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Surface Restructuring, Thermal Desorption, Kinetic Bistability, and Chemical Waves

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Adsorbate-induced surface restructuring is treated in the framework of a statistical lattice-gas model taking into account the possibility of formation of a metastable substrate structure on the clean surface and stabilization of this structure by adsorbate–substrate interaction. With these assumptions, surface restructuring is described in terms of the theory of first-order phase transitions. The proposed model is then employed to analyze (i) the influence of adsorbate-induced changes in the surface on thermal desorption spectra and (ii) the effect of surface restructuring on the propagation of chemical waves in the $2A + B_2 \rightarrow 2AB$ reaction. The interplay between reaction-diffusion kinetics and surface restructuring is shown to result in formation of chemical waves with atomistically sharp spatial features.

KEY WORDS: Lattice-gas model; lateral interactions; metastable and stable structures; first-order phase transitions; reaction-diffusion kinetics.

1. INTRODUCTION

Kinetics of elementary processes in adsorbed overlayers at finite coverages are usually complicated by (i) lateral interactions between adsorbed particles, (ii) surface heterogeneity, and (iii) adsorbate-induced changes of the substrate surface structure. During the past decade, the effects resulting from the first two factors have been studied and understood in detail (see refs. 1, 2 and 3, respectively). On the other hand, the manifestation of surface restructuring in the apparent kinetics is in spite of considerable

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attention still not quite clear. The latter is partly explained by the fact that the bulk of detailed experimental data on surface reconstruction has been obtained only recently (an extensive list of references to experimental studies carried out before 1989 is presented in the review by Somorjai and Van Hove;(4) more recent references can be found in a few comprehensive reviews edited by King and Woodruff(5)). In addition, the statistical models describing adsorbate-induced structural phase transitions on the surface are not well developed. Progress in this field is however rather rapid (see the reviews(6, 7)), and the results obtained will stimulate in the nearest future advances in simulations of rate processes complicated by adsorbate-induced changes in the surface.

In general, one might expect that the influence of surface restructuring on elementary rate processes in adsorbed overlayers could be significant because typical energies involved are usually much higher than the thermal energy. The available (limited) experience of simulations of elementary kinetic processes accompanied by structural changes in the surface (for a review see ref. 8) indicates however that the effect of such changes on the apparent kinetics is often hidden. Illustrating the latter, we may refer to the analysis of the kinetics of temperature-programmed desorption (TPD) for the H/W(001) and CO/Pt(110) systems (the way how to measure TPD spectra is described in Section 3). In the former case, the surface reconstructs spontaneously at low temperatures, and hydrogen adsorption facilitates formation of the reconstructed $c(2 \times 2)$ structure at low coverages and results in the appearance of incommensurate structures at high coverages. The simplest statistical model describing this phenomenon (at low coverages) has been constructed by Lau and Yang(9) employing the phenomenological Landau–Ginzburg expression with a two-component order parameter for the free energy of the clean surface and the lattice-gas model [with the mean-field (MF) approximation] for hydrogen atoms. This model (with minor modifications) has been used by Inaoka and Yoshimori(10) to simulate the TPD spectra for H/W(001). In the latter case, CO adsorption on Pt(110) results in suppressing the (2×1) missing-row reconstruction if the surface coverage is higher than a quarter of the monolayer, $\theta > 0.25$ ML. The kinetics of thermal desorption of CO from Pt(110) has been simulated(11) by employing (with modifications) the Ising-type model proposed by Campuzano *et al.*(12) In both cases [H/W(001) and CO/Pt(110)], the models reproduce the splitting of the TPD spectra (the term “splitting” means the existence of two maxima in the graph). Qualitatively-similar features of the spectra might however be formally obtained by taking into account only adsorbate-adsorbate interactions. The Ising-type model has also been used(13) to interpret the TPD spectra for the O/Ag(110) system [oxygen induces formation of the missing-row

(1×2) structure]. In this case, experiment$^{(14)}$ indicates that the kinetics of associative desorption of oxygen $[\mathrm{O}_{\mathrm{ads}} + \mathrm{O}_{\mathrm{ads}} \rightarrow (\mathrm{O}_2)_{\mathrm{gas}}]$ can be accurately fitted by employing the first-order law (this law is typical of ideal monomolecular desorption). The apparent first order of the desorption kinetics was shown$^{(13)}$ to be directly connected with surface restructuring.

Affecting the kinetics of elementary steps of heterogeneous reactions, the adsorbate-induced restructuring of the surface may play a crucial role in such interesting and important phenomena as bistability and kinetic oscillations (see the pioneering experimental$^{(15)}$ and theoretical$^{(16,17)}$ studies of CO oxidation on Pt(001) by Ertl *et al.* and also the recent reviews$^{(18-20)}$).

The goal of the present paper is to formulate a relatively simple statistical model describing adsorbate-induced surface restructuring in terms of the theory of first-order phase transitions (Section 2) and to illustrate the effect of this phenomenon on desorption kinetics (Section 3), and on bistability and chemical waves in the $2\mathrm{A} + \mathrm{B}_2 \rightarrow 2\mathrm{AB}$ reaction (Section 4). The model employed is based on the two-state approximation (every surface atom is either in the "stable" or "metastable" state). This approximation has already been used to construct a phase diagram of the adsorbate-substrate system,$^{(22)}$ to interpret (qualitatively) the TPD spectra for H/Pt(001),$^{(23)}$ and to simulate oscillations and spatial self-organization in CO oxidation on Pt(001).$^{(17,24)}$ Compared to the earlier studies,$^{(17,22-24)}$ our treatment contains some important new ingredients:

(1) The earlier analysis$^{(23)}$ of thermal desorption based on the model formulated in ref. 22 ignored the tendency of surface atoms to be either all in the stable or all in the metastable state and also the correlations in the arrangement of adsorbed particles. In addition, the TPD spectra were analyzed$^{(23)}$ assuming that desorption occurs at $T > T_c$ (T_c is the critical temperature). The present treatment of thermal desorption is free of all these restrictions.

(2) Earlier Monte Carlo simulations$^{(17)}$ of spatio-temporal patterns, employing the two-state approximation, were based on empirical rules prescribing the transition from one state to another with increasing or decreasing adsorbate coverage. A weak point of this approach is the lack of a microscopic statistical background justifying the rules used. In addition, the authors$^{(17)}$ have ignored adsorbate diffusion. In reality, CO diffusion on Pt is very fast and accordingly important for understanding spatial self-organization. The other phenomenological approach of the same group$^{(16)}$ (see also the review$^{(19)}$) to describing oscillatory kinetics of CO oxidation on Pt is based on the conventional kinetic equations. The latter model, taking into account CO diffusion and predicting very interesting results, assumes coexistence of two phases at all the spatial points. Physically

this means that the phase boundaries are omitted from the analysis. For this reason, the phenomenological approach(16) is able to predict only "mesoscopic" patterns. In particular, the characteristic size of chemical waves in this case, $l \sim (D\tau)^{1/2}$ (D is the CO diffusion coefficient, and τ is the time scale of the other elementary steps), is much larger that the lattice spacing. Meanwhile, the patterns observed in real systems are often atomistically sharp.(25) The latter seems to be directly connected with phase boundaries. In our treatment of chemical waves, the phase boundary is analyzed explicitly. Employing a generic reaction scheme, we show that the interplay between reaction-diffusion kinetics and surface restructuring does result in formation of chemical waves with atomistically sharp spatial features.

