

Kinetics of rapid reactions on nanometer catalyst particles

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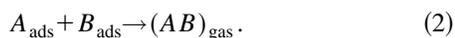
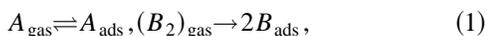
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Steady-state kinetics of the practically important catalytic reaction $2A + B_2 \rightarrow 2AB$ (e.g., $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ on Pt, Rh or Pd), occurring on nanometer supported catalyst particles, is analyzed by employing two schemes taking into account, respectively, (i) the interplay of the reaction on different facets of the catalyst particle and (ii) the possibility of adsorption of reactants on the support followed by diffusion to the catalyst. The results obtained demonstrate that the kinetics for these two cases can be remarkably different compared to those corresponding to the infinite surface. [S0163-1829(97)12707-2]

Model studies of rate processes in adsorbed overlayers have usually focused on the case when the surface is infinite.¹ In contrast, the length scale of real supported catalysts is often a few nanometers.² The assumption of an infinite surface is not valid for such catalysts, and solid understanding of the kinetic effects which are possible in this size limit is in fact lacking.³ It is therefore important to develop simulation schemes, where reactions occur on finite supported particles. The importance of such simulations is expected to increase both because of the practical relevance and because modern nanofabrication technologies⁴ provide the opportunity to create mesoscopic model systems of supported catalysts, with a controlled size, shape, and distribution on the support.

In the present paper, we will successively analyze two important factors which might change the reaction kinetics on supported systems, namely, (i) the interplay of the reaction on different facets of the catalyst particle and (ii) the possibility of adsorption of reactants on the support followed by diffusion to the catalyst. In both cases, the model reaction is assumed to occur via the Langmuir-Hinshelwood (LH) mechanism,



This reaction mimics, e.g., CO or hydrogen oxidation on transition metals (A stands for CO or hydrogen, and B_2 for O_2). During the past decade its kinetics for the infinite surface have been studied in detail in the mean-field (MF) approximation [where surface diffusion of both reactants is implicitly assumed to be rapid compared to step (2)] and also in the case of limited mobility of the reactants [see a pioneering paper by Ziff *et al.*⁵ and the review (Ref. 6)].

Discussing the interplay of different facets, we neglect desorption of A molecules. The kinetics of the other steps will be explored with realistic ratio between the corresponding rate constants by employing Monte Carlo (MC) simulations (i.e., beyond the MF approximation). Such simulations are far from straightforward because in the situations corre-

sponding to real reactions the ratio of the rate constants of different steps varies over many orders of magnitude. Usually, the LH step (2) is *rapid* compared to adsorption and slow compared to diffusion of A particles; B diffusion is often negligible by comparison. In this limit, quantitative results are presently lacking even for the infinite overlayer. Some relevant simulations have only been done⁷ for the case when the rate constants of the reaction and adsorption are *comparable*, A diffusion is rapid, and B diffusion is slow. The idea making it possible to realize the calculations is fairly simple:⁷ if diffusion of A particles is rapid, one may distribute these reactants on the sites (which are free of B particles) either at random (if there is no lateral interactions) or according to the canonical distribution (with lateral interactions). This natural prescription, assuming a canonical distribution of A particles on all the non- B sites, even if these sites are topologically disconnected by B regions, is completely correct for the “precursor” mechanism of A diffusion. If, however, the latter process occurs via nearest-neighbor jumps, the rule outlined above is just a reasonable approximation.⁷

To simulate rapid diffusion of A particles, we use the prescription proposed in Ref. 7 and in addition take *explicitly* into account that the LH step is rapid compared to adsorption (the algorithm described earlier⁷ is not specially oriented to the case under consideration and for this reason is too time consuming). In this limit, one of the reactant coverages will at steady state always be low compared to the other. If the surface is predominantly covered by A particles, the reaction can be described by employing the MF approximation because A particles are distributed at random (we ignore lateral interactions in our MC simulations). This case is, however, not interesting (for the infinite overlayer, the surface will, for example, be completely covered by A particles). For this reason, our attention will be focused on the situation when the surface is predominantly covered by B particles. If the reaction rate constant for the LH step is very high, the average number of A particles on a lattice with a limited number of sites (e.g., 100×100) will be much lower than unity. Physically, this means that in this limit every A particle ar-

