



ELECTROCHEMICAL PROMOTION IN CATALYSIS: NON-FARADAIC ELECTROCHEMICAL MODIFICATION OF CATALYTIC ACTIVITY

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Abstract—The catalytic activity and selectivity of the gas-exposed electrode surface of metal electrodes in solid electrolyte cells is altered dramatically and reversibly upon polarizing the metal–solid electrolyte interface. The induced steady-state change in *catalytic* rate can be up to 9000% higher than the normal (open-circuit) catalytic rate and up to 3×10^5 higher than the steady-state rate of ion supply. This new effect of non-faradaic electrochemical modification of catalytic activity (NEMCA) has been already demonstrated for more than 30 catalytic reactions on Pt, Pd, Rh, Ag, Au and Ni surface by using O^{2-} , F^- , Na^+ and H^+ conducting solid electrolytes. There is also a recent demonstration for an aqueous electrolyte system. In this paper the common features of previous NEMCA studies are summarized and the origin of the effect is discussed in light of recent *in situ* work function and XPS measurements which showed that: (1) solid electrolyte cells with metal electrodes are work function probes and work function controllers, via potential application, for their gas-exposed electrode surfaces; and (2) NEMCA is due to an electrochemically driven and controlled spillover of ions from the solid electrolyte onto the gas-exposed electrode surface. These spillover ions establish an effective electrochemical double layer and act as promoters for catalytic reactions. This interfacing of electrochemistry and catalysis offers several exciting theoretical and technological possibilities.

Key words: solid electrolyte, zirconia, $\beta''-Al_2O_3$, electrochemical promotion, NEMCA, metal electrode, ion spillover, activity and selectivity modification, work function.

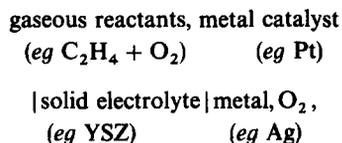
INTRODUCTION

The use of solid electrolyte galvanic cells to study catalytic phenomena was first proposed by C. Wagner[1]. This led to the technique of solid electrolyte potentiometry (SEP)[2] for measuring *in situ* the activity of oxygen on metal catalysts. Work in this area has been summarized in several reviews[3–6].

During the last few years, however, it has become apparent that the “active” use of solid electrolyte cells offers some far more interesting possibilities in heterogeneous catalysis: it was found that they can be used not only to study but also to influence catalytic phenomena on metal surfaces in a very pronounced and reversible manner. Work in this area prior to 1988 had been reviewed by Vayenas[3]. Then in 1988 the first reports on the effect of non-faradaic electrochemical modification of catalytic activity (NEMCA) appeared in the literature[7, 8]. Since then the NEMCA effect has been described for more than 30 catalytic reactions[6–13] and work prior to 1992 has been reviewed in a monograph[6]. In addition to the group which first reported this novel effect[6–13] the groups of Sobyanyin[14, 15], Lambert[16], Stoukides[17] and Haller[18] have also contributed recently to the NEMCA literature. Very recently the NEMCA effect was also demon-

strated in an aqueous electrolyte system by Heitbaum *et al.*[19]. The term “electrochemical promotion in catalysis” has also been proposed by Pritchard to describe the NEMCA effect[20].

In brief it has been found that the catalytic activity and selectivity of porous metal catalyst films deposited on solid electrolytes can be altered in a dramatic, reversible and, to some extent, predictable manner by carrying out the catalytic reaction in solid electrolyte cells of the type:



where the metal catalyst also serves as an electrode and by applying currents or potentials to the cell with a concomitant supply or removal of ions, O^{2-} , F^- , Na^+ , H^+ , to or from the catalyst surface.

The NEMCA effect was first demonstrated on Pt and Ag electrodes using 8 mol% Y_2O_3 -stabilized- ZrO_2 (YSZ), an O^{2-} conductor, as the solid electrolyte[7–9]. Electrochemical O^{2-} pumping to the catalyst–electrode was found to cause up to 60-fold (6000%) steady-state reversible enhancement in the rate of C_2H_4 oxidation[9]. Furthermore this

steady-state rate increase was found to be up to 3×10^5 times higher than the steady-state rate of supply of O^{2-} to the catalyst, *ie* the enhancement factor Λ [6, 9] or apparent faradaic efficiency for the process is 3×10^5 [9]. More recently the rate of C_2H_4 oxidation on Rh electrodes supported on YSZ was found to reversible increase by a factor of 90, again with faradaic efficiency values of the order of 10^5 [21].

