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Non-Faradaic Electrochemical Modification of Catalytic Activity

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It was found that catalytic activity and selectivity of metal catalysts can be altered dramatically and in a reversible manner. This is accomplished by electrochemically supplying oxygen anions onto catalytic surfaces via polarized solid electrolyte cells. Oxygen anions, forced electrochemically to adsorb on the catalyst surface, alter the catalyst work function in a predictable way and lead to reaction rate increases of the order of 1500%. Changes in catalytic reaction rates typically exceed the rate of O^{2-} transport to or from the catalyst surface by 10^2–10^4. The case of several catalytic reactions in which this new phenomenon has been observed is discussed.

Modification of the electronic and concomitant catalytic properties of metal and metal oxide catalysts has been a long-sought goal since the early 1950s when the importance of the electronic factor in heterogeneous catalysis was widely realized.[1] The catalytic properties of solid catalysts can be modified by doping of the active phase or of the catalyst support. It is usually accepted that such catalytic property modifications result from changes in the electronic state of the catalyst surface and consequent changes in the binding energies of chemisorbed species.[2,3] Geometric interpretations have also been proposed.[2]

We have now found a means of altering the catalytic activity and selectivity of metal surfaces in a dramatic, reversible, and apparently predictable manner. This is accomplished by electrochemically supplying or removing oxygen anions, O^{2-}, to or from catalyst surfaces in solid electrolyte cells of the type

$$\text{gaseous reactants, metal catalyst}/ZrO_2(8\text{ mol \% }Y_2O_3)/M, O_2 \quad (1)$$

where the metal M catalyzes the reaction

$$O_2 + 4e^- \rightleftharpoons 2O^{2-} \quad (2)$$

and serves as a means of supplying O^{2-} to the catalyst through the yttria-stabilized zirconia electrolyte under the influence of an external voltage (Figure 1).

Cells of this type are known from sensor applications[4] and have been already used for the cogeneration of chemicals, such as NO, and power[5,6] and also to influence the rate of catalytic reactions such as NO decomposition,[7,8] CO hydrogenation,[9,10] and ethylbenzene conversion to styrene.[11] In these cases the observed changes in catalytic rate, Δr, were approximately equal to the rate of supply or removal of O^{2-}, i.e., $i/2F$, where i is the applied current and F is Faraday's constant. Consequently, in these cases, the enhancement factor Λ, defined by

$$\Lambda = \Delta r(\text{catalytic})/(i/2F) \quad (3)$$

is unity and the behavior is purely Faradaic.

The first report of a "non-Faradaic" electrochemical effect on catalytic activity was for the case of ethylene and propylene epoxidation on Ag catalysts where Λ values of the order of 300 were measured.[12,13]

We now report results which show conclusively that the non-Faradaic electrochemical modification of catalytic activity (NEMCA effect) is not a peculiarity of the ethylene and propylene epoxidation systems but a general effect in heterogeneous catalysis. We also report, for the first time, enhancement factors as high as 15 000, obtained during ethylene and methanol oxidation on Pt. A semiquantitative explanation of this new phenomenon is also proposed.

The continuous flow, atmospheric pressure experimental apparatus has been described in previous communications,[11-15] where catalyst preparation and surface characterization details are also presented. On-line gas chromatography, mass spectrometry, and IR spectroscopy were used for reactant and product analysis. The active solid electrolyte surface area was 2 cm^2. The thickness of the porous metal catalyst electrodes was 5–10 μm and their surface area, measured by surface titration techniques,[12-15] was typically 500–2000 cm^2. The three-electrode system, which is shown in Figure 1, used in conjunction with the current interruption technique, permitted accurate measurement of the catalyst–electrode overpotential, η, and of the catalyst–solid electrolyte exchange current density, i_o. An AMEL 553 galvanostat was used to apply constant currents between the catalyst and the counter electrode.

Table I shows the catalytic reactions for which the NEMCA effect has been observed. Dramatic alterations in catalytic activity and selectivity are obtained upon polarization of the catalyst–solid electrolyte interface. No reaction has been found yet for which the NEMCA effect is not operative in the presence of significant (i.e., a few hundred millivolts) activation overpotential.

