

Rules and Mathematical Modeling of Electrochemical and Classical Promotion

2. Modeling

S. Brosda and C. G. Vayenas¹

Department of Chemical Engineering, Caratheodory 1 St, University of Patras, Patras, GR-26500, Greece

Received July 16, 2001; revised January 30, 2002; accepted January 30, 2002

A physical and corresponding mathematical model is developed to describe the kinetics of electrochemically or chemically (classically) promoted catalytic reactions. The model, which can be viewed as an extension of Langmuir–Hinshelwood–Hougen–Watson kinetics is based on electrochemical Langmuir-type adsorption isotherms which can account explicitly for the attractive or repulsive electrostatic interactions between the adsorbates and the “effective double layer” present at the catalyst–gas interface. The model, which contains only measurable parameters and leads to mathematically tractable rate expressions, predicts directly the recently established promotional rules of catalysis and is in good semiquantitative agreement with experiment regarding the dependence of catalytic rates on the partial pressures of the reactants and on catalyst work function. © 2002 Elsevier Science (USA)

1. INTRODUCTION

Promotion plays a key role in heterogeneous catalysis. It is necessary for the design of successful industrial catalysts (2–4) but can also serve for a better understanding of catalysis itself (5, 6). It has been shown recently that classical (chemical) promotion is closely related not only to the effect of electrochemical promotion (7–11) but also to the phenomenon of metal–support interactions on oxide supports (12–14).

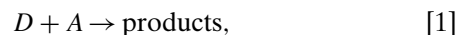
In a companion paper (1) we have described the rules of electrochemical and chemical promotion which enable one to predict the dependence of catalytic rates, r , on electropositive or electronegative promoter coverage (or, equivalently on catalyst surface work function, Φ) on the basis of the unpromoted kinetics, i.e., on the basis of the rate dependence on the reactant partial pressures p_D and p_A (of the electron donor D , and the electron acceptor reactant A) in the absence of promoters. These rigorous rules, derived on the basis of 50 electrochemical and chemical

promotion studies, are listed in Tables 1–8. As discussed in (1) there appear to be no exceptions to these rules in the electrochemical and chemical promotion literature.

In this communication we show how all these rules can be described mathematically by a simple kinetic model based on fundamental thermodynamic and catalytic principles.

Such a model should be as simple as possible, without however missing any of the underlying thermodynamic and physicochemical factors which cause electrochemical and chemical promotion. In particular it is shown that the use of electrochemical Langmuir-type adsorption isotherms, derived by accounting explicitly for the electrostatic interaction between adsorbate dipoles and the effective double layer field created by the promoters, suffices to describe *all* the experimentally observed rules G1–G7 (Tables 2–6) as well as practically all other observations regarding electrochemical promotion, including the effect of work function on heats of adsorption (1, 9, 14) as well as on kinetics and reaction orders (9, 14).

Thus, for an arbitrary catalytic reaction,



where D is an electron donor (e.g., C_2H_4 or H_2) and A is an electron acceptor (e.g., O_2), we develop a general rate expression,

$$r = r(k_R, k_D, k_A, p_D, p_A, \Phi, T), \quad [2]$$

where k_R is the surface reaction rate constant between chemisorbed D and A and k_D and k_A are the adsorption equilibrium constants of D and A , respectively, which is able to describe the following:

(a) The dependence of r on Φ (thus also on catalyst potential U_{WR} (1, 7, 9)) for fixed p_D and p_A (purely electrophobic, purely electrophilic, volcano, inverted volcano).

(b) The dependence of r on p_D (or p_A) at fixed p_D (or p_A) and Φ (positive- and negative-order kinetics and transition between positive- and negative-order kinetics).

¹ To whom correspondence should be addressed. E-mail: cat@zeus.chemeng.upatras.gr.

TABLE 1
Local Rules

Type of reaction	$D + A \rightarrow$ products			
Donicity of reactants	D : Electron donor, $\partial\Phi/\partial\theta_D < 0$		A : Electron acceptor, $\partial\Phi/\partial\theta_A > 0$	
Kinetics	Rate-positive order in D , $\partial r/\partial p_D > 0$	Rate-negative order in A , $\partial r/\partial p_A < 0$	Rate-negative order in D , $\partial r/\partial p_D < 0$	Rate-positive order in A , $\partial r/\partial p_A > 0$
Predicted NEMCA behavior	Rule L1: Electrophobic behavior, $\partial r/\partial\Phi > 0$, $\Lambda > 1$		Rule L2: Electrophilic behavior, $\partial r/\partial\Phi < 0$, $\Lambda < -1$	

The problem posed by Eq. [2], without the additional complication of the Φ dependence, is a classical problem in heterogeneous catalysis. The usual approach is to use Langmuir isotherms to describe reactant (and sometimes product) adsorption. This leads to the well-known Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetics (2). The advantage of this approach is mathematical simplicity: the weakness is inherent in the assumptions and limitations of the Langmuir isotherm. Thus LHHW kinetics usually provide only a qualitative and, in several instances, semiquantitative description of actual experimental kinetics. More-realistic isotherms (Temkin, Freundlich, Guggenheim) lead to large numbers of adjustable parameters and mathematically intractable expressions.

Consequently the only realistic approach to the problem posed by Eq. [2] is a Langmuirian approach in which, however, one describes explicitly the dependence of k_R , k_D , and k_A on catalyst potential U_{WR} or, equivalently, work function Φ .

2. RESULTS AND DISCUSSION

2.1. Adsorption in the Presence of a Double Layer

We consider the adsorption of a single molecule, j , on a metal film M . The film is deposited on a solid electrolyte, e.g., YSZ, or is partly covered by a promoter, or simply has a significant coverage of adsorbed reactants and products on its surface, so that we may consider that an *effective double layer* is present at the metal–gas interface (Fig. 1). The existence of this overall neutral double layer at the catalyst–gas interface of metal catalysts in contact with solid elec-

trolytes is well documented via XPS, UPS, work function measurements, AC impedance spectroscopy, cyclic voltammetry, TPD, and PEEM, as described in Refs. (1, 14, 15) and in references therein.

The double layer is described by its effective thickness, d , and by its field strength \tilde{E} (Fig. 1). The adsorbed molecule has a dipole moment \tilde{P} . It is well documented (15, 16) that the local field strength \tilde{E} can affect strongly not only the chemisorptive bond strength but also the preferred orientation of the adsorbate (Fig. 2).

In the case of electrochemically promoted (NEMCA) catalysts we concentrate on the adsorption on the gas-exposed electrode surface and not at the three-phase boundaries (tpb). The “surface area,” N_{tpb} , of the three-phase boundaries is usually at least a factor of 100 smaller than the gas-exposed catalyst–electrode surface area, N_G . Adsorption at the tpb plays an important role in the electrocatalysis at the tpb, which can affect indirectly the NEMCA behavior of the electrode. But it contributes little directly to the measured catalytic rate and thus can be neglected. Its effect is built into U_{WR} and Φ .

We first assume Langmuir-type adsorption ($\tilde{E} = 0$ or $\tilde{P}_j = 0$), which implies negligible lateral interactions between adsorbed molecules and negligible inherent or induced heterogeneity of the catalyst–electrode surface:

$$k_j p_j = \theta_j / (1 - \theta_j). \quad [3]$$

Equation [3] is obtained assuming equilibrium between gaseous and adsorbed species S_j :



TABLE 2
Global Rules G1 and G2

Type of reaction	$D + A \rightarrow$ products			
Donicity of reactants	D : Electron donor, $\partial\Phi/\partial\theta_D < 0$		A : Electron acceptor, $\partial\Phi/\partial\theta_A > 0$	
Open-circuit kinetics and strength of adsorption	Rate-positive order in D , $\partial r/\partial p_D > 0$	Rate-zeroth or -negative order in A , $\partial r/\partial p_A \leq 0$	Rate-zeroth or -negative order in D , $\partial r/\partial p_D \leq 0$	Rate-positive order in A , $\partial r/\partial p_A > 0$
	D weakly adsorbed, A strongly adsorbed, $k_D p_D \ll k_A p_A$ & $1 \ll k_A p_A$		D strongly adsorbed, A weakly adsorbed, $k_D p_D \gg k_A p_A$ & $k_D p_D \gg 1$	
Predicted NEMCA behavior	Purely electrophobic behavior, $\partial r/\partial\Phi > 0$		Purely electrophilic behavior, $\partial r/\partial\Phi < 0$	

TABLE 3
Global Rule G3

Type of reaction	$D + A \rightarrow$ products			
Donicity of reactants	Electron donor, $\partial\Phi/\partial\theta_D < 0$		Electron acceptor, $\partial\Phi/\partial\theta_A > 0$	
Open-circuit kinetics and strength of adsorption	Strong adsorption, rate-positive order in D , $\partial r/\partial p_D > 0$	Strong adsorption, rate-negative order in A , $\partial r/\partial p_A < 0$	Strong adsorption, rate-negative order in D , $\partial r/\partial p_D < 0$	Strong adsorption, rate-positive order in A , $\partial r/\partial p_A > 0$
Predicted NEMCA behavior	$k_A p_A > k_D p_D > 1$		$k_D p_D > k_A p_A > 1$	
	D and A strongly adsorbed			
	Volcano-type behavior			

TABLE 4
Global Rule G4

Type of reaction	$D + A \rightarrow$ products	
Donicity of reactants	Electron donor, $\partial\Phi/\partial\theta_D < 0$	Electron acceptor, $\partial\Phi/\partial\theta_A > 0$
Open-circuit kinetics and strength of adsorption	Rate-positive order in D , $\partial r/\partial p_D > 0$, weak adsorption	Rate-positive order in A , $\partial r/\partial p_A > 0$, weak adsorption
Predicted NEMCA behavior	Inverted volcano-type behavior	

TABLE 5
Global Rule G6

Type of reaction	$D \rightarrow$ products, $A \rightarrow$ products	
Donicity of reactants	D : Electron donor, $\partial\Phi/\partial\theta_D < 0$	A : Electron acceptor, $\partial\Phi/\partial\theta_A > 0$
Open-circuit kinetics	Rate-positive order in D , $\partial r/\partial p_D > 0$	Rate-positive order in A , $\partial r/\partial p_A > 0$
Predicted NEMCA behavior	Purely electrophobic behavior	Purely electrophilic behavior

TABLE 6
Rules G5 and G7

- Rule G5: Rules G1–G4 are also valid when D and A are both electron acceptors or electron donors. In this case D is the stronger electron donor or weaker electron acceptor and A is the weaker electron donor or stronger electron acceptor.
- Rule G7: The maximum rate enhancement (r_{\max}/r_{\min}) for every fixed $\Delta\Phi$ increases with increasing difference in the electron acceptor–electron donor character of the two reactants.

