

Non-Faradaic Electrochemical Modification of Catalytic Activity

REVERSIBLE PROMOTION OF PLATINUM METALS CATALYSTS

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The catalytic activity and selectivity of platinum metals can be altered dramatically and reversibly by interfacing the metal with a solid electrolyte which supplies ions onto the catalyst surface under the influence of an external potential. The induced change in catalytic rate is orders of magnitude higher than the rate of ion supply. This new effect has revealed a surprisingly simple exponential relationship between catalytic activity and catalyst work function. The effect appears to apply to all heterogeneously catalysed reactions, but is particularly pronounced for platinum. This interfacing of electrochemistry and catalysis appears to offer some exciting theoretical and technological possibilities.

It has been found recently 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 (1-8). This is achieved by carrying out the catalytic reaction in solid electrolyte cells of the type:

gaseous reactants, metal catalyst|solid electrolyte|
metal, O₂

and by applying a certain voltage or current to the cell, with a concomitant supply or removal of ions, for example O²⁻, Na⁺, to or from the catalyst surface through the gas-impermeable solid electrolyte. This is shown diagrammatically in Figure 1.

The term Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) has been used to describe this new phenomenon, since the steady-state catalytic rate increase can be up to a factor of 3×10^3 higher than the steady-state rate of ion transfer through the electrolyte (1, 5, 6).

The observed dramatic changes in the catalytic rate are up to a factor of 70 higher than

the regular (open-circuit) catalytic rate, and have been successfully correlated with changes in the average work function of the gas-exposed catalyst surface (1, 5-7). As anticipated theoretically and proved experimentally (1), this work function change equals $e\eta$, where η is the catalyst activation overpotential. The activation overpotential is a measure of the "difficulty" of charge transfer at the catalyst-solid electrolyte interface. This interface is where partially charged species are produced. These then "spill-over" onto the catalyst surface, together with their compensating charge in the metal, and alter the metal catalyst average work function.

The NEMCA effect can be viewed as a special kind of catalytic promotion (2), actually an electrochemical one, which enables continuous and controlled in situ variation and monitoring of the amount of the promoter. From a theoretical point of view it provides evidence that long-range electronic interactions may play an important role in heterocatalytic reactions.

