13) is not subject to this restriction. The derivation of Eqs. (12) and (13) is quite straightforward [9]. It is based on the standard definition of the work function [9, 37 – 39] and on the fact that the average Volta electrode potential Ψ vanishes at the electrode-gas interface, since no net charge can be sustained there [9].

The validity of Eqs. (12) and (13) was demonstrated in situ by using a Kelvin probe to measure in situ $e\Phi$ on catalyst surfaces subject to electrochemical promotion [5, 7, 9].

Therefore by applying currents or potentials in NEMCA experiments and by thus varying V_{WR}, one is also varying the average catalyst surface work function $e\Phi$ (Eq. 13). Positive currents increase $e\Phi$ and negative currents decrease it. Physically the variation in $e\Phi$ is due to spillover of ions to or from the catalyst surface.

Dependence of Catalytic Rates and Activation Energies on $e\Phi$

In view of Eq. (13) it follows that NEMCA experiments permit one to directly examine the effect of catalyst work function $e\Phi$ on catalytic rates. From a fundamental viewpoint the most interesting finding of all previous NEMCA studies is that over wide ranges of catalyst work function $e\Phi$ catalytic rates depend exponentially on $e\Phi$ and catalytic activation energies vary linearly with $e\Phi$ [4, 9].

A typical example is shown on Fig. 8 for the catalytic oxidation of C_2H_4 and of CH_4 on Pt. Both reactions exhibit electrophobic behaviour which is due to the weakening of the Pt = O chemisorptive bond with increasing $e\Phi$ [4, 9]. Chemisorbed atomic oxygen is an electron acceptor, thus increasing $e\Phi$ causes a weakening in the Pt = O bond, cleavage of which is involved in the rate-limiting step of the catalytic oxidation, and thus a linear decrease in activation energy and an exponential increase in catalytic rate is observed. In general, increasing $e\Phi$ weakens the chemisorptive bond of electron acceptor adsorbates such as oxygen [9]. Fig. 4 provides another example. The abrupt rate increases are due to reduction of surface Rh oxide [16]. Increasing $e\Phi$ weakens the Rh – O bond and destabilizes the oxide, thus causing the observed dramatic rate enhancement.

XPS Spectroscopic, Voltammetric and TPD Identification of Backspillover Ions as the Cause of NEMCA

The first XPS investigation of Ag electrodes on YSZ under O^{2-} pumping conditions was published in 1983 [40]. That study provided direct evidence for the creation of backspillover oxide ions on Ag (O 1s at 529.2 eV) upon positive current application. More recently Göpel and coworkers have used XPS, UPS and EELS to study Ag/YSZ catalyst surfaces under NEMCA conditions [32]. Their XPS spectra are similar to those in Ref. [40].

Very recently a similar detailed XPS study was performed on Pt films interfaced with YSZ [31]. This study showed that:

I. Backspillover oxide ions (O 1s at 528.8 eV) are generated on the gas-exposed electrode surface upon positive current application (peak δ in Fig. 9 top).
II. Normally chemisorbed atom oxygen (O 1s at 530.2 eV) is also formed upon positive current application (peak γ in Fig. 9 top). The coverages of the γ and δ states of oxygen are comparable and of the order of 0.5 each [31].
III. Oxidic spillover oxygen (δ-state) is *less* reactive than normally chemisorbed atomic oxygen (γ-state) with the reducing (H_2 and CO) ultra high vacuum background [31].