(3) Earlier simulations of spatial self-organization in CO oxidation on Pt(001),(24) using the two-state approximation, were based on the Landau–Ginzburg equation for describing the kinetics of surface restructuring. The correlations in the arrangement of adsorbed particles in this case are ignored. The phase boundaries are not analyzed explicitly either. Our analysis incorporates these factors.

2. MODEL

Outlining the model of adsorbate-induced surface restructuring, we need first to recall the definitions of a few relevant terms such as "surface reconstruction", "stable structure", and "metastable structure". The term "surface reconstruction" means a deviation of the arrangement of substrate atoms from a simple truncation of the bulk structure. The term "metastable structure" is used for a structure whose free energy is a local, but not an absolute, minimum with respect to structural changes (there is an energy barrier which prevents the system from reaching the minimum of free energy corresponding to the stable structure). The relationship between the terms "unreconstructed" and "reconstructed" on the one hand and "stable" and "unstable" on the other is not unique. If the clean surface reconstructs spontaneously, the reconstructed arrangement is stable, and the "truncated" arrangement is metastable. Otherwise, the "truncated" arrangement is stable, and the reconstructed structure is metastable (or unstable).

Surface restructuring under the influence of adsorption can usually be discussed in terms of the theory of phase transitions. In our model, the adsorbate-induced restructuring of the substrate layer is treated as a first-order phase transition. As we have already noted in the Introduction, the model is oriented to such real systems as CO or hydrogen on Pt(001). In this case, the stable and metastable arrangements of substrate atoms on the clean surface have the "hex" and (1 × 1) symmetry, respectively, and accordingly the term "adsorbate-induced surface restructuring" implies the adsorbate-induced transition from the "hex" arrangement of substrate atoms to the (1 × 1) surface structure. This phase transition is of the first order because formation of the (1 × 1) islands occurs even at low adsorbate coverages. The driving force for stabilization of the metastable (1 × 1) structure by adsorbed particles is a higher value of the adsorption energy on this structure compared to that on the "hex" phase.(26)

In real systems [e.g., on Pt(001)], the surface densities of substrate atoms in the stable and metastable structures are slightly different and the phase transition is then accompanied by forcing up some of the substrate atoms. Full-scale simulations of the latter phenomenon are hardly possible at present. In our analysis, this complicating factor is ignored, i.e., the densities of substrate atoms in the stable and metastable structure are considered to be equal. In this case, the adsorbate-induced phase transition can be described by employing the lattice-gas model as shown for example in Fig. 1. The main ingredients of this model are as follows:

(i) Substrate atoms are assumed to form a square lattice. Every atom may be in the stable or metastable state (the terms "stable" and "metastable states" will hereafter always refer to the states which are stable and metastable on the clean surface). The energy difference of these states is ΔE. The nearest-neighbour substrate-substrate interaction is considered to be attractive, $-\varepsilon_s$ ($\varepsilon_s > 0$), if the atoms are in the same states, and repulsive, ε_s, if the states are different (really, the total nearest-neighbour substrate-substrate interactions are of course attractive; the interactions

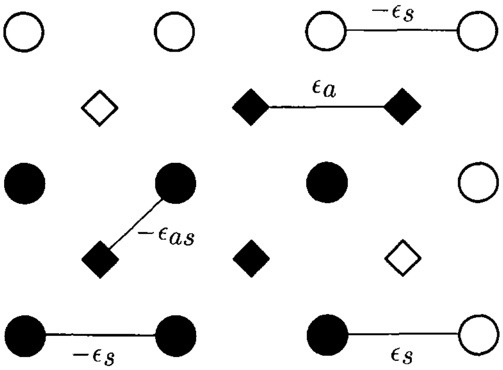

Fig. 1. Schematic arrangement of particles on the surface. Open and filled circles show substrate atoms in the ground and metastable states. Open and filled diamonds exhibit vacant and occupied adsorption sites, respectively.

$-\varepsilon_s$ and $+\varepsilon_s$ introduced describe the deviation from the average value). The next-nearest-neighbour interactions are ignored. With this choice of the substrate-substrate interactions, the model describes the tendency of substrate atoms to be either all in the stable or all in the metastable state.

(ii) Adsorbed particles are assumed to occupy hollow sites [this assumption is not essential, because in the case of adsorption on top sites the formal equations will be the same (one needs only redefine some parameters)]. The adsorption energy of a given adsorbed particle is considered to increase linearly with the number of nearest-neighbour substrate atoms located in the metastable state (as we have already noted, this is a driving force for the phase transition). The corresponding contribution to the adsorbate energy is given by $-\varepsilon_{as}n$, where $\varepsilon_{as} > 0$ is the increase of the adsorption energy after the transition of one nearest-neighbour substrate atom from the stable to the metastable state.

(iii) The nearest-neighbour adsorbate-adsorbate interaction is assumed to be repulsive, $\varepsilon_a > 0$. [For CO adsorption on Pt(001), it is evident, for example from the formation of the $c(2\times 2)$ structure on the (1×1) spots, that the adsorbate-adsorbate interaction is of this type.]

Mathematically, the lattice-gas model outlined above is equivalent to a model consisting of two subsystems of Ising spins with rather complicated interactions: ferromagnetic on one sublattice, antiferromagnetic on another with ferromagnetic interaction between sublattices. In addition, a magnetic field is applied to one of the sublattices, but in the second sublattice the magnetic moment is held fixed. To our knowledge, an analysis of the phase diagram of such a model is lacking in the literature. Our treatment presented below will be based on the MF approximation. This approximation is well known to yield reasonable results only if it corresponds to the physics of a problem under consideration. To clarify the physics behind our model, we need to analyze possible ordered and disordered structures at $T=0$. Assuming that the adsorbate coverage is not too high, one can easily calculate in this limit the energy per adparticle, $\mathscr{E}$, for the following most important situations: (i) adparticles are disordered and dilute, the surface is not restructured (i.e., the substrate atoms are in the ground state), $\mathscr{E}=0$; (ii) adparticles are disordered and dilute, the surface is locally restructured (i.e., the substrate atoms adjacent to a given adsorbed particle are in the metastable state), $\mathscr{E}=4(\Delta E-\varepsilon_{as})+16\varepsilon_s$; (iii) the adsorbate forms close-packed islands, the surface is restructured inside the islands, $\mathscr{E}=\Delta E-4\varepsilon_{as}+2\varepsilon_a$; (iv) the adsorbate forms $c(2\times 2)$ islands, the surface is restructured inside the islands, $\mathscr{E}=2\,\Delta E-4\varepsilon_{as}$. From this analysis, it is clear that the formation of adsorbate islands accompanied by surface restructuring (i.e., a first-order phase transition) is favorable if the adsorbate-substrate interaction, ε_{as}, is strong.