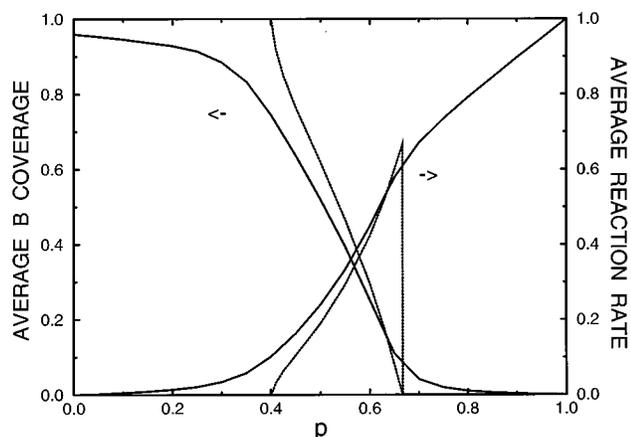


FIG. 1. Average reaction rate (A molecule site $^{-1}$ MCS $^{-1}$) and B coverage after 10^4 MCS. Solid and dotted lines correspond to a 50×50 lattice (with the boundary conditions described in the text) and to the infinite adsorbed overlayer (a 500×500 lattice with periodic boundary conditions), respectively.

iving at the surface will react with very high probability *before* the next A particle arrives. Thus, we only need to keep B particles on the $L \times L$ lattice (L is the lattice size). Then, the MC algorithm is as follows: (i) The arriving molecule is chosen to be A with a probability p and B_2 with the probability $1 - p$ ($p \leq 1$ is the dimensionless A pressure). (ii) If the arriving molecule is A , a site (site 1) on the lattice is chosen at random. If that site is occupied, the trial ends. Otherwise, A reacts. In particular, an adjacent site (site 2) is randomly chosen, and if this site is occupied by a B particle this particle is removed from the lattice (i.e., AB leaves the surface). If the adjacent site is vacant, the A particle is replaced from site 1 to another vacant site randomly chosen on the lattice, and then it again tries to react as described above. The latter two steps (replacement and an attempt to react) are repeated up to the successful reaction event. (iii) If the arriving molecule is B_2 , two adjacent sites are chosen at random. If either site is occupied, the trial ends. Otherwise, B_2 dissociates and adsorbs on the chosen sites.

Complementing rules (i)–(iii) by periodic boundary condition, we have first simulated the reaction kinetics for the infinite adsorbed overlayer (Fig. 1). To demonstrate the magnitude by which of the kinetics occurring on the nanometer-size crystals deviates from those calculated for the infinite adsorbed overlayer, we approximate one facet of a catalyst particle by a 50×50 lattice corresponding to ~ 10 nm dimension. An interplay between the reaction on this facet and neighboring facets is imitated by introducing special boundary conditions: the bottom and top rows of sites are assumed to be adjacent to A -poisoned facets, and the left- and right-hand-side rows are adjacent to B -poisoned facets. (In a real system, this situation would be realized if, e.g., the adsorption probability ratio for A versus B particles were larger and smaller, respectively, on the top/bottom and left/right adjacent facets compared to the middle facet.) In particular, B particles deposited by adsorption on the bottom or top rows are assumed to react instantaneously with A particles sitting on the sites belonging to adjacent facets. Accordingly, an A particle “jumping” after adsorption in order to find a partner may react not only with B particles located on the facet

where it was adsorbed but also with B particles on adjacent facets, provided that it reaches the left- and right-hand-side rows of sites (the game rules are the same as described above). Refilling of A and B particles on the boundary sites of adjacent facets is considered to be rapid (this assumption is reasonable because the adjacent sites are poisoned by A or B particles). With the boundary conditions introduced, the central facet is almost completely poisoned (Fig. 1) for $p < p_1$ ($p_1 = 0.401$ and $p_2 = 2/3$ are the critical parameters for the kinetic phase transitions in the infinite overlayer). Reaction events occur in this case [with low local rate] only near the bottom and top rows of sites. At $p_1 < p < p_2$, the reaction behavior on the facet is close to that predicted for the infinite overlayer. The dramatic difference in the kinetics is observed at $p > p_2$. Here, the infinite surface is completely poisoned by A , i.e., the overlayer is in the unreactive state. In contrast, the central facet is almost empty and the reaction rate is high, because the large relative impingement rate of A particles, causing poisoning of the infinite surface, is compensated on the facet by reaction of some of these A particles at the left- or right-hand-side boundary sites, filled by B particles. This compensation will be maintained until the kinetic phase transition to an A covered surface takes place on the left- and right-hand-side adjacent facets (at $p \rightarrow 1$).

