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Rules and Mathematical Modeling of Electrochemical and Chemical Promotion

1. Reaction Classification and Promotional Rules

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The effect of electrochemical promotion has already been studied for more than 60 different catalytic systems. Its origin is electrochemically controlled introduction of promoting species on catalyst surfaces interfaced with solid electrolytes. The promoting mechanism is thus similar to classic (chemical) promotion where the promoting species is added during catalyst preparation or from the gas phase. In this work simple and rigorous rules are derived that govern the promotional action, i.e., the catalytic rate dependence on promoter concentration or on work function, Φ, of the catalyst surface. These rules enable one to predict the rate, r, dependence on Φ or on promoter concentration on the basis of the rate dependence on the electron donor (D) or electron acceptor (A) reactant partial pressures, p_D and p_A, on the unpromoted catalyst surface. The four main types of promotional behavior, i.e., electrophobic ($\partial r/\partial \Phi > 0$), electrophilic ($\partial r/\partial \Phi < 0$), volcano type, and inverted volcano type, are shown to correspond to strong adsorption of A, strong adsorption of D, strong adsorption of A and D, and weak adsorption of A and D, respectively. The rules are in excellent agreement with both the electrochemical and classic promotion literature and can be summarized by the inequalities $(\partial r/\partial \Phi)_{p_A,p_D}(\partial r/\partial_{p_D})_{\Phi,p_A} > 0$ and $(\partial r/\partial \Phi)_{p_A,p_D}(\partial r/\partial p_A)_{\Phi,p_D} < 0$, which dictate that for a reaction involving a strongly adsorbed electron donor/acceptor reactant, an electropositive (electron donor)/electronegative (electron acceptor) promoter is to be recommended. © 2001 Academic Press

INTRODUCTION

Promoters play a key role in heterogeneous catalysis. Their use is necessary for the design of successful industrial catalysts (1). Broadly speaking promoters can be divided into structural promoters and electronic promoters (1, 2). In the former case they enhance and stabilize the dispersion of the active phase on the carrier. In the latter case they enhance the catalytic properties of the active phase itself (1–3). This is due to their ability to modify the chemisorptive properties of the catalyst surface and to affect the chemisorptive bond strength of reactants and reaction intermediates. At the molecular level this results from direct electrostatic (through the vacuum) and indirect (through the metal) interactions.

While chemical promotion has been known, studied, and used for more than a century (2–7), the closely related phenomenon of electrochemical promotion or nonfaradaic electrochemical modification of catalytic activity (NEMCA effect) was first discovered in the eighties (8–15). Work in this area has been reviewed (16–21). The significance of electrochemical promotion in electrochemistry (22, 23), surface science (24), and catalysis (25) has been discussed by Bockris and Minevski (22) and Lu and Wieckowski (23), Pritchard (24), and Grzybowska-Swierkosz and Haber (25), respectively, together with its similarities, but also some interesting operational differences, with classic (chemical) promotion (16–21) but also with metal–support interactions (26–28).

The operational principle of electrochemical promotion is shown in Fig. 1. On application of electrical current, I, or potential (±1 V) between the catalyst and a catalytically inert counterelectrode, also deposited on the solid electrolyte, ionic species are supplied to the catalyst at a rate I/nF, where n is the ion charge in the solid electrolyte support. The electrochemically generated ionically bonded species ($O^{\delta-}$ in the case of O^{2-} conductors such as Y_2O_3-stabilized ZrO_2 (YSZ) (16–21), $Na^{\delta+}$ in the case of Na^+ conductors such as β''-Al_2O_3) (29) migrate (backspillover) over the entire gas-exposed catalyst-electrode surface and establish an effective double layer at the catalyst/gas interface (30–33). Each backspillover species is accompanied by its compensating (image) charge in the metal so that the effective double layer is overall neutral, as is the case with every double layer (20, 30–33) (Fig. 2).

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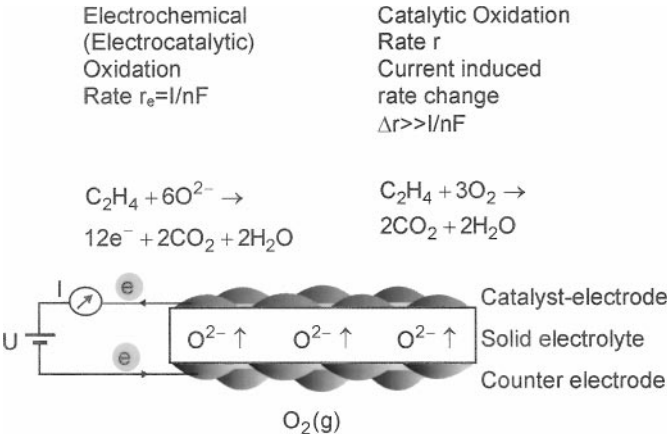

FIG. 1. Principle and basic experimental setup for electrochemical promotion (NEMCA) studies using an O^{2-}-conducting solid electrolyte.

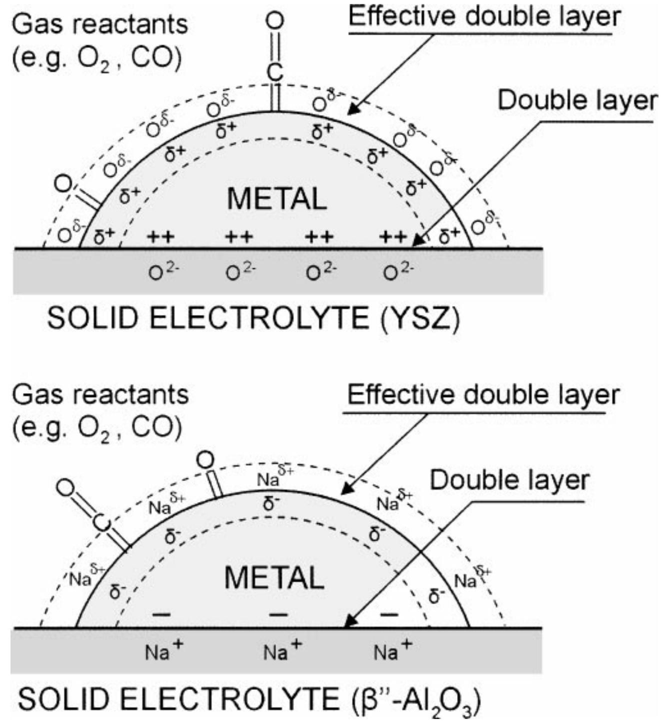

FIG. 2. Schematic representation of a metal catalyst-electrode deposited on an O^{2-}-conducting electrolyte and a Na^+-conducting solid electrolyte, showing the location of the metal-solid electrolyte double layer and of the effective double layer created at the metal/gas interface due to potential-controlled ion migration (backspillover).

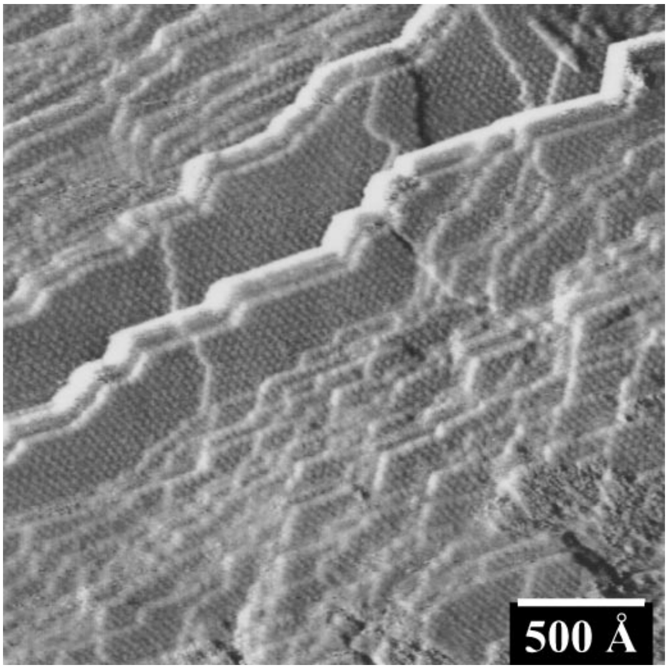

FIG. 3. Atomic resolution STM of a part of the surface of a Pt single crystal, which is interfaced with β''-Al_2O_3, showing the creation of the effective double layer at the metal/gas interface. Each sphere on the Pt(111) terraces is a Na atom. The Na coverage is ~0.01 and the Na atoms form an (12 × 12) overlayer on the Pt(111) surface. The Na coverage can be controlled by the applied potential U_{WR} (42). Sodium can be totally and reversibly removed via positive (anodic) potential or current application. Further experimental details can be found in Ref.(41). Tunneling current and voltage: $I = 10$ nA, $U = -0.16$ V.

The presence of the effective double layer at the catalyst/gas interface has been confirmed using a variety of surface spectroscopic and electrochemical techniques including X-ray photoelectron spectroscopy (XPS) (34, 35), ultraviolet photoelectron spectroscopy (UPS) (36), temperature-programmed desorption (TPD) (37), cyclic voltammetry (34, 38) impedance spectroscopy (39, 40), scanning tunneling microscopy (STM) (41, 42) (Fig. 3), and work function measurements (10, 30, 33, 36, 43–47) via the Kelvin probe technique (10, 30, 33, 43–47) or via the electron cutoff energy in UPS (36). The work function measurements (10, 30, 33, 36, 43–47) have shown that the work function, Φ, of the catalyst surface is related, over wide and well-defined conditions described below (30, 31, 33), to the catalyst-working (W) electrode potential, U_{WR}, with respect to a reference (R) electrode via the equation

$$e\Delta U_{WR} = \Delta\Phi. \qquad [1]$$

Thus the work function of the catalyst surface can be *in situ* controlled via the applied potential U_{WR} and thus electrochemical promotion is, simply, catalysis in the presence of an electrochemically controllable double layer at the catalyst/gas interface (21).

The effective double layer affects the binding strength of chemisorbed reactants and reaction intermediates and thus affects the catalytic rate in a very pronounced and reversible manner.

It should be noted that in general in electrochemistry (20, 21, 48) one has

$$e\Delta U_{\mathrm{WR}} = -\Delta\bar{\mu}(= -\Delta E_{\mathrm{F}}) = \Delta\Phi + e\Delta\Psi, \qquad [2]$$

where $\bar{\mu}$ is the electrochemical potential of electrons in the catalyst electrode, $E_{\mathrm{F}}(=\bar{\mu})$ is the Fermi level of the catalyst-electrode, and Ψ is the outer (Volta) potential of the metal catalyst-electrode in the gas outside the metal/gas interface. The latter vanishes ($\Psi = 0$, $\Delta\psi = 0$) when no *net* charge resides at the metal/gas interface (30, 31, 33). This is the case when an "effective" double layer is present at the metal/gas interface (21, 30, 31, 33), which as every double layer is overall neutral, and thus in this case Eq. [2] reduces to the experimental equation [1]. At the molecular level the stability of the effective double layer and thus the validity of Eq. [1] require that the migration (backspillover) of the promoting ion ($O^{\delta-}$, $Na^{\delta+}$) is fast relative to its desorption or catalytic consumption (31, 49–51). When this condition is not met (e.g., high T or nonporous electrodes) or also when the limits of zero or saturation coverage of the promoting ion are reached (at very positive or negative ΔU_{WR}) then deviations from Eq. [1] are observed (31, 49–52) and only Eq. [2] is satisfied.

It is important to note that a change in Ψ (corresponding to the introduction of a net charge at the metal/gas interface) does not cause any measurable change in catalytic rates (21, 53) as also confirmed by introducing $e\Delta\Psi$ (thus $(-\Delta\bar{\mu})$ changes of up to 10^4 eV via a van de Graaf machine on metal catalysts interfaced with solid electrolytes and observing no change in catalytic rate (21)). This is due to the very small charge density (surface coverage 10^{-7}–10^{-9}) required to induce large changes in the outer potential Ψ of metal particles of micrometer dimensions (53). Thus it is the change, $\Delta\Phi$, in work function and not the change $-\Delta\bar{\mu}$ in Fermi level that is relevant for describing electrochemical promotion (21, 53) as experimentally observed (9–21). Thus even when Eq. [1] is not satisfied for the reasons outlined above and the more general Eq. [2] is fulfilled one must keep in mind that only the change $\Delta\Phi$ (and not the $e\Delta\Psi$ term) is relevant to promotion and catalysis as only $\Delta\Phi$ corresponds to a measurable change in the coverage of the promoting ions at the metal/gas interface.

Similarities and Differences between Electrochemical and Classic Promotion

It should be noted that once the backspillover species originating from the solid electrolyte have migrated at the metal/gas interface, they act as normal (chemical) promoters for catalytic reactions. For example, Lambert and coworkers via elegant use of XPS (35) have shown that the state of sodium introduced via evaporation on a Pt surface interfaced with β''-Al_2O_3 is indistinguishable from $Na^{\delta+}$ introduced on the same Pt surface via negative (cathodic) potential application.

Thus the only real difference between electrochemical and classic promotion is that in the former case one can control *in situ* the amount of promoter on the catalyst surface. This implies that if the promoting species has a short lifetime (e.g., 10–10^3 s) on the catalyst surface (e.g., O^{2-} originating from YSZ) (16–21) it can still be used as a promoter since its coverage on the catalyst surface can be fixed by appropriate setting of the potential U_{WR}. The promoting $O^{\delta-}$ species is thus replenished on the catalyst surface at a rate $I/2F$, where I is the applied current and F is Faraday's constant. Thus the promoting species is generated at the three-phase boundary (tpb) catalyst–solid electrolyte–gas in an electrocatalytic (faradaic) process. At steady state the promoting species, which migrates (backspillovers) at the metal/gas interface, is consumed there at a rate $I/2F$. It therefore acts as a sacrificial promoter (20, 21, 46, 54–56). The difference between electrochemical and classic promotion is thus operational and not functional.