For the model under consideration, the free energy can be represented as a sum of terms describing substrate atoms, adsorbate particles, and an interaction between them,

$$F(\kappa, \theta) = F_s(\kappa) + F_a(\theta) + F_{int}(\kappa, \theta) \tag{1}$$

where κ is the fraction of substrate atoms in the metastable state, and θ the surface coverage (i.e., the fraction of occupied sites).

The type of approximations desirable for calculating different terms in Eq. (1) depends on our goals. In particular, the tendency of substrate atoms to be either all in the stable or all in the metastable state, resulting in a first-order phase transition in the adsorbate/substrate system, can be taken into account by employing the simplest MF approximation. This approximation (with proper parameterization) is known to describe quantitatively almost all the special features of first-order phase transitions (accurate calculation of the critical exponents is of course not possible; but in our work we do not discuss the latter problem). The MF expression for the free energy of substrate atoms is given by (we use $k_B = 1$)

$$F_s(\kappa) = \kappa\, \Delta E - A(\kappa - 1/2)^2/2 + T[\kappa \ln \kappa + (1 - \kappa) \ln(1 - \kappa)] \tag{2}$$

where $A = 4z\varepsilon_s$ is a coefficient proportional to the substrate-substrate interaction, and $z = 4$ the number of nearest-neighbour sites. The interaction between the substrate and adsorbate subsystems is represented as

$$F_{int}(\kappa, \theta) = -B\kappa\theta \tag{3}$$

where $B = z\varepsilon_{as}$.

At thermodynamic equilibrium, we have $\partial F/\partial\kappa = 0$, or

$$\Delta E - B\theta - A(\kappa - 1/2) + T \ln[\kappa/(1 - \kappa)] = 0 \tag{4}$$

In analogy with the Ising model of a ferromagnet in an external field, this equation, together with the Maxwell construction, predicts (Fig. 2) that the dependence of κ on $\Delta E - B\theta$ is smooth for $T > T_s$ and stepwise when $T < T_s$, where $T_s = A/4$ is the critical temperature for the substrate subsystem. The discontinuity of κ takes place at $\theta_{cr} = \Delta E/B$ (this coverage corresponds to zero field in the Ising model). For $T \ll T_s$, the substrate subsystem is in the state with $\kappa \simeq 0$ when $\theta < \theta_{cr}$ and with $\kappa \simeq 1$ when $\theta > \theta_{cr}$.

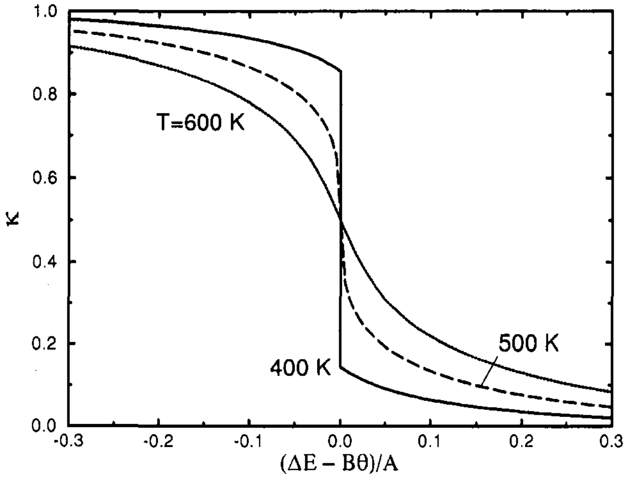

Fig. 2. Fraction of the substrate atoms in the metastable state as a function of the parameter $(\Delta E - B\theta)/A$ at $T = 400$, 500 and 600 K [according to Eq. (4) with $A = B = 2000$ K and $\Delta E = 500$ K].

To calculate the phase diagram of the adsorbate/substrate system and also the desorption rate, we need the chemical potential of adsorbed particles. According to definition, one has

$$\mu(\theta) = \partial F/\partial\theta = -B\kappa + \partial F_a/\partial\theta \tag{5}$$

The parameter κ in this equation is implicitly dependent on θ [as given by Eq. (4)]. The second term in Eq. (5), $\partial F_a/\partial\theta$, can in principle be calculated in the MF approximation. This approximation ignores, however, correlations in the arrangement of adsorbed particles. Such correlations affect the thermodynamics and kinetics.(1) Better results can be obtained in the quasi-chemical (QC) approximation (Sec. 3.3.2 in ref. 1), which yields(1)

$$\frac{\partial F_a}{\partial\theta} = T \ln\left[\frac{\theta}{1-\theta}\left(\frac{\mathscr{P}_{AA}\exp(\varepsilon_a/T) + 0.5\mathscr{P}_{A0}}{\mathscr{P}_{AA} + 0.5\mathscr{P}_{A0}}\right)^z\right] \tag{6}$$

where

$$\mathscr{P}_{AA} = \theta - \{1 - [1 - 2\beta\theta(1-\theta)]^{1/2}\}/\beta$$

and

$$\mathscr{P}_{A0} = 2\{1 - [1 - 2\beta\theta(1-\theta)]^{1/2}\}/\beta$$

are the QC probabilities that two adjacent sites are occupied by two or one particles, and $\beta = 2[1 - \exp(-\varepsilon_a/T)]$. Employing Eq. (6), we take into account only short-range correlations in the arrangement of adsorbed particles. The long-range correlations, which might arise due to "antiferromagnetic" adsorbate-adsorbate interactions, are ignored. Physically, the latter correlations are connected with a second-order phase transition in the adsorbed overlayer (this phase transition is neglected in our analysis because its effect on the surface restructuring, which is treated as a first-order phase transition, and on the rate process in the adsorbed overlayer is very weak).