The most spectacular effect has been observed for the case of ethylene oxidation on Pt, where, as shown in Figures 2 and 3, 10-fold increases in catalytic reaction rate have been observed, with Λ values as high as 15 000. This implies that for each O^{2-} supplied to the catalyst surface under steady-state conditions, 15 000 chemisorbed oxygen atoms react and 5000 CO_2 molecules are formed. This dramatic increase in reaction rate r was found to be caused primarily by a decrease in the activation energy E of the catalytic reaction, which is first order of ethylene and zero order in oxygen under the conditions shown in Figure 2, i.e., $r = KP_{ET}$.

Figure 3 shows that the kinetic constant K depends exponentially on the catalyst activation overpotential η above a threshold value η^*, i.e.

$$\ln (K/K_o) = \alpha e(\eta - \eta^*)/k_bT \quad (4)$$

where K_o is the kinetic constant value for $\eta = 0$, k_b is Boltzmann's constant, $\eta^* = 80$ mV, and $\alpha = 0.6 \pm 0.05$. The product $e\eta$ can be shown to be practically equal to the change in the catalyst work function $e\Delta\phi$.[16,17] This change is caused by the accumulation of negatively charged oxygen anions on the catalyst surface which

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(1) Boudart, M. *J. Am. Chem. Soc.* **1952**, *74*, 3556.

(2) Imelik, B., et al. *Stud. Surf. Sci. Catal.* **1982**, *11*.

(3) Akubuiro, E. C.; Verykios, X. E. *J. Catal.* **1987**, *103*, 320.

(4) Worrell, W. L. In *Electrochemistry and Solid State Science Education*; Smyrl, W. R., McLarnon, F., Eds.; The Electrochemical Society: Pennington, NJ, 1986.

(5) Vayenas, C. G.; Farr, R. D. *Science (Washington, D.C.)* **1980**, *208*, 593.

(6) Farr, R. D.; Vayenas, C. G. *J. Electrochem. Soc.* **1980**, *127*, 1478.

(7) Pancharatnam, S.; Huggins, R. A.; Mason, D. M. *J. Electrochem. Soc.* **1975**, *122*, 869.

(8) Gür, T. M.; Huggins, R. A. *J. Electrochem. Soc.* **1979**, *126*, 1067.

(9) Gür, T. M.; Huggins, R. A. *Science (Washington, D.C.)* **1983**, *219*, 967.

(10) Gür, T. M.; Huggins, R. A. *J. Catal.* **1986**, *102*, 443.

(11) Michaels, J. N.; Vayenas, C. G. *J. Catal.* **1984**, *85*, 477.

(12) Stoukides, M.; Vayenas, C. G. *J. Catal.* **1981**, *70*, 137.

(13) Stoukides, M.; Vayenas, C. G. *J. Electrochem. Soc.* **1984**, *131*, 839.

(14) Vayenas, C. G.; Lee, B.; Michaels, J. N. *J. Catal.* **1980**, *66*, 36.

(15) Yentekakis, I. V.; Vayenas, C. G. *J. Catal.* **1988**, *111*, 170.

(16) Bebelis, S.; Vayenas, C. G., submitted for publication in *J. Catal.*

(17) Neophytides, S.; Vayenas, C. G. submitted for publication in *J. Catal.*

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TABLE I: List of Catalytic Reactions Found To Exhibit the NEMCA Effect

reactants	products	catalyst	T, °C	Λ values	ref
$CH_2{=}CH_2$, O_2	ethylene oxide, CO_2	Ag	320–420	<300	12[a]
propylene, O_2	propylene oxide, CO_2	Ag	320–420	<300	13[a]
CO, O_2	CO_2	Pt	300–550	<500	15
$CH_2{=}CH_2$, O_2	CO_2, H_2O	Pt	260–420	<15 000	this work
CH_3OH	H_2CO, CO, H_2	Ag	550–700	−10	this work[a]
CH_3OH, O_2	CO_2, H_2CO	Pt	400–500	<12 000	this work[a]

[a] Change in product selectivity observed.