TABLE 7
Fundamental Rules F1 and F2

$$\left(\frac{\partial\theta_D}{\partial\Phi}\right)_{p_A, p_D} \geq 0$$

$$\left(\frac{\partial\theta_A}{\partial\Phi}\right)_{p_A, p_D} \leq 0$$

Thus

$$\mu_j(g) = \mu_j(\text{ad}), \quad [5]$$

or equivalently

$$\mu_j^o(g) + RT \ln p_j = \mu_j^o(\text{ad}) + RT \ln(\theta_j/(1 - \theta_j)), \quad [6]$$

where the standard chemical potential, $\mu_j^o(\text{ad})$, of adsorbed j corresponds to a standard state of $\theta_j = 0.5$. The Langmuir isotherm [3] is directly obtained from Eq. [6] with

$$k_j = \exp((\mu_j^o(g) - \mu_j^o(\text{ad}))/RT). \quad [7]$$

The larger the value of k_j , the stronger the adsorption of j on the catalyst–electrode surface. More generally the Langmuir isotherm [3] can be written as

$$k_j a_j = \theta_j/(1 - \theta_j), \quad [8]$$

where a_j is the activity of j on the catalyst surface. The latter is defined using the gaseous j standard state:

$$\mu_j = \mu_j^o(g) + RT \ln a_j. \quad [9]$$

It should be noted that within the context of the Langmuir isotherm (energetically equivalent adsorption sites, no lateral interactions) Eq. [8], which relates *two surface properties*, i.e., a_j and θ_j , remains valid even when the surface activity of S_j , a_j , is different from the gaseous activity, p_j , i.e., when $\mu_j(g) \neq \mu_j(\text{ad})$.

We start by noting that the Langmuir isotherm approach does not take into account the electrostatic interaction between the dipole of the adsorbate and the field of the double layer. This interaction however is quite important, as

TABLE 8
Practical Rules

- P1: $\theta_A \rightarrow 1 \Rightarrow$ Electronegative promoter recommended
 P2: $\theta_D \rightarrow 1 \Rightarrow$ Electropositive promoter recommended
 P3: $\theta_A, \theta_D \ll 1 \Rightarrow$ Electropositive or electronegative promoter recommended

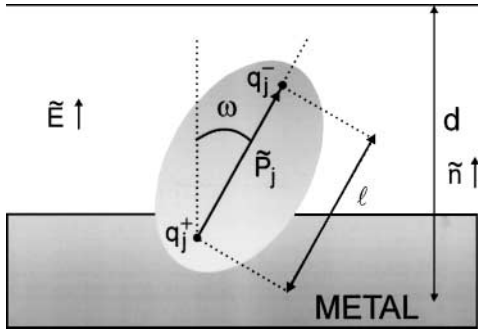
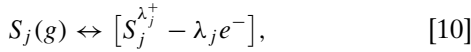


FIG. 1. Schematic of an adsorbate, modeled as a surface dipole, in the presence of the metal/gas effective double layer.

discussed in the companion paper (1). In order to account explicitly for this interaction one can write the adsorption equilibrium (Eq. [4]) in the form



where the partial charge transfer parameter λ_j is the net number of electrons donated by the adsorbate to the metal during chemisorptive bond formation (Fig. 1). The right hand side of Eq. [10] represents the overall neutral dipole adsorbate formed on the catalyst surface and accounts explicitly for the partial charge transfer between the adsorbate and the metal. The quantity λ_j is zero for a truly covalent chemisorptive bond, positive for an electron donor adsorbate, and negative for an electron acceptor adsorbate.

The partial electron transfer parameter λ_j is directly related to the dipole moment, P_j , of adsorbed j via

$$P_j = -q_j \ell / 2 = -\lambda_j e \ell / 2, \quad [11]$$

where ℓ is the distance between the centers of the positive and negative charges in the adsorbed dipole.

We then write the equilibrium condition for reaction [10].

$$\bar{\mu}_j(g) = \bar{\mu}_j(\text{ad}), \quad \text{i.e.,} \quad \mu_j(g) = \bar{\mu}_j(\text{ad}), \quad [12]$$

where now the use of the electrochemical potential $\bar{\mu}_j(\text{ad})$ of the adsorbed species is necessary since the adsorbate dipole interacts electrostatically with its surroundings.

In view of the assumed lack of individual lateral adsorbate-adsorbate interactions the only electrostatic en-

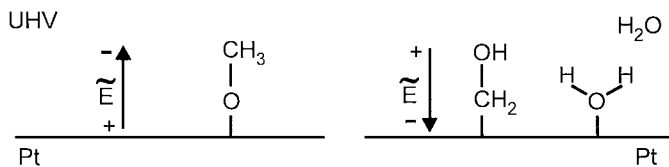


FIG. 2. Different adsorption intermediates formed upon adsorption of CH_3OH on Pt under ultrahigh vacuum (left) and in aqueous solutions (right) showing qualitatively the effect of local electrostatic field and surface work function on the mode of adsorption (16).

ergy to be accounted for in expressing the electrochemical potential, $\bar{\mu}_j$, of the adsorbate is the electrostatic energy of interaction of the adsorbate dipole with the effective double layer field. This is accounted for by

$$\bar{\mu}_j(\text{ad}) = \mu_j(\text{ad}) + \tilde{P}_j \cdot \tilde{E} N_{\text{AV}}, \quad [13]$$

where \tilde{P}_j , here taken as a vector, is the adsorbate dipole, \tilde{E} is the field strength, and N_{AV} is Avogadro's constant. Equation [13] shows that the electrochemical potential of an adsorbate is increased when its dipole moment is in the same orientation with the double layer field (dipole repulsion) and is decreased when it is in the opposite direction with the field (dipole attraction).

The double layer is assumed homogeneous with a thickness d and a uniform electric field \tilde{E} (Fig. 1). The electric field strength \tilde{E} , a vector, can be computed from

$$\tilde{E} = (\Delta\Phi / ed) \tilde{n}, \quad [14]$$

where \tilde{n} is the unit vector normal to the catalyst surface, e is the electric charge, and $\Delta\Phi (= \Phi - \Phi_0)$ is the work function difference between that of the actual surface and that of the surface at its potential of zero charge (14, 15, 17), where the field strength in the double layer vanishes and $\Phi = \Phi_0$. Upon combining Eqs. [11], [13], and [14] one obtains

$$\bar{\mu}_{j,\text{ad}} = \mu_{j(\text{ad})} - \lambda_j \frac{\ell}{2d} \cos \omega \Delta\Phi N_{\text{AV}}, \quad [15]$$

where ω is the angle formed between the adsorbate dipole and the field (Fig. 1).

Equation [15] expresses the fact that the electrochemical potential of an electron donor ($\lambda_j > 0$) is lowered with increasing work function Φ ($\Delta\Phi > 0$). This favors adsorption. Similarly for an electron acceptor adsorbate ($\lambda_j < 0$), increasing work function ($\Delta\Phi > 0$) increases the electrochemical potential of the adsorbate. This hinders adsorption.

Upon combining Eqs. [12] and [15] one obtains

$$\begin{aligned} \mu_j^{\circ}(g) + RT \ln p_j &= \mu_j^{\circ}(\text{ad}) + RT \ln(\theta_j / (1 - \theta_j)) \\ &\quad - \lambda_j \frac{\ell}{2d} \cos \omega \Delta\Phi N_{\text{AV}}. \end{aligned} \quad [16]$$

The above equation reduces to the one used to derive the Langmuir isotherm (Eq. [6]) when $\lambda_j = 0$ or $\Delta\Phi = 0$.

Upon rearranging one obtains

$$k_j p_j = (\theta_j / (1 - \theta_j)) \exp(-\lambda_j \Pi), \quad [17]$$

with

$$\Pi = \Delta\Phi \left(\frac{\ell}{2d} \cos \omega \right) / k_b T, \quad [18]$$

$$k_j = \exp((\mu_j^{\circ}(g) - \mu_j^{\circ}(\text{ad})) / RT). \quad [7]$$

The latter equation ([7]) shows that the adsorption equilibrium constant k_j retains the same meaning as in the absence of the double layer. The standard state of the adsorbed phase is always that corresponding to $\theta_j = 0.5$ and $\Delta\Phi = 0$. Equation [17] is formally identical to the electrochemical Langmuir isotherm (18). Its dimensionless potential term, Π , however has a somehow different surface science meaning, as it reflects the interaction between the adsorbate dipole moment and the effective double layer present on the catalyst surface instead of the coulombic interaction between the adsorbed ion and the electrode, which is the case in electrochemistry (18). We can thus term it an effective double layer (EDL) isotherm. Note that the EDL isotherm is mathematically very simple (like the electrochemical Langmuir isotherm) as long as Π and $\Delta\Phi$ (Eq. [18]) can be treated as independently controllable variables (e.g., by fixing $\Delta\Phi$ via a promoter or via potentiostatic imposition of ΔU_{WR} in NEMCA systems). When this is not the case and $\Delta\Phi$, thus Π , is determined by θ_j , one obtains more-complex, Frumkin-type, isotherms, as we see in Section 2.2.

Using Eq. [15] with $\cos\omega = 1$ and the definition of the isosteric enthalpy of adsorption $H_{ad} = T^2(\partial(\bar{\mu}_{j(ad)}/T)/\partial p_j)$, θ_j one can show easily that the isosteric heat of adsorption, $\Delta H_{ad,j}$, is given by

$$\Delta H_{ad,j} = \Delta H_{ad,j}^0 + \lambda_j \frac{\ell}{2d} \cdot \Delta\Phi, \quad [19]$$

where $\Delta H_{ad,j}^0$ is the heat of adsorption for $\Delta\Phi = 0$. Also, if one assumes $\ell \approx d$,

$$\Delta H_{ad,j} \approx \Delta H_{ad,j}^0 + (\lambda_j/2)\Delta\Phi. \quad [20]$$

Thus for an electron acceptor adsorbate ($\lambda_j < 0$) Eqs. [19] and [20] predict a linear decrease in ΔH_{ad} with increasing $\Delta\Phi$, while for electron donor adsorbates ($\lambda_j > 0$) they predict a linear decrease in ΔH_{ad} with decreasing $\Delta\Phi$. Both predictions are in excellent agreement with experiment, as shown in the companion paper (1). Equation [20] is also in excellent qualitative agreement with rigorous quantum mechanical calculations (1, 14). This provides solid support for the effective double layer isotherm (Eq. [17]).

