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Non-Faradaic electrochemical modification of catalytic activity: solid electrolytes as active catalyst supports

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Solid electrolytes can act as active catalyst supports to induce the effect of Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA). The main features of NEMCA are summarized together with some new results on C_2H_4 epoxidation on Ag/YSZ and CO oxidation on β''-Al_2O_3. In situ XPS investigation of Pt/YSZ has confirmed that NEMCA is due to an electrochemically controlled ion spillover from the solid electrolyte onto the metal electrode surface.

1. Introduction

The use of solid electrolytes to study catalytic phenomena was first proposed by C. Wagner [1]. This led to the technique of solid electrolyte potentiometry (SEP) initially demonstrated by Vayenas and Saltsburg [2] for in situ measuring the activity of oxygen on metal catalysts. Work in this area has been reviewed by Vayenas [3], Stoukides [4], Gellings et al. [5] and more recently by Vayenas et al. [6].

During the last few years, however, it has become apparent that the "active" use of solid electrolyte cells offers some far more interesting opportunities not only to study but also to influence catalytic phenomena on metal surfaces. Work prior to 1988 had been reviewed [3]. Then in 1988 the effect of non-Faradaic electrochemical modification of catalytic activity (NEMCA effect) was discovered [7–10] and has been described for more than twenty five catalytic reactions as reviewed by Vayenas et al. [6]. The groups of Sobyanin [11,12] and Stoukides [13] have also recently contributed to the NEMCA literature. Very recently the NEMCA effect was also demonstrated in an aqueous electrolyte system [14]. The term "Electrochemical promotion" has also been proposed [15] to describe the NEMCA effect.

In brief it has been found that the catalytic activity and selectivity of metal 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:

gaseous reactants, metal catalyst | solid electrolyte | metal, O_2

and by applying currents or potentials to the cell, with a concomitant supply or removal of ions, e.g. O^{2-} or Na^+, to or from the catalyst surface.

Up to 70-fold steady-state reversible enhancement in catalytic rate has been observed [6]. The steady state increase in the rate of catalytic reactions can be up to 3×10^5 times higher than the steady state rate of supply or removal of ions [6,9]. More than 25 catalytic reactions have been shown already to exhibit the NEMCA effect [6], which does not appear to be limited to any particular metal or solid electrolyte. Thus in addition to O^{2-} and Na^+ conducting solid electrolytes the NEMCA effect has also been demonstrated using H^+-conducting [11] and very recently F^--conducting solid electrolytes [16].

In this paper the main common features of previous NEMCA studies are summarized, some recent results on CO oxidation on Pt/β''-Al_2O_3 and ethylene epoxidation on Ag/YSZ are presented and the origin of the effect is discussed, in terms of a recent in situ XPS investigation.

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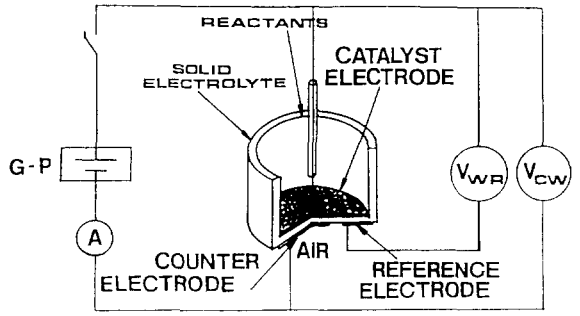

Fig. 1. Catalytic reactor configuration for NEMCA studies. G–P: Galvanostat–Potentiostat.

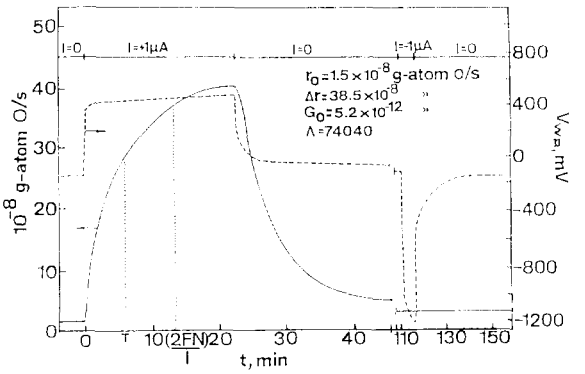

Fig. 2. Rate and catalyst potential response to step changes in applied current during C_2H_4 oxidation on Pt; $T=370\,°C$, $P_{O_2}=4.6$ kPa, $P_{C_2H_4}=0.36$ kPa. The steady-state rate increase Δr is 74000 times higher than the steady-state rate of supply of O^{2-} to the catalyst ($\Lambda=74000$).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

2. Experimental

The experimental setup is shown schematically on fig. 1. The metal catalyst, 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 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.

When a current or voltage is applied between the catalyst and the counter electrode, ions (O^{2-} in the case of doped ZrO_2, Na^+ in the case of β''-Al_2O_3) are supplied from (or to) the solid electrolyte to (or from) the catalyst surface. These is compelling evidence that these ions (together with their compensating charge in the metal thus forming surface dipoles) migrate (spillover) onto the catalyst surface [17–19]. Thus the solid electrolyte acts as an *active catalyst support.*

3. Results and discussion

3.1. Catalytic rate modification

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

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

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 g-atom O/s).