At temperatures below the critical one, $T < T_c$, the chemical potential given by Eqs. (5) and (6) is a nonmonotonous function of coverage (Fig. 3). The latter is indicative of phase separation (i.e., a first-order phase transition occurs for $T < T_c$). The real value of the chemical potential in the two-phase region and the coverages corresponding to the two pure phases are defined by the Maxwell rule (Fig. 4). Calculating the critical coverages at different temperatures makes it possible to construct the phase diagram of the adsorbate/substrate system. For example, Fig. 5 shows the phase diagram for $\Delta E = \varepsilon_{as} = \varepsilon_a = 4\varepsilon_s = 500$ K. In this case, the adsorbate should

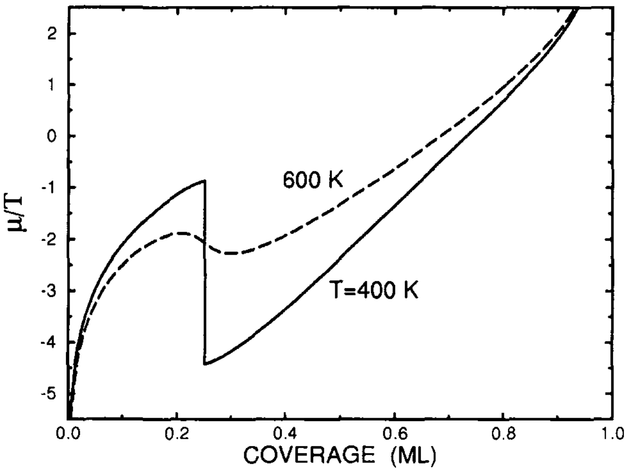

Fig. 3. Chemical potential of adsorbed particles as a function of coverage at $T = 400$ and 600 K [according to Eqs. (5) and (6) with $A = B = 2000$ K, $\Delta E = 500$ K, and $\varepsilon_a = 500$ K]. In the case under consideration, the critical temperature for the substrate subsystem is $T_s = 500$ K. The curve constructed for $T = 400$ K shows that at $T < T_s$ the chemical potential has a stepwise singularity near $\theta = \Delta E/B$. At $T_c > T > T_s$ (e. g., at 600 K), the chemical potential is a smooth but nonmonotonic function of coverage. At $T > T_c$ (the results for this case are not shown), the chemical potential monotonously increases with increasing coverage.

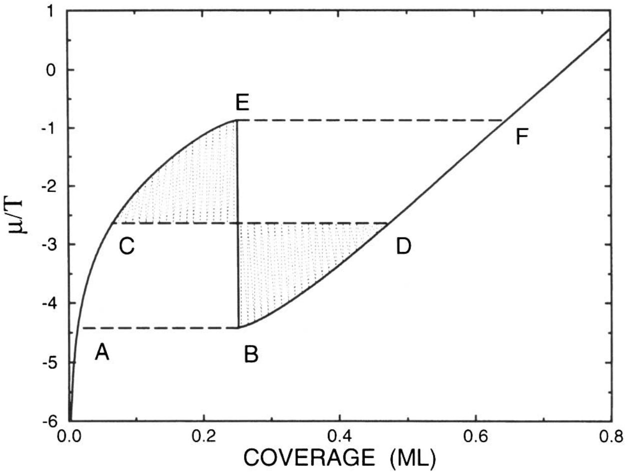

Fig. 4. Chemical potential of adsorbed particles as a function of coverage at $T < T_s$. The coexistence of two phases takes place along line *CD*. The value of the chemical potential in the two-phase region and the coverages corresponding to different phases are defined by the Maxwell rule (the shaded areas should be equal each other). Lines *CE* and *BD* indicate metastable states.

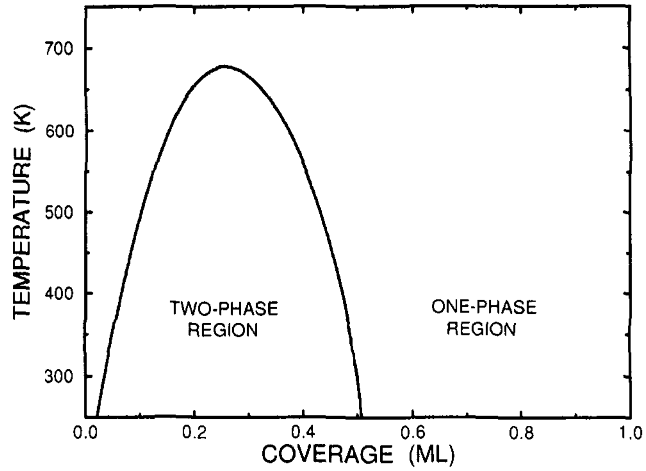

Fig. 5. Phase diagram showing the first-order phase transition in the adsorbate/substrate system (the parameters employed in calculations are the same as in Fig. 3). At temperatures slightly below 300 K, there is also a second-order $c(2 \times 2)$ phase transition (see the text) which is not shown.

at low temperatures be in $c(2 \times 2)$ restructured islands provided that the coverage is not too high (this point has already been discussed above). The critical temperature for the $c(2 \times 2)$ order-disorder phase transition can be estimated by using the well-known Onsager equation, $T_* = 0.573\varepsilon_a$. For a given set of parameters, this temperature is rather low (slightly below 300 K). For this reason, the $c(2 \times 2)$ order-disorder phase transition is not shown in Fig. 5 (construction of a phase diagram describing the interplay of the first-order and order-disorder phase transitions is a subtle problem which is beyond the goals of the present study). We may however note that even above T_* the islands in the two-phase region have short-range $c(2 \times 2)$ ordering which is taken into account in the QC approximation. Such islands can be formed as a diluted phase only at coverages up to 1/2 ML. In agreement with this general analysis, our model does predict a two-phase state only for $0 < \theta < 1/2$.

3. THERMAL DESORPTION

One of the most widely used techniques for studying the kinetics of elementary rate processes on solid surfaces is the thermal desorption method.(1, 27) It consists of adsorption at low temperature followed by desorption (or reaction) at the temperature rise, $T = T_0 + \beta t$, where T_0 is the initial temperature, and β is the heating rate. The temperature dependence of the desorption rate in the course of such measurements is called the temperature-programmed desorption (TPD) spectrum. A TPD experiment makes it possible to study the kinetics of the process for all the coverages from saturation to zero coverage over a short period of time. Analysis of the TPD spectra yields the dependence of the rate process of interest on temperature and coverage. This is the advantage of the TPD method and the reason of its widespread popularity. The goal of the present section is to demonstrate the effect of surface restructuring on the TPD spectra by employing the model introduced above.

The type of kinetic equations for describing desorption depends on the ratios between the rates of adsorbate diffusion, desorption, and surface restructuring, respectively. Diffusion of adsorbed particles is usually rapid compared to desorption. In this case, the adsorbed particles are expected to be in thermodynamic equilibrium, and the desorption rate can be expressed via the adsorbate chemical potential by employing the standard approach(1) for describing the rate processes in the framework of the lattice-gas approximation or alternatively by using the detailed balance principle for adsorption and desorption. In analogy with the one-phase case [see Eq. (4.2.11) in ref. 1 or ref. 28], we have the following equations for monomolecular and associative desorption, respectively,

$$d\theta/dt = -k_d^\circ \exp(\mu/T)[(1-\theta_1)S_1 + (1-\theta_2)S_2] \tag{7}$$

$$d\theta/dt = -k_d^\circ \exp(2\mu/T)[\mathscr{P}_{00}(\theta_1)S_1 + \mathscr{P}_{00}(\theta_2)S_2] \tag{8}$$