Despite the functional identity of classic and electrochemical promotion, the usefulness of the latter is not to be deemphasized. For example, more than 50 electrochemical promotion studies using YSZ or TiO_2 as the promoter donor on Pt, Rh, Pd, Ag, IrO_2, RuO_2, Au, and Ni surfaces (16–21) have revealed the great importance of $O^{\delta-}$ (probably O^{2-}) as an extremely effective promoting species for most catalytic oxidations. This promoting species was hitherto unknown from classic (chemical) promotion studies since its controlled formation on a metal surface without using an O^{2-}-conducting solid electrolyte is very difficult experimentally and, most importantly, because its lifetime, τ, on a metal catalyst surface under real oxidation reaction conditions at atmospheric pressure is typically 50–500 s (16–21), i.e., too short for any realistic practical catalyst application unless it is continuously replenished on the catalyst surface, as is the case in electrochemical promotion (NEMCA) studies using O^{2-} conductors (Fig. 4).

Another important operational advantage of electrochemical promotion is the direct possibility of controlling *in situ* the coverage of the promoting species on the catalyst surface (via current, I, or potential, U_{WR}, control) (Table 1). This allows for direct examination of the effect of promoter coverage and of Φ on the catalytic reaction kinetics. Such examples are shown in Figs. 5 and 6 (57–64) for the four main types of experimentally observed catalytic rate, r, versus work function, Φ, dependence:

1. Electrophobic $(\partial r/\partial\Phi)_{p_{\mathrm{A}},p_{\mathrm{D}}} > 0$.

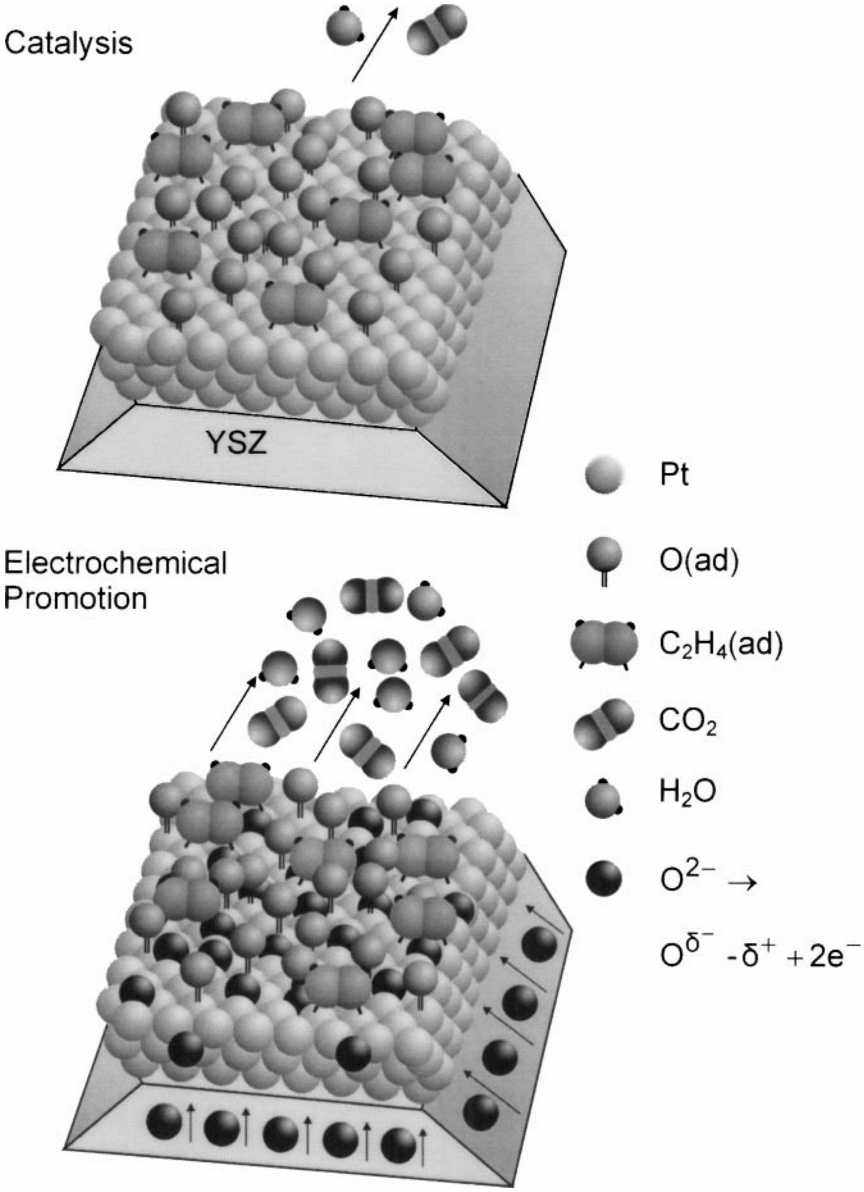

FIG. 4. Atomic visualization of electrochemical promotion (NEMCA) when using an O^{2-} conductor during C_2H_4 oxidation on Pt. The O^{2-} ions form $O^{\delta-}$–δ^+ backspillover dipoles which migrate (backspillover) at the metal/gas interface, forming an effective double layer which weakens the Pt=O bond and strengthens the Pt–C_2H_4 bond, thus enhancing catalytic activity. The lifetime of $O^{\delta-}$–δ^+ on the catalyst surface is Λ times longer than the lifetime of Pt=O (18, 20).

2. Electrophilic $(\partial r/\partial \Phi)_{p_A, p_D} < 0$.
3. Volcano type (r exhibits a maximum with respect to Φ).
4. Inverted volcano type (r exhibits a minimum with respect to Φ).

Thus although the rules presented here are applicable to both classic (Fig. 6, Refs. (61–64)) and electrochemical (Fig. 5, Refs. (57–60)) promotion, their extraction became possible only due to the systematic r versus Φ (as well as r vs p_A and r vs p_D at constant Φ) studies that electrochemical promotion enables one to perform efficiently and reversibly.

The goal of this work is (a) to classify previous electrochemical and classic promotion studies on the basis of the catalytic rate dependence on work function, Φ, or, equivalently, on coverage of the electropositive (electron donor) or electronegative (electron acceptor) promoter species in the four main categories shown in Figs. 5 and 6, and (b) to derive and rationalize the rules that govern which type of r versus Φ dependence a given catalytic reaction obeys.

TABLE 1

Relationship between Classic (Chemical) and Electrochemical Promotion

	Chemical promotion	Electrochemical promotion
Control variables	(Initial) promoter coverage θ_{P}	Catalyst potential U_{WR} or Fermi level E_{F} ($e\Delta U_{\mathrm{WR}} = -\Delta E_{\mathrm{F}}$) Rate, I/nF, of promoter supply to catalyst surface
Effect	Change in catalytic rate r Change in work function Φ Change in adsorption enthalpies $\lvert\Delta H_j\rvert$	
Action	Addition of electronegative promoter	Increase in U_{WR} Decrease in E_{F}
Result	$\Delta r > 0$: Electrophobic reactions $\Delta r < 0$: Electrophilic reactions $\Delta\Phi > 0$ $\Delta\lvert\Delta H_j\rvert > 0$: Electron donor adsorbates (D) $\Delta\lvert\Delta H_j\rvert < 0$: Electron acceptor adsorbates (A)	
Action	Addition of electropositive promoter	Decrease in U_{WR} Increase in E_{F}
Result	$\Delta r < 0$: Electrophobic reactions $\Delta r > 0$: Electrophilic reactions $\Delta\Phi < 0$ $\Delta\lvert\Delta H_j\rvert < 0$: Electron donor adsorbates (D) $\Delta\lvert\Delta H_j\rvert > 0$: Electron acceptor adsorbates (A)	

RESULTS AND DISCUSSION

1. Classification of Electrochemically and Classically Promoted Catalytic Reactions

Definitions and Some General Characteristics

The magnitude of electrochemical promotion for a given catalytic reaction is described in the literature (16–21) by three parameters:

1. The Faradaic efficiency, Λ, is defined by

$$\Lambda = (r - r_0)/(I/nF), \qquad [3]$$

where r is the electrochemically promoted catalytic rate, r_0 is the unpromoted (open-circuit) catalytic rate, I is the applied current, n is the charge of the promoting ion, and F (96,460 C/mol) is Faraday's constant. A reaction is electrochemically promoted when $|\Lambda| > 1$. For $|\Lambda| \leq 1$ one has electrocatalysis.

Values of Λ as high as 3×10^5 (11, 20) or as low as -3×10^4 (20) have been measured (Table 2). For oxidation reactions $\Lambda > 1$ implies electrophobic behavior $(\partial r/\partial\Phi) > 0$ and $\Lambda < -1$ implies electrophilic behavior $(\partial r/\partial\Phi < 0)$. For hydrogenation reactions using proton conductors the definitions are inverted, since proton supply to the catalyst corresponds to $I < 0$ and pure electrocatalysis must always correspond to $\Lambda = 1$ (65).

For oxidation reactions on metals supported on O^{2-} conductors, Λ also expresses the ratio of the lifetimes of the promoting O^{2-} species and of normally chemisorbed O on the catalyst surface (20, 21).

2. The rate enhancement ratio, ρ, is defined by

$$\rho = r/r_0. \qquad [4]$$

Values of ρ as high as 150 (66) or as low as zero (14) (complete catalyst poisoning) have been measured.

3. The promotional index PI_i of promoting species, i (e.g., $O^{\delta-}$, $Na^{\delta+}$), is defined by

$$\mathrm{PI}_i = \frac{\Delta r/r_0}{\Delta\theta_i}, \qquad [5]$$

where Δr is the promotionally induced rate enhancement $(r - r_0)$, and θ_i is the coverage of the promoting species on the catalyst surface. $\mathrm{PI}_i > 0$ corresponds to promotion; $\mathrm{PI}_i < 0$ corresponds to poisoning. Values of $\mathrm{PI}_{\mathrm{Na}^+}$ up to 6000 and of $\mathrm{PI}_{\mathrm{O}^{2-}}$ up to 100 have been measured (Table 2).

It should be noted that while Λ is a parameter relevant to electrochemical promotion (and to metal–support interactions (26, 27)) the other two parameters, ρ and PI_i, are relevant to both electrochemical and classic promotion.

Since the early days of electrochemical promotion (10, 11) it has been shown both experimentally and theoretically (16) that the order of magnitude of $|\Lambda|$, i.e., of the absolute value of Λ, for a given catalytic reaction, metal, and solid electrolyte can be estimated from

$$|\Lambda| \approx 2Fr_0/I_0, \qquad [6]$$

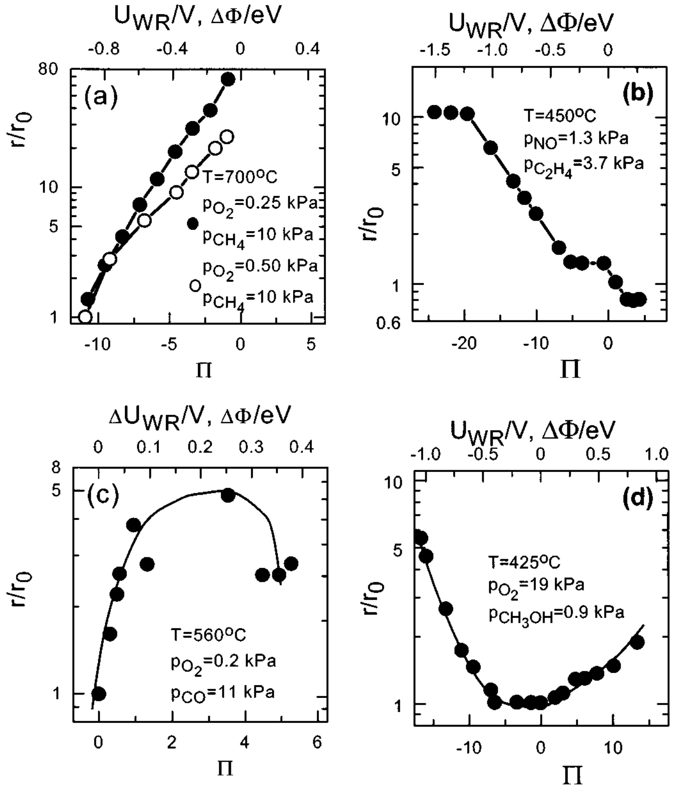

FIG. 5. Examples of the four types of electrochemical promotion behavior: (a) purely electrophobic, (b) purely electrophilic, (c) volcano type, (d) inverted volcano type. Effect of catalyst potential U_{WR}, work function Φ, change (vs $I=0$), and dimensionless catalyst potential $\Pi = F\Delta U_{\mathrm{WR}}/RT$ on the rates of: (a) CH_4 oxidation on Pt films deposited on YSZ for high (20 : 1 and 40 : 1) CH_4-to-O_2 feed ratios (57); (b) NO reduction by C_2H_4 on Pt films deposited on YSZ (58); (c) CO oxidation on Pt films deposited on YSZ (20); and (d) CH_3OH oxidative dehydrogenation to H_2CO on Pt films deposited on YSZ (18, 20).

where I_0 is the exchange current of the metal–solid electrolyte interface, measurable via $\ln I - \Delta U_{\mathrm{WR}}$ (Tafel) plots (16, 20). However, to date, no predictions whatsoever could be made about the sign of Λ or about the magnitude of ρ and PI_i. This is because Eq. [6] basically reflects that electrochemical promotion is due to electrochemical introduction of promoters on a catalyst surface (16), while the sign of Λ and the magnitude of ρ and PI_i refer to the purely fundamental aspects of promotion itself.

The prediction of the sign of Λ for any given catalytic reaction is one of the main goals of the present work while the estimation of the magnitude of ρ and PI_i is presented elsewhere (21, 67).