Two kinds of solid electrolytes have been

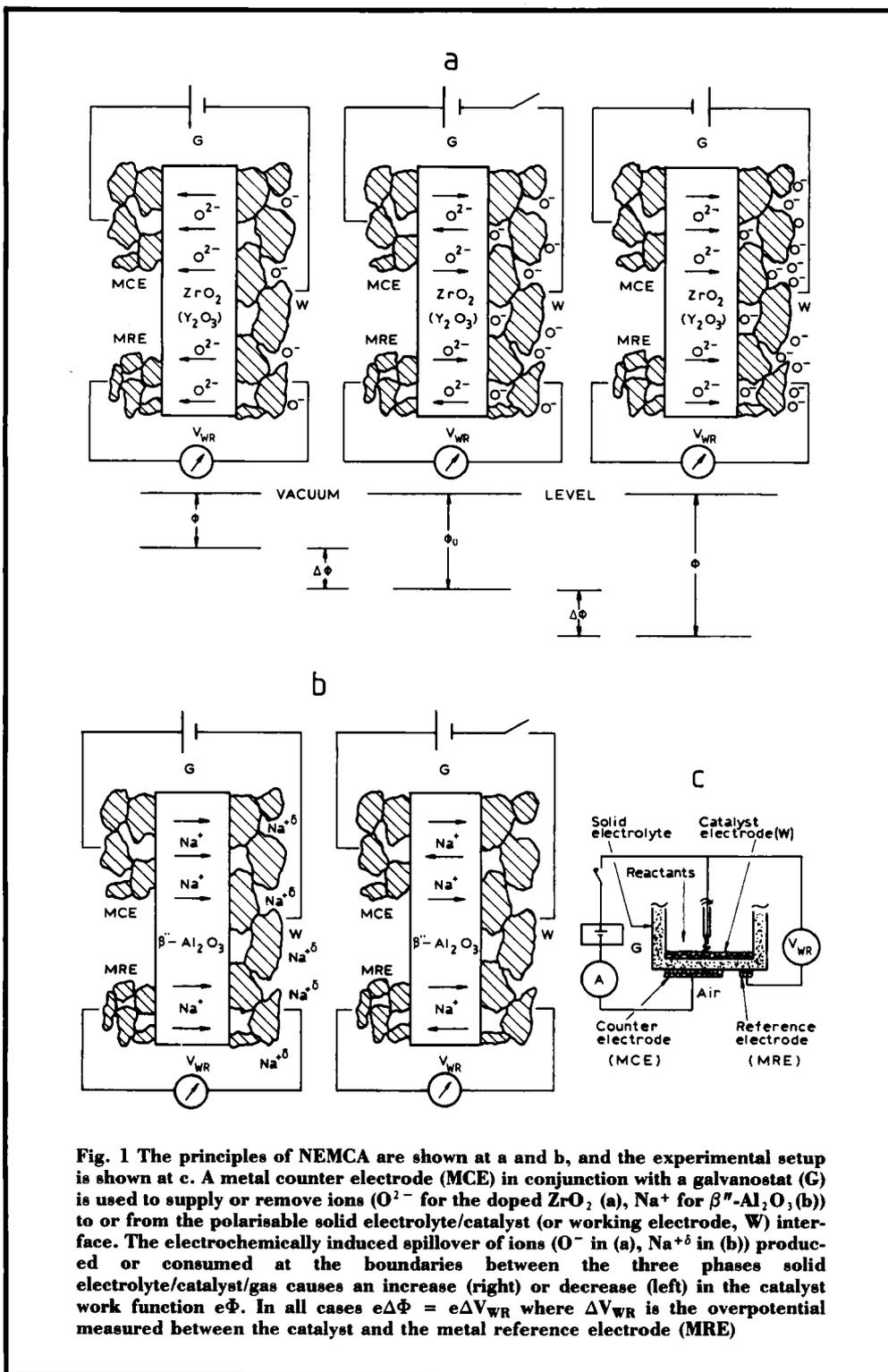


Fig. 1 The principles of NEMCA are shown at a and b, and the experimental setup is shown at c. A metal counter electrode (MCE) in conjunction with a galvanostat (G) is used to supply or remove ions (O^{2-} for the doped ZrO_2 (a), Na^+ for $\beta''-Al_2O_3$ (b)) to or from the polarisable solid electrolyte/catalyst (or working electrode, W) interface. The electrochemically induced spillover of ions (O^- in (a), $Na^{+\delta}$ in (b)) produced or consumed at the boundaries between the three phases solid electrolyte/catalyst/gas causes an increase (right) or decrease (left) in the catalyst work function $e\Phi$. In all cases $e\Delta\Phi = e\Delta V_{WR}$ where ΔV_{WR} is the overpotential measured between the catalyst and the metal reference electrode (MRE)

Catalytic Reactions Found to Exhibit the NEMCA Effect on Platinum, Palladium and Silver

I. Positive (Electrophobic) NEMCA effect ($\Delta r > 0$ with $I > 0^*$, $e\Delta\Phi > 0$)

Reactants	Products	Catalyst	Electrolyte	Temperature, °C	$\Delta r / (I/2F)$	r/r_0	References
C_2H_4, O_2	CO_2	Pt	$ZrO_2-Y_2O_3$	260–450	$[0,3 \times 10^5]$	<55	1,3,6
C_2H_4, O_2	CO_2	Pt	$\beta''-Al_2O_3$	180–300	$[0,5 \times 10^4]$	<4	1,9
CH_3OH, O_2	H_2CO, CO_2	Pt	$ZrO_2-Y_2O_3$	300–500	$[0,10^4]$	<3	10**
CO, O_2	CO_2	Pt	$ZrO_2-Y_2O_3$	300–550	$[0,500]$	<3	4,5,p
CO, O_2	CO_2	Pd	$ZrO_2-Y_2O_3$	400–550	$[0,10^3]$	<1.5	5
CH_4, O_2	CO_2	Pt	$ZrO_2-Y_2O_3$	650–750	$[0,5]$	<70	p
CH_4, O_2	CO, CO_2, C_2H_4	Ag	$ZrO_2-Y_2O_3$	650–750	$[0,5]$	<30	1**
C_2H_4, O_2	C_2H_4O, CO_2	Ag	$ZrO_2-Y_2O_3$	320–470	$[0,300]$	<3	5**
C_3H_6, O_2	C_3H_6O, CO_2	Ag	$ZrO_2-Y_2O_3$	320–420	$[0,300]$	<2	5**