where $\theta \equiv \theta_1 S_1 + \theta_2 S_2$ is the total coverage, S_1, $S_2 \equiv 1 - S_1$, θ_1 and θ_2 are the fractions of the surface and adsorbate coverages attributed to the first and second phases, $\mathscr{P}_{00}$ is the probability that two nearest-neighbour sites are vacant, and $k_d^\circ = \nu \exp(-E_d^\circ/T)$ is the desorption rate constant at low coverages in the case when all the substrate atoms are in the stable state. The relative value of the chemical potential depends on its asymptotic behaviour at low (or high) coverages. In Eqs. (7) and (8), the chemical potential is defined so that $\mu \approx T \ln \theta$ in the limit when $\theta \to 0$ (provided that all the substrate atoms are in the stable state). At finite coverages, the chemical potential is given in our model by Eq. (5) (as discussed in more detail below). A necessary condition for the applicability of Eqs. (7) and (8) is that the sticking coefficients for adsorption on both surface phases (at low coverages) are equal, $s_1 = s_2$. If the sticking coefficients are not equal, the contributions of the first and second phases (the terms proportional to S_1 and S_2, respectively) to the desorption rate would be proportional to the corresponding sticking coefficients. In our calculations presented below, the latter situation is not analyzed (because the results for $s_1 \neq s_2$ are very close to those for $s_1 = s_2$).

The ratio between the rates of desorption and surface restructuring may in principle be arbitrary. If surface restructuring is rapid, the adsorbate/substrate system is in fact in thermodynamic equilibrium in the course of TPD. Accordingly, the chemical potential of the adsorbed particles and the parameters θ_1, θ_2, S_1, and S_2 can be calculated by employing Eqs. (4)-(6). Typical TPD spectra for this case (Fig. 6a) contain a broad low-temperature peak and very narrow high-temperature peak. With decreasing initial coverage, the temperature corresponding to maximum desorption rate is seen to decrease. All these features are directly connected with surface restructuring. If the coverage is high and the temperature is low, the surface is in the state with $\kappa \simeq 1$. Under such circumstances, the desorption rate is relatively low (even if we have repulsive adsorbate-adsorbate interactions which are responsible for the appearance of a low-temperature peak). Increasing temperature and decreasing coverage are accompanied by surface restructuring (Fig. 6b). The latter in turn stimulates desorption because the adsorption energy on the unrestructured spots is lower. This positive feedback results in surface explosion-type kinetics.

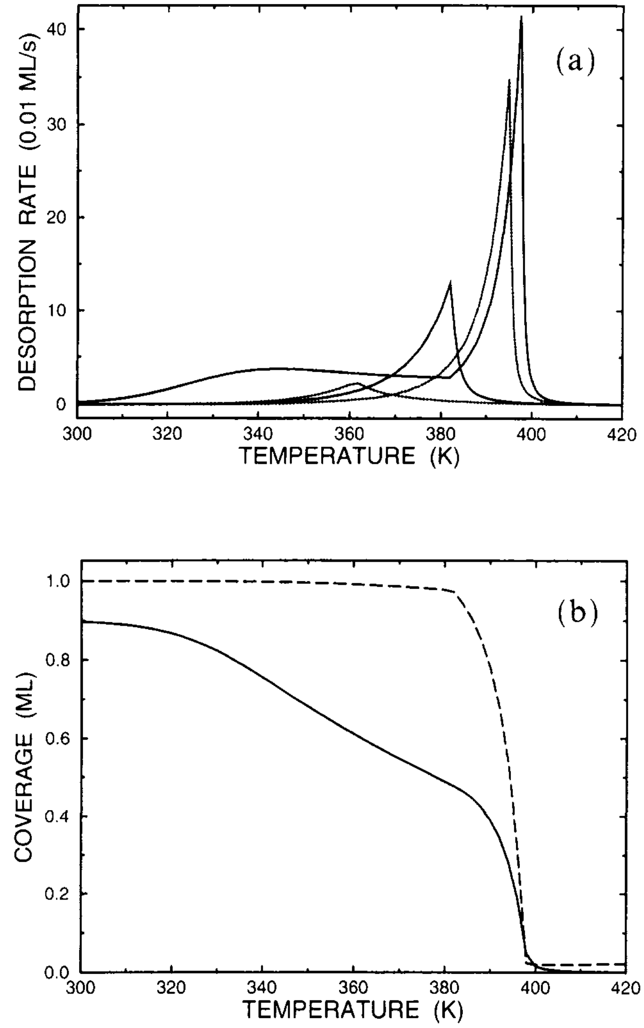

Fig. 6. (a) TPD spectra in the case when surface restructuring is rapid compared to desorption. The initial coverages are 0.9, 0.5, 0.3, and 0.1 ML (the integral intensities of spectra are proportional to the initial coverages). (b) Adsorbate coverage (solid line) and the fraction of substrate atoms in the metastable state (dashed line) as a function of temperature for the initial coverage of 0.9 ML. The Arrhenius parameter, heating rate, and initial temperature employed in calculations are $E_d^0 = 20$ kcal/mol, $\nu = 10^{13}$ s^{-1}, $\beta = 5$ K/s, and $T(0) = 250$ K, respectively. The parameters used to describe surface restructuring are the same as in Fig. 3.

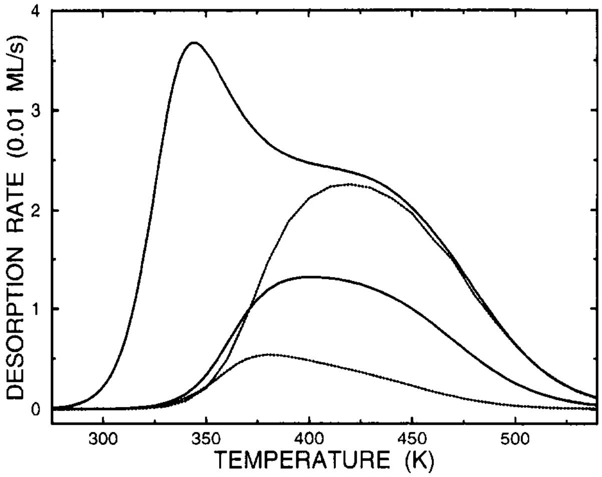

Fig. 7. TPD spectra in the case when surface restructuring is slow compared to desorption. The initial coverages are 0.9, 0.5, 0.3, and 0.1 ML (the integral intensities of spectra are proportional to the initial coverages). The parameters employed in calculations are the same as in Fig. 6.