Reaction Classification

Table 2 (8–21, 29, 38, 53, 57–60, 65–109) classifies practically all hitherto published electrochemical promotion studies on the basis of the solid electrolyte support and corresponding promoting ion used. The table also provides the catalyst used, the operating temperature range, and the measured maximum ($\Lambda > 1$) or minimum ($\Lambda < -1$) Λ value, as well as the measured maximum ($\rho > 1$) or minimum ($\rho < 1$) ρ and the maximum measured PI_i value. Note that for the case of nonreacting promoters (e.g., Na^+) no Λ values are given in many cases as they are not very useful. They tend, in principle, to $\pm\infty$ at steady state. In practice $|\Lambda|$ is finite due to some unavoidable promoter evaporation and is usually larger than 10^5 (93).

Table 3 classifies again the published electrochemical promotion studies of Table 2, which include complete and partial oxidations, NO reduction studies, catalytic hydrogenations, dehydrogenations, and isomerizations. This table is focused on the purely catalytic (chemical) aspects of electrochemical promotion and provides three additional important parameters:

i. The range of p_A/p_D values used in the investigation, where p_A and p_D are the partial pressures of the electron acceptor (e.g., O_2) and electron donor (e.g., hydrocarbon) reactant used.

ii. The observed kinetic order (positive order, negative order, or zero order) of the catalytic reaction with respect to the electron donor (D) and the electron acceptor (A).

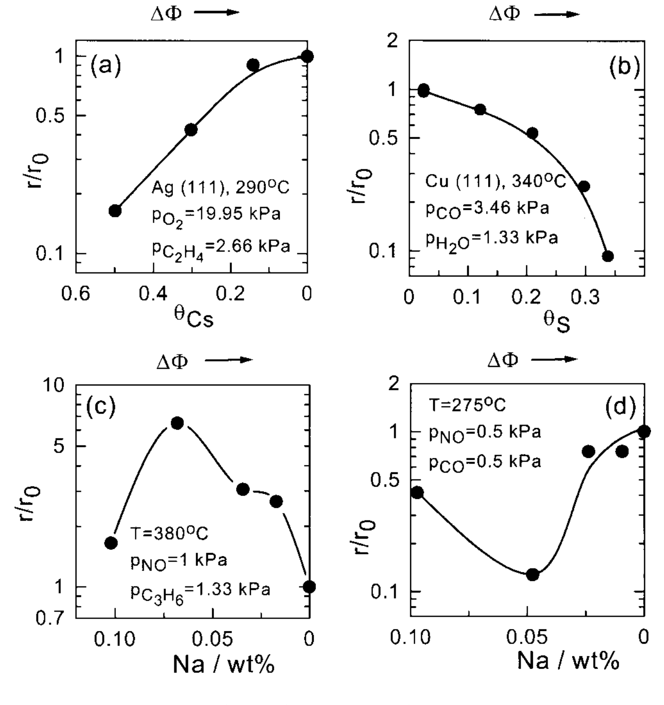

FIG. 6. Examples of the four types of classic promotion behavior: (a) purely electrophobic, (b) purely electrophilic, (c) volcano type, (d) inverted volcano type. Effect of decreasing electropositive (a,c,d) or increasing electronegative (b) promoter coverage and of concomitant $\Delta\Phi$ change on the rates of: (a) C_2H_4 epoxidation on Cs-promoted Ag(111) (61); (b) water–gas shift reaction on S-poisoned Cu(111) (2); (c) NO reduction by C_3H_6 on Na-promoted Pd supported on 8 mol% Y_2O_3-stabilized zirconia (YSZ) (54); and (d) NO reduction of CO on Na-promoted 0.5 wt% Rh supported on TiO_2 (4% WO_3) (64).

TABLE 2

Classification of Electrochemical Promotion (EP) Studies Based on the Type of Solid Electrolyte

1. EP studies using YSZ, promoting ion: O^{2-}

Reactants								
Electron donor (D)	Electron acceptor (A)	Product	Catalyst	T (°C)	Λ_{max} (>0) or Λ_{min} (<0)	ρ_{max} (>1) or ρ_{min} (<1)	$PI_{O^{2-}}$	Ref.
C_2H_4	O_2	CO_2	Pt	260–450	3×10^5	55	55	(11, 20)
C_2H_6	O_2	CO_2	Pt	270–500	300	20	20	(20, 68)
					−100	7	—	
CH_4	O_2	CO_2	Pt	600–750	5	70	70	(20, 57)
CO	O_2	CO_2	Pt	300–550	2×10^3	3	2	(20, 59)
					−500	6	—	
CO	O_2	CO_2	Pt	468–558	1000	5	5	(20, 69, 70)
CH_3OH	O_2	H_2CO,CO_2	Pt	300–500	1×10^4	$4{,}15^a$	3	(20, 60)
C_3H_6	O_2	CO_2	Pt	350–480	-3×10^3	6	—	(20, 71)
CH_3OH		H_2CO,CO, CH_4	Pt	400–500	−10	3^a	—	(18, 20, 60)
C_2H_4	NO	CO,CO_2, N_2, N_2O	Pt	380–500	−50	7	—	(58)
C_2H_4	O_2	CO_2	Rh	250–400	5×10^4	90	90	(20, 72)
H_2	CO_2	CH_4, CO	Rh	300–450	200	3^a	2	(20)
C_3H_6	NO, O_2	N_2,N_2O,CO_2	Rh	250–450	1×10^3	150^a	150	(66)
CO	NO, O_2	N_2,N_2O,CO_2	Rh	250–450	20	20^*	20	(73)
CO	O_2	CO_2	Pd	400–550	1×10^3	2	1	(18, 20)
H_2	CO	$C_xH_y,C_xH_yO_z$	Pd	300–370	10	3^a	2	(20)
H_2S		S_x, H_2	Pt	600–750	—	11	10	(20, 74)
CH_4	O_2	CO_2	Pd	380–440	2×10^3	90	90	(75)
H_2	CO_2	CO	Pd	500–590	−50	10	—	(18, 20)
CO	NO	CO_2,N_2,N_2O	Pd	320–480	−700	3	—	(76)
CO	N_2O	CO_2,N_2	Pd	440	−20	2	—	(76)
C_2H_4	O_2	C_2H_4O,CO_2	Ag	320–470	300	30^a	30	(8, 20, 53, 77, 78)
C_3H_6	O_2	C_3H_6O,CO_2	Ag	320–420	300	2^a	1	(20, 79)
CH_4	O_2	CO_2,C_2H_4, C_2H_6	Ag	650–850	5	30^a	30	(20, 80)
CO	O_2	CO_2	Ag	350–450	20	15	15	(20, 81)
CH_3OH		H_2CO, CO,CH_4	Ag	550–750	−25	6^a	—	(20, 82)
CH_3OH	O_2	H_2CO, CO_2	Ag	500	−95	2	—	(83)
CH_4	O_2	C_2H_4,C_2H_6, CO_2	Ag	700–750	−1.2	8^a	—	(20, 84, 85)
CO	O_2	CO_2	Ag–Pd	450–500	30	5	4	(86)
CH_4	H_2O	CO, CO_2	Ni	600–900	12	2^a	—	(20, 87)
CO	O_2	CO_2	Au	450–600	−60	3	—	(20, 84, 85)
CH_4	O_2	CO_2	Au	700–750	−3	3^a	—	(20, 84, 85)
C_2H_4	O_2	CO_2	IrO_2	350–400	200	6	5	(15, 20, 107)
C_2H_4	O_2	CO_2	RuO_2	240–500	4×10^3	115	115	(88)

2. EP studies using F^- conductors

Reactants									
Electron donor (D)	Electron acceptor (A)	Product	Catalyst	Solid electrolyte	T (°C)	Λ_{max} (>0) or Λ_{min} (<0)	ρ_{max} (>1) or ρ_{min} (<1)	PI_{F^-}	Ref.
CO	O_2	CO_2	Pt	CaF_2	500–700	200	2.5	1.5	(20, 89)

3. EP studies using mixed conductors

Reactants									
Electron donor (D)	Electron acceptor (A)	Product	Catalyst	Solid electrolyte	T (°C)	Λ_{max} (>0)or Λ_{min} (<0)	ρ_{max} (>1) or ρ_{min} (<1)	PI_{F^-}	Ref.
C_2H_4	O_2	CO_2	Pt	TiO_2 (TiO_x^+, O^{2-})	450–600	5×10^3	20	20	(20, 90)
C_2H_4	O_2	CO_2	Pt	CeO_2 (CeO_x^+, O^{2-})	500	-10^5	3	—	(91)
C_2H_4	O_2	CO_2	Pt	YZTi 10^b	400–475	−250	2	—	(92)
C_3H_6	O_2	CO_2	Pt	YZTi 10^b	400–500	1000 −1000	2.4	—	(92)

TABLE 2—*Continued*

4. EP studies using Na^+ conductors

Reactants									
Electron donor (D)	Electron acceptor (A)	Product	Catalyst	Solid electrolyte	T (°C)	Λ_{max} (>0) or Λ_{min} (<0)	ρ_{max} (>1) or ρ_{min} (<1)	PI_{Na^+}	Ref.
C_2H_4	O_2	CO_2	Pt	β''-Al_2O_3	180–300	5×10^4	0.25	−30	(20, 93)
CO	O_2	CO_2	Pt	β''-Al_2O_3	300–450	1×10^5	0.3	−30	(20, 29)
						-1×10^5	8	250	
H_2	C_6H_6	C_6H_{12}	Pt	β''-Al_2O_3	100–150	—	~0	−10	(14, 20, 44)
H_2	C_2H_2	C_2H_4, C_2H_6	Pt	β''-Al_2O_3	100–300	—	—*	—	(94)
C_2H_4	NO	CO_2, N_2, N_2O	Pt	β''-Al_2O_3	280–400	—	∞	500	(13, 20)
CO	NO	CO_2, N_2, N_2O	Pt	β''-Al_2O_3	320–400	—	13*	200	(95)
C_3H_6	NO	CO_2, N_2, N_2O	Pt	β''-Al_2O_3	375	—	10	—	(96)
H_2	NO	N_2, N_2O	Pt	β''-Al_2O_3	360–400	—	30	6000	(97)
H_2	C_2H_2, C_2H_4	C_2H_4 C_2H_6	Pd	β''-Al_2O_3	70–100	—	0.13	—	(98)
C_2H_4	O_2	C_2H_4O, CO_2	Ag	β''-Al_2O_3	240–280	—	—	40	(99)
CO	O_2	CO_2	Ag	β''-Al_2O_3	360–420	—	2	—	(20)
C_2H_4	O_2	CO_2	Pt	$Na_3Zr_2Si_2PO_{12}$	430	—	10	300	(100)

5. EP studies using K^+ conductors

Reactants									
Electron donor (D)	Electron acceptor (A)	Product	Catalyst	Solid electrolyte	T (°C)	Λ_{max} (>0) or Λ_{min} (<0)	ρ_{max} (>1) or ρ_{min} (<1)	PI_{K^+}	Ref.
NH_3		N_2, H_2	Fe	$K_2YZr(PO_4)_3$	500–700	—	4.5	—	(101)

6. EP studies using H^+ conductors

Reactants									
Electron donor (D)	Electron acceptor (A)	Product	Catalyst	Solid electrolyte	T (°C)	Λ_{max}(>0) or Λ_{min}(<0)	ρ_{max}(>1) or ρ_{min}(<1)	PI_{H^+}	Ref.
C_2H_4	O_2	CO_2	Pt	$CaZr_{0.9}In_{0.1}O_{3-a}$	385–470	-3×10^4	5	—	(102)
H_2	N_2	NH_3	Fe	$CaZr_{0.9}In_{0.1}O_{3-a}$	440	6	12	6	(65)
NH_3		N_2, H_2	Fe	$CaZr_{0.9}In_{0.1}O_{3-a}$	530–600	150	3.6	—	(101)
CH_4		C_2H_6, C_2H_4	Ag	$SrCe_{0.95}Yb_{0.05}O_3$	750	—	8*	10	(20, 103)
H_2	C_2H_4	C_2H_6	Ni	C_sHSO_4	150–170	300	2	12	(12, 20)
H_2	O_2	H_2O	Pt	Nafion	25	20	6	5	(20, 104)
1-C_4H_8		C_4H_{10}, 2-C_4H_8(*cis, trans*)	Pd	Nafion	70	−28	40*	—	(105)

7. EP studies using aqueous alkaline solutions

Reactants									
Electron donor (D)	Electron acceptor (A)	Product	Catalyst	Solid electrolyte	T (°C)	Λ_{max} (>0) or Λ_{min} (<0)	ρ_{max} (>1) or ρ_{min} (<1)	PI_{OH^-}	Ref.
H_2	O_2	H_2O	Pt	H_2O–0.1 N KOH	25–50	20	6	20	(20, 38)

8. EP studies utilizing molten salts

Reactants								
Electron donor (D)	Electron acceptor (A)	Product	Catalyst	Solid electrolyte	T (°C)	Λ_{max} (>0) or Λ_{min} (<0)	ρ_{max} (>1) or ρ_{min} (<1)	Ref.
SO_2	O_2	SO_3	Pt	V_2O_5–K_2SO_4	350–450	−100	6	(106)

[a] Change in product selectivity observed.

[b] 4.5 mol% Y_2O_3–10 mol% TiO_2–85.5 mol% ZrO_2.

iii. The observed global r versus work function Φ behavior, i.e., purely electrophobic $(\partial r/\partial \Phi) > 0$, purely electrophilic $(\partial r/\partial \Phi) < 0$, volcano type, and inverted volcano type. The term "global" denotes the behavior observed over the entire U_{WR} and thus Φ range investigated (typically from −1.5 to +1.5 eV vs open-circuit) as opposed to "local," which denotes the r versus Φ behavior at a specific U_{WR} and Φ value.