II. Negative (Electrophilic) NEMCA effect ($\Delta r > 0$ with $I < 0$, $e\Delta\Phi < 0$)

CO, O_2	CO_2	Pt	$ZrO_2-Y_2O_3$	300–550	$[0, -500]$	<6	4,5,p
CH_3OH, O_2	H_2CO, CO_2	Pt	$ZrO_2-Y_2O_3$	300–550	$[0, -10^4]$	<15	10**
CH_3OH	H_2CO, CO, CH_4	Pt	$ZrO_2-Y_2O_3$	400–500	$[0, -10]$	<3	5**
CH_3OH	H_2CO, CO, CH_4	Ag	$ZrO_2-Y_2O_3$	550–750	$[0, -25]$	<6	7**

* Current is defined as positive when O^{2-} are supplied to or Na^+ removed from the catalyst surface

** Change in product selectivity observed

p Present work

used in studies of the NEMCA effect, both exhibiting quite similar behaviours: [a] ZrO_2 (8 mol% Y_2O_3), which is an O^{2-} conductor, and [b] $\beta''-Al_2O_3$, which is a Na^+ conductor. The reactions examined were mainly oxidations, and porous platinum, palladium and silver films were used as catalysts and auxiliary electrodes. These films were deposited on the solid electrolyte using platinum, palladium and silver metal pastes (3–7), followed by calcination at temperatures of 600–850°C. The films typically have thicknesses of about 5 μm , porosities around 30 per cent, superficial surface areas of 1 to 2 cm^2 and true surface areas of 100–500 cm^2 , as measured by surface titration techniques (3–7). All reactions studied so far exhibit the NEMCA effect, as shown in the Table, in the presence of significant activation overpotential η , of a few hundred mV. The latter can be easily measured as the difference between the

ohmic-drop-free (IR-free) catalyst potential V_{WR} , with respect to a reference electrode, and the open-circuit potential $V_{WR,0}$:

$$\eta = V_{WR} - V_{WR,0} \quad (i)$$

The enhancement factor Λ and the rate enhancement ratio ρ are two useful quantities in comparing different reactions. The enhancement factor is defined as the ratio of the catalytic rate change to the rate of ion transport through the electrolyte upon application of a current or potential to the cell, while the rate enhancement ratio expresses the ratio of the catalytic rate r under closed circuit conditions to the one, r_0 , under open circuit conditions. Catalytic systems exhibiting the NEMCA effect are characterised by values of $|\Lambda| \gg 1$.

There are some main features of the NEMCA effect which have been observed in all the catalytic systems studied so far (1, 3–8):

[1] Catalytic rates depend exponentially on V_{WR} , over wide ranges of conditions:

$$\ln (r/r_0) = \alpha F(V_{WR} - V_{WR}^*)/RT \quad (ii)$$

where α and V_{WR}^* are catalyst and reaction-specific constants, and F is Faraday's constant. Equation (ii) can also be written as:

$$\ln (r/r_0) = \alpha e(\Phi - \Phi^*)/k_b T \quad (iii)$$

where $e\Phi$ is the average catalyst work function and Φ^* is, again, a catalyst and reaction specific constant. Equation (ii) is based on the equality relation between overpotential η and induced work function change, as shown both theoretically (5-7) and experimentally (1).

[2] The order of magnitude of the enhancement factor Λ can be estimated from:

