

Standing fronts in bistable reactions on composite catalytic surfaces

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Using as an example the $2A + B_2 \rightarrow 2AB$ reaction occurring via the standard Langmuir-Hinshelwood mechanism, we show by Monte Carlo simulations that the shape of the standing fronts, which can be observed in bistable reactions at the surface of a catalyst composed of two active metals, is crucially dependent on the energetics of adsorption on the metals forming a catalyst.

To understand the kinetics of heterogeneous catalytic reactions is of high practical importance, because heterogeneous catalysis is the mainstay of the chemical industry (more than 90 % of the chemical manufacturing processes in use throughout the world utilize catalysis, primarily heterogeneous catalysis,¹ which is also a vital component of current and future environmental and energy technologies). From the physical point of view, the kinetics of heterogeneous catalytic reactions are of interest due to their richness and complexity related to such factors as surface heterogeneity, adsorbate-adsorbate lateral interactions, and/or spontaneous and adsorbate-induced surface restructuring,²⁻⁴ and manifested in such phenomena as chemical waves, kinetic oscillations, and chaos.^{2,5} In academic studies, surface heterogeneity is usually considered as an undesirable factor. In practice, however, controlled heterogeneities can be employed to improve the activity of catalysts. Also from an academic point of view, the new features appearing due to heterogeneity are interesting.

To show the type of nontrivial kinetic effects related to catalyst heterogeneities, we treat in this paper the generic case when a reaction occurs on a surface composed of two catalytically active metals (such structures can be manufactured with a variety of nanotechnology techniques⁶ at length scales from nm to μm). Specifically, we analyze the most interesting situation when the reaction is bistable [practically important examples are CO and H_2 oxidation or NO reduction on catalysts like Pt or Rh (Ref. 7)]. On uniform surfaces (i.e., without heterogeneity), the reaction bistability may result in *propagation* of a chemical wave.⁷ On the surface of a catalyst consisting of two metals, one can realize a steady-state reaction regime corresponding to a *standing* chemical wave, with high reaction rate on one part of the surface and low reaction rate on the other part. Our goal is to demonstrate the adsorbate distributions in the reaction front corresponding to such reaction regimes.

In principle, chemical waves on the surface of a catalyst consisting of two metals can be described by using the conventional mean-field reaction-diffusion (MFRD) equations with *appropriate* boundary conditions (see a related treatment⁸ of propagation of chemical waves complicated by adsorbate-induced surface restructuring) near the line, dividing the two parts of the catalyst surface,

$$D_L \theta_x^L|_l = D_R \theta_x^R|_l, \quad (1)$$

$$\mu^L|_l = \mu^R|_l, \quad (2)$$

where θ^L , θ^R , D_L , and D_R are the adsorbate coverages and coefficients of diffusion on the left and right parts of the surface, μ is the adsorbate chemical potential, and $x=l$ is the coordinate corresponding to the boundary. Equation (2) can be rewritten as

$$\theta^L|_l = K \theta^R|_l, \quad (3)$$

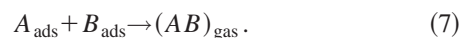
where K is the constant dependent on the difference of the binding energies on the two metals and also on coverage (if the coverage is appreciable). Physically, Eqs. (1) and (2) [or (3)] describe the mass conservation and local equilibrium near the boundary.

Recently, the MFRD equations were employed by Shvartsman *et al.*⁹ to explore chemical waves on composite catalysts, but referring to earlier related studies (e.g., Ref. 10) they used instead of condition (2) [or (3)] an incorrect boundary condition (for corrections, see Ref. 11):

$$\theta^L|_l = \theta^R|_l. \quad (4)$$

For this reason, the reaction fronts obtained by Shvartsman *et al.*⁹ are artificially smooth. Even with the corrections,¹¹ their analysis does not exhibit the whole richness of the reaction behavior near the boundary between the catalyst counterparts.

One of the shortcomings of the MFRD equations is that they do not take properly into account the coverage dependence of the adsorbate diffusion coefficients (for example, Shvartsman *et al.*^{9,11} ignore this factor), while at the same time the changes in coverages inside the front are often dramatic, which cause large variations in the coverage dependence of the diffusion coefficients as well. To overcome this and other shortcomings of the MFRD approach, we use Monte Carlo (MC) simulations. As an example, we treat the generic catalytic $A + B_2$ reaction occurring via the standard Langmuir-Hinshelwood (LH) mechanism,



This reaction mimics the essential behavior of, e.g., CO or hydrogen oxidation on noble metals (A stands for CO or hydrogen, and B_2 for O_2). During the past decade, its MC kinetics for the infinite uniform surface have been studied in detail (see the seminal paper by Ziff *et al.*¹² and the review⁷). Aiming at real reactions, we analyze one of the most important situations (for justification, see Refs. 13 and 14) when the LH step (7) is fast compared to A and B_2 adsorption, B particles are immobile, and A diffusion is rapid compared to the LH step. In addition, we take into account that strong repulsive lateral interactions between nearest-neighbor (nn) oxygen atoms prevent adsorption on nn sites. To mimic this effect, we consider that B_2 adsorption occurs on next-nearest-neighbor (nnn) sites. This detail is significant,^{13,14} because it prevents poisoning of the surface by B .