A reactant, j, is defined as electron acceptor (A) when it increases the work function of the surface, i.e.,

TABLE 3

Classification of Electrochemical Promotion Studies on the Basis of Global r versus Φ Behavior

A. Purely electrophobic reactions

Reactants						Kinetics $(\partial r/\partial p)_\Phi$			
(D)	(A)	Catalyst	Solid electrolyte	p_A/p_D	T (°C)	In D	In A	Rule	Ref.
C_2H_4	O_2	Pt	ZrO_2 (Y_2O_3)	12–16	260–450	+	0	G1	(11, 20)
C_2H_4	O_2	Pt	β''-Al_2O_3	238	180–300	+	0	G1	(20, 93)
C_2H_4	O_2	Pt	TiO_2	3.5–12	450–600	+	0	G1	(20, 90)
C_2H_4	O_2	Rh	ZrO_2 (Y_2O_3)	0.05–2.6	250–400	+	0	G1	(20, 72)
C_2H_4	O_2	Ag	ZrO_2 (Y_2O_3)	0.2–1.1	320–470	+	0	G1	(20, 78)
C_2H_4	O_2	IrO_2	ZrO_2 (Y_2O_3)	300	350–400	+	0	G1	(15, 20, 107)
C_2H_4	O_2	RuO_2	ZrO_2 (Y_2O_3)	155	240–500	+	≤0	G1	(88)
CO	O_2	Pt	CaF_2	11–17	500–700	+	0	G1	(20, 89)
CO	O_2	Pd	ZrO_2 (Y_2O_3)	500	400–550	?[a]	?	?	(18, 20)
CH_4	O_2	Pd	ZrO_2 (Y_2O_3)	0.2–4.8	380–440	+	0	G1	(75)
C_3H_6	O_2	Ag	ZrO_2 (Y_2O_3)	20–120	320–420	+	≤0	G1	(20, 79)
CH_4	O_2	Ag	ZrO_2 (Y_2O_3)	0.02–2	650–850	+	0	G1	(20, 80)
C_6H_6	H_2	Pt	β''-Al_2O_3	0.02–0.12	100–150	≥0	∼0	G1	(14, 20, 44)
C_2H_2	H_2	Pt	β''-Al_2O_3	1.7–9	100–300	?	?	?	(94)
H_2	CO_2	Rh	ZrO_2 (Y_2O_3)	0.03–0.7	300–450	+	0	G1	(20)
H_2	C_2H_2, C_2H_4	Pd	β''-Al_2O_3	0.1–5.9[b]	70–100	≥0	0	G1	(98)
H_2S	—	Pt	ZrO_2 (Y_2O_3)	—	600–750	?		?	(20, 74)
CH_4	—	Ag	$SrCe_{0.95}Yb_{0.05}O_3$	—	750	?		?	(20, 103)
NH_3	—	Fe	$CaZr_{0.9}In_{0.1}O_{3-a}$	4–12kPa	530–600	+		G1	(101)
NH_3	—	Fe	$K_2YZr(PO_4)_3$	4–12kPa	500–700	+		G1	(101)
CH_4	H_2O	Ni	ZrO_2 (Y_2O_3)	0.05–3.5	600–900	+	≤0	G1	(20, 87)

B. Purely electrophilic reactions

Reactants						Kinetics $(\partial r/\partial p)_\Phi$			
(D)	(A)	Catalyst	Solid electrolyte	p_A/p_D	T (°C)	In D	In A	Rule	Ref.
C_2H_4	O_2	Pt	$CaZr_{0.9}In_{0.1}O_{3-a}$	4.8	385–470	−	+	G2	(102)
C_2H_4	O_2	Pt	CeO_2	1.6–3.7	500	−	+	G2	(91)
C_2H_4	O_2	Pt	YZTi10	3	400–475	?	?	?	(92)
C_2H_4	O_2	Ag	β''-Al_2O_3	0.3–0.4	240–280	−	+	G2	(99)
CO	O_2	Ag	β''-Al_2O_3	0.1–10	360–420	0	+	G2	(20)
C_3H_6	O_2	Pt	ZrO_2 (Y_2O_3)	0.9–55	350–480	≤0	+	G2	(20, 71)
CH_3OH	O_2	Ag	ZrO_2 (Y_2O_3)	0–2	500	?	+	G2	(83)
CH_4	O_2	Au	ZrO_2 (Y_2O_3)	0.1–0.7	700–750	0	+	G2	(20, 84, 85)
H_2	N_2	Fe	$CaZr_{0.9}In_{0.1}O_{3-a}$	0–3	440	?	?	?	(65)
H_2	C_2H_4	Ni	$CsHSO_4$	1	150–170	?	?	?	(12, 20)
	CH_3OH	Pt	ZrO_2 (Y_2O_3)	—	400–500		?	?	(18, 20)
	CH_3OH	Ag	ZrO_2 (Y_2O_3)	0–6 kPa	550–750		+	G2	(20, 82)
C_2H_4	NO	Pt	ZrO_2 (Y_2O_3)	0.2–10	380–500	0	+	G2	(58)
C_2H_4	NO	Pt	β''-Al_2O_3	0.1–1.1	280–400	?	?	?	(13, 20)
CO	NO	Pt	β''-Al_2O_3	0.3–5	320–400	≤0	+	G2	(95)
CO	NO	Pd	ZrO_2 (Y_2O_3)	0.5–6.5	320–480	∼0	+	G2	(76, 108)
CO	N_2O	Pd	ZrO_2 (Y_2O_3)	2–50	440	−	+	G2	(76)
	1-C_4H_8	Pd	Nafion	—	70		?	G2	(105)

C. Volcano-type reactions

Reactants						Kinetics $(\partial r/\partial p)_\Phi$			
(D)	(A)	Catalyst	Solid electrolyte	p_A/p_D	T (°C)	In D	In A	Rule	Ref.
C_2H_4	O_2	Pt	$Na_3Zr_2Si_2PO_{12}$	1.3–3.8	430	−	+	G3	(100)
CO	O_2	Pt	ZrO_2 (Y_2O_3)	0.2–55	468–558	+	−	G3	(20)
CO	O_2	Pt	β''-Al_2O_3	0.5–20	300–450	−	+	G3	(20, 29)
H_2	O_2	Pt	H_2O–0.1 N KOH	0.3–3	25–50	+	−	G3	(20, 38)
H_2	O_2	Pt	Nafion	0.2–5	25	+	−	G3	(20, 104)
SO_2	O_2	Pt	V_2O_5–$K_2S_2O_7$	1.8	350–450	?	?	?	(106)
C_3H_6	NO	Pt	β''-Al_2O_3	2–70	375	−	+	G3	(96)
H_2	NO	Pt	β''-Al_2O_3	0.3–6	360–400	−	+	G3	(97)

TABLE 3—*Continued*

D. Inverted volcano-type reactions

Reactants						Kinetics $(\partial r/\partial p)_\Phi$			
(D)	(A)	Catalyst	Solid electrolyte	p_A/p_D	T (°C)	In D	In A	Rule	Ref.
C_2H_4	O_2	Pt	TiO_2	0.2–0.3^c	450–600	+	+	G4	(20, 90)
C_3H_6	O_2	Pt	YZTi10	5	400–500	?	?	?	(92)
CO	O_2	Ag	ZrO_2 (Y_2O_3)	0.6–14	350–450	+	+	G4	(20, 81)
CO	O_2	Ag–Pd alloy	ZrO_2 (Y_2O_3)	3.5–12.5	450–500	+	+	G4	(86)
CO	O_2	Au	ZrO_2 (Y_2O_3)	3–53	450–600	+	≥ 0	G4	(20, 84, 85)
C_2H_6	O_2	Pt	ZrO_2 (Y_2O_3)	0.06–7	270–500	+	+	G4	(20, 68)
CH_4	O_2	Pt	ZrO_2 (Y_2O_3)	0.02–7	600–750	+	+	G4	(20, 57)
CH_3OH	O_2	Pt	ZrO_2 (Y_2O_3)	3–45	300–500	+	?	?	(20, 60)
H_2	CO_2	Pd	ZrO_2 (Y_2O_3)	0.2–1.1	500–590	+	+	G4	(18, 20)
C_3H_6	NO, O_2	Rh	ZrO_2 (Y_2O_3)	0.08–8^d	250–450	+	NO: + O_2: 0	G4	(66)
CO	NO, O_2	Rh	ZrO_2 (Y_2O_3)	0.33^d	250–450	+	NO: + O_2 : 0	G4	(73)

[a] (?) No data available.

[b] $p_D = p_{C_2H_2} + p_{C_2H_4}$.

[c] Low p_A/p_D region.

[d] p_A/p_D is the ratio $p_{NO}/p_{C_3H_6}$ and p_{NO}/p_{CO}. The p_{O_2} range is 0–6 kPa.

$$\partial\Phi/\partial\theta_j)_{\theta_{i\neq j}} > 0, \qquad [7]$$

and as an electron donor (D) when it decreases the work function of the surface, i.e.,

$$\partial\Phi/\partial\theta_j)_{\theta_{i\neq j}} < 0. \qquad [8]$$

Table 3 shows that the global r versus Φ behavior can often change from one type to the other even for the same reaction and metal catalyst on changing the solid electrolyte support or the gaseous composition. No clear pattern regarding the r versus Φ behavior has been reported so far, except some limiting observations, e.g., that C_2H_4 oxidation is always electrophobic at very high p_A/p_D ($=p_{O_2}/p_{C_2H_4}$) ratios (109).

On classifying the reactions in this way (Table 3) several clear patterns and regularities appear.

2. Promotional Rules

The rules of electrochemical promotion follow directly from Table 3. For example, as shown in Table 3 all purely electrophobic reactions are positive order in D and zero or negative order in A. All purely electrophilic reactions are positive order in A and zero or negative order in D. Volcano-type reactions are always positive order in one reactant and purely negative order in the other. Inverted volcano-type reactions are positive order in both reactants.

Thus the following promotional rules can be formulated:

Electrophobic Reactions

Inspection of Table 3 shows the following rule for electrophobic reactions:

Rule G1: *A reaction exhibits purely electrophobic behavior* ($(\partial r/\partial\Phi)_{p_A,p_D} > 0$) *when the kinetics are positive order in the electron donor (D) reactant and negative or zero order in the electron acceptor (A) reactant.*

Table 3 lists 21 purely electrophobic reactions. Sufficient information (kinetics) exists for 17 cases. In all 17 cases rule G1 is confirmed. There are no exceptions. A typical example from the literature (11, 14) is shown in Fig. 7.

An equivalent formulation of rule G1 is the following:

Rule G1′: *A reaction exhibits purely electrophobic behavior* ($(\partial r/\partial\Phi)_{p_A,p_D} > 0$) *when the electron acceptor reactant (A) is strongly adsorbed and much more strongly adsorbed on the catalyst surface than the electron donor reactant (D).*

In the context of adsorption equilibrium constants k_A and k_D, the latter can be expressed simply as

$$k_A p_A \gg 1 \quad \text{and} \quad k_A p_A \gg k_D p_D \Rightarrow (\partial r/\partial\Phi)_{p_A,p_D} > 0, \qquad [9]$$

where k_A and k_D are the adsorption equilibrium constants of A and D on the catalyst surface. The dependence of k_A and k_D on work function Φ is discussed elsewhere (21, 67).

Electrophilic Reactions

Inspection of Table 3 shows the following rule for electrophilic reactions:

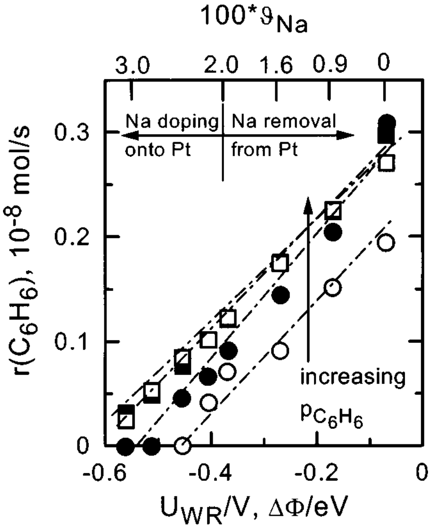

FIG. 7. Example of rule G1 (electrophobic behavior): Effect of Na coverage and concomitant work function change on the rate of C_6H_6 hydrogenation on Pt deposited on β''-Al_2O_3 (44). Note that the rate is positive order in C_6H_6 (D). It is also near zero order in H_2 (44).

Rule G2: *A reaction exhibits purely electrophilic behavior* $((\partial r/\partial\Phi)_{p_A,p_D} < 0)$ *when the kinetics are positive order in the electron acceptor (A) reactant and negative or zero order in the electron donor (D) reactant.*

Table 3 lists 18 purely electrophilic reactions. Sufficient information (kinetics) exist in 13 cases. In all 13 cases rule G2 is confirmed. There are no exceptions. A typical example from the electrochemical promotion literature (102) is shown in Fig. 8.

An equivalent formulation of rule G2 is the following:

Rule G2′: *A reaction exhibits purely electrophilic behavior* $((\partial r/\partial\Phi)_{p_A,p_D} < 0)$ *when the electron donor reactant (D) is strongly adsorbed and much more strongly adsorbed on the catalyst surface than the electron acceptor reactant (A).*

In the context of adsorption equilibrium constants the latter can be expressed simply as

$$1 \ll k_D p_D \quad \text{and} \quad k_A p_A \ll k_D p_D \Rightarrow (\partial r/\partial\Phi)_{p_A,p_D} < 0. \tag{10}$$

Volcano-Type Reactions

Inspection of Table 3 shows the following rule for volcano-type reactions:

Rule G3: *A reaction exhibits volcano-type (maximum type) behavior with respect to* Φ *when the kinetics also exhibit a maximum with respect to A (at fixed* p_D*) and D (at fixed* p_A*) so that the rate is always positive order in A or D and at the same time negative (not zero) order in D or A, respectively.*

Thus the following equivalent rule is derived:

Rule G3′: *A reaction exhibits volcano-type behavior when both the electron donor D and electron acceptor A are strongly adsorbed on the catalyst surface.*

Table 3 lists eight volcano-type reactions. Sufficient information (kinetics) exists in seven cases. In all seven cases rule G3 is confirmed. There are no exceptions. A typical example from the literature (38) is shown in Fig. 9.