Figure 3 shows the isotherms resulting from Eq. [17] for various values of the dimensionless work function Π and of the partial electron transfer parameter λ_j .

Equation [17] can be written in the form

$$\theta_j/(1 - \theta_j) = k_j p_j \exp(\lambda_j \Pi), \quad [21]$$

or equivalently

$$\theta_j/(1 - \theta_j) = k_j a_j \exp(\lambda_j \Pi); \quad [22]$$

thus Fig. 3 shows the isotherms resulting from Eqs. [21] or [22] for various values of the parameter $\lambda_j \Pi$. It should be

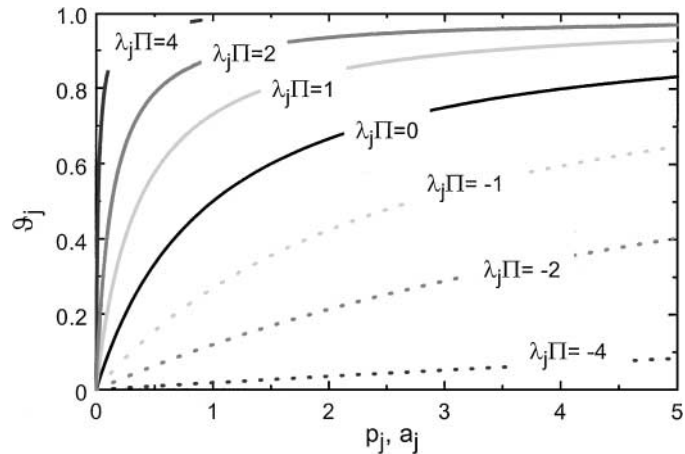


FIG. 3. Effective double layer adsorption equilibrium isotherms for $k_j = 1$ and various values of the parameter $\lambda_j \Pi$.

noted that $\lambda_j \Pi < 0$ implies *repulsive* electrostatic interactions between the adsorbate j and the double layer while $\lambda_j \Pi > 0$ corresponds to *attractive* interactions. Thus $\lambda_j \Pi < 0$ causes a decrease in θ_j , for any fixed P_j (or a_j) in relation to the value it would have in the absence of the double layer ($\Pi = 0$, Fig. 3). The opposite holds for $\lambda_j \Pi > 0$.

Conversely Fig. 3 shows that when $\lambda_j \Pi < 0$, then for any fixed θ_j one has an increase in p_j , or surface activity a_j , in relation to the p_j or a_j value corresponding to $\Pi = 0$. In fact, denoting by p_j^0 or a_j^0 the activity of species j in absence of the double layer ($\Pi = 0$), then one obtains from Eqs. [21] or [22] for any fixed θ_j

$$p_j = p_j^0 \exp(-\lambda_j \Pi), \quad [23]$$

$$a_j = a_j^0 \exp(-\lambda_j \Pi). \quad [24]$$

Thus for the case of O chemisorption ($\lambda_O < 0$) Eqs. [23] and [24] imply an increase in oxygen activity with increasing Π (or Φ or U_{WR}) for any fixed oxygen coverage. This is due to the increasing strength of repulsive lateral interactions between chemisorbed O and the double layer. If oxygen is chemisorbed on the metal surface as O^{2-} ($\lambda_O = -2$) then in view of $\Delta\Phi = e\Delta U_{WR}$ (1, 9, 14), and assuming $\ell = d$, $\cos\omega = 1$, it follows from Eq. [24] that

$$a_{O_2} = a_{O_2}^0 \exp(2e\Delta U_{WR}/k_b T) = a_{O_2}^0 \exp(2F\Delta U_{WR}/RT). \quad [25]$$

By further taking into account the dissociative oxygen chemisorption equilibrium condition ($a_{O_2}^0 = p_{O_2}$) one obtains

$$p_{O_2} = p_{O_2}^0 \exp(4e\Delta U_{WR}/k_b T) = p_{O_2}^0 \exp(4F\Delta U_{WR}/RT), \quad [26]$$

$$a_{O_2} = a_{O_2}^0 \exp(4e\Delta U_{WR}/k_b T) = a_{O_2}^0 \exp(4F\Delta U_{WR}/RT). \quad [27]$$

These are the equations commonly used to describe the variation in surface oxygen activity on an electrode deposited on YSZ due to the application of an overpotential ΔU_{WR} in solid state electrochemistry (14). These equations are equivalent to

$$\mu_{O_2}(\text{ad}) = \mu_{O_2}^0(\text{ad}) + 4F \Delta U_{WR}, \quad [28]$$

where $\mu_{O_2}^0(\text{ad})$ is the chemical potential of oxygen on the electrode in the absence of an applied overpotential ΔU_{WR} . But it is worth noting that this equation, as well as Eqs. [26] and [27], are only valid for fixed coverage (any fixed coverage) of the adsorbate on the electrode surface.

This point is important to remember for the following reason, which is significant when modeling catalytic kinetics in presence of a double layer. When θ_j is not fixed, and instead a_j (or p_j) is fixed due to equilibrium with gaseous $S_j(a_j = p_j)$, then for $\lambda_j < 0$ (e.g., O chemisorption) upon increasing Π (or $\Delta\Phi$ or ΔU_{WR}) the surface coverage θ_j decreases (Fig. 3). This is perhaps at the beginning somehow not intuitively obvious (e.g., how an increase in catalyst–electrode potential and work function causes a decrease in O coverage) but is in excellent agreement with all catalytic oxidation promotional kinetics, both electrochemical and classical, and, of course, with the modified electrochemical Langmuir isotherm described by Eq. [17]. The reason is the increasing electrochemical potential of electron acceptor adsorbates with increasing Φ or U_{WR} due to repulsive lateral interactions with the double layer (Eqs. [13] or [17]).

Strictly speaking the partial charge transfer parameter λ_j which appears in the modified electrochemical Langmuir isotherm [17] or [21] is not a constant but may vary with θ_j or Π . This is because, in view of Eq. [11], λ_j is given by

$$\lambda_j = -\frac{2P_j}{e\ell}, \quad [29]$$

and both P_j and ℓ may be, to some extent, coverage dependent.

2.2. Adsorption in the Absence of a Coadsorbing Species

In the previous section we assumed that $\Delta\Phi$, thus Π , is an independently controllable variable, such as p_j . This is true both in electrochemical promotion experiments, since in the presence of the effective double layer at the metal–gas interface it is $\Delta\Phi = e\Delta U_{WR}$ (1, 14), and in classical promotion experiments where $\Delta\Phi$ can largely be controlled, albeit not *in situ*, by the amount of promoter species deposited on the catalyst surface.

We now examine what happens to the modified effective double layer isotherm (Eq. [17]) when $\Delta\Phi$ is created only by the presence of the adsorbate j , i.e., in absence of any coadsorbing ionic species. Substituting Eq. [29] into Eq. [17]

and expressing $\Delta\Phi$ via the Helmholtz equation

$$\Delta\Phi = \frac{eN_M}{\epsilon_0} \Delta(P_j\theta_j), \quad [30]$$

where e is the electron charge (1.6×10^{-19} C), N_M is the surface atom density (atom/m²), ϵ_0 is the electric permeability of vacuum ($\epsilon_0 = 8.85 \times 10^{-12}$ C²/Jm), and P_j is the dipole moment of the adsorbate, j , in the adsorbed state, one obtains

$$k_j p_j = (\theta_j / (1 - \theta_j)) \exp\left(\frac{N_M \cos \omega}{\epsilon_0 d k_b T} P_j^2 \theta_j\right), \quad [31]$$

which is a Frumkin- or Fowler–Guggenheim-type isotherm (18–22) and the exponential term accounts for the lateral repulsive interactions between the adsorbed j molecules.

More precisely, and accounting for the possible variation of P_j with θ_j , one can write Eq. [31] in the form

$$k_j p_j = \theta_j / (1 - \theta_j) \exp\left(\frac{N_M \cos \omega}{\epsilon_0 d k_b T} \int_0^{\theta_j} P_j^2(\theta_j') d\theta_j'\right). \quad [32]$$

To the extent that P_j may be assumed constant one can then show that the variation in the isosteric heat of adsorption $\Delta H_{ad,j}$, with coverage θ_j , is given by

$$\Delta H_{ad,j} = \Delta H_{ad,j}^0 - \frac{N_M \cos \omega}{\epsilon_0 d} P_j^2 \theta_j, \quad [33]$$

where $\Delta H_{ad,j}^0$ refers again to $\theta_j = 0$, $\Delta\Phi = 0$. As noted in the companion paper (1) Eq. [33] is often found to be in good agreement with experiment, regarding the linear variation in heats of adsorption with coverage.

In view of Eqs. [32] and [33] one can now appreciate the advantages of the effective medium double layer approach used to derive Eq. [17]. Even with the simpler Frumkin or Fowler–Guggenheim approach (Eqs. [31] and [32]), treating the coadsorption and surface reaction of different adsorbates leads immediately to mathematically intractable expressions and to the introduction of new parameters, whereas Eq. [17] leads to mathematically simple catalytic rate expressions, as is shown in the next section.

2.3. Catalytic Kinetics in the Presence of a Double Layer

So far we have established that the modified electrochemical Langmuir or effective double layer isotherm,

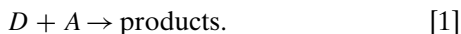
$$\theta_j / (1 - \theta_j) = k_j p_j \exp(\lambda_j \Pi), \quad [21]$$

is consistent with the main experimental finding regarding the effect of promotion on adsorption, i.e., with the observed linear variation of heats of adsorption with $\Delta\Phi$ (1, 14):

$$\Delta H_{ad,j} = \Delta H_{ad,j}^0 + (\lambda_j / 2) \Delta\Phi. \quad [20]$$

The crucial task remains of examining to what extent it can also describe the effect of promotion, electrochemical or classical, on catalytic reaction kinetics. More specifically we examine to what extent it can predict the four main types of global r vs Φ dependence (1) and all the associated local and global electrochemical and chemical promotional rules (Tables 1–8).