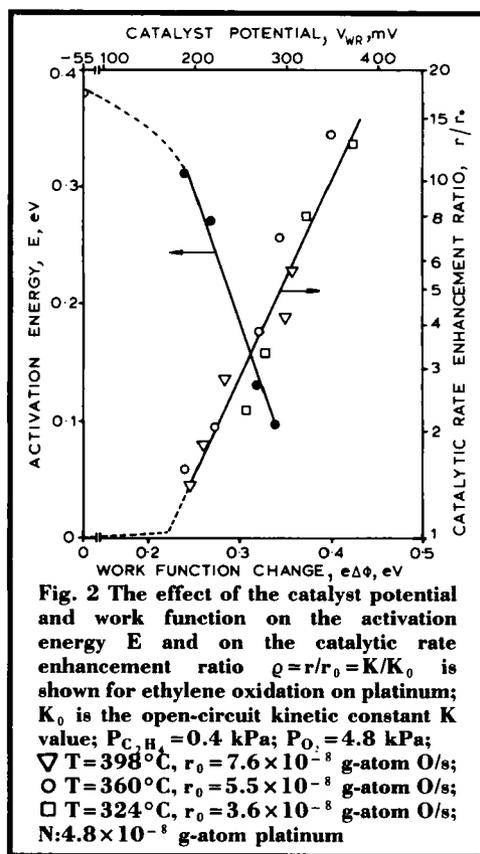
$$\Lambda = 2Fr_0/I_0 \quad (iv)$$

where I_0 is the exchange current of the catalyst-solid electrolyte interface (3-7).

[3] The catalytic rate relaxation time constant τ during galvanostatic transients (3-7) is proportional to N/I , where N is the catalyst true surface area expressed in g-atoms, and I is the applied current. Actually τ has been found to be comparable to the time required for a certain ion coverage to be established on the catalyst surface, corresponding to the induced average work function change of the catalyst. This implies that the NEMCA effect is not an electrocatalytic effect localised at the three phase boundaries between the catalyst electrolyte gas phase, but a catalytic effect taking place over the entire catalyst surface.

NEMCA Effect on Platinum Metals

Although the NEMCA effect is not limited to a particular metal catalyst or solid electrolyte (1), in most of the reactions examined so far platinum metals, and especially platinum, have been used as catalysts (1, 3-6). This choice has been dictated both by the importance of platinum metals as oxidation catalysts, and also by their particular suitability for NEMCA studies, as they exhibit in general high turnover frequencies and low values of I_0 , compared to



other metals, such as silver (Equation (iv)). Some examples are reviewed here and some new results are also presented.

Ethylene Oxidation on Pt/ZrO₂ (8 per cent Y₂O₃)

The kinetics of this reaction have been described in detail recently (6). Under fuel-lean conditions, $P_{O_2} \gg P_{C_2H_4}$, where the catalytic rate is first order in ethylene pressure $P_{C_2H_4}$, and zeroth order in oxygen pressure P_{O_2} , that is $r = KP_{C_2H_4}$, rate enhancement ratios ρ up to 55 and enhancement factor values up to 3×10^5 were measured (6). Both the open-circuit and the NEMCA induced kinetic behaviours were modelled quantitatively (6). It was found that the kinetic constant K of the reaction between adsorbed oxygen and gas phase ethylene depends exponentially on V_{WR} and work function $e\Phi$, see Figure 2, with