The Pt catalyst film with a surface area corresponding to $N=4.2\times10^{-9}$ 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. The corresponding turnover frequency (TOF), i.e., 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 μA 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 $G_O=I/2F=5.2\times10^{-12}$ g-atom O/s. (Current is defined positive when anions are supplied to or cations removed from the catalyst). The catalytic rate starts increasing (fig. 2) and within 25 min gradually reaches a value $r=40.0\times10^{-8}$ g-atom O/s, which is 26 times larger than r_0. The new TOF is 95 s^{-1}. The increase in catalytic rate $\Delta r=r-r_0=38.5\times10^{-8}$ g-atom 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 [6], of the type:

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

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.:

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

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 $I/2F$, 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, 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. Negative current application has practically no effect on the rate of this particular reaction.

3.2. Definitions and the role of the exchange current I_0

The NEMCA effect has been already studied for more than twenty 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 refs. [6] and [20].

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

$$\Lambda = \Delta r/(I/nF) , \quad (4)$$

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, i.e. 2 for case of doped ZrO_2 and 1 for β''-Al_2O_3. The current I is taken to be positive when the catalyst is positive with respect to the counter electrode, i.e., when anions are supplied to the catalyst or cations removed from it.

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:

$$\rho = r/r_0 . \quad (5)$$

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

As it turns out experimentally (fig. 3) 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:

$$|\Lambda| \approx 2Fr_0/I_0 , \quad (6)$$

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 versus η (Tafel) plots [6,9]. The overpotential η is defined from:

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

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:

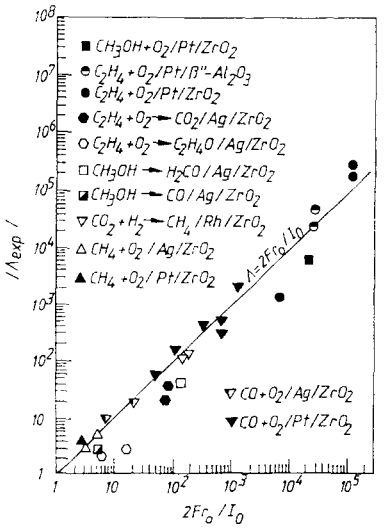

Fig. 3. Comparison of predicted and measured enhancement factor Λ values for the catalytic reactions found to exhibit the NEMCA effect.

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

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 deelectronation reaction at the tpb, e.g.:

$$O^{2-} \leftrightharpoons O(a)+2e^-\ , \quad (9)$$

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. 3, eq. (6) is in very good agreement with the 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 NEMCA 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. (6)). The parameter I_0 is proportional to the tpb length [21] and can be controlled during catalyst film preparation by varying the sintering temperature and thus metal crystallite size and tpb length [6].

3.3. Selectivity modification

One of the most promising applications of NEMCA is in product selectivity modification. An example is shown on fig. 4 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 $V_{WR}<-0.4$ V some acetaldehyde) at various levels of addition of gas-phase chlorinated hydrocarbon "moderators". With no $C_2H_4Cl_2$ present in the feed, the selectivity to ethylene oxide is varied between 0 and 56% by varying V_{WR}. Combination of NEMCA and $C_2H_4Cl_2$ addition gives selectivities well above 75%.

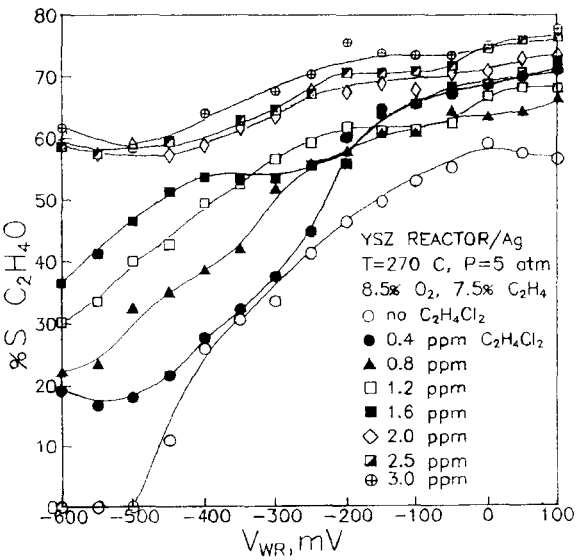

Fig. 4. Effect of catalyst potential V_{WR} on the selectivity to ethylene oxide during C_2H_4 oxidation on Ag at various levels of addition of the gas-phase "moderator" $C_2H_4Cl_2$.

3.4. The work function of catalyst films interfaced with solid electrolytes

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 [6,10]. It was shown both theoretically and experimentally that:

$$eV^0_{WR} = e\Phi_W - e\Phi_R \quad (10)$$

and

$$e\Delta V_{WR} = \Delta e\Phi_W , \quad (11)$$

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. (10) to hold, but eq. (11) is not subject to this restriction.