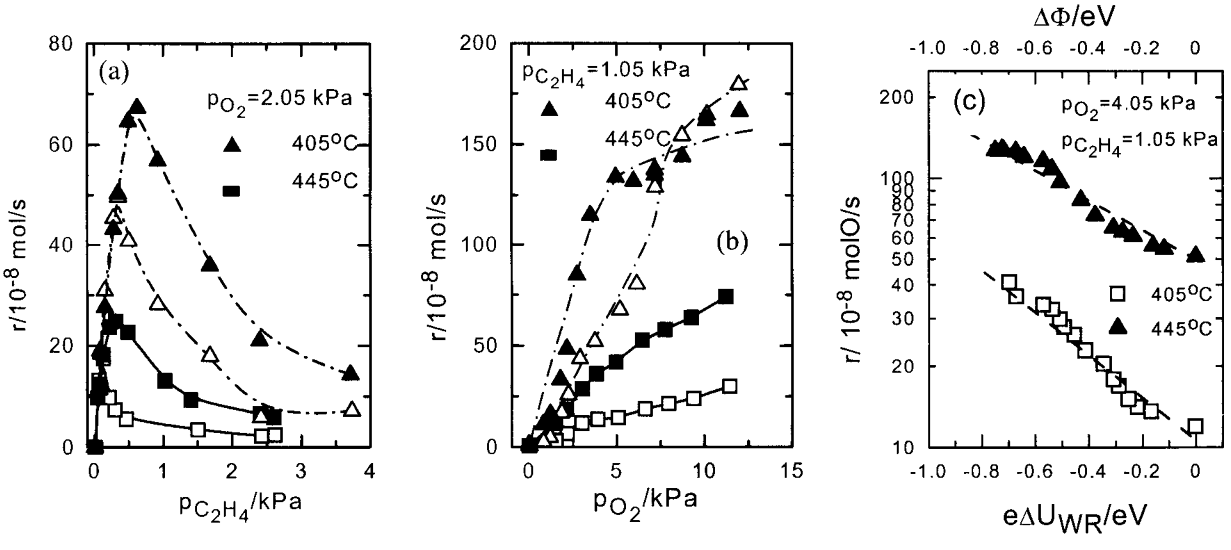

FIG. 8. Example of rule G2 (electrophilic behavior): Effect of $p_{C_2H_4}(=p_D)$ (a), p_{O_2} $(=p_A)$ (b), and $\Delta\Phi$ (c) on the rate of C_2H_4 oxidation on Pt films interfaced with $CaZr_{0.9}In_{0.1}O_{3-\alpha}$, a H^+ conductor (102). Note that (c) is obtained under gaseous composition where the rate is positive order in O_2 and negative order in C_2H_4 (a,b).

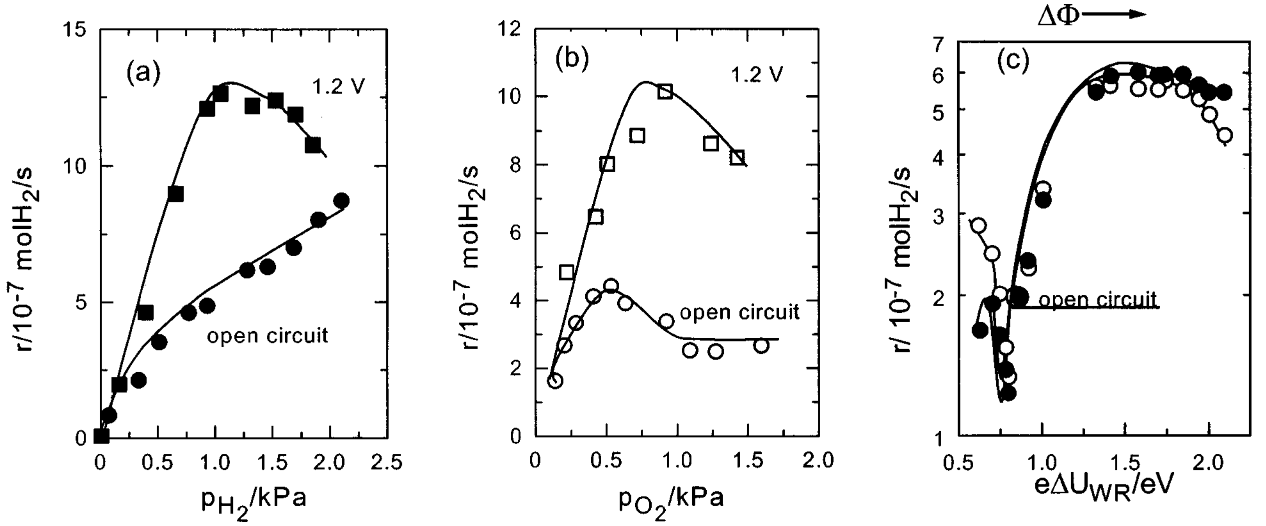

FIG. 9. Example of rule G3 (volcano-type behavior): Effect of $p_{H_2}(=p_D)$ (a), $p_{O_2}(=p_A)$ (b), and potential U_{WR} and $\Delta\Phi$ (c) on the rate of H_2 oxidation on Pt/graphite in aqueous 0.1 M KOH solutions (38). Note that under the p_{H_2}, p_{O_2} conditions of (c) the open-circuit rate is positive order in H_2 (a) and negative order in O_2 (b) and that the orders are reversed with the applied positive potential (U_{WR} = 1.2 V). At this potential the rate passes through its maximum (volcano) value (c).

In the context of adsorption equilibrium constants the latter can be expressed as

$$k_A p_A, k_D p_D \gg 1 \Rightarrow \begin{cases} (\partial r/\partial\Phi)_{p_A,p_D} > 0, & \Phi < \Phi_M, \\ (\partial r/\partial\Phi)_{p_A,p_D} = 0, & \Phi = \Phi_M, \\ (\partial r/\partial\Phi)_{p_A,p_D} < 0, & \Phi > \Phi_M, \end{cases} \qquad [11]$$

where Φ_M is the work function value at the rate maximum (volcano maximum).

Inverted Volcano (Minimum)-Type Reactions

Inspection of Table 3 shows the following rule for inverted volcano-type reactions:

Rule G4: *A reaction exhibits inverted volcano (minimum rate) type behavior when the kinetics are positive order in both the electron acceptor (A) and electron donor (D) reactant.*

Table 3 lists 11 inverted volcano reactions. Sufficient information (kinetics) exists in 9 cases. In all 9 cases rule G4 is confirmed. There are no exceptions. A typical example from the literature (81) is shown in Fig. 10.

An equivalent formulation of rule G4 is the following:

Rule G4′: *A reaction exhibits inverted volcano-type behaviour when both the electron donor D and the electron acceptor A are weakly adsorbed on the catalyst surface.*

In the context of adsorption equilibrium constants, rule G4′ can be expressed as

$$k_A p_A, k_D p_D \ll 1 \Rightarrow \begin{cases} (\partial r/\partial\Phi)_{p_A,p_D} < 0, & \Phi < \Phi_m, \\ (\partial r/\partial\Phi)_{p_A,p_D} = 0, & \Phi = \Phi_m, \\ (\partial r/\partial\Phi)_{p_A,p_D} > 0, & \Phi > \Phi_m, \end{cases} \qquad [12]$$

where Φ_m is the work function value at the rate minimum.

More Complex Examples

The excellent agreement between the above rules and the classic and electrochemical promotion literature can also be appreciated from Figs. 11 to 13 which show some more complex examples that nevertheless can be fully described by the above rules:

Figure 11 refers to C_2H_4 oxidation on Pt/TiO_2 (90). The kinetics change dramatically with potential (Figs. 11a, 11b). For high potential U_{WR} and thus Φ values the rate is positive order in O_2 (A) and negative order in C_2H_4 (D). For low Φ values the rate is positive order in C_2H_4 (D) and even becomes negative order in O_2 (A) for high p_{O_2} values (Fig. 11b). But in all cases the above rules G1 to G4 apply. For example for low $p_{O_2}(=p_A)$ to $p_{C_2H_4}(=p_D)$ ratios (e.g., $p_{O_2} = 1.45$ kPa, $p_{C_2H_4} = 5.6$ kPa) the open-circuit rate is positive order both in A and in D (Figs. 11a, 11b); thus inverted volcano behavior is obtained, according to rule G4, (Fig. 11d). For high $p_{O_2}(=p_A)$ to $p_{C_2H_4}(=p_D)$ ratios (e.g., $p_{O_2} = 1.45$ kPa, $p_{C_2H_4} = 0.6$ kPa) the open-circuit rate becomes near zero order in O_2 (=A) and positive order in C_2H_4(=D) (Figs. 11a, 11b); thus purely electrophobic behavior is obtained (rule G1, Fig. 11c).

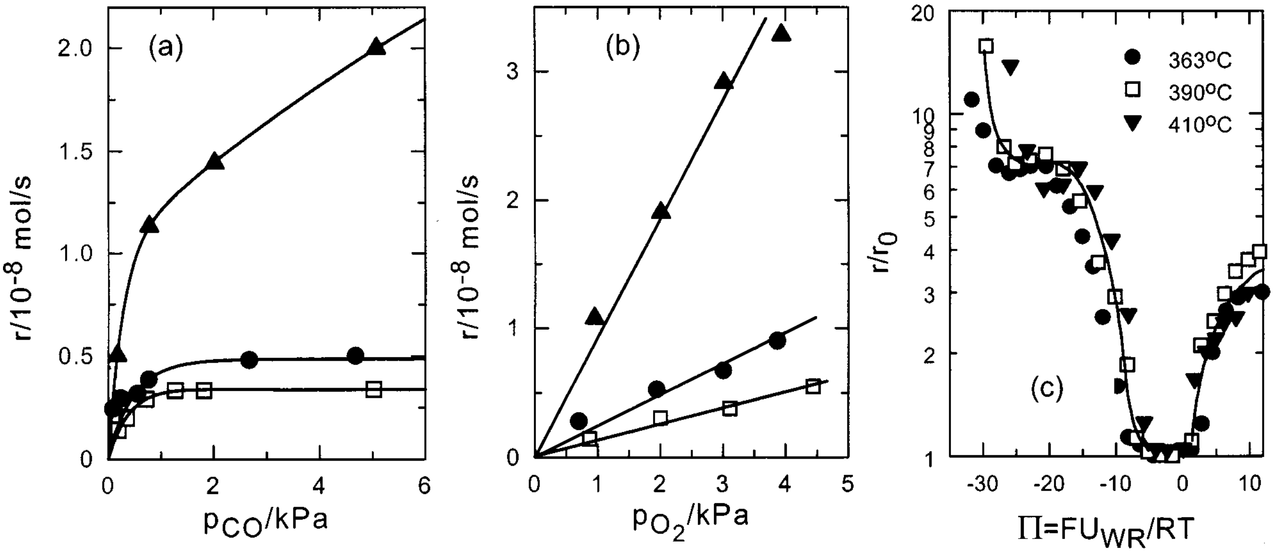

FIG. 10. Example of rule G4 (inverted volcano-type behavior): Effect of p_{CO} $(=p_{\mathrm{D}})$ (a), $p_{\mathrm{O_2}}(=p_{\mathrm{A}})$ (b), and $\Delta\Phi$ and dimensionless catalyst potential Π $(=FU_{\mathrm{WR}}/RT)$ (c) on the rate of CO oxidation on Ag films deposited on YSZ (81). $T = 415$°C. (a) $p_{\mathrm{O_2}} = 3$ kPa: □, open-circuit; ●, $U_{\mathrm{WR}} = 475$ mV; ▲, $U_{\mathrm{WR}} = -1300$ mV. (b) $p_{\mathrm{CO}} = 5$ kPa: □, open-circuit; ●, $U_{\mathrm{WR}} = 475$ mV; ▲, $U_{\mathrm{WR}} = -1300$ mV. (c) $p_{\mathrm{O_2}} = 3$ kPa, $p_{\mathrm{CO}} = 5$ kPa: ●, $T = 363$°C, $r_0 = 2.7$ nmol O/s; □, $T = 390$°C; ▼, $r_0 = 3.4$ nmol O/s; ▽, $T = 410$°C, $r_0 = 5.5$ nmol O/s.

Figure 12 comes from the classic promotion literature and refers to CO oxidation on Pt(111) promoted with Li(110). As with every alkali promoter, decreasing Li content on the catalyst surface corresponds to increasing Φ (21, 111). Here O_2 is the electron acceptor (A) and CO plays the role of the electron donor (D). For low $p_{\mathrm{CO}}/p_{\mathrm{O_2}}(=p_{\mathrm{D}}/p_{\mathrm{A}})$ ratios where the rate is positive order in CO the rate is dramatically enhanced with increasing Φ, i.e., with decreasing Li coverage (Figs. 12a, 12b; rule G1). For high $p_{\mathrm{CO}}/p_{\mathrm{O_2}}$ ratios, where the rate is negative order in CO, electrophilic behavior is observed for low Li coverages (Figs. 12a, 12b; rule G2).

The behavior is qualitatively similar for CO oxidation on Pt deposited on β''-$\mathrm{Al_2O_3}$, a $\mathrm{Na^+}$ conductor and promoter donor, as shown in Fig. 13 which comes from the electrochemical promotion literature (29). Here when the rate is negative order in CO(=D) electrophilic behavior $(\partial r/\partial\Phi < 0)$ is obtained (Fig. 13, rule G2). When the rate is positive order in CO, weak electrophobic behavior is observed (Fig. 13, rule G1). Note that the rate exhibits volcano-type behavior with respect to both Φ and p_{CO} (rule G3).

Connection between Φ and Adsorbate Coverage

The work function Φ can be directly related to the coverage, θ_i, of the promoting ion via the Helmholtz equation (20, 112)

$$\Delta\Phi = \frac{eN_{\mathrm{M}}}{\varepsilon_0} P_i \Delta\theta_i, \qquad [13]$$

where e is the unit electron charge (1.6×10^{-19} C/atom), N_{M} is the surface atom density of the catalyst surface (atom/m^2), $\varepsilon_0 = 8.85 \times 10^{-12}$ $\mathrm{C^2/J \cdot m}$, and P_i $(\mathrm{C \cdot m})$ is the dipole moment of the promoting species i. Typically P_i is of the order of 1–5 D (1 D (Debye) $= 3.36 \times 10^{-30}$ $\mathrm{C \cdot m}$).