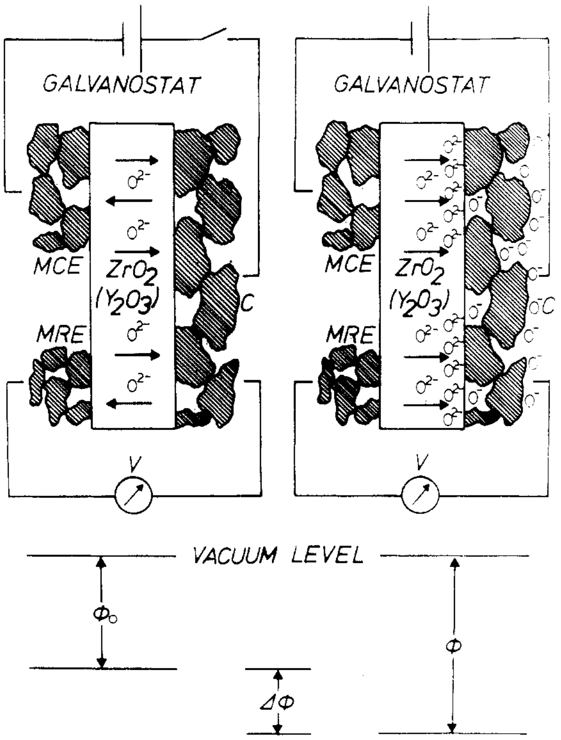

Figure 1. Principle of non-Faradaic electrochemical modification of catalytic activity (NEMCA): oxygen anions (O^{2-}) pumped electrochemically from the counter electrode (MCE) to the polarizable solid electrolyte–catalyst (C) interface accumulate near the solid electrolyte–catalyst–gas-phase three-phase boundaries and are only partly oxidized to O^- which diffuses over the entire catalyst surface causing an increase in the catalyst work function $e\Delta\phi$. It is $\Delta\phi \approx \eta$, where η is the overpotential measured between the catalyst and the reference electrode (MRE).

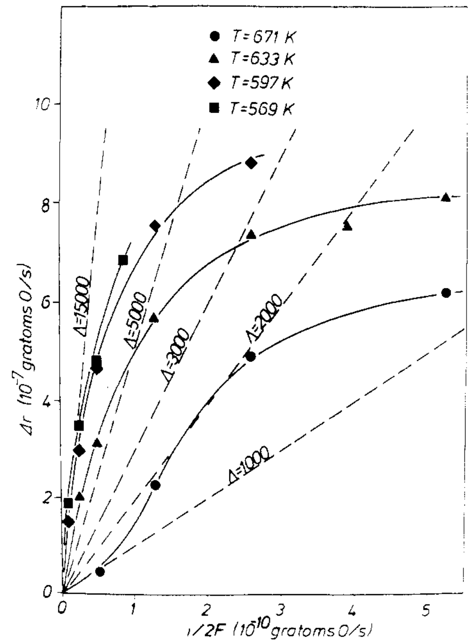

Figure 2. Effect of applied current on the rate of ethylene oxidation to CO_2, on Pt. Dashed lines are constant enhancement factor lines; $P_{ET} = 4.6 \times 10^{-3}$ bar, $p_{O_2} = 4.7 \times 10^{-2}$ bar, open-circuit rate $r_o = 5.04 \times 10^{-8}$ g-atom of O/s at 569 K.

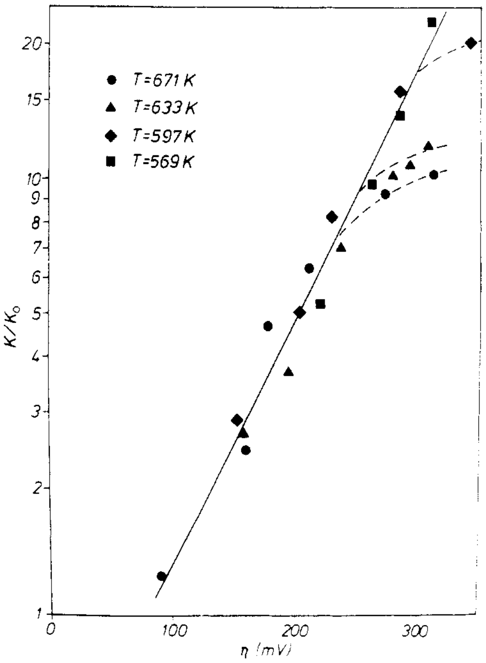

Figure 3. Effect of the change in catalyst work function $e\Delta\phi = e\eta$ on the kinetic constant of ethylene oxidation to CO_2 on Pt. Conditions as in Figure 2. Deviations from the straight line appear when the order of the reaction with respect to ethylene decreases from 1 to 0.