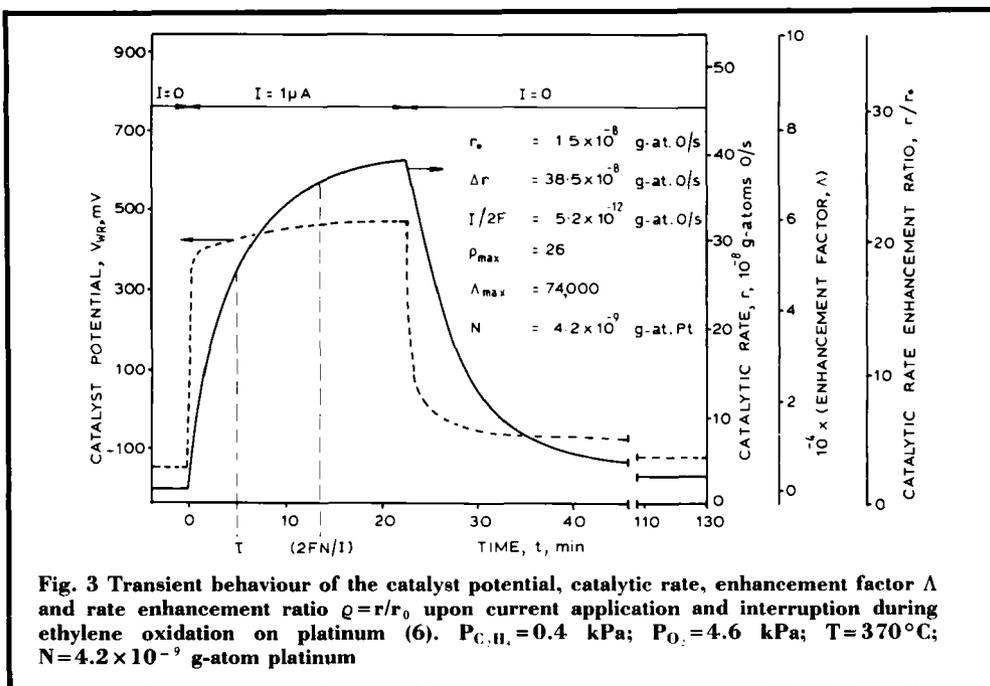


Fig. 3 Transient behaviour of the catalyst potential, catalytic rate, enhancement factor Λ and rate enhancement ratio $q=r/r_0$ upon current application and interruption during ethylene oxidation on platinum (6). $P_{C,H_2}=0.4$ kPa; $P_{O_2}=4.6$ kPa; $T=370^\circ\text{C}$; $N=4.2 \times 10^9$ g-atom platinum

values of $\alpha = 0.5-1.0$ (Equations (ii) and (iii)). The activation energy was found to decrease linearly with $e\Phi$. This decrease counterbalances the compensating decrease in the pre-exponential factor K^0 , $K = K^0 \exp(-E/RT)$ (6), yielding to the experimentally observed exponential increase of K with V_{WR} and $e\Phi$, also shown in Figure 2. Figure 3 shows a typical transient response of the catalytic rate and catalyst potential upon imposition of a constant current (galvanostatic transient). It can be seen that the effect is reversible and that the steady-state rate increase Δr is a factor of 26 higher than r_0 , and a factor of 74,000 higher than the rate $I/2F$ of O^{2-} supply. Also the relaxation time constant τ is of the order of $2FN/I$, where N is the total catalyst film surface area.

Ethylene Oxidation on Pt/ β'' - Al_2O_3

This behaviour is qualitatively similar to that observed when using stabilised-zirconia as the solid electrolyte. As shown in Figure 4, the catalytic rate constant K decreases exponentially up to a certain point with decreasing work

function $e\Phi$ caused by Na^+ supply to the catalyst. The maximum rate constant decrease is over 90 per cent and corresponds to a sodium coverage of only 0.015 (9).

Measured Λ values were of the order of 10^3 to 5×10^4 . The open circuit kinetic model developed in (6) was found to describe adequately the NEMCA catalytic behaviour (indicated by the dotted line on Figure 4) with the kinetic constant K (see above) depending exponentially on $e\Phi$ with slope $0.28/k_b T$. The observed catalytic rate relaxation time constants τ during galvanostatic transients were approximated well by:

$$\tau \sim NF\theta_{Na}/I \quad (v)$$

which is very similar to $\tau \approx 2FN/I$, used for τ estimation for O^{2-} conducting solid electrolytes.

Methanol Oxidation on Pt/ ZrO_2 (8 per cent Y_2O_3)

This system is quite interesting as it exhibits both positive ($I > 0, \Lambda > 0$) and negative ($I < 0, \Lambda < 0$) NEMCA behaviour at temperatures of