In general P_i is coverage-dependent and also the Helmholtz equation has to be written in its general form

$$\Delta\Phi = \frac{eN_{\mathrm{M}}}{\varepsilon_0} \sum_j P_j \Delta\theta_j, \qquad [14]$$

where the summation extends over all adsorbed reactants, intermediates, and promoters. This is because when the coverage, θ_i, of a promoting species, i, is varied in an electrochemical (or classical) promotion experiment, it is reasonable to expect that the coverages of coadsorbed reactants, $\theta_{j \neq i}$, will also change. Since, however, the dipole moment, P_i, of electropositive $(P_i < 0)$ or electronegative $(P_i > 0)$ promoters, such as $\mathrm{Na^{\delta+}}$ and $\mathrm{O^{2-}}$, is typically a factor of 5 larger than the dipole moments of more covalently adsorbed reactants and intermediates (112–115), experiment has shown that Equation [13] rather than its more general form [14] can be used to a good approximation (20, 29, 115).

This enables one to formulate the above promotional rules G1 to G4 (Eqs. [9] to [12]) also in terms of promoter coverage by simply replacing $\partial\Phi$ by $\partial\theta_i$ (for electronegative promoters i) and by $-\partial\theta_i$ (for electropositive promoters i).

Local Promotional Rules

When examining the rate dependence on Φ at any specific work function Φ value, two possibilities exist:

$$(\partial r/\partial\Phi)_{p_{\mathrm{A}},p_{\mathrm{D}}} > 0 \text{ (electrophobic behavior)}, \qquad [15]$$

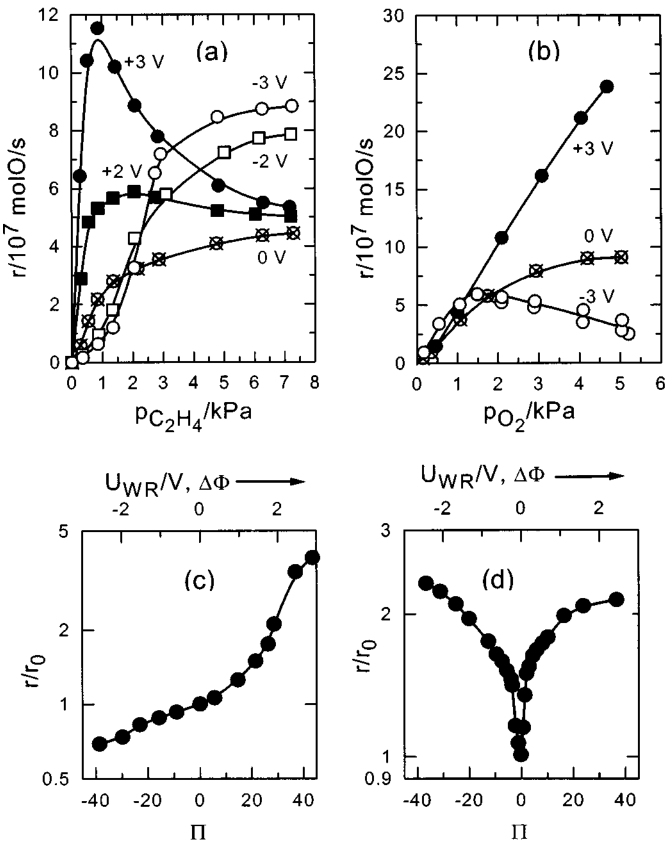

FIG. 11. Example of rules G1 and G4: Effect of $p_{C_2H_4}$ ($=p_D$) (a), p_{O_2}($=p_A$) (b), and $\Delta\Phi$ and Π ($=FU_{WR}/RT$) (c), on the rate of C_2H_4 oxidation on Pt films deposited on TiO_2 (90). Numbers (in V) refer to ΔU_{WR}, which is a factor of 10 larger than $\Delta\Phi$ (82). (a) $p_{O_2} = 1.45$ kPa; ●, +3 V; ■, +2 V; ⊗, open-circuit; □, −2 V; ○, −3 V. (b) $p_{CO} = 3$ kPa; ●, +3 V; ⊗, open-circuit; ○, −3 V. (c, left) $p_{C_2H_4} = 0.6$ kPa; $p_{O_2} = 1.45$ kPa, rule G1; (c, right) $p_{C_2H_4} = 5.6$ kPa, $p_{O_2} = 1.45$ kPa, rule G4.

$$(\partial r/\partial\Phi)_{p_A,p_D} < 0 \text{ (electrophilic behavior).} \qquad [16]$$

On the basis of the above global promotional rules the following two very simple local (L) rules can be directly derived:

Rule L1: *When the electron acceptor reactant (A) is more strongly adsorbed than the electron donor reactant (D) then the reaction exhibits local electrophobic behavior.*

Mathematically this is expressed as

$$k_A p_A \gg k_D p_D \Rightarrow (\partial r/\partial\Phi)_{p_A,p_D} > 0. \qquad [17]$$

Rule L2: *When the electron acceptor reactant (A) is more weakly adsorbed than the electron donor reactant (D) then the reaction exhibits local electrophilic behavior.*

Mathematically this is expressed as

$$k_A p_A \ll k_D p_D \Rightarrow (\partial r/\partial\Phi)_{p_A,p_D} < 0. \qquad [18]$$

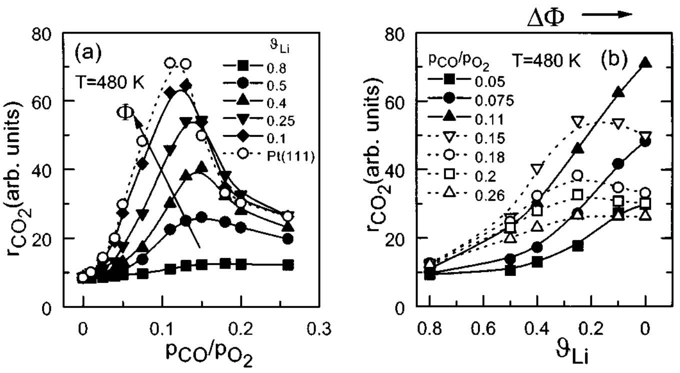

FIG. 12. Examples of rules G1, G2, and G3. Effect of p_{CO}/p_{O_2} ($=p_D/p_A$) and of Li coverage on the rate of CO oxidation on Pt(111). Note that $\partial r/\partial\Phi$ always traces $\partial r/\partial p_{CO}$ (a) and that volcano-type r versus Φ dependence is obtained for high p_{CO}/p_{O_2} ratios (b) where the rate shifts to negative order in CO (rule G3). Based on the data of Ref. (110).

The local rules L1 and L2 can also be expressed in the following equivalent way:

Rule L1′: *When the rate is negative or zero order in the electron acceptor A and positive order in the electron donor D then the reaction exhibits electrophobic behavior.*

Rule L2′: *When the rate is positive order in the electron acceptor A and negative or zero order in the electron donor D then the reaction exhibits electrophilic behavior.*

Rules L1 and L2 (or L1′ and L2′) are exemplified in Table 3 and Figs. 7 to 13.

It is also clear that the global promotional rules G1 to G3 stem directly from rules L1 and L2, so that if rules L1 and L2 can be rationalized at the molecular level, then rules G1 to G3 can also be rationalized.

Before proceeding with this rationalization at the molecular level we first present a direct mathematical

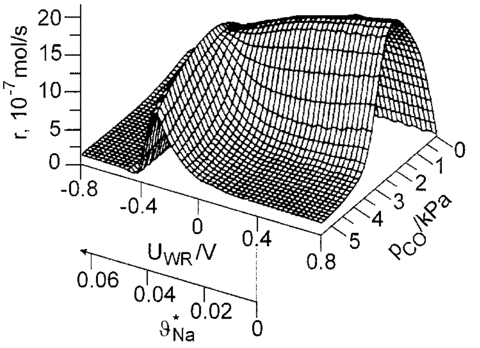

FIG. 13. Examples of rules G1, G2, and G3: Effect of p_{CO} ($=p_D$) and of Na coverage and corresponding U_{WR} value on the rate of CO oxidation on Pt films deposited on β''-Al_2O_3 at fixed $p_{O_2} = 6$ kPa (29). Note that $\partial r/\partial\Phi$ always traces $\partial r/\partial p_{CO}$ for negative, positive, and zero (volcano peak) values.

consequence of rules L1′ and L2′:

$$\left(\frac{\partial r}{\partial \Phi}\right)_{p_\mathrm{A},p_\mathrm{D}} \left(\frac{\partial r}{\partial p_\mathrm{D}}\right)_{\Phi,p_\mathrm{A}} > 0, \qquad [19]$$

$$\left(\frac{\partial r}{\partial \Phi}\right)_{p_\mathrm{A},p_\mathrm{D}} \left(\frac{\partial r}{\partial p_\mathrm{A}}\right)_{\Phi,p_\mathrm{D}} < 0. \qquad [20]$$

These surprisingly simple inequalities contain mathematically not only the local rules L1 and L2 but also the global rules G1 to G3. This is also clear from Table 3 and from Figs. 7 to 13.

This is not surprising in view of the fact that rules G1, G1′, G2, G2′, and G3 and hence L1, L1′, L2, and L2′, as well as the practical rules P1 and P2 discussed below, are all expressions of the same simple idea: In the presence of an adsorbate that is so strongly adsorbed that it is slowing the catalytic rate due to site blocking, then the reaction rate can be increased by decreasing the strength of that adsorption and hence lowering the coverage.

Inequality [19] dictates that (unless both A and D are very weakly adsorbed, rule G4) the r versus Φ dependence always follows (has the same sign with) the r versus p_D behavior.

This again can be confirmed from Table 3 and Figs. 7 to 10 as well as from the more complex Figs. 11 to 13 which show the transition from one global behavior to another as p_A and p_D are varied. Note, for example, in Fig. 13 that when a reaction exhibits a maximum in the r versus $p_\mathrm{D}(=p_\mathrm{CO})$ behavior, it also exhibits a maximum (volcano) in the r versus Φ behavior.

One might rightly ask why this close and preferential connection exists between the r versus Φ and r versus p_D dependencies. The answer is straightforward and has simply to do with the definitions of Φ and Fermi level E_F (or electrochemical potential of electrons $\bar{\mu}(=E_\mathrm{F})$ (20, 112)) which are connected via (20, 33, 112)

$$-\bar{\mu} = \Phi + e\Psi, \qquad [21]$$

where Ψ is the outer (or Volta) potential of the catalyst surface. For an overall neutral catalyst surface (as is usually the case, e.g., when it is covered by the effective double layer, Fig. 2) it is $\Psi = 0$ (20, 30, 33) and thus

$$-\bar{\mu} = \Phi, \quad -E_\mathrm{F} = \Phi. \qquad [22]$$

Consequently the generalized promotional rules [19] and [20] can also be written as

$$\left(\frac{\partial r}{\partial E_\mathrm{F}}\right)_{p_\mathrm{A},p_\mathrm{D}} \left(\frac{\partial r}{\partial p_\mathrm{D}}\right)_{E_\mathrm{F},p_\mathrm{A}} < 0, \qquad [23]$$

$$\left(\frac{\partial r}{\partial E_\mathrm{F}}\right)_{p_\mathrm{A},p_\mathrm{D}} \left(\frac{\partial r}{\partial p_\mathrm{A}}\right)_{E_\mathrm{F},p_\mathrm{D}} > 0, \qquad [24]$$

and now one sees from Eqs. [23] and [24] that the r versus E_F dependence follows the r versus p_A (electron acceptor) dependence. So $(\partial r/\partial\Phi)$ traces $(\partial r/\partial p_\mathrm{D})$, Eq. [19], and $(\partial r/\partial E_\mathrm{F})$ traces $(\partial r/\partial p_\mathrm{A})$, Eq. [24].

Contrary to rules G1, G1′, G2, G2′, and G3 (which refer to strong adsorption of either D or A or both D and A), rule G4 (as well as rule P3 which follows) refers to the case of weak adsorption of both D and A in which case both $(\partial r/\partial p_\mathrm{D})$ and $(\partial r/\partial p_\mathrm{A})$ are positive. In this case Eqs. [19] and [20] are not valid and are simply replaced by

$$(\Phi - \Phi_\mathrm{m})\left(\frac{\partial r}{\partial \Phi}\right)_{p_\mathrm{A},p_\mathrm{D}} > 0 \qquad [25]$$

or, equivalently for an overall neutral surface (20, 30, 33), by

$$(E_\mathrm{F} - E_\mathrm{F,m})\left(\frac{\partial r}{\partial E_\mathrm{F}}\right)_{p_\mathrm{A},p_\mathrm{D}} > 0. \qquad [26]$$

Equation [25] is rule G4 (Fig. 10) and is discussed and rationalized in Appendix A.

Practical Considerations

The above global and local promotional rules suggest, in a straightforward manner, the following three practical rules for promoter selection with respect to rate maximization:

Rule P1: *If a catalyst surface is covered predominantly by an electron acceptor adsorbate, then an electron acceptor (electronegative) promoter is to be recommended.*

Rule P2: *If a catalyst surface is covered predominantly by an electron donor adsorbate, then an electron donor (electropositive) promoter is to be recommended.*

Rule P3: *If a catalyst surface has very low coverages of both electron acceptor and electron donor adsorbates, then both an electron acceptor and electron donor promoter will enhance the rate.*

Needless to say, the above practical promotional rules are applicable for modest (e.g., <0.2) coverages of the promoting species so that site blocking by the promoter does not become the dominant factor limiting the catalytic rate.