The validity of eqs. (10) and (11) has been demonstrated by using a Kelvin probe to measure in situ $e\Phi$ on catalyst surfaces subject to electrochemical promotion [10].

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. (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.

In view of eq. (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 range 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. 5 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 $e\Phi$ [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.

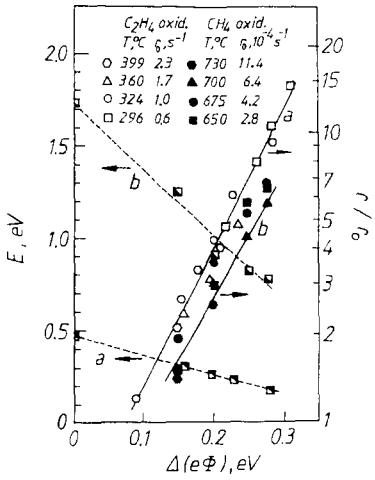

Fig. 5. Effect of catalyst work function $e\Phi$ on the activation energy E and catalytic rate enhancement ratio r/r_0 for C_2H_4 oxidation on Pt(a) ($P_{C_2H_4}$=0.4 kPa; P_{O_2}=4.8 kPa) and CH_4 oxidation on Pt(b) ($P_{CH_4}=P_{O_2}$=2 kPa).

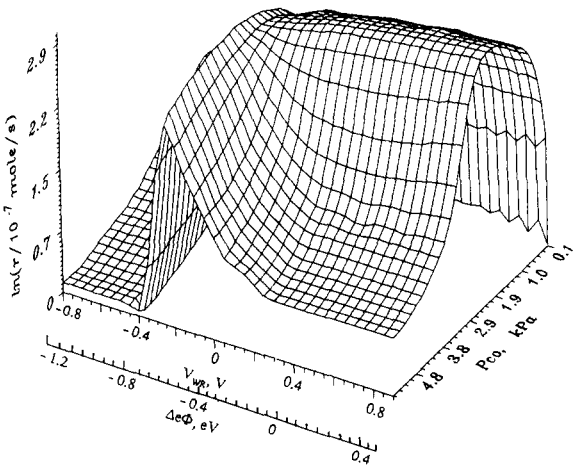

Fig. 6. Effect of catalyst potential V_{WR}, work function $e\Phi$ and partial pressure of CO on the rate of CO oxidation on Pt/β″-Al_2O_3; T=350°C, P_{O_2}=6 kPa.

In other cases the dependence of catalytic rates on work function $e\Phi$ is more complex. An example is shown on fig. 6 for the case of CO oxidation on Pt deposited on β″-Al_2O_3, a Na^+ conductor. For V_{WR}>0.4 V (or $\Delta e\Phi$>0) the Pt surface is Na-free and the classical Langmuir–Hinshelwood type rate

dependence on P_{CO} is observed. For high P_{CO} values the rate is negative-order in CO, since the Pt surface is predominantly covered by CO. By decreasing V_{WR} and $e\Phi$ via Na introduction on the surface, an exponential increase in the rate is obtained due to enhanced chemisorption of oxygen on the Pt surface [22]. Upon further decreasing $e\Phi$ the rate drops abruptly due to the formation of a CO–Na–Pt surface complex [22]. For low P_{CO} values, Na has no promoting effect on the rate (fig. 6) since the surface is already predominantly covered by oxygen. It is worth noting that small changes in Na coverage on the Pt surface θ_{Na} suffice to cause the interesting volcano-type behaviour depicted on fig. 6 for high P_{CO} values. Thus θ_{Na} varies on fig. 6 from 0 ($\Delta e\Phi=0$) to 0.08 ($\Delta e\Phi=-1.2$ eV) [22].

3.5. Spectroscopic evidence for spillover ions as the cause of NEMCA

Until recently there was only one in situ XPS investigation of catalyst surfaces (Ag) subject to NEMCA conditions [17]. That study provided direct evidence for the creation of spillover oxide ions on Ag (O1s at 529.2 eV) upon positive current application which also affected the coverage of covalently bonded atomically adsorbed oxygen (O1s at 532.6 eV). More recently Göpel and coworkers [18] have used XPS, UPS and EELS to study Ag/YSZ catalyst surfaces under NEMCA conditions.

Very recently Ladas et al. [19] have obtained similar XPS results on Pt films interfaced with YSZ. Spillover oxide ions (O1s at 528.8 eV) are generated upon positive current application and are less reactive with the reducing UHV background than atomically chemisorbed oxygen (O1s at 530.2 eV). This provides a straightforward explanation for the origin of NEMCA: Spillover oxide ions generated upon electrochemical O^{2-} pumping to the catalyst spread over the catalyst surface and establish an effective electrochemical double layer which increases the catalyst surface work function and affects the strength of chemisorptive bonds 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 [23] on well-characterized surfaces under UHV conditions.

4. 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 surface.

The study of NEMCA has revealed that over the 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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