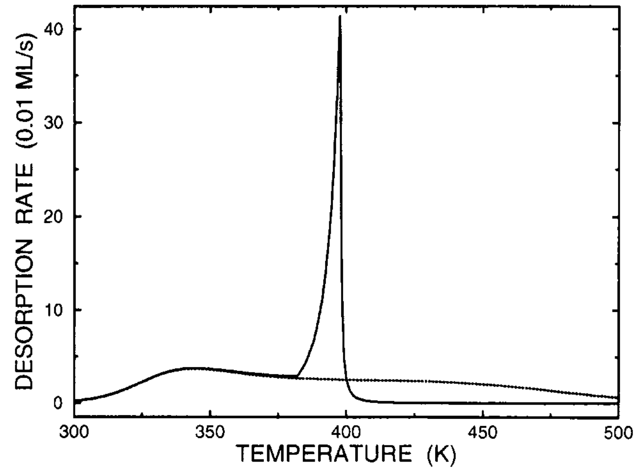

Fig. 8. Comparison of the TPD spectra corresponding to rapid (solid line) and slow (dotted line) surface restructuring. The initial coverage is 0.9 ML. The parameters employed in calculations are the same as in Fig. 3.

The other limit we want to discuss briefly is when surface restructuring is slow compared to desorption. In this case, the substrate subsystem is not expected to be in the equilibrium state during TPD. Accordingly, the TPD spectra should be explicitly dependent on the kinetics of surface restructuring. The latter kinetics can be explored in the framework of the model described by using Monte Carlo simulations. Such simulations are however beyond the scope of the present study. Our intention is only to demonstrate the scale of changes in TPD spectra corresponding to slow restructuring compared to those obtained for the equilibrium situation (Fig. 6a). This can be done by assuming that the adsorbate/substrate system is in equilibrium at the initial temperature and that, with increasing temperature, surface restructuring does not occur at all, i.e. (i) the fractions of the surface attributed to the first and second phases are constant, and

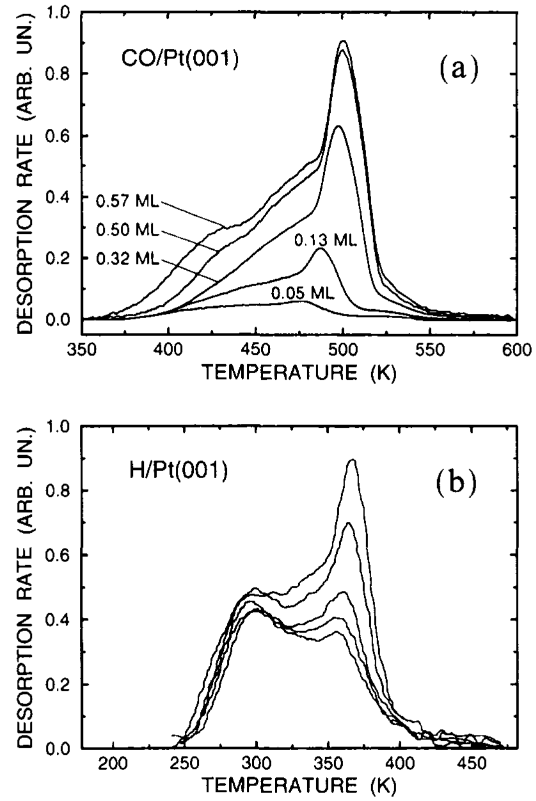

Fig. 9. TPD spectra for (a) CO and (b) hydrogen on an initial Pt(001)-hex-*R* surface.[29, 30] The initial CO coverages are shown in the panel. The maximum initial hydrogen coverage is about 0.5 ML.

(ii) the adsorbate structure on the spots corresponding to different phases is frozen (mathematically, the latter means that the values of κ for the first and second phases are kept constant). The adsorbate coverages corresponding to different phases can be obtained in this case from the grand canonical distribution taking into account that the adsorbate chemical potential [Eq. (5)] is the same for both the phases. The desorption rate is then given by Eqs. (7) or (8) (these equations hold even if the substrate subsystem is far from equilibrium). The TPD spectra (Fig. 7) calculated with the conditions corresponding to the frozen substrate are quite different compared to those exhibited in Fig. 6a (see also Fig. 8) because the positive feedback is now lacking.

Typical experimental data illustrating the manifestation of surface restructuring in thermal desorption are shown in Fig. 9, which displays the TPD spectra for CO and hydrogen on an initial Pt(001)-hex-*R* surface.(29, 30) In both cases, adsorption is accompanied by the "hex" → (1×1) surface restructuring. With increasing temperature and decreasing coverage, the "hex" structure is recovered. The latter is expected to result in formation of a relatively narrow high-temperature TPD peak. With increasing initial coverage, the temperature corresponding to maximum desorption rate is seen to increase. All these special features of the TPD spectra are in qualitative agreement with the results shown in Fig. 6a. In fact, the model overestimates the effect of surface restructuring on TPD spectra (compared to the experiment). The latter seems to indicate that in the experiment the rates of desorption and surface restructuring are comparable, i.e. the adsorbate/substrate system is not in complete thermodynamic equilibrium.

4. BISTABILITY AND CHEMICAL WAVES

First-order *kinetic* phase transitions connected with bistability and resulting in chemical waves usually occur in rapid surface reactions. General properties of such phase transitions in systems without surface restructuring are well understood.(20, 21) On the other hand, studies of kinetic phase transition and chemical waves complicated by surface restructuring are in fact lacking. Below, we briefly recall elementary ideas employed in this field of surface kinetics (Section 4.1) and then explore the effect of surface restructuring on propagation of chemical waves (Section 4.2).

4.1. Chemical Waves without Surface Restructuring

The simplest bistable reaction, $2A + B_2 \rightarrow 2AB$, occurs via irreversible adsorption of reactants, $A_{gas} \rightarrow A_{ads}$ and $(B_2)_{gas} \rightarrow 2B_{ads}$, and the Langmuir–Hinshelwood (LH) reaction between them, $A_{ads} + B_{ads} \rightarrow (AB)_{gas}$. The analysis of steady-state regimes and chemical waves for this reaction on the stable surface (i.e., without surface restructuring) is fairly simple provided that the LH step is rapid, i.e., $k_r \to \infty$.(20) In this case, any given region of the surface at any given moment will be covered predominantly by A or B species, and the reaction rate is in fact controlled by the rates of adsorption. In the A-dominated region, the reaction-diffusion equation is(20)

$$\partial \theta_A / \partial t = D_A \, \partial^2 \theta_A / \partial x^2 + W_A(\theta_A) \tag{9}$$

where D_A is the diffusion coefficient, $W_A(\theta_A) = P_A(1-\theta_A) - 2P_{B2}(1-\theta_A)^2$ the reaction rate, and P_A and P_{B2} are the effective pressures (i.e. pressures multiplied by the adsorption rate constants). If the surface is predominantly covered by B particles, we have

$$\partial \theta_B / \partial t = D_B \, \partial^2 \theta_B / \partial x^2 + W_B(\theta_B) \tag{10}$$

where $W_B(\theta_B) = 2P_{B2}(1-\theta_B)^2 - P_A(1-\theta_B)$.

To prevent confusion, we have to emphasize once more that Eqs. (9) and (10) are applicable in *different* (A- and B-dominated) regions. Thus, these equations do not form a system of coupled equations. Instead, they should be solved independently [i.e., Eq. (9) should be solved in the A-dominated region, and Eq. (10) has to be solved in the B-dominated region, respectively]. The only coupling between Eqs. (9) and (10) is introduced via the boundary condition near the point (or points) separating the A- and B-dominated regions.