3. RATIONALIZATION OF THE PROMOTIONAL RULES

Previous electrochemical promotion studies have used (9–11, 13–21, 29, 38, 53, 57–60, 65–109) two very simple qualitative rules to explain all the observed effects of varying potential U_WR or work function Φ on the reaction kinetics (16–21):

Rule F1: *Increasing work function Φ (e.g., via addition of electronegative promoters) strengthens the chemisorptive bond of electron donor adsorbates (D) and weakens the chemisorptive bond of electron acceptor adsorbates (A).*

Rule F2: *Decreasing work function Φ (e.g., via addition of electropositive promoters) weakens the chemisorptive bond of electron donor adsorbates (D) and strengthens the chemisorptive bond of electron acceptor adsorbates (A).*

These two complementary rules are intuitively obvious; e.g., can be simply derived by considering the lateral attractive and repulsive interactions of coadsorbed reactants and promoters (Appendix B). They can explain all the observed promotionally induced kinetics for more than sixty different catalytic systems (Table 3). As an example these two rules can explain all the observed changes in kinetics orders with Φ shown in Figs. 8 to 13 in a straightforward manner.

We are not aware of any exceptions to these rules even in cases where they lead at a first glance to surprising predictions, e.g., that addition of O^{2-} on a Rh surface destabilizes formation of surface Rh_2O_3 (72) or that anodic ($\Delta U_{WR} > 0$) polarization of Pt both on solid electrolyte surfaces (11, 20) and in aqueous media (38) weakens the Pt=O chemisorptive bond and leads to massive O_2 desorption (37, 115) or that alkali addition on transition metal surfaces enhances O chemisorption and thus promotes hydrocarbon oxidation under fuel-rich conditions (29, 99). All these predictions have been confirmed experimentally (11, 20, 37, 38, 72, 115) and, for many cases, also theoretically via rigorous quantum-mechanical calculations using metal clusters (116, 117).

It therefore becomes important to discuss: (a) How the "fundamental" rules F1 and F2 lead to the experimentally observed promotional rules L1, L2, and G1–G4. (b) How the "fundamental" rules F1 and F2 follow from fundamental first principles.

Derivation of the Experimental Local Rules L1 and L2 from the Fundamental Rules F1 and F2

The two "fundamental" rules F1 and F2 can be expressed mathematically as

$$\left(\frac{\partial \theta_D}{\partial \Phi}\right)_{p_A, p_D} \geq 0, \qquad [27]$$

$$\left(\frac{\partial \theta_A}{\partial \Phi}\right)_{p_A, p_D} \leq 0. \qquad [28]$$

As shown in Appendix A these two "fundamental" rules lead directly mathematically to the experimental rules L1 and L2 (Eqs. [17], [18] and, for low coverages, to rule G4, Eq. [25]). Henceforth the global rules G1 to G4 are all derived on the basis of the "fundamental" rules F1 and F2.

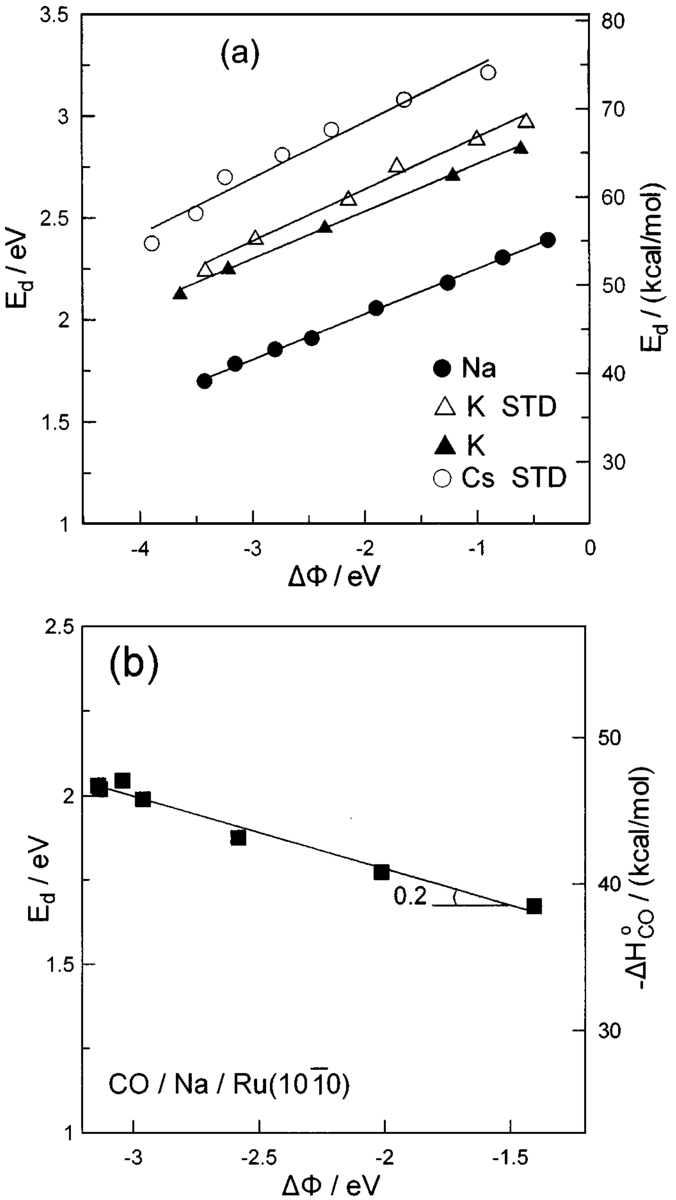

FIG. 14. (a) Alkali adsorption on Ru(0001). Effect of work function change on chemisorptive bond strength; based on the data of Ref. (119). (b) CO chemisorption on alkali-modified Ru(10$\bar{1}$0). Effect of work function change on the adsorption enthalpy of CO. Based on the data of Refs. (120, 121).

It should be noted that the two fundamental rules F1 and F2 (Eqs. [27] and [28]) are neither mathematically nor physically identical to the definitions of electron acceptor and electron donor adsorbates (Eqs. [7] and [8]) although obviously they are related. Mathematically the difference is in the subscripts (i.e., what is kept constant). Physically the difference is the following: Equations [7] and [8] are based on the Helmholz equation [13] and simply describe how Φ varies with changing θ_A or θ_D (keeping all other coverages constant). On the other hand Eqs. [27] and [28] (rules F1 and F2) describe how θ_A and θ_D vary with changing Φ (at fixed p_A, p_D, i.e., under usual experimental catalytic or electrochemical promotion conditions) via, for example addition of a promoter or potential application in electrochemical promotion experiments.

Experimental Confirmation and First Principle Rationalization of Rules F1 and F2

The variation in the enthalpy of adsorption of electron acceptor (e.g., O), electron donor (e.g., C_2H_4), and amphoteric (e.g., H, CO) adsorbates with varying promoter coverage and thus work function Φ has been studied experimentally using mostly the technique of temperature-programmed desorption (TPD) (2, 37, 115, 116, 118). Here (Figs. 14, 15) we show a few such results both from the classic promotion and from the electrochemical promotion literature (2, 115, 118–121).

All these results conform nicely to the approximate equation

$$\Delta|\Delta H_j| \approx \alpha_{H_j} \cdot \Delta\Phi, \qquad [29]$$

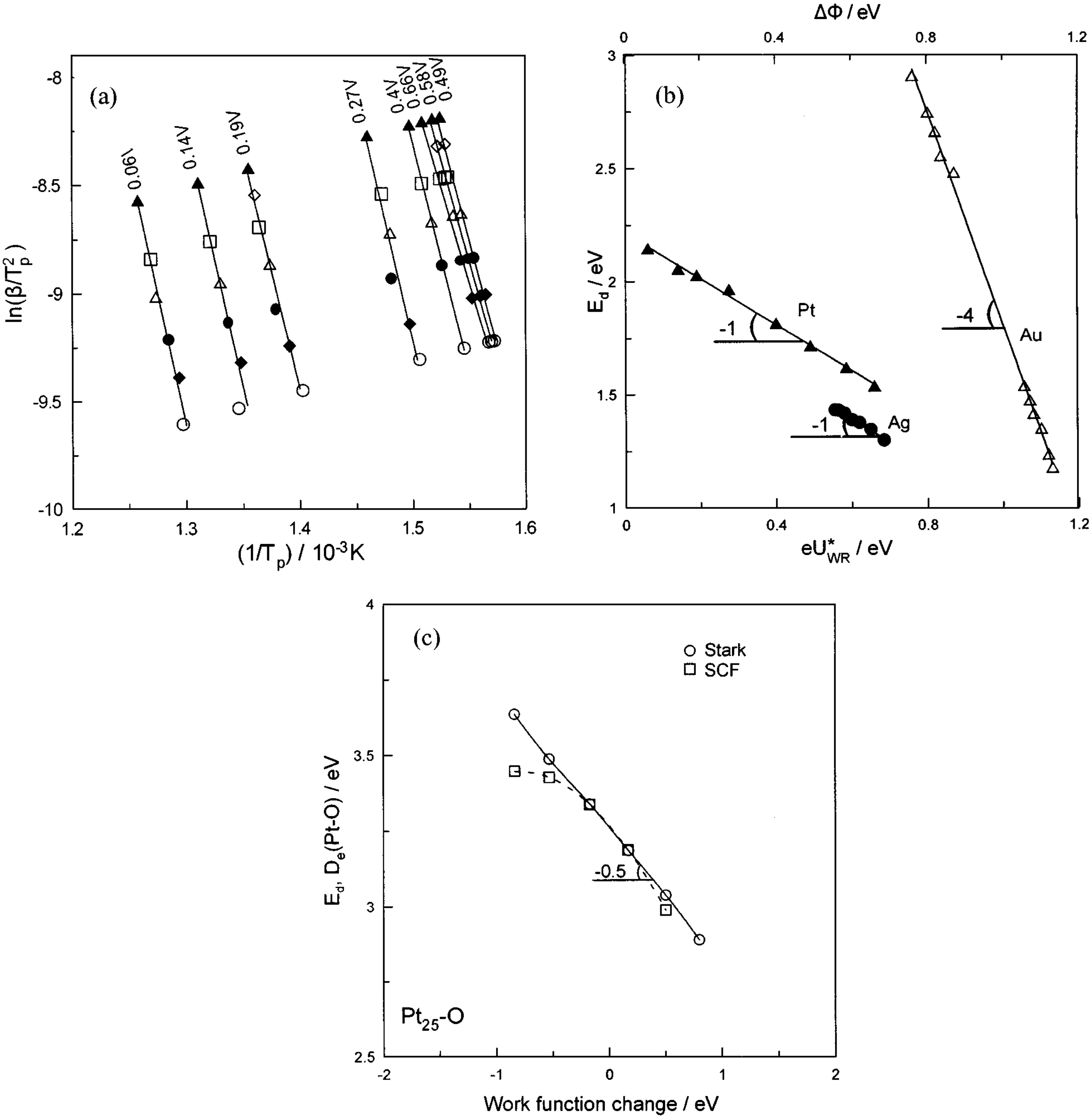

FIG. 15. Oxygen chemisorption on polycrystalline Pt, Ag, and Au films deposited on YSZ at low ($\theta_O < 0.1$) coverages (115, 118). (a) Redhead plots obtained at various imposed $\Delta\Phi$ values for O chemisorption on Pt (115). (b) Effect of $\Delta\Phi$ on the adsorption enthalpy of O on Pt, Ag, and Au (118). (c) Effect of $\Delta\Phi$ on the adsorption enthalpy of O on Pt from the cluster quantum-mechanical calculations of Pacchioni *et al.* (107). SCF, self-consistent field. Note that (i) on considering only electrostatic (Stark) effects a straight line is obtained (107) as in Appendix B (ii) the electrostatic (Stark) effect is dominant, as only minor deviations are obtained on solving the full SCF equations.

where the parameter α_{H_j} ($\alpha_{H_j} \approx 0.2$–1) is positive for electropositive (electron donor) adsorbates and negative for electronegative (electron acceptor) adsorbates. This correlation is similar in form to that proposed by Boudart many years ago (122), has a firm electrostatic (Appendix B) and quantum mechanical (116, 117) basis, and as shown in Figs. 14 and 15, provides an excellent description for the adsorption of alkalis on Ru(0001) (119), CO on alkali (Na, K, Cs)-modified Ru(10$\bar{1}$0) (120, 121), and O on polycrystalline Pt, Ag, and Au surface interfaced with YSZ and modified by O^{2-} (2, 37, 115, 118). We do not imply that equation [29] is a general fundamental equation, although, as shown in Fig. 15, the ab initio quantum-mechanical calculations of Pacchioni and Illas (116, 117) are in excellent agreement with it and although it can be rigorously derived on the basis of a simple electrostatic model that accounts only for through-the-vacuum adsorbate interactions as shown in Appendix B, which also provides a natural meaning to the parameter α_{H_j} on the basis of the dipole moment P_j of adsorbate j.

But we are also not aware of any published exceptions to the physical meaning it conveys, i.e., that the enthalpy of adsorption and thus, according to any isotherm, the coverage of an electron acceptor/donor adsorbate decreases/increases with increasing work function Φ and thus decreasing Fermi level E_F.

As shown in Figs. 14 and 15 the experimental α_{H_j} values are ∼0.2 for alkalis on Ru(0001) (Fig. 14a), ∼−0.2 for CO on Na-modified Ru(10$\bar{1}$0) (Fig. 14b, here CO behaves as an electron acceptor as is very often the case (2)), −1 for O on Pt and Ag (Fig. 15b), and −4 for O on Au (Fig. 15b). These values imply dipole moment, P_i, values on the order of 1–5 D, in good agreement with the literature (20, 112–114) as also discussed in Appendix B.

Thus Eq. [29] and the semiquantitative trends it conveys can be rationalized on the basis of both lateral coadsorbate interactions (Appendix B) and rigorous quantum-mechanical calculations on clusters (116) (which have shown that 80% of the repulsive O^{2-}–O interaction is indeed an electrostatic (Stark) through-the-vacuum interaction). Qualitatively similar conclusions can be reached also by the more recent quantum-mechanical calculations of Koper and van Santen regarding the adsorption of CO on metal surfaces (123).