is known to induce an increase in the average work function of the catalyst crystallites.[18]

When the catalyst work function changes, the binding energies of chemisorbed species change and the activation energy of the catalytic reaction is also expected to change dramatically. Our results for the Pt-catalyzed ethylene oxidation show that indeed the product $\alpha e\eta$ is approximately equal to the decrease in activation energy, i.e.

$$\Delta E = -\alpha e\eta = -\alpha e\Delta\phi \qquad (5)$$

Figure 4 shows a case where a negative current, i.e., O^{2-} removal from a Ag catalyst, causes a non-Faradaic increase in the rates of methanol decomposition to formaldehyde and to CO and H_2. Selectivity to formaldehyde decreases with decreasing current and overpotential η.

A possible explanation of the NEMCA effect is the following: Oxygen anions (O^{2-}) pumped electrochemically to the polarizable solid electrolyte–catalyst interface accumulate near the solid electrolyte–catalyst–gas-phase three-phase boundaries and get oxidized by the reaction

$$O^{2-} \rightarrow O(ads) + 2e^- \qquad (6)$$

where O(ads) is chemisorbed oxygen, covalently bonded to the catalyst surface. When the exchange current density of reaction 6 is small (e.g., 10^{-7} A/cm^2 of electrolyte), the interface is polarizable and an activation overpotential develops at the catalyst

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(18) Gundry, P. M.; Tompkins, F. C. In *Experimental Methods in Catalytic Research*; Anderson, R. B., Ed.; Academic: New York, 1968; pp 100–168.

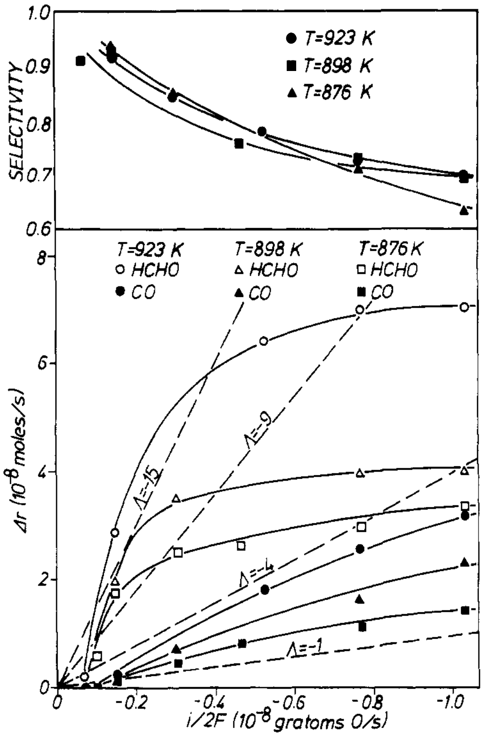

Figure 4. Effect of applied current on the rates of CH_3OH dehydrogenation to H_2CO and decomposition to CO and H_2 and on the selectivity to H_2CO. Ag catalyst, $p_{CH_3OH} = 5 \times 10^{-2}$ bar.