We thus consider an arbitrary catalytic reaction between an electron donor D ($\lambda_D > 0$) and an electron acceptor A ($\lambda_A < 0$):



We also first assume that adsorbed D and A are in equilibrium with gaseous D and A , respectively ($\mu_D(g) = \bar{\mu}_D(\text{ad})$, $\mu_A(g) = \bar{\mu}_A(\text{ad})$), and that product adsorption is relatively weak and their desorption fast, so that the reaction between adsorbed D and A is rate limiting. The cases of adsorption or desorption rate control are discussed in Section 2.4.

We start by noting that when D and A coadsorb, their adsorption isotherms are given by

$$\theta_D/\theta_v = k_D p_D \exp(\lambda_D \Pi); \quad \theta_A/\theta_v = k_A p_A \exp(\lambda_A \Pi), \quad [34]$$

where θ_v is the coverage of vacant sites on the catalyst surface. Adding these equations and noting that $\theta_A + \theta_D + \theta_v = 1$ one obtains

$$(1 - \theta_v)/\theta_v = k_D p_D \exp(\lambda_D \Pi) + k_A p_A \exp(\lambda_A \Pi); \quad [35]$$

therefore,

$$\theta_v = 1/(1 + k_D p_D \exp(\lambda_D \Pi) + k_A p_A \exp(\lambda_A \Pi)) \quad [36]$$

and combining it with Eq. [33] one obtains

$$\theta_D = \frac{k_D p_D \exp(\lambda_D \Pi)}{1 + k_D p_D \exp(\lambda_D \Pi) + k_A p_A \exp(\lambda_A \Pi)}, \quad [37]$$

$$\theta_A = \frac{k_A p_A \exp(\lambda_A \Pi)}{1 + k_D p_D \exp(\lambda_D \Pi) + k_A p_A \exp(\lambda_A \Pi)}, \quad [38]$$

$$r = k_R \theta_D \theta_A = \frac{k_R k_D k_A p_D p_A \exp[(\lambda_D + \lambda_A) \Pi]}{(1 + k_D p_D \exp(\lambda_D \Pi) + k_A p_A \exp(\lambda_A \Pi))^2}, \quad [39]$$

where the surface reaction rate constant k_R can in general be expressed as

$$k_R = k_R^0 \exp(\lambda_R \Pi). \quad [40]$$

Equation [40] has been observed experimentally for years (7, 9, 11). Metcalfe (23, 24) has recently modeled electrochemical promotion using O^{2-} conductors and derived Eq. [40] using transition state theory and the concept of a partially charged transition state (24).

In the context of the present effective double layer model the parameter λ_R in Eq. [40] is given by Eq. [29], i.e., equals $(-2P_R/e\ell)$, where P_R is the dipole moment of the transition state. Since P_R is difficult to measure, two alternative approaches can be followed for modeling purposes to estimate P_R and λ_R . The first is to assume that the dipole moment, \tilde{P}_R , of the transition state equals, to a first approximation, the sum of the dipole moment vectors, \tilde{P}_A and \tilde{P}_D , of the adsorbed reactants. This leads to $\lambda_R = \lambda_D + \lambda_A$. Since $\lambda_D > 0$ and $\lambda_A < 0$, this leads, in general, to small $|\lambda_R|$ values. The alternative approach is to assume that the dipole moment of the transition state formed between the electron acceptor and donor adsorbates is negligible in comparison with the dipole moments of the adsorbates themselves, and thus to set $\lambda_R \approx 0$. Both approaches have been tried and both lead to good agreement with experiment. The advantage of both approaches is that no adjustable parameter is introduced into the model and thus, as shown below, it is possible to derive all local and global promotional rules in terms of only four, measurable, parameters:

(a) The two adsorption coefficients k_D and k_A , which quantify the chemisorptive bond strength of D and A at the potential of zero charge of the double layer.

(b) The two partial charge transfer parameters λ_D (> 0) and λ_A (< 0), which describe the electron donicity of the reactants. The values of λ_D and λ_A will be considered fixed except for the case of very weak adsorption ($k_D p_D$, $k_A p_A < 10^{-2}$), where λ_D and λ_A are assumed to vanish in the Π range of repulsive interactions ($\Pi < 0$ and $\Pi > 0$, respectively). This means that in the region of low coverages ($\theta_D, \theta_A < 10^{-2}$) repulsive interactions are neglected, as analyzed in (1). All four parameters are amenable to direct experimental measurement.

2.4. Model Predictions

The mathematical model of Eqs. [37]–[39] is in excellent qualitative agreement with experiment, as shown in Figs. 4–11. It describes in a semiquantitative manner all electrochemical promotion studies to date and predicts the local and global electrochemical and classical promotion rules L1, L2, and G1–G7.

Figure 4 shows how the model predicts the four main types of r vs Φ global behavior (electrophobic, electrophilic, volcano, inverted volcano) for fixed λ_D and λ_A , p_D and p_A , by just varying the adsorption equilibrium constants k_D and k_A . Note that in Fig. 4 and in the other figures we omit the units of p_D and p_A (e.g., kPa) and k_D, k_A (e.g., kPa^{-1}), unless we refer to experimental data. This is because one is free to use any consistent set of units, since only the dimensionless products $k_A p_A$ and $k_D p_D$ enter the calculations.

In Figs. 4 to 6 one can note the following.

(a) In Fig. 4a it is $k_D p_D \ll k_A p_A$, i.e., strong adsorption of A and weak adsorption of D . This leads to *purely*

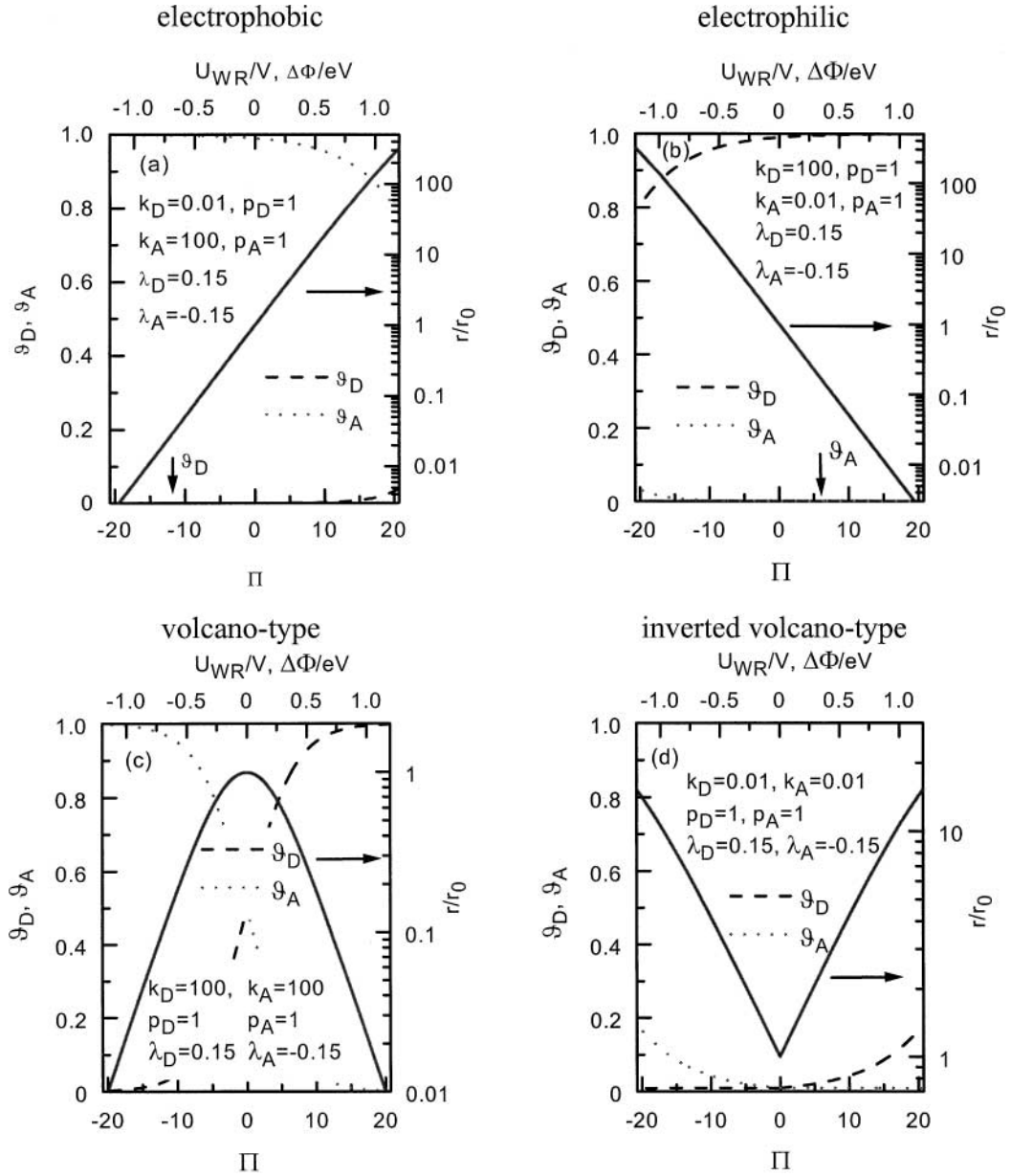


FIG. 4. Model-predicted electrochemical promotion behavior: (a) electrophobic, (b) electrophilic, (c) volcano-type, and (d) inverted volcano-type reactions.

electrophobic behavior. As also shown in Figs. 5a and 5b with these parameter values ($k_D = 10^{-2}$, $k_A = 10^2$) the rate is first order in D for every Φ (or ΔU_{WR}) value. It is also negative order in A (for $p_A > 10^{-2}$) for every Φ (or ΔU_{WR}) value. Thus *rule G1* is predicted exactly.