Now we will turn our attention to the possibility of adsorption of reactants on the support followed by diffusion to the catalyst (and vice versa). This is usually referred to as the “spillover” effect in catalysis.⁸ The role of this channel has already been discussed in the literature. In particular, there are experimental reports⁹ that the supply of CO molecules via the support is important in CO oxidation on model nanometer catalysts obtained by evaporating Pd onto mica, Al_2O_3 , and SiO_2 . There exist also a few theoretical MF treatments^{10–12} of the phenomenon under consideration. The formalism of Refs. 10 and 11 is primarily focused on diffusion along the support. The reaction kinetics on the catalyst in such circumstances have, however, not been analyzed explicitly.^{10,11} The models¹² treat the reaction kinetics but do not describe in detail diffusion on the support (instead of solving the partial differential equations for diffusion, the authors¹² employed ordinary equations of the same type as those used for the well-stirred reactor). We present below the first *self-consistent* study of the kinetics of a catalytic reaction [steps (1) and (2)] accompanied by reactant supply from the support. MC simulations in this case are hardly possible. For this reason, our analysis will be based on the MF approximation.

Assuming the LH step to be rapid, we conclude (in analogy with the first part of the paper) that the surface is (near the steady state) covered predominantly by A or B species. When the ratio of the reactant pressures P_A/P_{B_2} is small, the B_2 adsorption dominates, i.e., $\theta_B \gg \theta_A$ and $\theta \approx \theta_B$ ($\theta \equiv \theta_A + \theta_B$), the A coverage is low, and the A desorption rate is to a first approximation negligible due to rapid A reaction with B , and accordingly the evolution of θ for the infinite surface is only dependent on the adsorption rates,

$$d\theta/dt = k_{B_2}^a P_{B_2} (1 - \theta)^2 - k_A^d P_A (1 - \theta). \quad (3)$$

In analogy, the A -dominated regime (where P_A/P_{B_2} is sufficiently large and $\theta \approx \theta_A$) is described as

$$d\theta/dt = k_A^a P_A (1-\theta) - k_A^d \theta - k_{B_2}^a P_{B_2} (1-\theta)^2, \quad (4)$$

where k_A^a , k_A^d , $k_{B_2}^a$, and k_r are the rate constants for adsorption, desorption, and reaction.

To simulate the reaction kinetics for a system of small, supported catalyst particles, the catalyst shape is taken to be circular with radius R . In addition to the reaction steps (1) and (2) on the particle, A molecules are also assumed to adsorb on the support. B_2 adsorption on the support is neglected. The catalyst particles are considered to be widely separated (no interference of the kinetics on different particles). Adsorbate diffusion on the catalyst is assumed to be rapid (no concentration gradients on catalyst particles). To describe the reaction kinetics, we can in this case employ Eqs. (3) and (4), complemented with the terms corresponding to diffusion of A molecules from the support to the catalyst. The equation for the latter process is as follows:

$$\frac{\partial \Theta}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left[r \frac{\partial \Theta}{\partial r} \right] + \mathcal{K}_A^a P_A - \mathcal{K}_A^d \Theta, \quad (5)$$

where $\Theta \ll 1$ is the A coverage on the support ($\Theta \ll 1$ if the A binding energy on the support is sufficiently low), D is the diffusion coefficient, and \mathcal{K}_A^a and \mathcal{K}_A^d are the rate constants for adsorption and desorption on the support, respectively. The boundary condition for Eq. (5) at $r=R$ is given by

$$(D/a) \partial \Theta / \partial r |_{r=R} = k_{\text{eff}} \Theta(R), \quad (6)$$

where a is the lattice spacing, $k_{\text{eff}} \Theta(R)$ the net flux (per boundary site) of A molecules from the support to the catalyst particle, and k_{eff} the ‘‘effective’’ rate constant connecting the net flux with $\Theta(R)$ [k_{eff} should be calculated by solving self-consistently Eqs. (5) and (3) or (5) and (4)]. The steady-state solution to Eq. (5) with condition (6) is known to be