More than 30 catalytic reactions on Pt, Pd, Rh, Ag, Au and Ni have been shown already to exhibit the NEMCA effect[6, 13] which does not appear to be limited to any particular metal, solid electrolyte or group of catalytic reactions. Thus in addition to O^{2-} conducting solid electrolytes[6-9, 11, 12], the NEMCA effect has also been demonstrated using Na^+ -conducting solid electrolytes such as $\beta''-Al_2O_3$ [10, 16], H^+ -conducting solid electrolytes such as $CsHSO_4$ [14] and very recently F^- conducting solid electrolytes, such as CaF_2 [22]. Also in addition to complete[8, 9] and partial oxidation reactions[11] the NEMCA effect has also been demonstrated for dehydrogenation, hydrogenation and decomposition reactions[6, 13].

In this paper we summarize the common features of previous NEMCA studies together with some new results on C_2H_4 epoxidation on Ag and C_2H_4 oxidation on Rh and discuss the origin of the effect in the light of recent work function[10], X-ray photo electron spectroscopic (XPS)[23] and cyclic voltammetric[24] investigations.

EXPERIMENTAL

The basic experimental setup is shown schematically on Fig. 1 (top). 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 (*eg* Y_2O_3 -stabilized- ZrO_2 (YSZ) an O^{2-} conductor, or $\beta''-Al_2O_3$, a Na^+ conductor). Catalyst, counter and reference electrode preparation and characterization details have been presented in detail elsewhere[6] 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 5-10³ cm^2 as measured via surface titration of oxygen and CO or C_2H_4 [6-13]. The catalyst electrode is exposed to the reactive gas mixture (*eg* $C_2H_4 + O_2$) 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, *eg* 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 $\beta''-Al_2O_3$) are supplied from (or to) the solid electrolyte to (or from) the catalyst-electrode surface. The current is defined

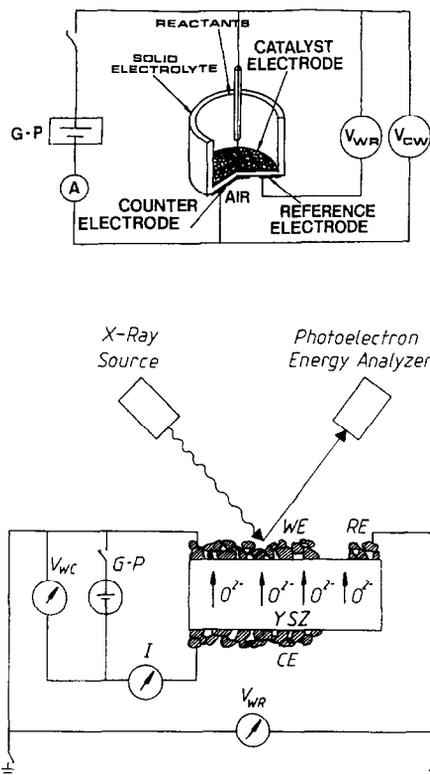


Fig. 1. Schematic of the experimental setup for NEMCA studies (top), and for using XPS (bottom) G-P: galvanostat-potentiostat.

positive when anions are supplied to or cations removed from the catalyst electrode. There is compelling evidence 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[6, 10, 23]. Thus the solid electrolyte acts as an active catalyst support and establishes an effective electrochemical double layer on the gas-exposed, *ie* catalytically active, electrode surface.

The (average) work function of the gas-exposed catalyst-electrode surface was measured *in situ*, *ie* 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[10, 25].

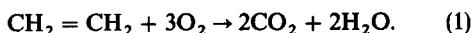
The experimental setup for using XPS to investigate metal electrode surfaces under conditions of electrochemical O^{2-} pumping is shown schematically in Fig. 1 (bottom). A 2-mm thick YSZ slab (10 × 13 mm) with a Pt catalyst electrode film, a Pt reference electrode and a Ag counter electrode was mounted 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 of 25-525°C by XPS using a Leybold HS-12 analyser operated at constant ΔE mode with 100-eV pass energy and a sampling area of 5 × 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[23].