To gain some additional insight we note that the general rate expression [39] is now reduced to

$$r \approx k_R \frac{k_D p_D}{k_A p_A} \exp[(\lambda_D - \lambda_A)\Pi], \quad [41]$$

where, since $\lambda_D > 0$ and $\lambda_A < 0$, $\lambda_D - \lambda_A > 0$. Thus the slope

in the $\ln r$ vs Π line in Fig. 4a is $\lambda_D - \lambda_A$. Note also that Eq. [41] explains the experimentally observed exponential dependence of r on Φ (1, 9, 14).

$$\ln(r/r_0) = \alpha(\Phi - \Phi^*)/k_b T \quad [42]$$

and provides the following physical meaning to the NEMCA coefficient α .

$$\alpha = \frac{\ell}{2d} (\cos \omega_D \lambda_D - \cos \omega_A \lambda_A), \quad [43]$$

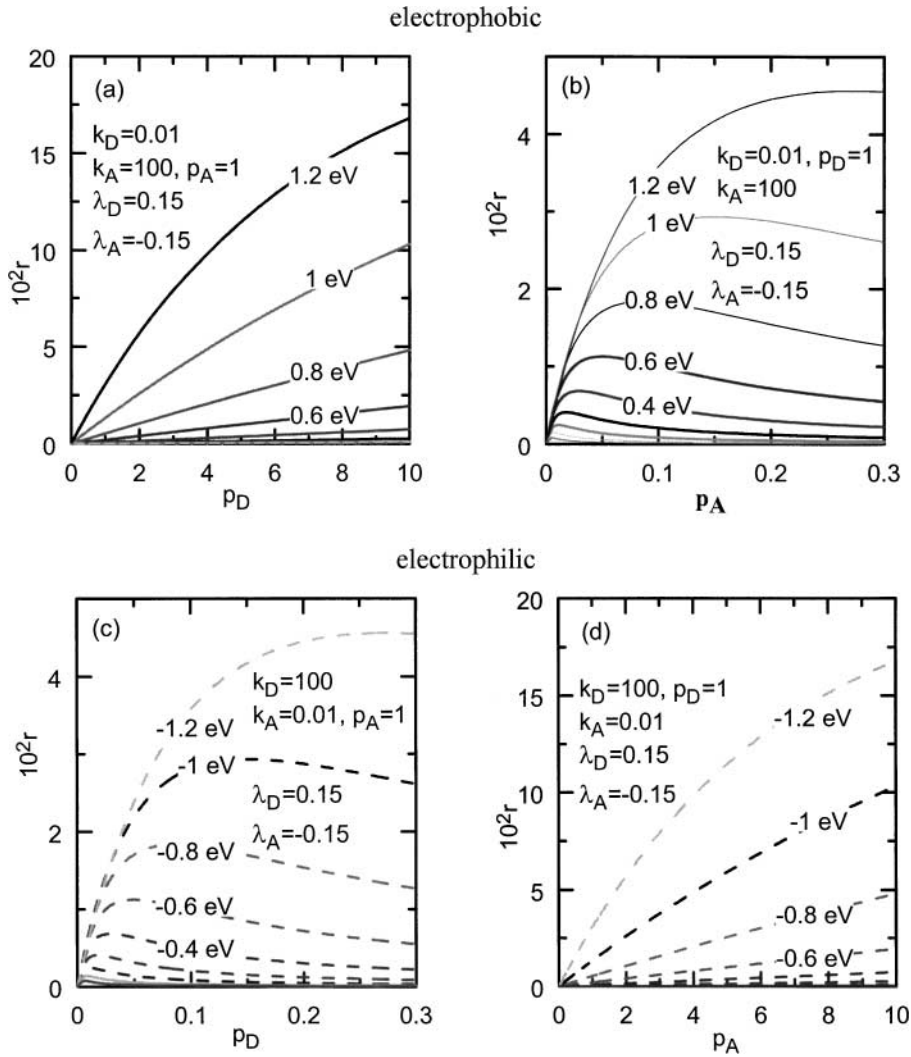


FIG. 5. Model-predicted electrochemical promotion kinetic behavior: (a, b) electrophobic reaction, (c, d) electrophilic reaction. Numbers, in eV, indicate $\Delta\Phi$ value; $(\ell/2d)\cos\omega = 1$, $T = 673$ K.

which for the case of nonzero λ_R in Eq. [40] becomes

$$\alpha = \frac{\ell}{2d}(\lambda_R + \cos\omega_D\lambda_D - \cos\omega_A\lambda_A) \quad [44]$$

or approximately ($\ell \approx 2d$, $\omega_D = \omega_A = 0$):

$$\alpha \approx \lambda_R + \lambda_D - \lambda_A. \quad [45]$$

(b) In Fig. 4b it is $k_D p_D \gg 1 \gg k_A p_A$, i.e., strong adsorption of the electron donor D and weak adsorption of the electron acceptor A . This leads to *purely electrophilic behavior*. As also shown in Figs. 5c and 5d with these parameter values ($k_D = 10^2$, $k_A = 10^{-2}$) the rate is negative order D (for $p_D > 10^{-2}$) for every Φ value. It is also first order in A for every Φ value. Thus *rule G2 is predicted exactly*.

The general rate expression [39] now reduces to

$$r = k_R \frac{k_A p_A}{k_D p_D} \exp[(\lambda_A - \lambda_D)\Pi], \quad [46]$$

where $\lambda_A - \lambda_D < 0$. This is the slope value in Fig. 4b. The experimental equation [42] is also nicely predicted while the (negative for electrophilic reactions) NEMCA coefficient α is given by

$$\alpha = \frac{\ell}{2d}[\lambda_A \cos\omega_A - \lambda_D \cos\omega_D], \quad [47]$$

or more generally by

$$\alpha = \frac{\ell}{2d}[\lambda_R + \lambda_A \cos\omega_A - \lambda_D \cos\omega_D] \quad [48]$$

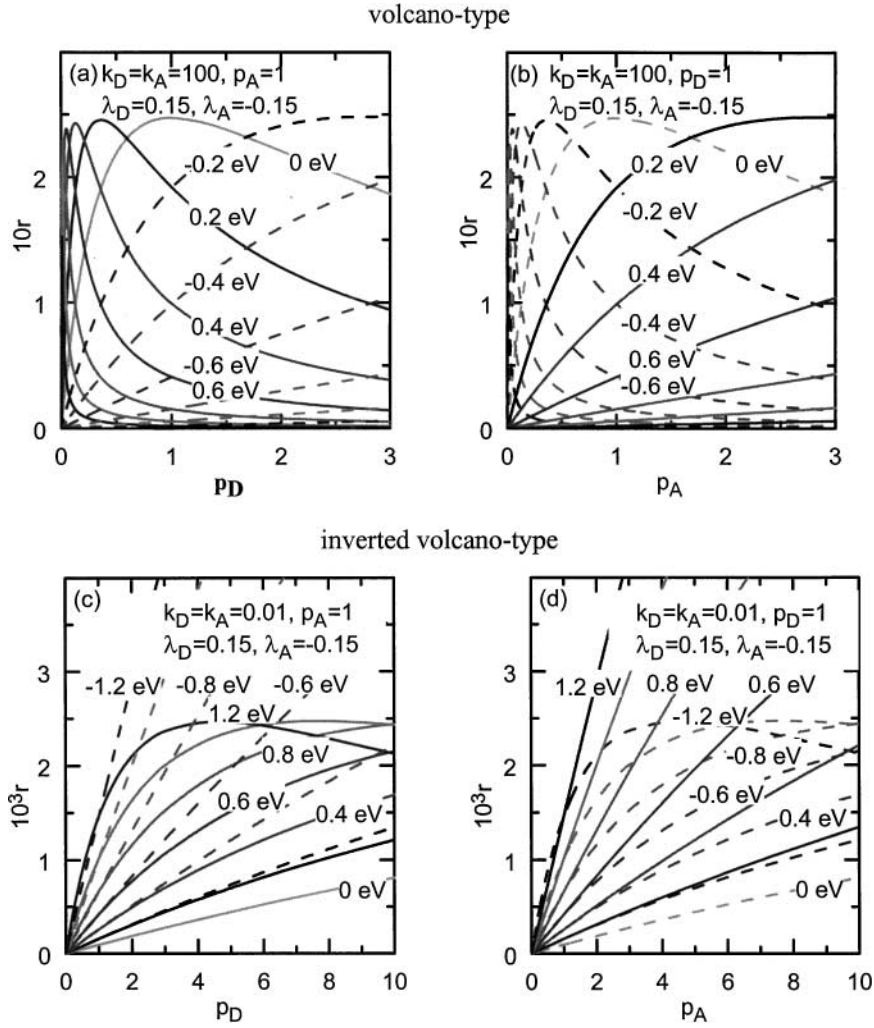


FIG. 6. Model-predicted electrochemical promotion kinetic behavior: (a, b) volcano-type reaction, (c, d) inverted volcano-type reaction. Numbers, in eV, indicate $\Delta\Phi$ value; $(\ell/2d) \cos \omega = 1$, $T = 673$ K.

or approximately ($\ell \approx 2d$, $\omega_A = \omega_D = 0$):

$$\alpha = \lambda_R + \lambda_A - \lambda_D. \quad [49]$$

Next we examine strong adsorption of both D and A ($k_D p_D = k_A p_A = 10^2$). This leads to volcano behavior (Fig. 4c). The rate dependence of r on p_D and p_A (Figs. 6a and 6b) shifts from negative order in D and positive order in A at high positive Φ values to positive order in D and negative order in A at low (negative) Φ values. The similarity with the r vs p_{H_2} and r vs p_{O_2} behavior during H_2 oxidation on Pt in alkaline solutions which exhibits volcano r vs Φ behavior (1) is noteworthy. *Rule G3 is predicted exactly.*

The general rate expression [39] now reduces to

$$r = k_R \frac{\frac{k_D p_D}{k_A p_A} \exp[(\lambda_D - \lambda_A)\Pi]}{\left[1 + \frac{k_D p_D}{k_A p_A} \exp[(\lambda_D - \lambda_A)\Pi]\right]^2}; \quad [50]$$

thus the asymptotes in the volcano $\ln r$ vs Π plot (Fig. 4c) are $\lambda_D - \lambda_A$ (>0) for low Π and $\lambda_A - \lambda_D$ (<0) for high Π .

Furthermore simple differentiation of Eq. [50] shows that the rate is maximized ($\theta_D = \theta_A$) when

$$\frac{k_D p_D}{k_A p_A} \exp[(\lambda_D - \lambda_A)\Pi] \approx 1. \quad [51]$$

This equation, solved in terms of p_D , for fixed p_A and Π (or $\Delta\Phi$), gives the location of the rate maxima in Fig. 6a. When solved in terms of p_A , for fixed p_D and Π (or $\Delta\Phi$) it gives the location of the rate maxima in Fig. 6b. And when solved in terms of Π (or $\Delta\Phi$) for fixed p_D and p_A it gives the location of the volcano peak (Fig. 4c).