$$\Theta(r) = [1 - \mathcal{A} K_0(r/l)] \mathcal{K}_A^a P_A / \mathcal{K}_A^d, \quad (7)$$

where $\mathcal{A} = 1/[K_0(R/l) - (D/alk_{\text{eff}})K_1(R/l)]$, $l = (D/\mathcal{K}_A^d)^{1/2}$, $K_0(x)$ is a modified Bessel function of the second kind of zero order, and $K_1(x) = dK_0(x)/dx$ the corresponding function of first order. For small catalyst particles, we may consider that $l \gg R$. In this limit, $K_0(x) \approx -\ln(x)$, and

$$\Theta(R) \approx (D\mathcal{K}_A^a P_A / aR\mathcal{K}_A^d) / [k_{\text{eff}} \ln(l/R) + D/aR]. \quad (8)$$

The total diffusion flux to the particle is accordingly given by

$$F = (2\pi R/a) k_{\text{eff}} \Theta(R) \approx \frac{2\pi D \mathcal{K}_A^a k_{\text{eff}} P_A}{a^2 \mathcal{K}_A^d [k_{\text{eff}} \ln(l/R) + D/aR]}. \quad (9)$$

The flux per one site on the catalyst particle \mathcal{F} is obtained by dividing the total flux by the number of sites on the particle ($\approx \pi R^2/a^2$), i.e.,

$$\mathcal{F} \approx \frac{2D\mathcal{K}_A^a k_{\text{eff}} P_A}{R^2 \mathcal{K}_A^d [k_{\text{eff}} \ln(l/R) + D/aR]}. \quad (10)$$

If the catalyst particle is primarily covered by B , the A molecules diffusing from the support to the catalyst are rap-

idly consumed due to reaction. In this case, A jumps onto the catalyst are irreversible, and $k_{\text{eff}} = (1-\theta)\mathcal{K}_{10}$, where \mathcal{K}_{10} is the jump rate constant for the case when the spot is empty. Substituting this expression for k_{eff} into Eq. (10) yields

$$\mathcal{F} \approx \frac{2D\mathcal{K}_A^a \mathcal{K}_{10} P_A (1-\theta)}{R^2 \mathcal{K}_A^d [(1-\theta)\mathcal{K}_{10} \ln(l/R) + D/aR]}. \quad (11)$$

Adding the flux (11) into Eq. (3), we get the following equation for the reaction on the catalyst particle in the B dominated regime

$$d\theta/dt = k_{B_2}^a P_{B_2} (1-\theta)^2 - k_A^a P_A^{\text{eff}} (1-\theta). \quad (12)$$

The only difference between Eqs. (3) and (12) is that P_A [in Eq. (3)] is replaced by a new effective A pressure

$$P_A^{\text{eff}} \approx \left(1 + \frac{2D\mathcal{K}_A^a \mathcal{K}_{10}}{R^2 \mathcal{K}_A^d k_A^a [(1-\theta)\mathcal{K}_{10} \ln(l/R) + D/aR]} \right) P_A. \quad (13)$$