CONCLUSIONS

Careful classification and examination of the electrochemical promotion and classic promotion literature have revealed four simple and rigorous experimental rules (G1–G4) which enable one to predict the rate versus work function, Φ, behavior of catalytic reactions (electrophobic, electrophilic, volcano, inverted volcano) on the basis of the rate dependence on the reactants on the unpromoted surface. The rate versus Φ dependence traces, generally, the rate versus p_D dependence except at very low coverages.

These experimental "global" rules G1 to G4 lead to three practical rules, P1 to P3, which dictate the choice of promoter type (electropositive or electronegative) on the basis of the nature (electron donor or acceptor) of the most strongly bonded reactant species.

The experimental global rules are intimately based on two fundamental rules, F1 and F2, dictating the effect of work function change induced by the promoter on the binding strength of electron donor and electron acceptor adsorbates. These fundamental rules are strongly supported both by the experimental surface science literature and by rigorous model ab initio quantum-mechanical calculations.

The rules presented here allow one to make some very clear predictions. Although we have found no exceptions in more than 60 cases, it will be interesting to compare these rules with more catalytic systems where the r versus p_A, p_D, and Φ dependence is studied in detail.

APPENDIX A

Here we first show that the local rules L1′ and L2′ (Eqs. [19], [20]) and thus also rules G1 to G3 follow from the "fundamental" rules F1 and F2 (Eqs. [27], [28]). At the end we also show that rules F1 and F2 also lead to rule G4 as a limiting case of very low coverages of both reactants.

We start from Eqs. [27] and [28] written as pure inequalities:

$$\left(\frac{\partial \theta_D}{\partial \Phi}\right)_{p_A, p_D} > 0, \qquad [A1]$$

$$\left(\frac{\partial \theta_A}{\partial \Phi}\right)_{p_A, p_D} < 0. \qquad [A2]$$

We examine Eq. [A1] and consider two cases:

$$\text{I.} \quad \left(\frac{\partial r}{\partial \theta_D}\right)_{p_A, p_D} > 0, \qquad [A3]$$

$$\text{II.} \quad \left(\frac{\partial r}{\partial \theta_D}\right)_{p_A, p_D} < 0. \qquad [A4]$$

Broadly speaking, case I corresponds to low coverage of D and case II corresponds to high coverage of D. Thus in case I,

$$\left(\frac{\partial r}{\partial p_D}\right)_{\Phi, p_A} > 0, \qquad [A5]$$

and in case II,

$$\left(\frac{\partial r}{\partial p_D}\right)_{\Phi, p_A} < 0. \qquad [A6]$$

Case I. On multiplying inequalities [A1] and [A3] one obtains

$$\left(\frac{\partial r}{\partial \Phi}\right)_{p_A, p_D} > 0. \qquad [A7]$$

From [A5] and [A7] it follows that

$$\left(\frac{\partial r}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}}\left(\frac{\partial r}{\partial P_{\mathrm{D}}}\right)_{\Phi,p_{\mathrm{A}}} > 0, \qquad [A8]$$

which is inequality [19], i.e., Rule L1′.

Case II. On multiplying inequalities [A1] and [A4] one obtains

$$\left(\frac{\partial r}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}} < 0. \qquad [A9]$$

From [A6] and [A9] it follows that

$$\left(\frac{\partial r}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}}\left(\frac{\partial r}{\partial p_{\mathrm{D}}}\right)_{\Phi,p_{\mathrm{A}}} > 0, \qquad [A8]$$

which is again Rule L1′. Thus in both cases I and II, inequality [A8], i.e., rule L1′, has been proven.

The procedure is identical for deriving rule L2′, i.e., inequality [20]: We start from inequality [A2] and consider two cases:

$$\text{I.}\quad \left(\frac{\partial r}{\partial \theta_{\mathrm{A}}}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}} > 0, \qquad [A10]$$

$$\text{II.}\quad \left(\frac{\partial r}{\partial \theta_{\mathrm{A}}}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}} < 0. \qquad [A11]$$

In case I,

$$\left(\frac{\partial r}{\partial p_{\mathrm{A}}}\right)_{\Phi,p_{\mathrm{D}}} > 0, \qquad [A12]$$

and in case II,

$$\left(\frac{\partial r}{\partial p_{\mathrm{A}}}\right)_{\Phi,p_{\mathrm{D}}} < 0. \qquad [A13]$$

Case I. On multiplying inequalities [A2] and [A10] one obtains

$$\left(\frac{\partial r}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}} < 0. \qquad [A14]$$

From [A12] and [A14] it follows that

$$\left(\frac{\partial r}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}}\left(\frac{\partial r}{\partial p_{\mathrm{A}}}\right)_{\Phi,p_{\mathrm{D}}} < 0, \qquad [A15]$$

which is inequality [20], i.e., rule L2′.

Case II. On multiplying inequalities [A2] and [A11] one obtains

$$\left(\frac{\partial r}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}} > 0. \qquad [A7]$$

From [A13] and [A7] one obtains again

$$\left(\frac{\partial r}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}}\left(\frac{\partial r}{\partial p_{\mathrm{A}}}\right)_{\Phi,p_{\mathrm{D}}} < 0, \qquad [A15]$$

which is again inequality [20], i.e., rule L2′.

When both θ_{A} and θ_{D} are low, it can be reasonably assumed that repulsive lateral interactions between the adsorbates and the promoter are negligible in comparison to the attractive ones. This can be easily understood as follows: Consider a catalyst surface with very low coverages of A and D, e.g., very low adsorption equilibrium constants k_{A} and k_{D}, where an electropositive (or electronegative) promoter is introduced, also at a low coverage θ_{P}. The presence of the electropositive (electronegative) promoter will locally ($\sim\theta_{\mathrm{p}}$) enhance the local sticking coefficient, $k_{\mathrm{S,A}}$ (or $k_{\mathrm{S,D}}$), of the electron acceptor A (or electron donor D) reactant very significantly (up to two or three orders of magnitude (1, 2, 20, 21)) and thus will enhance significantly the average sticking coefficient of A (or D) on the catalyst surface. At the same time the average sticking coefficient of D (or A) will be only marginally affected since a fraction $1-\theta_{\mathrm{p}}\approx 1$ of the catalyst surface is still available for the adsorption of D or A.

Thus, at low coverages, an electropositive (electronegative) promoter will enhance the sticking coefficient of the electron acceptor (donor) reactant without practically changing the sticking coefficient of the electron donor (acceptor) reactant.

By the same argument one can see that the desorption rate constants $k_{\mathrm{d,A}}$ and $k_{\mathrm{d,D}}$ of A and D will not be significantly affected by the presence of the promoter.

Thus the adsorption equilibrium constant of A (or D), $k_{\mathrm{A}} = k_{\mathrm{S,A}}/k_{\mathrm{d,A}}$ ($k_{\mathrm{D}} = k_{\mathrm{S,D}}/k_{\mathrm{d,D}}$), will be enhanced but that of D (or A) will remain practically unaffected. This leads to the following limiting expression of rules F1 and F2:

$$\left(\frac{\partial \theta_{\mathrm{D}}}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}} > 0, \quad \Phi \geq \Phi_{\mathrm{m}}, \qquad [A16]$$

$$\left(\frac{\partial \theta_{\mathrm{D}}}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}} = 0, \quad \Phi < \Phi_{\mathrm{m}}, \qquad [A17]$$

$$\left(\frac{\partial \theta_{\mathrm{A}}}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}} < 0, \quad \Phi < \Phi_{\mathrm{m}}, \qquad [A18]$$

$$\left(\frac{\partial \theta_{\mathrm{A}}}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}} = 0, \quad \Phi \geq \Phi_{\mathrm{m}}, \qquad [A19]$$

where Φ_{m} is the work function at the point of zero charge (pzc) (48). Equations [A16] to [A19] express that, at very low coverages, the promoter can enhance θ_{A} and θ_{D} only by enhancing one of the two sticking coefficients as described above. Since at low coverages,

$$\left(\frac{\partial r}{\partial \theta_{\mathrm{A}}}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}} > 0, \quad \left(\frac{\partial r}{\partial \theta_{\mathrm{D}}}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}} > 0, \qquad [A20]$$

it follows directly from inequalities [A16] to [A20] that

$$\left(\frac{\partial r}{\partial \Phi}\right)_{p_{\mathrm{A}},p_{\mathrm{D}}}(\Phi - \Phi_{\mathrm{m}}) > 0. \qquad \text{[A21]}$$

Thus rule G4, as well as rules L1′ and L2′ (and therefore rules G1 to G3), follows directly from the "fundamental" rules F1 and F2 (Eqs. [27], [28]). Rule G4 is a special case corresponding to low coverages of both reactants. Repulsive lateral interactions that play an important role at high coverages (rules G1 to G3) here become negligible.

APPENDIX B: ELECTROSTATIC INTERACTIONS OF ADSORBATES IN A DOUBLE LAYER

Here we show that Eq. [29] relating $\Delta\Phi$ and change in adsorption enthalpy can be derived by simply taking into account the electrostatic interactions between the adsorbate and the effective double layer.

We consider the adsorbate shown schematically in Fig. 16a in the presence of the double layer formed by the backspillover ions on the catalyst surface. Specific examples of the effective double layer for surfaces promoted by $O^{\delta-}$ and $Na^{\delta+}$ are shown schematically in Fig. 16b. The double layer is assumed homogeneous with a thickness d and a uniform field strength $\tilde{E}$ which can be computed from

$$\mathbf{E} = (\Delta\Phi/ed)\mathbf{n}, \qquad \text{[B1]}$$

where $\Delta\Phi(= \Phi - \Phi_{\mathrm{m}})$ is the work function difference between that of the actual surface and that of the surface at its pzc (30, 31, 33, 48), and $\mathbf{n}$ is the unit vector normal to the surface and pointing to the vacuum.

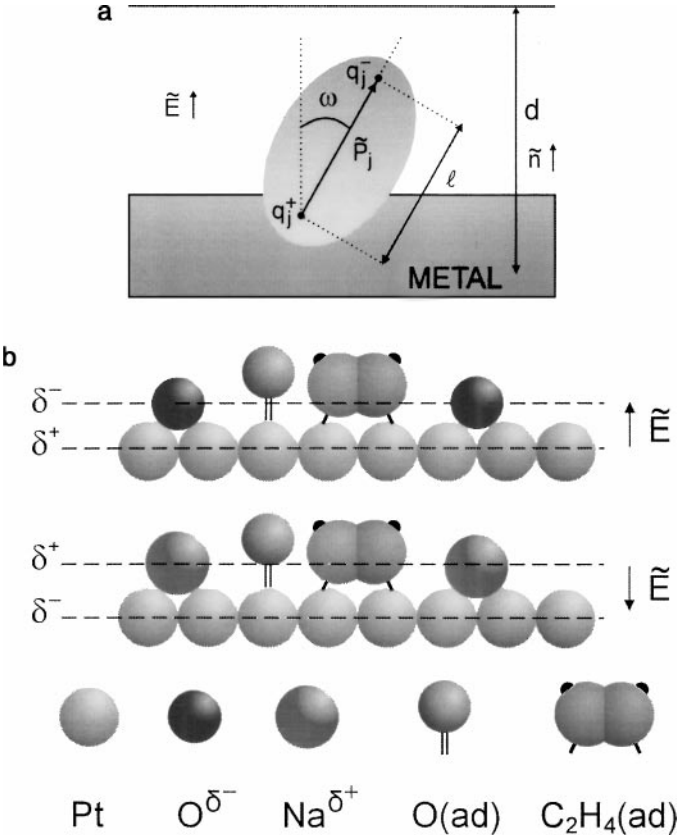

FIG. 16. (a) Schematic representation of an adsorbed molecule with dipole moment $\tilde{P}_j$ in the effective double layer formed at a metal/gas interface. (b) Schematic of the double layer during C_2H_4 oxidation promoted by $O^{\delta-}$ and $Na^{\delta+}$.

It is clear from electrostatics that the change ΔH in the potential energy, and thus internal energy and enthalpy of the adsorbed molecule, j, with dipole moment $\tilde{P}_j$, due to the presence of the field is

$$\Delta H_j = \mathbf{E}\mathbf{P}_j; \qquad \text{[B2]}$$

thus

$$\Delta H_j = \Delta\Phi \cdot \left(\frac{q_j}{e}\right)\left(\frac{l}{2d}\right)\cos\omega, \qquad \text{[B3]}$$

and, therefore, Eq. [29] has been derived, with $\alpha_{H_j} = (q_j/e)(l/2d)\cos\,\omega$.

An increase in the enthalpy, H, of the adsorbate causes an equal decrease in its activation energy for desorption, E_d, i.e., $\Delta H = -\Delta E_d$; thus,

$$\Delta E_{d,j} = -\Delta\Phi \cdot \left(\frac{q_j}{e}\right)\left(\frac{l}{2d}\right)\cos\omega. \qquad \text{[B4]}$$

Thus for the case of O chemisorbed on Pt where $\cos\omega = 1$, if one reasonably assumes $l = d$, then one obtains

$$\Delta E_{d,j} = -\left(\frac{n_j}{2e}\right)\Delta\Phi, \quad \Delta E_{d,j} = \frac{\lambda_j}{2}\Delta\Phi, \qquad \text{[B5]}$$

where $\lambda_j(= n_j/e)$ is the partial charge transfer parameter of adsorbate j, which is positive for an electron donor and negative for an electron acceptor.

Equation [B5] is in excellent agreement with experiment (Fig. 15) and allows one to speculate that the partial charge transfer λ_0 is near -2 for the case of O chemisorption on Pt. In fact one can speculate that Eq. [B5] can even account qualitatively for the decrease in the ΔE versus Φ slope from (-1 to -4) as one goes (Fig. 15b) from Pt and Ag (-1) to Au (-4) where d can be reasonably expected to be smaller due to the lower O^{2-} coverage (115, 118) and, thus, less "dense" double layer.

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