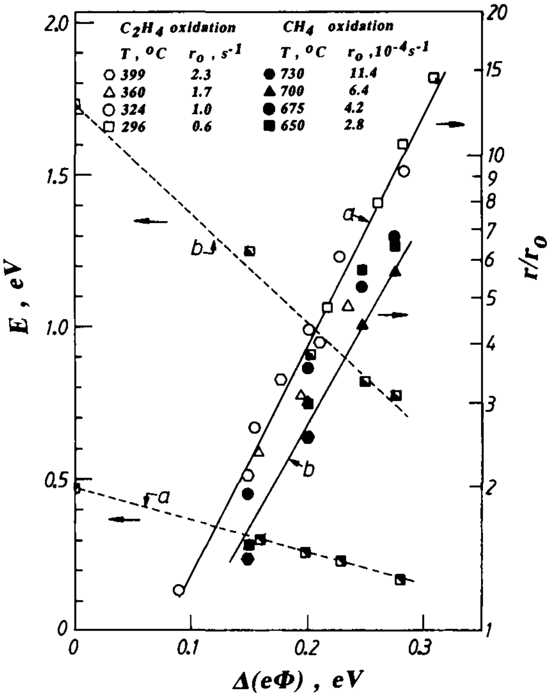

Fig. 8
Effect of catalyst work function $e\Phi$ on the activation energy E and catalytic rate enhancement ratio r/r_0 for C_2H_4 oxidation on Pt (a) and CH_4 oxidation on Pt (b) (Refs. 4, 9)

These observations provide a straightforward explanation for the origin of NEMCA when using YSZ: Spillover oxide ions (O^{2-} or O^-) generated at the tpb upon electrochemical O^{2-} pumping to the catalyst spread over the gas-exposed catalyst-electrode surface. They are accompanied by their compensating charge in the metal, thus forming spillover dipoles. They thus establish an effective electrochemical double layer which increases the catalyst surface work function and affects the strength of chemisorptive bonds such as that of normally chemisorbed oxygen via through-the-metal or through-the-vacuum interactions. This change in chemisorptive bond strength causes the observed dramatic changes in catalytic rates. It thus appears that the physicochemical origin of NEMCA is closely related to the very interesting electrical polarization- (0.3 V/Å) and work function change-induced effects on chemisorption recently observed by Yates and coworkers on well-characterized surfaces under UHV conditions [41].

The creation of two types of chemisorbed oxygen on Pt surfaces subject to NEMCA conditions has been recently confirmed by means of linear potential sweep voltammetry (Fig. 9 bottom, Ref. [35]). The first oxygen reduction peak corresponds to normally chemisorbed oxygen (γ-state) and the second reduction peak which appears only after prolonged positive current application [35] corresponds to the δ-state of oxygen, i.e. spillover oxidic oxygen.

The most lucid demonstration of the two types of oxygen formed on Pt has been provided by TPD [34] (Fig. 10). The