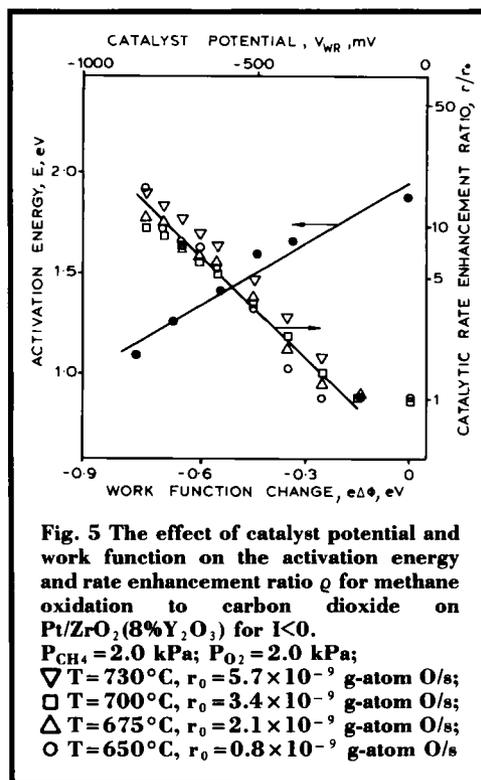
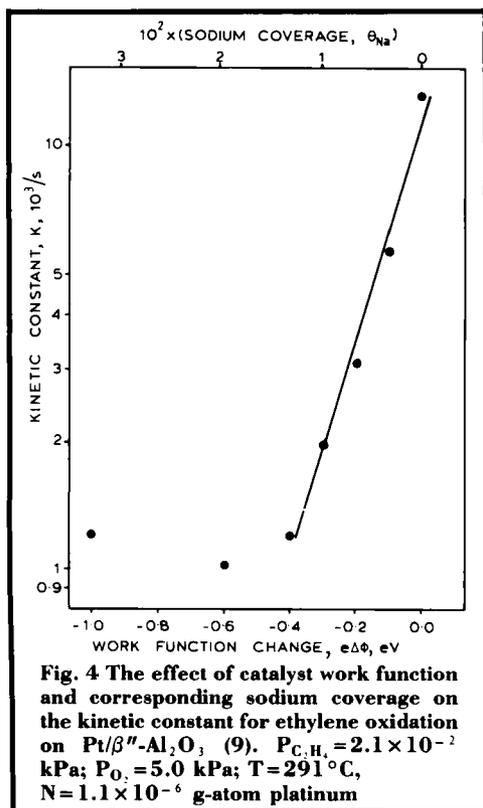
350 to 650°C (10). As in other NEMCA studies the kinetic constants K_i for the formation of the main products, which are formaldehyde and carbon dioxide, depend exponentially on catalyst work function:

$$\ln(K_i/K_{i,0}) = \alpha_i e(\Phi - \Phi^*)/k_b T \quad (\text{vi})$$

with $K_i/K_{i,0}$ ratios up to 10 for negative currents (removal of O^{2-} from the catalyst) and up to 3 for positive currents. Measured Λ values were of the order of 10^3 to 10^4 (10). Selectivity to formaldehyde can be varied deliberately between 35 and 60 per cent by controlling the catalyst potential. Unfortunately selectivity goes through a maximum near the open circuit potential (10).

Methane Oxidation on Pt/ZrO₂ (8 per cent Y₂O₃)

This reaction also exhibits both positive and negative NEMCA behaviour, at temperatures



650 to 750°C and for a 1:1 ratio of oxygen to methane. Equation (iii) is again valid with α values +0.8 and -0.3 for increasing and decreasing work function, respectively. This is shown, for the latter case ($I < 0$), in Figure 5. Again the activation energy changes linearly with work function. The slope is 1.05 ± 0.1 . Enhancement ratios ρ up to 70 and Λ values up to 5 have been measured.

Carbon Monoxide Oxidation on Platinum and Palladium

These are well known oscillatory reactions and both were found to exhibit the NEMCA effect. In the case of the palladium catalysed carbon monoxide oxidation Λ values of the order of 10^3 were measured at $T = 290^\circ\text{C}$, $P_{CO} = 3 \times 10^{-4}$ bar and $P_{O_2} = 0.15$ bar. For the oxidation of carbon monoxide on platinum both negative and positive NEMCA behaviour has been observed, with rate enhancement ratios up to 6 and $|\Lambda|$ values up to 500 (4). As shown in

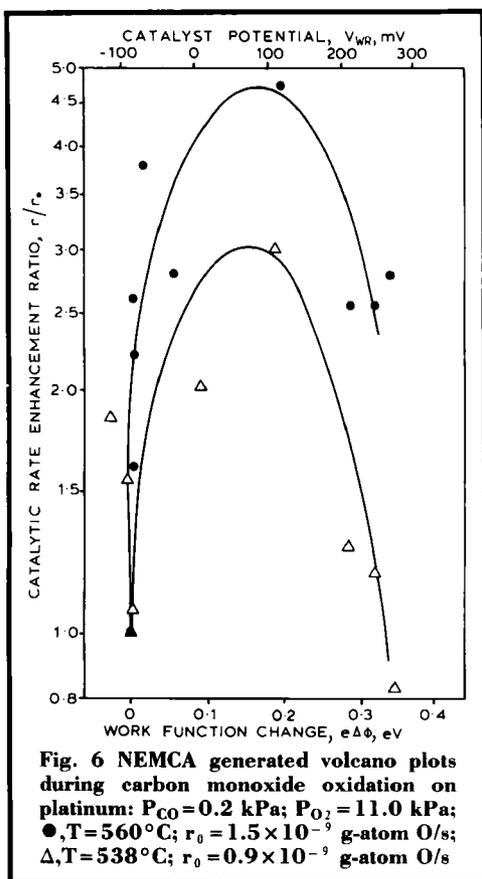


Figure 6 one can use NEMCA to create "volcano" type plots. These are, apparently, the first volcano plots generated for a single metal by changing its work function. Oscillatory states can also be induced, stopped or modified by controlling the catalyst potential (3, 5).