RESULTS AND DISCUSSION

3.1. Catalytic rate modification

Figure 2 shows a typical NEMCA experiment carried out in the setup depicted on Fig. 1 (top). The catalytic reaction under study is the complete oxidation of C_2H_4 on Pt[9]:



The figure shows a typical galvanostatic transient, *ie* it depicts the transient effect of a constant applied current on the rate of C_2H_4 oxidation (expressed in g-atom $O s^{-1}$).

The Pt catalyst film with a surface area corresponding to $N = 4.2 \times 10^{-9}$ g-atom Pt, as measured by surface titration techniques[6], 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. 1. Initially ($t < 0$) the circuit is open ($I = 0$) and the open-circuit catalytic rate r_0 is 1.5×10^{-8} g-atom $O s^{-1}$. The corresponding turnover frequency (TOF), *ie* oxygen atoms reacting per site per s is $3.57 s^{-1}$.

Then at $t = 0$ a galvanostat is used to apply a constant current of $+1 \mu A$ between the catalyst and the counter electrode (Fig. 1). Now oxygen ions O^{2-} are supplied to the catalyst-gas-solid electrolyte three-phase-boundaries (tpb) at a rate $G_O = I/2F = 5.2 \times 10^{-12}$ g-atom $O s^{-1}$. The catalytic rate starts increasing (Fig. 2) and within 25 min gradually reaches a value $r = 40 \times 10^{-8}$ g-atom $O s^{-1}$, which is 26 times larger than r_0 . The new TOF is $95.2 s^{-1}$. The increase in catalytic rate $\Delta r = r - r_0 = 38.5 \times 10^{-8}$ g-atom $O s^{-1}$ is 74,000 times larger than $I/2F$. This means that each O^{2-} supplied to the Pt catalyst causes at steady state 74,000 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 (*ie* constant current) operation are found in NEMCA studies to be usually, but not always[6], of the type:

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

ie 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, *ie* 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 , *ie*

$$\tau \approx 2FN/I. \quad (3)$$

What this observation shows is that NEMCA is a catalytic effect, it takes place over the entire gas-exposed catalyst surface and is not an electro-catalytic 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[6]. It is worth noting that if NEMCA were restricted to the tpb, *ie* if the observed rate increase were due to an electro-catalytic reaction, then τ would be practically zero during galvanostatic transients.

As shown on Fig. 2 NEMCA is reversible, *ie* 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[22]. Negative current application has practically no effect on the rate of this particular reaction.

3.2. Effect of gaseous composition on regular (open-circuit) and NEMCA-induced reaction rate

Figure 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. 1). 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 60 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[6, 9].

Figure 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 imposed values of V_{WR} . Increasing V_{WR} causes up to 90-fold (9000%) rate enhancement relative to the open-circuit rate value. The dramatic rate

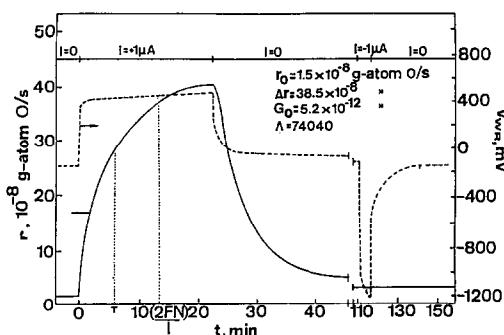


Fig. 2. Rate and catalyst potential response to step changes in applied current during C_2H_4 oxidation on Pt; $T = 370^\circ C$, $P_{O_2} = 4.6$ kPa, $P_{C_2H_4} = 0.36$ kPa. The steady-state rate increase Δr is 74,000 times higher than the steady-state rate of supply of O^{2-} to the catalyst ($\Lambda = 74,000$).