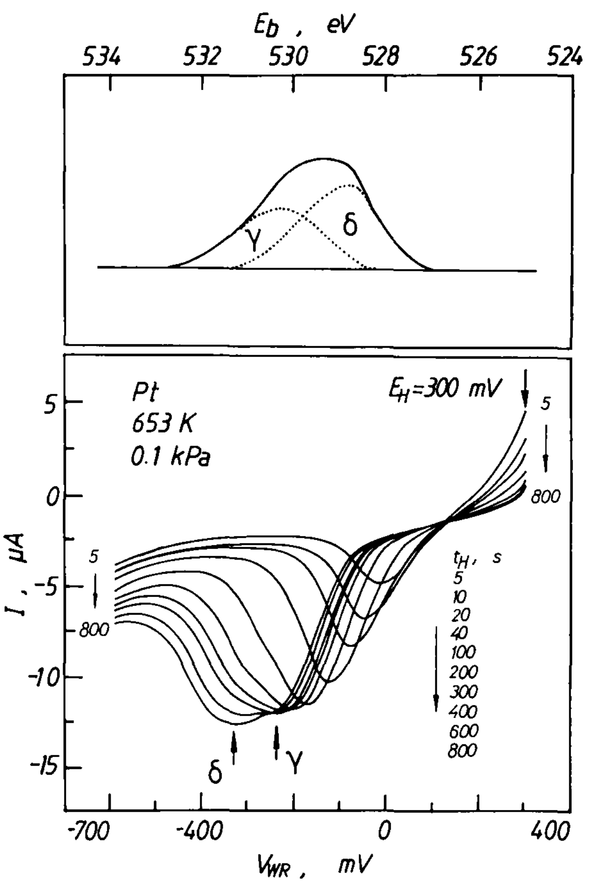

Fig. 9

Top: O 1s photoelectron spectrum of oxygen adsorbed on a Pt electrode supported on YSZ under UHV conditions after applying a constant overpotential ΔV_{WR} = 1.2 V corresponding to a steady state current I = 40 μA for 15 min at 673 K (Ref. 31). The same O 1s spectrum was maintained after turning off the potentiostat and rapidly cooling to 400 K (Ref. 31). The γ-state is normally chemisorbed atomic oxygen (E_b = 530.2 eV) and the δ-state is backspillover oxidic oxygen (E_b = 528.8 eV). Bottom: Linear potential sweep voltammogram obtained at T = 653 K and P_{O_2} = 0.1 kPa on a Pt electrode supported on YSZ showing the effect of holding time t_H at V_{WR} = 300 mV on the reduction of the γ- and δ-states of adsorbed oxygen; sweep rate: 30 mV/s (Ref. 35)

strongly bonded backspillover oxygen species (peak desorption temperature $T_p \approx 750-780$ K) displaces the normally chemisorbed oxygen from the gas phase ($T_p = 740$ K) to much more weakly bonded state ($T_p \approx 680$ K). Thus Figs. 9 and 10 provide a straightforward explanation of NEMCA when using O^{2-} conductors. A recent XPS investigation [42] has also confirmed that Na backspillover is the origin of NEMCA when using Na^+-conducting solid electrolytes.

4. Conclusions

Solid electrolytes can be used as active catalyst supports to promote reversibly catalyst surfaces. The promoting action is due to an electrochemically driven and controlled backspillover of ionic species on the catalyst surface. These species, which in some cases cannot form via gas phase adsorption, alter the catalyst work function and affect the binding strengths of chemisorbed reactants and intermediates, thus causing very pronounced modifications in catalytic activity and selectivity. In addition to potential technological applications these new phenomena allow for a systematic study of the role of promoters in heterogeneous catalysis.

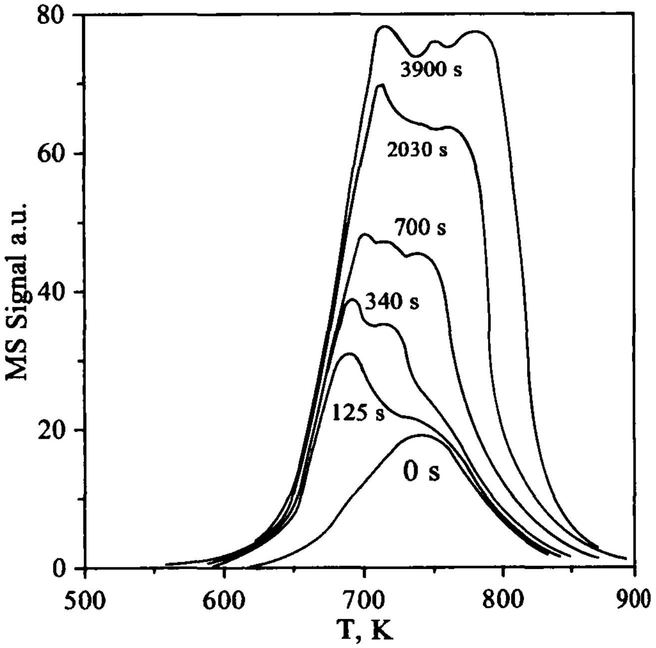

Fig. 10

Oxygen TPD spectra after gaseous oxygen adsorption at 673 K and $P_{O_2} = 4\cdot 10^{-6}$ Torr for 1800s (7.2 kL) followed by electrochemical O^{2-} supply (I = 15 μA) for various time periods (Ref. 34)

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