Last we examine the case of weak adsorption of both D and A ($k_D p_D = k_A p_A = 10^{-2}$). In this case, since as previously noted only attractive interactions are considered and the repulsive interactions are neglected (1), the coverage

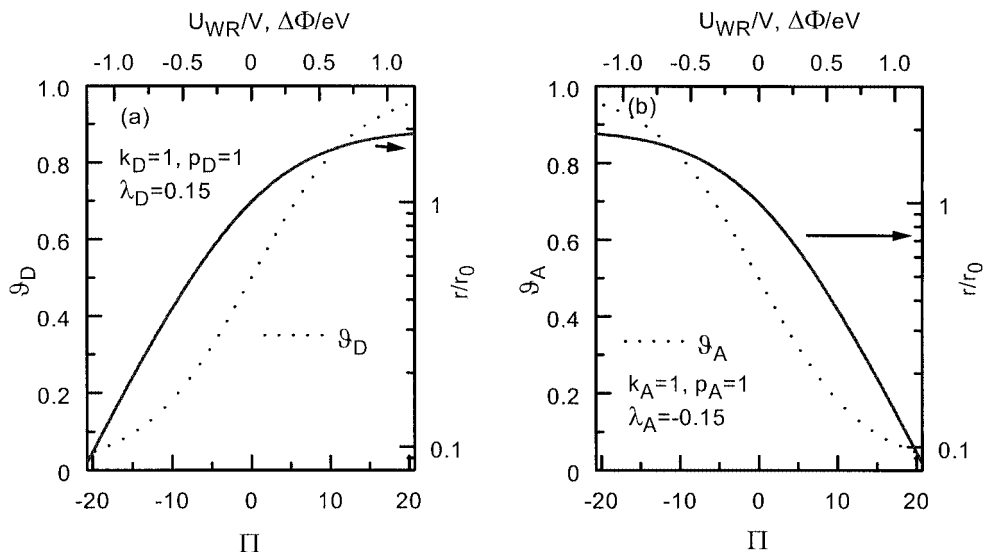


FIG. 7. Model-predicted electrochemical promotion behavior for a monomolecular reaction: (a) electrophobic, (b) electrophilic.

equations [37] and [38] take the form

$$\theta_D = \frac{k_D p_D \exp[\max(0, \lambda_D \Pi)]}{1 + k_D p_D \exp[\max(0, \lambda_D \Pi)] + k_A p_A \exp[\max(0, \lambda_A \Pi)]}, \quad [52]$$

$$\theta_A = \frac{k_A p_A \exp[\max(0, \lambda_A \Pi)]}{1 + k_D p_D \exp[\max(0, \lambda_D \Pi)] + k_A p_A \exp[\max(0, \lambda_A \Pi)]}, \quad [53]$$

where the symbol $\max(\alpha, \beta)$ denotes α when $\alpha > \beta$, β when $\alpha < \beta$, and α (or β) when $\alpha = \beta$.

The resulting r vs Π behavior is shown in Fig. 4d. In excellent agreement with *global rule G4*, *inverted volcano* behavior is predicted with a minimum at the point of zero charge. Furthermore the r vs p_D behavior shifts from first order in D for negative $\Delta\Phi$ to Langmuir-type or even negative order in D for high Φ (Fig. 6c).

Conversely the r vs p_A behavior (Fig. 6d) shifts from first order in A for positive $\Delta\Phi$ to Langmuir-type or even negative order in A for very low Φ . Thus *global rule G4* is confirmed exactly.

Monomolecular reactions. Two cases have to be examined here:

$$D \rightarrow \text{products}, \quad [54]$$

$$A \rightarrow \text{products}. \quad [55]$$

In both cases the rate expression is

$$r = k_R \theta_j = k_R \frac{k_j p_j \exp(\lambda_j \Pi)}{1 + k_j p_j \exp(\lambda_j \Pi)}, \quad [56]$$

where j stands for D or A and in the former case $\lambda_D > 0$

whereas in the latter $\lambda_A < 0$. The resulting r vs Π and r vs p_D (or p_A) behavior is shown in Figs. 7 and 8.

In the former case ($\lambda_D > 0$) the r vs Φ behavior is electrophobic and the reaction order with respect to p_D decreases with increasing Φ . This confirms *rule G6*.

In the latter case ($\lambda_A < 0$) the r vs Φ behavior is electrophilic and the reaction order increases with increasing Φ . This also confirms *rule G6*.

Effect of partial electron transfer parameter. Figure 9 depicts the effect of the value of the partial charge transfer parameter λ_D for fixed $\lambda_A (= -0.15)$ on the rate-enhancement ratio $\rho (=r/r_0)$ for the four main types of promotional behavior, i.e., electrophobic, electrophilic, volcano, and inverted volcano. The main feature of the figure is that it confirms in general the *global rules G5* and *G7*. Regarding *global rule G5* it can be seen in Figs. 9a–9c that as long as $\lambda_D > \lambda_A$, *rules G1–G3* remain valid regardless of the sign of λ_D , with some deviations predicted only for *rule G4* in the case of positive Π (in this case a shift from inverted volcano to electrophilic behavior is predicted when both λ_A and λ_D are negative (Fig. 9d)).

With respect to *rule G7*, Figs. 9a–9c show that, indeed, the larger the value of $|\lambda_D - \lambda_A|$, the stronger the rate dependence on potential and thus the larger the maximum obtainable $\rho (=r/r_0)$ value. Some deviations are again predicted for the case of inverted volcano reactions (Fig. 9d), where it is the value of λ_D (at fixed λ_A) and not the difference $|\lambda_D - \lambda_A|$ which dictates the maximum $\rho (=r/r_0)$ value.

In the case of strong adsorption of A (Fig. 9a) $\rho (=r/r_0)$ is an increasing function of λ_D except for very high λ_D , where volcano-type behavior is predicted. This is because in this case the coverage of A decreases significantly at very

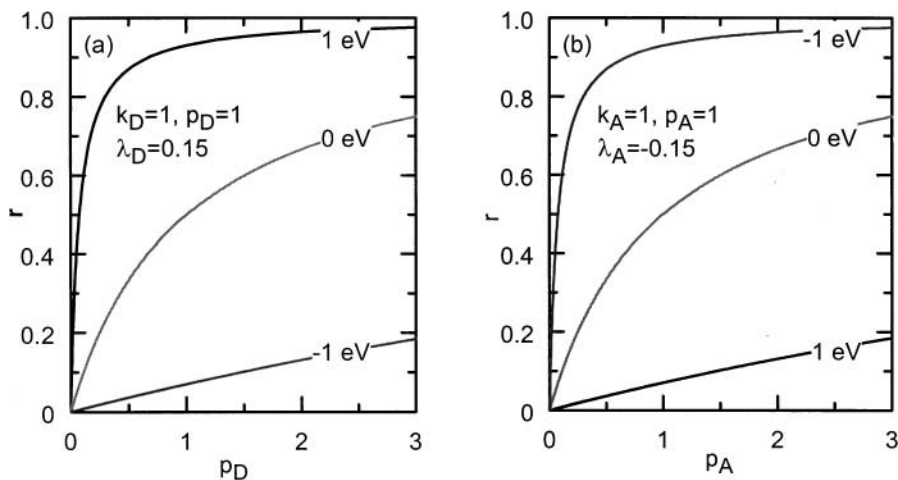


FIG. 8. Model-predicted electrochemical promotion kinetic behavior for a monomolecular reaction of an electron donor (a) and an electron acceptor (b) adsorbate. Numbers, in eV, indicate $\Delta\Phi$ value; $(\ell/2d)\cos\omega = 1$, $T = 673$ K.

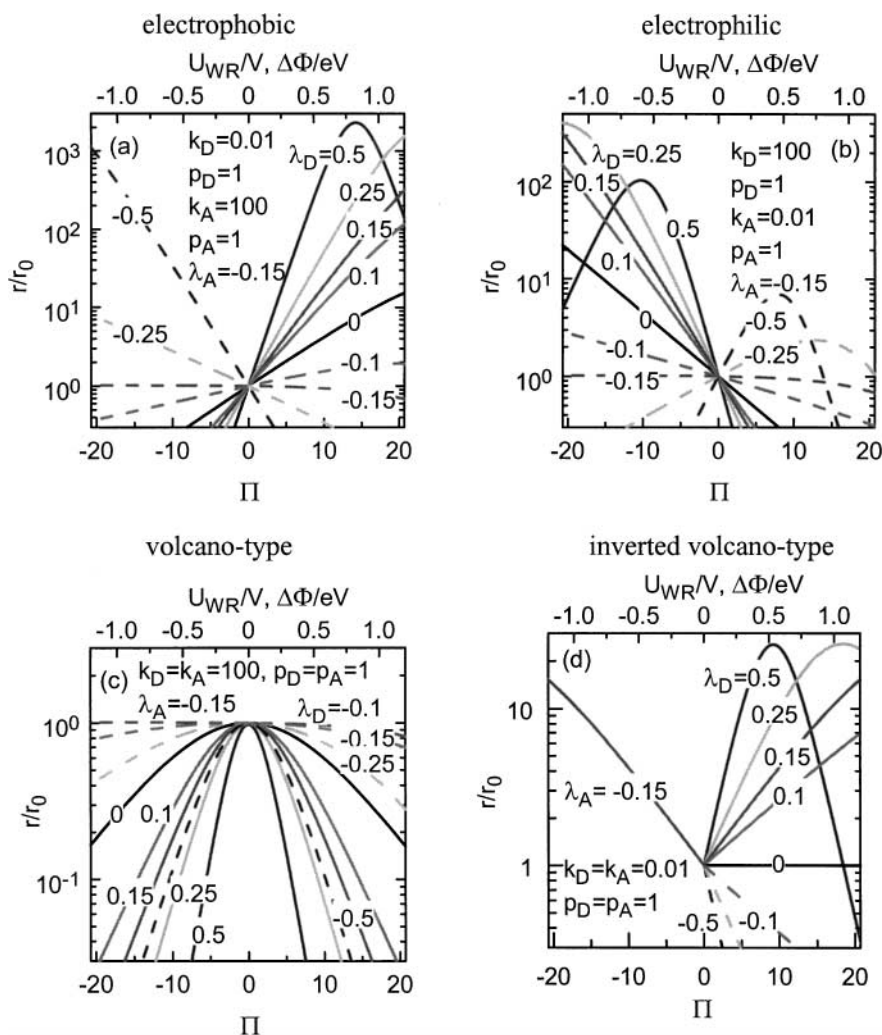


FIG. 9. Effect of partial charge transfer coefficient λ_D on catalyst performance for fixed λ_A as a function of dimensionless work function Π ; (a) electrophobic, (b) electrophilic, (c) volcano-type, and (d) inverted volcano-type.

positive potentials. When λ_D also becomes negative (like λ_A), then volcano-type behavior is again predicted (Fig. 9a).