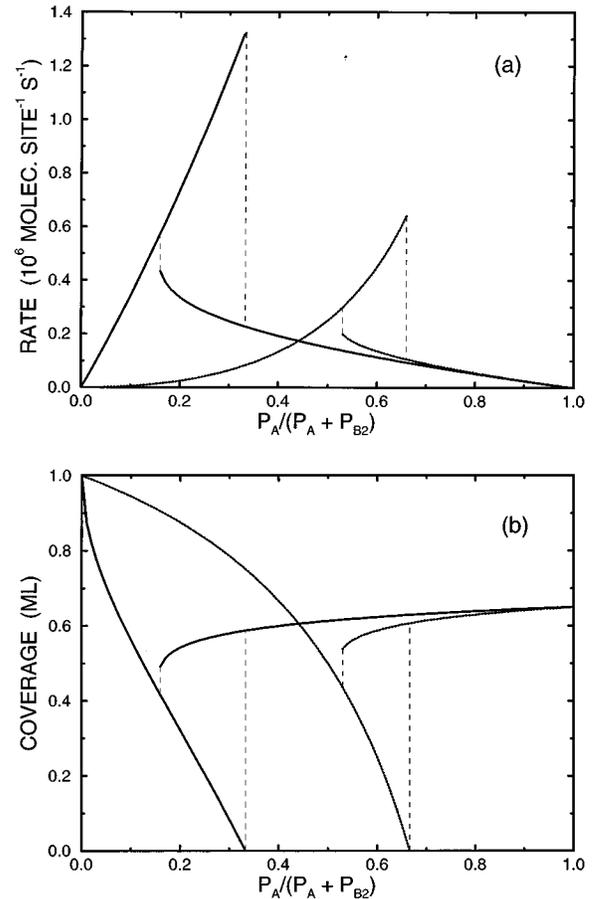


FIG. 2. (a) Reaction rate and (b) reactant coverages for rapid $2A + B_2 \rightarrow 2AB$ reaction under steady-state conditions. The dotted lines show the kinetics for the infinite adsorbed overlayer [Eqs. (3) and (4)]. The solid lines correspond to reaction on the catalyst particles [Eqs. (12) and (16) with Eqs. (14) and (18) for P_A^{eff} , respectively]. The input data for calculations are as follows: Reaction conditions, $T = 450$ K, $P_A + P_{B_2} = 0.01$ bar; A adsorption, $k_A^a = 10^8$ s $^{-1}$ bar $^{-1}$; B_2 adsorption, $k_{B_2}^a = 2 \times 10^8$ s $^{-1}$ bar $^{-1}$; A desorption, $k_A^d = \nu_A^d \exp(-E_A^d/T)$; $\nu_A^d = 10^{16}$ s $^{-1}$, $E_A^d = 35 - 15\theta_A$ kcal/mol; processes on the catalyst, $D\mathcal{K}_A^a / [R^2 \mathcal{K}_A^d k_A^a \ln(l/R)] = 1.5$.

If the A -consumption rate is high ($\mathcal{K}_{10} \gg D/aR$), the effective pressure is given by

$$P_A^{\text{eff}} \simeq \left(1 + \frac{2D\mathcal{K}_A^a}{R^2\mathcal{K}_A^d k_A^a \ln(l/R)(1-\theta)} \right) P_A. \quad (14)$$

If the catalyst particle is primarily covered by A molecules, we must take into account A jumps both from the support to the catalyst and from the catalyst to the support. In this case, the net A flux (per boundary site) from the support to the spot is given by

$$k_{\text{eff}}\Theta(R) \equiv (1-\theta)\mathcal{K}_{10}\Theta(R) - \mathcal{K}_{01}\theta, \quad (15)$$

where \mathcal{K}_{01} is the rate constant for jumps from the catalyst onto the support. Solving Eq. (15) together with Eq. (7) [or with Eq. (8)] and taking into account that the different rate constants in these equations are interconnected via the relationship $\mathcal{K}_{01}\mathcal{K}_A^d k_A^a = \mathcal{K}_{10}\mathcal{K}_A^a k_A^d$ given by the detailed balance principle for the A adsorption-desorption equilibrium, one can obtain explicit expressions for k_{eff} and $\Theta(R)$ and then for the flux \mathcal{F} . In particular, combining Eqs. (8) and (15), we have [cf. Eq. (4)]

$$d\theta/dt = k_A^a P_A^{\text{eff}}(1-\theta) - k_A^d \theta - k_{B_2}^a P_{B_2}(1-\theta)^2, \quad (16)$$

where

$$P_A^{\text{eff}} \simeq \left(1 + \frac{2D\mathcal{K}_A^a \mathcal{K}_{10} [1 - k_A^d \theta / k_A^a P_A (1-\theta)]}{R^2 \mathcal{K}_A^d k_A^a [(1-\theta)\mathcal{K}_{10} \ln(l/R) + D/aR]} \right) P_A. \quad (17)$$

If the jumps from the support to the catalyst are rapid ($\mathcal{K}_{10} \gg D/aR$), the effective A pressure is given by

$$P_A^{\text{eff}} \simeq \left(1 + \frac{2D\mathcal{K}_A^a [1 - k_A^d \theta / k_A^a P_A (1-\theta)]}{R^2 \mathcal{K}_A^d k_A^a \ln(l/R)(1-\theta)} \right) P_A. \quad (18)$$