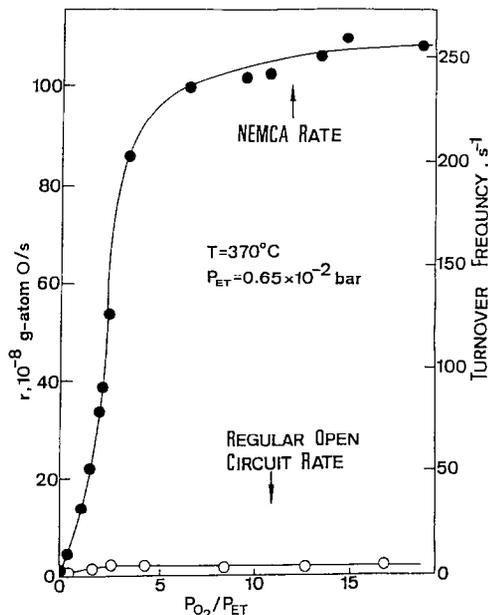


Fig. 3. Effect of gaseous composition on the regular (open-circuit) steady-state rate of C_2H_4 oxidation on Pt and on NEMCA-induced catalytic rate when the catalyst film is maintained at $V_{WR} = 1$ V.

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[6, 9, 21].

3.3. Definitions and the role of the exchange current I_0

The NEMCA effect has already been studied for more than 30 catalytic reactions on Pt, Rh, Pd, Ag, Ni and Au surfaces and using O^{2-} , Na^+ , H^+ and, very recently, F^- -conducting solid electrolytes. A list of these reactions is given in[6] and [13].

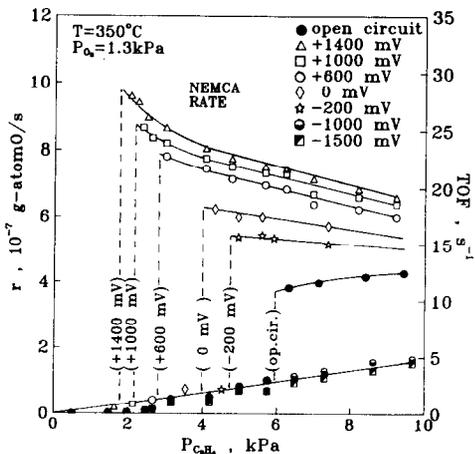


Fig. 4. Effect of gaseous composition and catalyst potential V_{WR} on the steady-state rate of C_2H_4 oxidation on Rh.

In order to compare different catalytic reactions, it is useful to define two dimensionless parameters, *ie* the enhancement factor or faradaic efficiency Λ and the rate enhancement ratio ρ [6]. The former is defined from:

$$\Lambda = \Delta r / (I/nF), \tag{4}$$

where the change in catalytic rate Δr is expressed in terms of g-atom or g-equivalent of oxygen consumed or produced and n is the absolute value of the ion charge, *ie* 2 for the case of doped ZrO_2 and 1 for $\beta''-Al_2O_3$.

A catalytic reaction is said to exhibit NEMCA when $|\Lambda| > 1$. When $\Lambda > 1$, as *eg* 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:

$$\rho = r/r_0. \tag{5}$$

In the C_2H_4 oxidation example presented on Fig. 2 and discussed above the Λ and r values at steady state are $\Lambda = 74,000$ and $\rho = 26$.

As it turns out experimentally (Fig. 5) and can be explained theoretically[6] 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:

$$|\Lambda| \approx 2Fr_0/I_0 \tag{6}$$

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[6, 9]. The over-

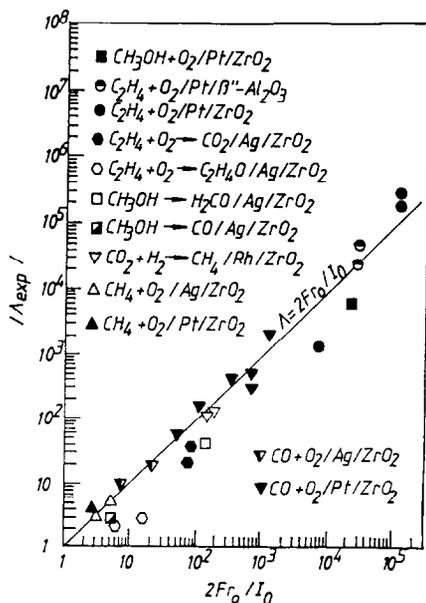


Fig. 5. Comparison of predicted and measured enhancement factor Λ values for the first 12 catalytic reactions found to exhibit the NEMCA effect.