The steady-state solutions of Eqs. (9) and (10) are customarily classified(20) by employing the dimensionless parameter $\alpha \equiv P_A/(P_A + P_{B2})$. Under steady-state conditions, Eq. (9) always (i.e., at $0 < \alpha \leqslant 1$) has a trivial stable solution, $\theta_A = 1$ (in this case, $\theta_B = 0$), corresponding to the "unreactive" state. A stable "reactive" solution (Fig. 10) with $\theta_B = 1 - P_A/2P_{B2}$ ($\theta_A \simeq 0$) and $W = P_A^2/2P_{B2}$ is given by Eq. (10) for $P_A < 2P_{B2}$, i.e., for $\alpha \leqslant \alpha_{cr}^0 \equiv 2/3$. All the other solutions to Eqs. (9) and (10) are unstable.

The steady-state solutions described above are stable if we ignore surface diffusion. Including the latter process into the reaction scheme opens up the possibility of formation of chemical waves and makes it possible to introduce a parameter α_{cr}^* ($0 \leqslant \alpha_{cr}^* \leqslant \alpha_{cr}^0$) corresponding to equistability of two kinetic phases. In the bistable region, the mean-field solution describing the reactive regime is absolutely stable for $\alpha \leqslant \alpha_{cr}^*$ and metastable for $\alpha_{cr}^* \leqslant \alpha \leqslant \alpha_{cr}^0$. The self-poisoning solution with $\theta_A = 1$ is metastable for $\alpha \leqslant \alpha_{cr}^*$ and absolutely stable when $\alpha \geqslant \alpha_{cr}^*$. Suppose, for example, that one part of the surface (e.g. the part where $x > 0$) is initially completely covered

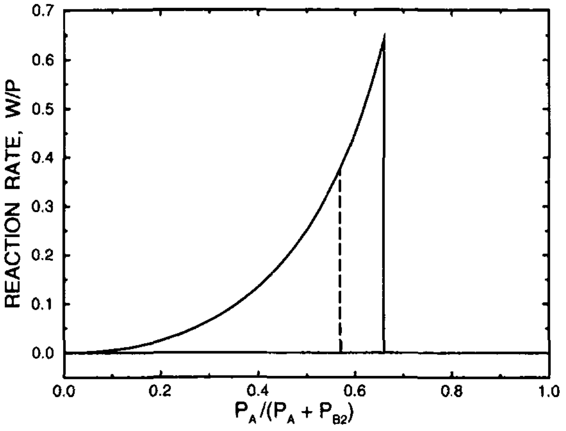

Fig. 10. Steady-state reaction rate as a function of the relative concentration of A molecules in the gas phase for the $2A + B_2 \rightarrow 2AB$ reaction with irreversible adsorption at $P/k_r \rightarrow 0$ $(P \equiv P_A + P_{B2})$. For the unreactive regime, the reaction rate is zero, $W = 0$, for all the conditions. The reactive regime with $W \neq 0$ is possible when $P_A < 2P_{B2}$. The dashed line corresponds to the equistability condition (for $D_A \gg D_B$).

by the A species while the other part (with $x < 0$) is in the reactive steady state. As time increases the interface which started at $x = 0$ will move. This is a chemical wave due to diffusion and the chemical reaction. If $\alpha < \alpha^*_{cr}$, so that the region with $x > 0$ is metastable and the other is stable, then the interface will move in the positive x-direction. If $\alpha > \alpha^*_{cr}$, then the region with $x < 0$ is metastable, and the interface will move in the opposite direction. If $\alpha = \alpha^*_{cr}$, the two regions are equistable, and the interface does not move. The value of α^*_{cr} depends on the ratio of the diffusion coefficients D_A and D_B. As an example, we consider below that $D_A \gg D_B$. In this case,(20) $\alpha^*_{cr} = 4/7 = 0.571$.

A chemical wave, realizing the transition from the metastable kinetic phase to the stable state and moving at a velocity v, is given by a special solution to Eqs. (9) and (10)

$$\theta = \theta(\xi), \qquad \xi = x - vt \tag{11}$$

that satisfies the relevant boundary conditions. Assuming the boundary between the A-rich and B-rich regions to be located at $\xi = 0$ and substituting (11) into Eqs. (9) and (10), we have for $\xi > 0$ and $\xi < 0$, respectively, the following equations

$$D_A\, d^2\theta_A/d\xi^2 + v\, d\theta_A/d\xi + W_A(\theta_A) = 0 \tag{12}$$

$$D_B\, d^2\theta_B/d\xi^2 + v\, d\theta_B/d\xi + W_B(\theta_B) = 0 \tag{13}$$

At $\xi \to +\infty$, the surface is completely covered by A molecules, i.e. $\theta_A = 1$ and $d\theta_A/d\xi = 0$. Accordingly at $\xi \to -\infty$, the boundary conditions are: $\theta_B = \theta_B^{st}$ and $d\theta_B/d\xi = 0$, where θ_B^{st} is the steady-state coverage corresponding to the reactive regime. In addition, at $\xi = 0$, we should have

$$\theta_A = \theta_B = 0 \tag{14}$$

and

$$D_A(d\theta_A/d\xi)|_{\xi \to +0} = -D_B(d\theta_B/d\xi)|_{\xi \to -0} \tag{15}$$

Physically, Eq. (14) shows that for $k_r \to \infty$, the adsorbate coverages should be very low near the boundary because the reaction is rapid. Condition (15) means that when $\xi \to 0$, the diffusion fluxes of A and B particles are equal and directed towards the boundary. Thus, these fluxes compensate each other at the boundary due to rapid reaction and accordingly the mass balance is sustained. If $D_A \gg D_B$, the diffusion flux of B particles is low and we can in fact rewrite condition (15) as

$$d\theta_A/d\xi|_{\xi \to +0} = 0 \tag{16}$$

If, for example, $\alpha < \alpha_{cr}^*$ and $v > 0$, the propagation of the B-rich region is maintained primarily by B_2 adsorption. In this case, we can neglect the first (diffusion) term in Eq. (13) (because $D_A \gg D_B$). Then, integrating this equation yields

$$\ln(1-\theta_B) - \ln[(1-\chi-\theta_B)/(1-\chi)] = -(P_A/v)\,\xi \tag{17}$$

where $\chi = P_A/2P_{B2}$. To obtain v, we need to integrate Eq. (12) numerically with the boundary conditions described above.