For strong adsorption of D (Fig. 9b), ρ is again an increasing function of λ_D and for negative λ_D values a transition to inverted-volcano-type behavior is predicted.

Rules G5 and G7 are also predicted for the case of strong adsorption of both D and A (Fig. 9c), i.e., for the case of volcano behavior. In the case of weak adsorption of D and A (Fig. 9d) a transition from inverted volcano to purely electrophilic behavior is predicted when λ_D is negative, as already noted.

The excellent prediction by the model of all global promotion rules is not only qualitative. The predicted ρ values ($\sim 10^2$ for 1V variation in U_{WR} , Fig. 4a) are in excellent agreement with experiment (9, 14). Also the ρ_{\max} values (~ 10 – 20) predicted for *volcano* and *inverted volcano* behavior are in very good agreement with experiment (1, 9, 14). Finally the λ_D, λ_A which are used (± 0.15) are physically very reasonable for predominantly covalently bonded adsorbates. For example, for $U_{WR} = 1$ V at 673 K, it is $\Pi \approx 17$; thus the λ_D and λ_A values used in the simulations give $\exp(\lambda_j \Pi)$, and thus ρ , values between 10^{-2} and 10^2 , in good qualitative agreement with experiment (1, 9, 14).

Adsorption or desorption rate control. The previous analysis was focused on surface reaction rate control. However the effective double layer kinetics can be easily extended to the cases of reactant adsorption control or product desorption control.

Denoting by $k_{a,A}, k_{a,D}, k_{a,Pr}$ the kinetic adsorption rate constants of A, D , and products and by $k_{d,A}, k_{d,D}, k_{d,Pr}$ the corresponding kinetic desorption rate constants, one can easily derive, as shown in the Appendix, the following rate expressions.

Adsorption of D controlling. In this case one has

$$r = k_{a,D} P_D / [1 + k_A P_A \exp(\lambda_A \Pi)]. \quad [57]$$

Note that since $\partial k_{a,D} / \partial \Pi \geq 0$ (electron donor adsorbate) and $\lambda_A < 0$, it follows that

$$(\partial r / \partial P_D)_{\Phi, P_A} > 0, \quad (\partial r / \partial P_A)_{\Phi, P_D} < 0, \quad (\partial r / \partial \Phi)_{P_A, P_D} > 0, \quad [58]$$

i.e., *rule G1 (electrophobic behavior) is predicted exactly.* This is very reasonable since Eq. [57] is very similar to Eq. [41], i.e., corresponds to weak adsorption of D .

Adsorption of A controlling. In this case one has

$$r = k_{a,A} P_A / [1 + k_D P_D \exp(\lambda_D \Pi)]. \quad [59]$$

Note that since $\partial k_{a,A} / \partial \Pi \leq 0$ (electron acceptor adsorbate) and $\lambda_D > 0$ it follows that

$$(\partial r / \partial P_A)_{\Phi, P_D} > 0, \quad (\partial r / \partial P_D)_{\Phi, P_A} < 0, \quad (\partial r / \partial \Phi)_{P_A, P_D} < 0, \quad [60]$$

i.e., *rule G2 (electrophilic behavior) is predicted exactly.* This is quite reasonable since Eq. [59] is very similar to Eq. [46], i.e., weak adsorption of A .

Product desorption rate controlling. In this case one has

$$r = k_{a,Pr} P_{Pr} \exp(\lambda_{Pr} \Pi) / [1 + k_D P_D \exp(\lambda_D \Pi) + k_A P_A \exp(\lambda_A \Pi) + k_{Pr} P_{Pr} \exp(\lambda_{Pr} \Pi)] \quad [61]$$

When the product is electron donor ($\lambda_{Pr} > 0, \partial r / \partial k_{a,Pr} \geq 0$), Eq. [61] predicts electrophobic behavior unless λ_D is much larger than λ_{Pr} .

When the product is electron acceptor ($\lambda_{Pr} < 0, \partial r / \partial k_{a,Pr} \leq 0$), Eq. [61] predicts electrophilic behavior unless λ_A is much smaller than λ_{Pr} . In general this case is very similar to that of the monomolecular reactions described above, except for the additional complication due to the coadsorption of the reactants.

2.5. Comparison with Complex Promotional Kinetics

The success of the model can be appreciated from Fig. 10, which compares model predictions (Figs. 10a and 10b) with some truly interesting and complex experimental results (Figs. 10c and 10d) obtained during C_2H_4 oxidation on Pt/TiO₂ (25). As shown in Figs. 10c and 10d the rate dependence on U_{WR} and Π shifts from inverted volcano (Fig. 10c) to purely electrophobic (Fig. 10d) as $p_{C_2H_4}$ ($= p_D$) is decreased by a factor of 10 at fixed p_{O_2} .

As shown in Figs. 10a and 10b the model predicts the shift in global behavior in a truly impressive semiquantitative manner and in fact with very reasonable λ_D and λ_A values ($\lambda_D > 0, \lambda_A < 0$).

Finally the success of the model can be judged from Figs. 11a and 11b, which show the experimental and model-predicted rate dependence on p_{CO} and work function during CO oxidation on Pt/ β'' -Al₂O₃ (8). Note the transition from a classical Langmuir–Hinshelwood to a positive-order rate dependence on p_{CO} with decreasing work function. Also notice that on every point of the experimental or model-predicted rate dependence, the basic promotional rule (1),

$$\left(\frac{\partial r}{\partial \Phi} \right)_{P_A, P_D} \left(\frac{\partial r}{\partial P_D} \right)_{\Phi, P_A} > 0, \quad [62]$$

is strictly obeyed. The optimal λ_D and λ_A values are again quite reasonable ($\lambda_D > 0, \lambda_A < 0$). The large optimal k_A and k_D values (~ 9) are also quite reasonable, as they indicate strong adsorption of both CO ($= D$) and oxygen ($= A$), which is the necessary and sufficient condition (Rule G3) for the appearance of volcano-type behavior.

In general Figs. 4–11, and in particular Figs. 4–6, 10, and 11 show, beyond any reasonable doubt, that the effective double layer model of promotion, expressed mathematically

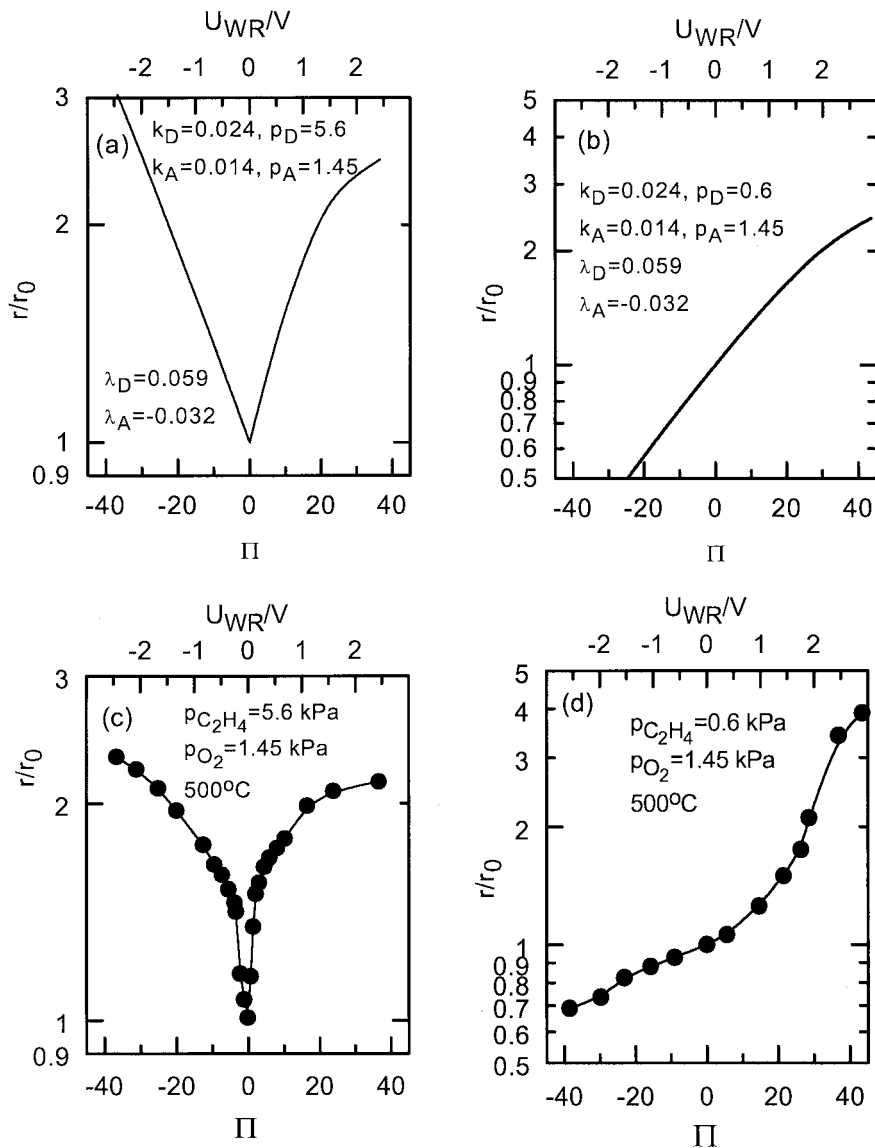


FIG. 10. Experimentally observed (c, d) and model predicted (a, b) transition from inverted volcano to electrophobic behavior upon increasing the O_2 to ethylene (i.e., A/D) ratio by a factor of 10; C_2H_4 oxidation on Pt/TiO_2 (25).

by Eqs. [39] and [40], provides a satisfactory description of promotional kinetics.

Despite the success of the effective double layer kinetic model in describing promotional kinetics in a semiquantitative manner, it is also worth mentioning some of its limitations. As an effective medium model, it does not account for local effects, which may become increasingly important at very low promoter coverages. Also the model in its present form does not account explicitly for promoter site-blocking effects, which can become important at high promoter coverages.