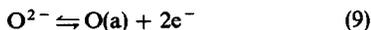
potential η is defined from:

$$\eta = V_{\text{WR}} - V_{\text{WR}}^0, \quad (7)$$

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[26]:

$$(I/I_0) = \exp(\alpha_a F\eta/RT) - \exp(-\alpha_c F\eta/RT) \quad (8)$$

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 de-electronation reaction at the tpb, *eg*:



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, equation (6) 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, *ie* high I_0 electrode–electrolyte interfaces are desirable to minimize activation overpotential losses, exactly the opposite is true for catalytic applications, *ie* I_0 must be low in order to obtain high Λ values, *ie* 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 [equation (6)]. The parameter I_0 is proportional to the tpb length[27] and can be controlled during catalyst film preparation by varying the sintering temperature and thus metal crystallite size and tpb length[6].

3.4. Selectivity modification

One of the most promising applications of NEMCA is in product selectivity modification. An example is shown on Fig. 6 for the case of C_2H_4 oxidation on Ag. The figure shows the effect of varying catalyst potential V_{WR} on the selectivity to ethylene oxide (the other products being CO_2 and for $V_{\text{WR}} < -0.4\text{V}$ some acetaldehyde) at various levels of addition of gas-phase chlorinated hydrocarbon “moderators”. With no $\text{C}_2\text{H}_4\text{Cl}_2$ present in the feed the selectivity to ethylene oxide is varied between 0 and 56% by varying V_{WR} . Combination of NEMCA and $\text{C}_2\text{H}_4\text{Cl}_2$ addition gives selectivities well above 75%. The beneficial effect of increasing $e\Phi$ and Cl coverage is due to the weakening of the binding strength of chemisorbed atomic oxygen[6] which makes it more selective for epoxidation[6, 11].

3.5. 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

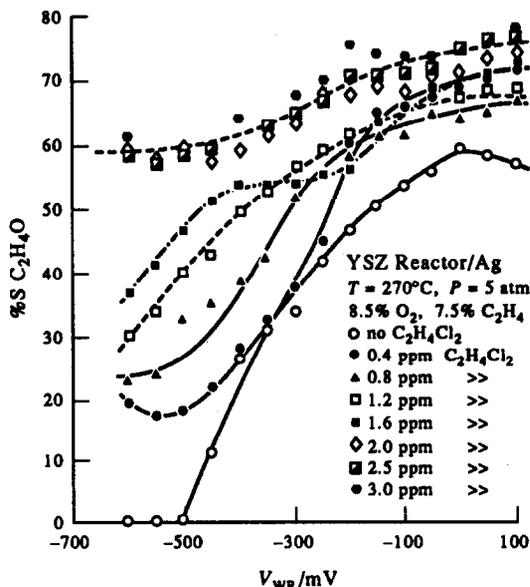


Fig. 6. Effect of catalyst potential V_{WR} on the selectivity to ethylene oxide during C_2H_4 oxidation on Ag at various levels of gas-phase “moderator” $\text{C}_2\text{H}_4\text{Cl}_2$.

cells can be used both to monitor and to control the work function of the gas-exposed surfaces of their electrodes[6, 10]. It was shown both theoretically[6] and experimentally[10, 25] that:

$$eV_{\text{WR}}^0 = e\Phi_{\text{W}} - e\Phi_{\text{R}}, \quad (10)$$

and

$$e\Delta V_{\text{WR}} = \Delta(e\Phi_{\text{W}}), \quad (11)$$

where $e\Phi_{\text{W}}$ is the catalyst surface work function and $e\Phi_{\text{R}}$ is the work function of the reference electrode surface. The reference electrode must be of the same material as the catalyst for equation (10) to hold, but equation (11) is not subject to this restriction. The derivation of equations (10) and (11) is quite straightforward[6]. It is based on the standard definition of the work function[6, 26, 28, 29] 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[6].

The validity of equations (10) and (11) was demonstrated *in situ* by using a Kelvin probe to measure *in situ* $e\Phi$ on catalyst surfaces subject to electrochemical promotion[10, 25].

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 $e\Phi$ [equation (11)]. 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.

3.6. Dependence of catalytic rates and activation energies on $e\Phi$

In view of equation (11) it follows that NEMCA experiments permit 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 $e\Phi$ [6,10].

A typical example is shown on Fig. 7 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 $e\Phi$ [6, 9, 12]. 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[6]. Figure 4 provides another example. The abrupt rate increases are due to reduction of surface Rh oxide[21]. Increasing $e\Phi$ weakens the Rh—O bond and destabilizes the oxide, thus causing the observed dramatic rate enhancement.