The Origin of NEMCA

The experimental features of all previous NEMCA studies can be adequately explained by a semiquantitative model, which is based on a uniform change of the catalyst work function induced by an electrochemically controlled spillover of ions onto the catalyst surface, and on the concomitant controlled change in the strength of chemisorptive bonds (1, 3, 6, 7, 11). The induced work function changes require only a small coverage of ions (typically <5 per cent

of a monolayer, as calculated using the Helmholtz equation (1, 9)) which does not significantly affect the coverages of covalently bonded species. The creation of such spillover ions depends solely on the presence of significant catalyst-electrolyte overpotential, so that the NEMCA effect seems to be of general interest and not restricted to any particular catalytic system. The surprisingly simple relationship (Equation (iii)) between catalytic activity and catalyst work function, measured in situ and for the first time varied at constant reactant composition, quantifies the importance of the electronic factor in heterogeneous catalysis, offering some new insights into the action of promoters.

As a result of NEMCA studies it was found that the e.m.f. of solid electrolyte cells with electrodes made of the same material provides a direct measure of the work function difference between the catalyst (working electrode) and the gas-exposed surfaces of the reference electrode (1). This observation is of particular importance for a deeper understanding of solid electrolyte potentiometric measurements, which have been used in recent years in catalyst research (8, 12).

The catalytic reactions for which the NEMCA effect has been studied so far are given in the Table. They fall into two groups: those exhibiting "positive" NEMCA behaviour, that is $\Delta > 0$, or equivalently, rate acceleration with increasing catalyst work function, and those exhibiting "negative" NEMCA behaviour, that is $\Delta < 0$ or equivalently, rate acceleration with decreasing catalyst work function. The terms "electrophobic" and "electrophilic" have been proposed, respectively, for these two groups of reactions (1, 7).

The rate limiting step in electrophobic reactions, such as ethylene oxidation on platinum, involves cleavage of a metal/electron-acceptor adsorbate bond (6). In this case it is expected, provided that the nature of the activating complex is unchanging, that the rate of the reaction will increase exponentially with decreasing heat of adsorption of the adsorbate, for example atomic oxygen, ($-\Delta H_{ad}$) and consequently with

$e\Delta\Phi$, if one takes into account the semi-theoretical linear relation between $\Delta(-\Delta H_{ad})$ and $e\Delta\Phi$, proposed by Boudart (11). This explains both Equation (iii) and the observed quasilinear decrease in activation energy with eV_{WR} and $e\Phi$ with slope of the order of -1 .

If, on the other hand, the rate limiting step of a catalytic reaction involves cleavage of an intra-adsorbate bond in an electron-acceptor adsorbate, then it is expected from classical bond order conservation considerations that the strengthening of the metal-adsorbate bond with decreasing work function will cause a weakening of the intra-adsorbate bonds, thus producing an exponential catalytic rate increase (7). This is the case with methanol oxidation on platinum, where lowering the catalyst work function facilitates the abstraction of hydrogen from adsorbed methanol intermediates. In this way the rates of formation of formaldehyde and chemisorbed carbon monoxide are accelerated, and the latter can be rapidly oxidised by chemisorbed oxygen, as experimentally observed (7, 10).

The almost linear correlation of work function change with activation energy, found in NEMCA studies, seems to imply that NEMCA is actually a "long-range" electronic effect mediated through the electronic band structure of the catalyst. Long-range effects have been predicted theoretically for some adsorbates on metal surfaces (13) and have been invoked to explain the dependence of the sticking coefficient of oxygen on alkali-doped germanium; this was found to depend exponentially on the alkali induced $e\Phi$ change, regardless of alkali type (14).