It is worth noting that promoters have, in general, high absolute values of their dipole moments, $|P_j|$, i.e., 5–10 D

(Debye) for alkalis and ~ 2 D for O^{2-} , used in electrochemical promotion (14). Thus for a surface with $N_M = 10^{19}$ atom/m², it follows directly from the Helmholtz equation [30] that a 1-eV work function change requires

$$(|P_j|/D)\theta_j \approx 0.26. \quad [63]$$

Thus for alkali promoters a coverage of 0.052–0.026 suffices to reduce the work function by 1 eV, but even for an O^{2-} promoter (14), a coverage of 0.13 is sufficient to increase the work function by the same amount. Thus, with strong promoters, site blocking effects are not dominant.

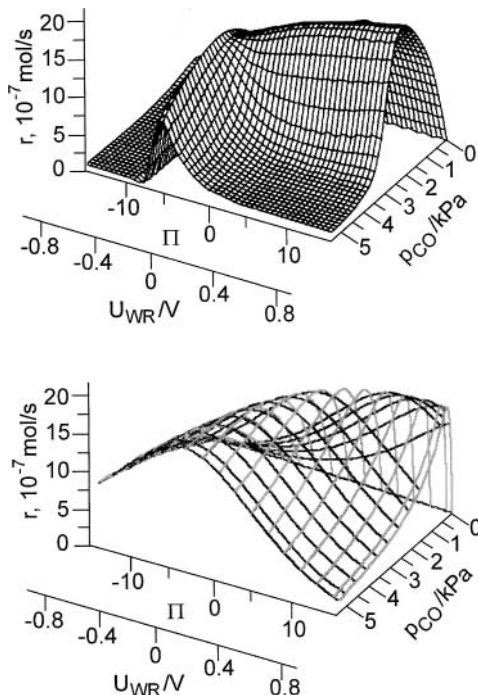


FIG. 11. Experimental (8) (top) and model-simulated (bottom) dependence of the rate of CO oxidation on Pt deposited on β'' -Al₂O₃ as a function of p_{CO} , catalyst potential U_{WR} , and dimensionless catalyst work function $\Pi (= \Delta\Phi/k_bT)$ at $p_{\text{O}_2} = 6$ kPa (8). Parameters used in Eqs. [39] and [40]: $k_A = 9.133$, $k_D = 8.715$, $\lambda_A = -0.08$, $\lambda_D = 0.09$, $\lambda_R = 0$, and $k_R = 6.19 \times 10^{-6}$.

3. CONCLUSIONS

A kinetic model has been developed which accounts explicitly for the electrostatic interactions between catalytic adsorbates and the effective double layer present at the metal-gas interface. This mean field effective double layer (EDL) model is mathematically simple and predicts all the recently established rules of electrochemical and chemical (classical) promotion (1). It is also in good qualitative agreement with more-complex promotional kinetics, where several of these rules are applicable in different operating conditions. The effective double layer isotherm, on which the kinetic model is based, predicts the experimentally observed linear variation in adsorption enthalpies with work function. Thus the EDL extension of LHHW kinetics appears to describe well the effect of promoters in catalytic kinetics.

APPENDIX

Here we derive effective double layer rate expressions for the irreversible reaction [1] and for the cases of reactant adsorption control or product desorption control.

Adsorption of D Rate Controlling

In this case the adsorption of A is in equilibrium and the coverage of D vanishes, as the irreversible surface reaction

step is in quasiequilibrium. Therefore,

$$\theta_A/(1 - \theta_A) = k_A P_A \exp(\lambda_A \Pi), \quad \theta_v = 1 - \theta_A, \quad [\text{A1}]$$

and thus

$$r = k_{a,D} P_D \theta_v = k_{a,D} P_D / (1 + k_A P_A \exp(\lambda_A \Pi)), \quad [\text{A2}]$$

where $k_{a,D}$ is the kinetic adsorption rate constant of D. This is Eq. [57]. It is interesting to notice that since D is an electron donor, it follows that

$$\partial k_{a,D} / \partial \Phi \geq 0, \quad [\text{A3}]$$

and since $\lambda_A < 0$, it follows from Eq. [A2] that

$$(\partial r / \partial P_D)_{\Phi, P_A} > 0, \quad (\partial r / \partial P_A)_{\Phi, P_D} < 0, \quad (\partial r / \partial \Phi)_{P_A, P_D} > 0, \quad [\text{A4}]$$

i.e., rule G1 is predicted exactly.

Adsorption of A Rate Controlling

In complete analogy with the previous case one obtains

$$r = k_{a,A} P_A / (1 + k_D P_D \exp(\lambda_D \Pi)), \quad [\text{A5}]$$

where $k_{a,A}$ is the kinetic adsorption rate constant of A, which is Eq. [59]. Since A is an electron acceptor, it follows that

$$\partial k_{a,A} / \partial \Phi \leq 0, \quad [\text{A6}]$$

and since $\lambda_D > 0$, it follows from Eq. [A5] that

$$(\partial r / \partial P_A)_{\Phi, P_D} > 0, \quad (\partial r / \partial P_D)_{\Phi, P_A} < 0, \quad (\partial r / \partial \Phi)_{P_A, P_D} < 0, \quad [\text{A7}]$$

i.e., rule G2 is predicted exactly.

Product Desorption Rate Controlling

We denote by k_{Pr} the adsorption equilibrium constant of the products and by $k_{a,Pr}$ and $k_{d,Pr}$ the adsorption and desorption kinetic rate constants. Clearly $k_{Pr} = k_{a,Pr} / k_{d,Pr}$. In this case the adsorption of A, D, and products is in quasiequilibrium; thus

$$\theta_A / \theta_v = k_D P_D \exp(\lambda_D \Pi), \quad \theta_A / \theta_v = k_A P_A \exp(\lambda_A \Pi), \quad [\text{A8}]$$

$$\theta_{Pr} / \theta_v = k_{Pr} P_{Pr} \exp(\lambda_{Pr} \Pi). \quad [\text{A9}]$$

From these equations and

$$r = k_{d,Pr} \theta_{Pr} \quad [\text{A10}]$$

it follows directly that

$$r = k_{a,Pr} P_{Pr} \exp(\lambda_{Pr} \Pi) / [1 + k_D P_D \exp(\lambda_D \Pi) + k_A P_A \exp(\lambda_A \Pi) + k_{Pr} P_{Pr} \exp(\lambda_{Pr} \Pi)], \quad [\text{A11}]$$

which is Eq. [61].

ACKNOWLEDGMENTS

We thank the TMR programme of the EU for financial support, and Dr. Haralambos Couris for his valuable collaboration in the numerical fitting of the data of Figs. 10 and 11.

REFERENCES

- Vayenas, C. G., Brosda, S., and Pliangos, C., *J. Catal.* **203**, 329 (2001).
- Hegedus, L. L., Aris, R., Bell, A. T., Boudart, M., Chen, N. Y., Gates, B. C., Haag, W. O., Somorjai, G. A., and Wei, J., "Catalyst Design: Progress and Perspectives." Wiley, New York, 1987.
- Ertl, G., Knötzing, H., and Weitcamp, J., "Handbook of Catalysis." VCH Publishers, Weinheim, 1997.
- Farrauto, R. J., and Bartholomew, C. H., "Fundamentals of Industrial Catalytic Processes." Chapman & Hall, London, 1997.
- Kiskinova, M., in "Poisoning and Promotion in Catalysis Based on Surface Science Concepts and Experiments," No. 70. Elsevier, Amsterdam, 1992.
- Volkenstein, T., "Elektronentheorie der Katalyse an Halbleitern." VEB Deutscher Verlag der Wissenschaften, Berlin, 1964.
- Vayenas, C. G., Bebelis, S., and Ladas, S., *Nature* **343**, 625 (1990).
- Yentekakis, I. V., Moggridge, G., Vayenas, C. G., and Lambert, R. M., *J. Catal.* **146**, 292 (1994).
- Vayenas, C. G., Jaksic, M. M., Bebelis, S., and Neophytides, S. G., in "The Electrochemical Activation of Catalysis" (J. O. M. Bockris, B. E. Conway, and R. E. White, Eds.), No. 29, p. 57. Kluwer Academic/Plenum Publishers, New York, 1996.
- Vayenas, C. G., Lambert, R. M., Ladas, S., Bebelis, S., Neophytides, S., Tikhov, M. S., Filkin, N. C., Makri, M., Tsiplakides, D., Cavalca, C., and Besocke, K., *Stud. Surf. Sci. Catal.* **112**, 39 (1997).
- Foti, G., Wodiunig, S., and Comninellis, C., *Curr. Top. Electrochem.* **7**, 1 (2000).
- Nicole, J., Tsiplakides, D., Pliangos, C., Verykios, X. E., Comninellis, C., and Vayenas, C. G., *J. Catal.* **204**, 23 (2001).
- Vayenas, C. G., and Pitselis, G., *Ind. Eng. Chem. Res.* **40**, 4209 (2001).
- Vayenas, C. G., Bebelis, S., Pliangos, C., Brosda, S., and Tsiplakides, D., "Electrochemical Activation of Catalysts: Promotion, Electrochemical Promotion and Metal-Support Interactions." Kluwer Academic/Plenum publishers, New York, 2001.
- Tsiplakides, D., and Vayenas, C. G., *J. Electrochem. Soc.* **148**(5), E189 (2001).
- Franaszczuk, K., Herrero, E., Zelenay, P., Wieckowski, A., Wang, J., and Masel, R. I., *J. Phys. Chem.* **96**(21), 8509 (1992).
- Bockris, J. O. M., Reddy, A. K. M., and Gamboa-Aldeo, M., "Modern Electrochemistry." Kluwer Academic/Plenum Publishers, New York, 2000.
- Gileadi, E., "Electrode Kinetics for Chemists, Chemical Engineers and Materials Scientists." Wiley-VCH, Weinheim, 1993.
- Somorjai, G. A., "Chemistry in Two Dimensions: Surfaces." Cornell University Press, Ithaca, NY, 1981.
- Adamson, A. W., "Physical Chemistry of Surfaces." Wiley, New York, 1990.
- Rudinski, W., and Everett, D. H., "Adsorption of Gases on Heterogeneous Surfaces." Academic Press, London, 1992.
- Rubinstein, I., "Physical Electrochemistry. Principles, Methods, and Applications." Dekker, New York, 1995.
- Metcalfe, I., *J. Catal.* **199**, 247 (2001).
- Metcalfe, I., *J. Catal.* **199**, 259 (2001).
- Pliangos, C., Yentekakis, I. V., Ladas, S., and Vayenas, C. G., *J. Catal.* **159**, 189 (1996).