3.7. XPS spectroscopic and voltammetric identification of spillover ions as the cause of NEMCA

The first XPS investigation of Ag electrodes on YSZ under O^{2-} -pumping conditions was published in 1983[30]. That study provided direct evidence for the creation of spillover oxide ions on Ag (O1s 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[31]. Their XPS spectra are similar to those in [30].

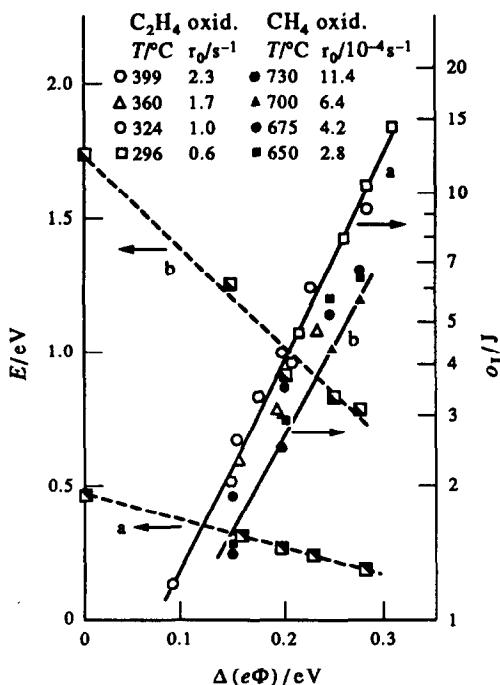


Fig. 7. Effect of catalyst work function $e\Phi$ on the activation energy E and catalytic rate enhancement ratio r/r_0 for C_2H_4 oxidation on Pt (a) and CH_4 oxidation on Pt (b).

Very recently a similar detailed XPS study was performed on Pt films interfaced with YSZ[23]. This study showed that:

(i) spillover oxide ions (O1s at 528.8 eV) are generated on the gas-exposed electrode surface upon positive current application (peak δ in Fig. 8 top);

(ii) normally chemisorbed atomic oxygen (O1s at 530.2 eV) is also formed upon positive current application (peak γ in Fig. 8 top). The coverages of the γ and δ states of oxygen are comparable and of the order of 0.5 each[23]; and

(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[23].

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

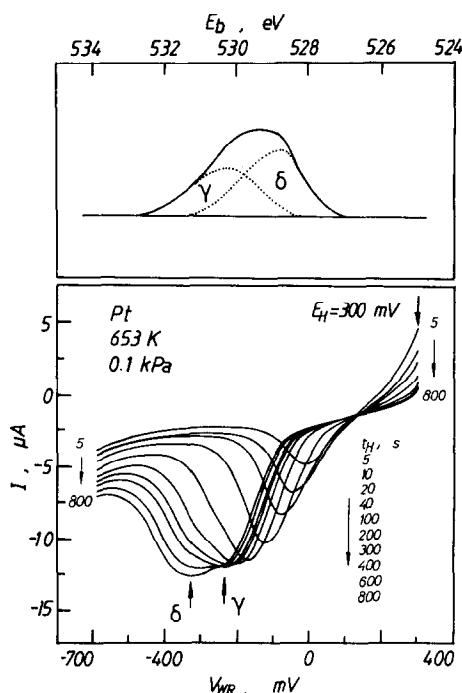


Fig. 8. Top: O1s photoelectron spectrum of oxygen adsorbed on a Pt electrode supported on YSZ under *uhv* conditions after applying a constant overpotential $\Delta V_{WR} = 1.2$ V corresponding to a steady-state current $I = 40 \mu A$ for 15 min at 673 K[23]. The γ -state is normally chemisorbed atomic oxygen ($E_b = 530.2$ eV) and the δ -state is spillover 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^{-1} [24].

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[32].

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. 8 bottom, [24]). 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[24] must correspond to the δ -state of oxygen, *ie* spillover oxidic oxygen.

CONCLUSIONS

Solid electrolytes can be used as active catalyst supports to reversibly promote catalyst surfaces. The promoting effect of solid electrolytes is due to an electrochemically driven and controlled spillover of ions on the catalyst-electrode surface.

The study of NEMCA has revealed that over wide ranges of work function $e\Phi$, catalytic rates depend exponentially on catalyst work function. Potential technological applications of NEMCA may emerge as more reactions are studied.

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