Nevertheless short-range effects involving sites adjacent to the spillover ions cannot be entirely ruled out as one could also observe, macroscopically in this case, a "long-range" effect if the spillover ion is fairly mobile on the catalyst surface. There is also convincing experimental and theoretical evidence for short-range effects in explaining the promoting and poisoning action of co-adsorbed electronegative and electropositive species (for example 2, 15). It is very likely that there is no universal answer

and that the long- or short-range electronic nature of NEMCA is catalyst- and spillover-ion-specific. The use of TPD and of in situ surface science techniques, such as XPS, UPS and STM (16) under conditions of NEMCA behaviour will definitely help the exact characterisation of the electrochemically created spillover species and the elucidation of the nature of their interaction with the catalyst surface.

Practical Applications of NEMCA

Apart from the interesting theoretical consideration briefly outlined above, it is clear that the NEMCA effect can be utilised in at least two different and practically meaningful ways:

First, as a means of selecting promoters for conventional supported catalysts. NEMCA can be used to determine if a given reaction exhibits electrophobic ($\Delta > 0$, $\alpha > 0$), or electrophilic ($\Delta < 0$, $\alpha < 0$) behaviour. In the former case, promoters based on fluorine, chlorine, bromine and other elements causing an increase in catalyst work function are expected to have a beneficial effect on catalyst performance. In the latter case alkali based promoters are the best choice for catalyst performance enhancement.

Second, for use in solid oxide fuel cell (SOFC) type reactors (12) to carry out reactions where NEMCA can give high selectivity to the desired valuable products. In this application, the reacting mixture should be fed to one side of the solid electrolyte, which is covered by the porous catalyst, while the other side, covered by a suitable electrocatalyst (12), is exposed to a suitable gaseous or liquid (9) environment, for the oxidation or reduction of the ions, which are pumped through the solid electrolyte to or from the catalyst. A suitable voltage is constantly applied between the catalyst and the electrocatalyst. Since current densities of a few $\mu\text{A}/\text{cm}^2$ suffice to induce significant overpotential and catalyst work function changes, provided the catalyst-solid electrolyte interface is polarisable (1, 3-10), the SOFC reactor can operate at low operating temperatures (200-650°C), which cover the vast majority of industrial chemical reactions.

In the latter application platinum group metals, of use in many catalytic reactions of technological interest, could naturally play a leading role.

There are sound theoretical reasons to expect that the NEMCA effect is more pronounced (higher α values) on metals with high local density of states (LDOS) near the Fermi level, as is the case for most of the platinum group metals.

However there is already some experimental evidence supporting this idea. The LDOS at the Fermi level is 2.2 and 2.3 states/eV atom, for platinum and palladium, respectively, while it is only 0.27 states/eV atom for silver. In comparison the absolute value of α is 0.3–1.0 for

platinum-catalysed reactions and 0.1–0.2 for reactions which are catalysed by silver.

Conclusions

Solid electrolytes can be used as ion donors or acceptors to control the work function of metal catalysts and to induce dramatic and reversible changes in catalytic activity and selectivity. The effect is very pronounced for platinum, but is not restricted to a particular metal or solid electrolyte. The use of NEMCA, that is of in situ electrochemical promotion of catalyst surfaces, allows for new areas of surface catalytic chemistry to be explored, and could lead to technological applications by influencing catalyst performance in desirable directions.

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Palladium Doped Semiconductor Alcohol Sensor

The detection and accurate measurement of the alcohol concentration in breath has been traditionally performed by a fuel cell, with the expired air being oxidised catalytically on a platinum electrode, and the small current generated being amplified (1).

Now Japanese researchers have produced a semiconductor detector which is capable of being used as a breathalyser, and which will selectively ignore other gases (2).

The basis of the detector is a porous alumina substrate, onto which a thick film (about 50 μm) of lanthanum oxide containing indium oxide and palladium was screen printed. Gold electrodes were attached and the whole was then calcined. Indium oxide was chosen as the semiconductor as previous attempts with tin(IV) oxide resulted in an unacceptably high increase in electrical resistance.

The addition of lanthanum oxide improved the sensitivity to ethanol vapour almost 7 fold, even though the electrical resistance and the response time also increased. The further addition of palladium was especially effective, dramatically increasing the sensitivity and shortening the 90% response time to about 35 seconds for 1000 ppm ethanol in air at 300°C.

The device has an "S" shaped response to alcohol gas concentrations between 0 and 1000 ppm at 300°C, being approximately linear from 0 to 100 ppm, and its selectivity to gases at 300°C, other than ethanol, is only modest.

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