electrode. The product $e\eta$ is practically equal to the change in the work function of the catalyst electrode.[16,17] This change in the catalyst work function results in dramatic changes in catalyst activity and selectivity. When O^{2-} anions are pumped *onto* the catalyst surface, then the catalyst work function *increases* with a consequent decrease in the heats of chemisorption, $-\Delta H_i$, of covalently bonded chemisorbed species on the catalyst surface. According to theoretical considerations of Boudart[1,18] and Mignolet[18] $\Delta(-\Delta H_i) = -e\Delta\phi/2$ or $\Delta(-\Delta H_i) = -e\Delta\phi$, respectively. Our experimental results for the case of ethylene oxidation on Pt, where $\Delta E \approx -e\Delta\phi/1.6$, are in qualitative agreement with these theoretical predictions since the observed change in the reaction activation energy is related to the heat of chemisorption of oxygen on the catalyst surface.[14,16] When oxygen anions are removed *from* a catalyst surface, then the average catalyst work function *decreases* and chemisorptive bonds become stronger. This is expected to promote cleavage of existing bonds in adsorbed species and to enhance the rate of adsorbate decomposition, as experimentally observed in the case of CH_3OH decomposition on Ag (Figure 4).

From a molecular viewpoint, the appearance of an activation overpotential η at the catalyst-electrolyte interface implies that O^{2-} from the electrolyte are queuing to the three-phase boundaries and an excess of O^{2-} is accumulated near the metal surface. Under these conditions reaction 6 is to a large extent restricted to its first step, i.e.

$$O^{2-} \rightarrow O^{-}(ads) + e^{-} \qquad (7)$$

Singly charged oxygen anions O^- thus formed cannot dispose of their charge and are forced to remain adsorbed on the catalyst, gradually diffusing over the entire surface within a time frame of the order of $S/(i/2F)$, where S is the number of surface catalyst gram atoms. It is well established[18] that negatively charged ions, forced to adsorb on a surface, cause a negative surface potential, i.e., a decrease in the surface potential χ and a consequent increase in the work function, $e\phi$ (Figure 1). This consideration explains why the experimentally observed galvanostatic transient relaxation time constants for the change in catalytic rate, Δr, are of the order of $S/(i/2F)$. The proposed explanation of the NEMCA effect is strongly supported by recent investigation of Ag electrodes in zirconia cells using in situ XPS which showed the appearance of O 1s signal corresponding to ionically bonded oxygen during electrochemical oxygen pumping.[19]

On the basis of the above physical considerations a simple mathematical model has been developed to relate catalytic reaction rate and catalyst overpotential η or change in work function $e\Delta\phi$.[16]

For the first-order Eley-Rideal-type reactions the model predicts

$$\ln (r/r_0) = \alpha F(\eta - \eta^*)/RT \qquad (8)$$

where η^* is a constant. This is in excellent agreement with experimental results as shown in Figure 3. Combining eq 8 with the high-field approximation of the classical Butler-Volmer equation, which relates η with i and i_0, one can obtain an approximate expression for Λ:[16,17]

$$\Lambda \approx 2Fr_0/Ai_0 \qquad (9)$$

where A is the active solid electrolyte surface area. Equation 9 is also in good qualitative agreement with experimental observation[16,17] and underlines that, in order to obtain the NEMCA effect, i.e., high Λ values, one must use highly polarizable (i.e., low i_0) metal-solid electrolyte interfaces. This can explain why in some recent studies[11,20,21] O^{2-} pumping to metal catalysts was found to have only a Faradaic effect on catalytic rates ($\Lambda \leq 1$). According to eq 9 this will indeed be the case if the intrinsic catalytic rate r_0 is not sufficiently high and the exchange current density i_0 is not sufficiently small.

The present results show that the work function of metal catalysts can be altered deliberately by using solid electrolyte cells. Changes in work function result in dramatic changes in catalytic activity and selectivity. This observation underlines the importance of the electronic factor in heterogeneous catalysis. From a practical viewpoint the work function of metal catalysts can now be considered a new controllable parameter which can be varied at will to influence catalytic performance in desirable directions. Although only the reactions shown in Table I have been investigated so far, it is almost certain that new technological applications will emerge as more reactions are explored.

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(19) Arakawa, T.; Saito, A.; Shiokawa, J. *Appl. Surf. Sci.* **1983**, *16*, 365.
(20) Seimanides, S.; Stoukides, M. *J. Electrochem. Soc.* **1986**, *133*, 1535.
(21) Otsuka, K.; Yokoyama, S.; Morikawa, A. *Chem. Lett., Chem. Soc. Jpn.* **1985**, 319.