The analysis above indicates [see, e.g., Eqs. (14) and (18)] that the A supply via the support is important if $D\mathcal{K}_A^a/R^2\mathcal{K}_A^d k_A^a > 1$. Often, $\mathcal{K}_A^a \approx k_A^a$. Taking in addition into account that $D = a^2\mathfrak{R}$ (\mathfrak{R} is the jump rate constant for diffusion), we can rewrite the condition above as $a^2\mathfrak{R}/R^2\mathcal{K}_A^d > 1$, or

$$(a^2\nu_{\text{dif}}/R^2\nu_{\text{des}})\exp[(\mathcal{E}_{\text{des}} - \mathcal{E}_{\text{dif}})/T] > 1, \quad (19)$$

where ν_{dif} , \mathcal{E}_{dif} , ν_{des} and \mathcal{E}_{des} are the Arrhenius parameters for A diffusion and desorption on the support, respectively. If for example $a^2/R^2 = 10^{-2}$, $\nu_{\text{dif}}/\nu_{\text{des}} = 10^{-2}$, and $T = 400$ K, the reactant supply via support is important provided that $\mathcal{E}_{\text{des}} - \mathcal{E}_{\text{dif}} > 7$ kcal/mol. This requirement is realistic for CO adsorption on oxides [e.g., for MgO (Ref. 13)].

Typical reaction kinetics calculated by employing Eqs. (12) and (16) [with Eqs. (14) and (18) for P_A^{eff}] are shown in Fig. 2 (solid lines). Due to the A supply from the support, the position of the maximum reaction rate is seen to be shifted to a lower value of the $P_A/(P_A + P_B)$ ratio. In addition, the dependence of the reaction rate on the reactant pressure (for the regime where the surface is predominantly covered by B) is changed considerably (it becomes linear) compared to the case without A diffusion from the support. As $P_A/(P_A + P_{B_2})$ increases from 0 to 1, the system exhibits a transition from a regime where the reaction rate is completely controlled by A supply from the support to a regime where diffusion from the support is negligible.

In summary, our study demonstrates that the reaction kinetics on nanometer supported catalyst particles can be remarkably different compared to those corresponding to the infinite surface.

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¹H.C. Kang and W.H. Weinberg, Chem. Rev. **95**, 667 (1995).

²J.T. Richardson, *Principles of Catalyst Development* (Plenum, New York, 1989).

³V. Gorogetskii, J. Lauterbach, H.-H. Rotermund, J.H. Block, and G. Ertl, Nature **370**, 276 (1994).

⁴P.W. Jacobs, F.H. Ribeiro, G.A. Somorjai, and S.J. Wind, Catal. Lett. **37**, 131 (1996).

⁵R.M. Ziff, E. Gulari, and Y. Barshad, Phys. Rev. Lett. **56**, 2553 (1986).

⁶V.P. Zhdanov and B. Kasemo, Surf. Sci. Rep. **20**, 111 (1994).

⁷M. Tammaro, M. Sabella, and J.W. Evans, J. Chem. Phys. **103**, 10 277 (1995).

⁸W.C. Conner, Jr., and J.L. Falconer, Chem. Rev. **95**, 759 (1995).

⁹V. Matolin and E. Gillet, Surf. Sci. **166**, L115 (1986); F. Rumpf,

H. Poppa, and M. Boudart, Langmuir **4**, 722 (1988); M. Eriksson and L.-G. Petersson, Surf. Sci. **311**, 139 (1994); C.R. Henry, C. Chaption, and C. Duriez, J. Chem. Phys. **95**, 700 (1991); Z. Phys. D **19**, 347 (1991); C. Becker and C.R. Henry, Surf. Sci. **352**, 457 (1996).

¹⁰R. Aris, J. Catal. **22**, 282 (1971); D.-J. Kuan, H.T. Davis, and R. Aris, Chem. Eng. Sci. **38**, 719 (1983).

¹¹V.P. Zhdanov, *Elementary Physicochemical Processes on Solid Surfaces* (Plenum, New York, 1991), Chap. 7.5.

¹²R.K. Edvinsson, R.R. Hudgins, and P.L. Silveston, in *New Aspects of Spillover Effects in Catalysis*, edited by T. Inui *et al.* (Elsevier, Amsterdam, 1993), p. 229; Y.W. Nam and P.L. Silveston, *ibid.*, p. 235.

¹³J.-W. He, J.S. Corneille, C.A. Estrada, M.-C. Wu, and D.W. Goodman, J. Vac. Sci. Technol. A **10**, 2248 (1992).