Results of calculations (Fig. 11) illustrate that the typical velocity, length (in the A domain), and time of the reaction front are given by

$$v \approx (D_A P_A)^{1/2}, \qquad l \approx (D_A/P_A)^{1/2}, \qquad \tau_f \approx l/v \approx 1/P_A \tag{18}$$

With $D_A \approx 10^{-8}$ cm^2/s ($D_A^{\circ} \approx 10^{-3}$ cm^2/s, $E_a \approx 10$ kcal/mol, and $T = 500$ K) and $P_A \approx 1$ s^{-1}, one has $v \approx 10^{-4}$ cm/s, $l \approx 10^{-4}$ cm, and $\tau_f \approx 1$ s.

4.2. Chemical Waves with Surface Restructuring

To show the effect of surface restructuring on the propagation of chemical waves, we keep the same reaction scheme as in Section 4.1 and assume that (i) adsorption of A molecules is accompanied by surface restructuring as described in Section 2, (ii) adsorption of B_2 molecules does

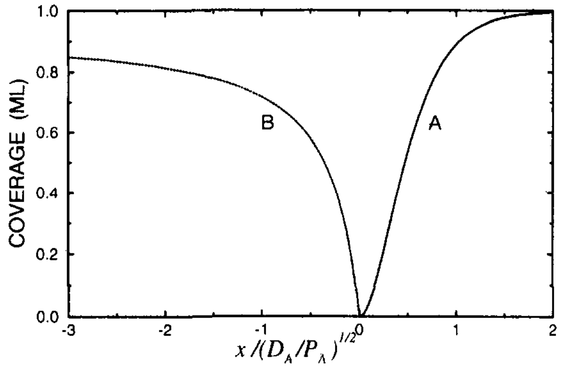

Fig. 11. Chemical wave for the $2A + B_2 \rightarrow 2AB$ reaction without surface restructuring for $D_A \gg D_B$ and $P_A/2P_{B2} = 0.1$ [in this case, $v = 3.01(D_A P_A)^{1/2}$]. A and B coverages are shown by solid and dotted lines, respectively.

not change the surface structure, and (iii) the rates of adsorption of A and B_2 molecules are independent of the state of the surface (the latter is assumed for pedagogical simplicity). In this case, the steady-state reaction regimes are the same as those described above (Fig. 10) because the reaction rate is limited by the rates of adsorption which in turn are independent of the surface structure. Thus, the system under consideration is kinetically bistable, and accordingly one can try to construct solutions to the reaction-diffusion equations corresponding to chemical waves by employing the approach outlined in Section 4.1 with modifications to take into account surface restructuring.

Some of the modifications required are trivial. For example, the model of surface restructuring employed in our analysis contains adsorbate-adsorbate interactions. With these interactions, the diffusion coefficients D_A and D_B are expected to be strongly dependent on coverage. Such effects do not, however, change the conceptual picture of chemical waves and can accordingly be ignored in the present treatment. To understand the type of modifications which are really important, we need to introduce the time scale τ_s characterizing the response of the substrate subsystem to the change in adsorbate coverage.

If the response of the substrate subsystem to the change in coverages is slow, i.e. $\tau_s \gg \tau_f$, the adsorbate-induced surface restructuring is not able to follow the reaction front. In this case, surface restructuring in fact does not affect the propagation of a chemical wave because it occurs only afterwards, i.e., far behind the reaction front.

The other limit is when $\tau_s \ll \tau_f$. In this case, the response of the substrate subsystem to the change in coverages is so fast that the adsorbate/substrate system is in local equilibrium. This simplification makes it possible to integrate the reaction-diffusion equations as described in Section 4.1. The new point is that, calculating the A coverage, we should take into account that at some distance $\xi = \xi_{cr} > 0$ the substrate subsystem changes the state. The boundary conditions near ξ_{cr} are

$$\mu|_{\xi \to \xi_{cr} - 0} = \mu|_{\xi \to \xi_{cr} + 0} = \mu_\circ \tag{19}$$

and

$$(D_A\, \partial\theta_A/\partial\xi + v\theta_A)|_{\xi \to \xi_{cr} - 0} = (D_A\, \partial\theta_A/\partial\xi + v\theta_A)|_{\xi \to \xi_{cr} + 0} \tag{20}$$

where $\mu_\circ$ is the chemical potential corresponding to coexistence of two phases (line *CD* in Fig. 4).

Physically, condition (19) indicates that the adsorbate/substrate system is in local equilibrium near the interface (this is a standard approximation employed for describing the kinetics of first-order phase transitions(31, 32)). It can be rewritten as

$$\theta_A|_{\xi \to \xi_{cr} - 0} = \theta_A^C \quad \text{and} \quad \theta_A|_{\xi \to \xi_{cr} + 0} = \theta_A^D \tag{21}$$

where θ_A^C and θ_A^D are coverages corresponding to the points *C* and *D* (Fig. 4). Condition (20) guarantees mass conservation near the phase boundary because it shows that the A-particle fluxes before and after ξ_{cr}

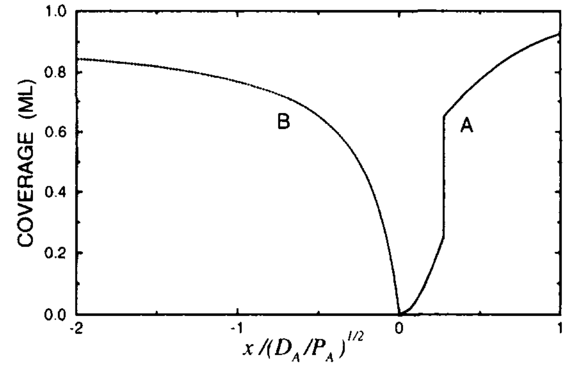

Fig. 12. Chemical wave for the $2A + B_2 \rightarrow 2AB$ reaction with surface restructuring for $D_A \gg D_B$, $\theta_A|_{\xi \to \xi_{cr} - 0} = 0.25$, $\theta_A|_{\xi \to \xi_{cr} + 0} = 0.65$, and $P_A/2P_{B2} = 0.1$ [in this case, $v = 2.16(D_A P_A)^{1/2}$]. The A and B coverages are shown by solid and dotted lines, respectively.

are equal. Using Eqs. (19) and (20), one can calculate ξ_{cr} and v self-consistently.

A typical chemical wave, obtained by numerical integration of the reaction-diffusion equations with the boundary conditions described above, is shown in Fig. 12. Surface restructuring is seen to result in formation of a reaction front with a stepwise singularity at $\xi = \xi_{cr}$.

5. CONCLUSION

We have proposed a statistical lattice-gas model describing adsorbate-induced surface restructuring in terms of the theory of first-order phase transitions. Employing this model, we have shown in detail the manifestation of surface restructuring in (i) thermal desorption and (ii) propagation of chemical waves in the $2A + B_2 \rightarrow 2AB$ reaction.

Our analysis has primarily been based on analytical approaches. The model presented is however very convenient for Monte Carlo simulations. Applying the latter technique to the model outlined, one can treat a wide class of phenomena in the case when the time scales of different kinetic process (e.g., surface reconstruction and desorption, or surface reconstruction and propagation of chemical waves) are comparable.

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