Our simulations are executed on a 400×400 square lattice. The left and right 200×400 sublattices of the lattice represent the two catalyst components. In general, the probabilities of all the kinetic processes on these two sublattices may be different. Our preliminary analysis, taking into account the experimental data available for CO (and H_2) oxidation on such catalytically active metals as Pt and Rh, has indicated that the most crucial factors for understanding the effects under consideration is the difference in the O_2 sticking probabilities and CO adsorption energies. In the present work, the B_2 (O_2) sticking coefficient for the left sublattice is taken to be ten times larger than that for the right sublattice (this assumption is actually quite realistic because the values of the O_2 sticking coefficient are very different for different metals and even for different faces of the same metal). The difference in the A (CO) adsorption energies, ΔE , results in an anisotropy of the A jumps between the nn sites located on the boundary between the sublattices. Specifically, the ratio of the rate constants for the boundary jumps in the two directions is $\exp(-\Delta E/k_B T)$. We analyze three cases when (a) there is no preference for A adsorption on the two sublattices ($\Delta E = 0$), (b) the right sublattice is preferable ($\Delta E < 0$), and (c) the left sublattice is preferable ($\Delta E > 0$), respectively. In case (a), all the A jump probabilities are considered to be equal. In case (b), the A jump probabilities on the two sublattices and from the left sublattice to the right sublattice are equal (the Schwoebel barrier is neglected), but the probability of A jump from the right sublattice to the left sublattice is considered to be ten times lower, i.e., $\exp(-\Delta E/k_B T) = 10$. Case (c) is the opposite to case (b), i.e., $\exp(-\Delta E/k_B T) = 0.1$. [In reality, case (a), corresponding to condition (4), cannot be realized, because even a relatively small difference in the adsorption energies on different metals results in considerable anisotropy of diffusion jumps. The results obtained for case (a) are however instructive from the tutorial point of view.] The probabilities of A (CO) adsorption on the two sublattices are considered to be equal (this is reasonable, because the CO sticking coefficient is close to unity on many metals). To not obscure the main message, the probabilities of the LH step on the two sublattices are assumed to be equal as well (in principle, the difference in these probabilities can easily be included into the model, but it is not necessary for our present goals).

To characterize the relative rates of the elementary steps, we introduce the four dimensionless parameters, p_{rea} , p_A , $p_{B_2}^L$, and $p_{B_2}^R$. The parameter p_{rea} is the ratio of the rates of

the LH step and A diffusion. The parameters p_A , $p_{B_2}^L$, and $p_{B_2}^R$ are the ratios of the rates of A and B_2 adsorption and the LH step (this means that these parameters are proportional to the product of reactant pressures and sticking coefficients). All these parameters are considered to be much lower than unity, because in real systems, as already noted, A diffusion is rapid compared to the LH step, which is in turn fast compared to A and B_2 adsorption.

With the specification above, the MC algorithm for simulating the reaction kinetics is as follows:

(1) A random number ρ ($\rho \leq 1$) is generated. If $\rho < p_{rea}$, an adsorption-reaction trial is realized [item (2)]. For $\rho > p_{rea}$, an A -diffusion trial is performed [item (3)].

(2) An adsorption-reaction attempt contains several steps. (i) An adsorption site is chosen at random. (ii) A new random number ρ' is generated. (iii) If the site selected is vacant, A or B_2 adsorption acts are realized provided that $\rho' < p_A$, $p_A < \rho' < p_A + p_{B_2}^L$ or $p_A < \rho' < p_A + p_{B_2}^R$, respectively. For B_2 adsorption, one of the nnn sites is chosen at random, and the trial is accepted provided that these sites have no nn sites occupied by B particles (the condition $p_A < \rho' < p_A + p_{B_2}^L$ is used if at least one of the two selected sites belongs to the left sublattice). (iv) If the site chosen is occupied by A , A tries to react. In particular, one of the nn sites is selected at random, and the trial is fulfilled if the latter site is occupied by B .

(3) For A diffusion, an adsorption site is chosen at random. If the site is vacant or occupied by B , the trial ends. Otherwise, an A particle located in this site tries to diffuse. In particular, an adjacent site is randomly selected, and if the latter site is vacant, the A particle jumps to it with unit probability if both sites belong to the same sublattice or if the jump occurs from one sublattice to another energetically preferable sublattice. If the jump occurs with the loss of energy, the jump probability is reduced down to 0.1.

The simulations have been executed for $p_{rea} = 0.01$, $p_A = 0.01$, $p_{B_2}^L = 0.04$, and $p_{B_2}^R = 0.004$ (with these parameters, A diffusion is two orders of magnitude faster than the LH step, and the LH step is in turn about two orders of magnitude faster than A and B_2 adsorption). First, we performed 10^5 MC steps (MCS) in order to reach the steady state and then used additional 10^5 MC in order to get the results (one MCS corresponds to 400×400 attempts to realize one of the adsorption-reaction-diffusion steps). The steady-state reaction fronts were found to be fairly stable. In particular, the same reactant distributions were reached starting from the clean lattice or from the $c(2 \times 2)$ B structure.

The results of the simulations are displayed in Figs. 1 and 2. In particular, Fig. 1 shows the A and B coverages along the coordinate perpendicular to the boundary between the two sublattices. Figure 2 exhibits typical snapshots of the central part of the lattice. The left and right sublattices are seen to be covered primarily by B and A particles, respectively, because the B_2 adsorption probability for the left sublattice is higher (the average reaction rates on these sublattices are accordingly high and low).

If the A adsorption energies on both sublattices are equal [case (a)], the A coverage smoothly increases [Figs. 1(a) and 2(a)] along the coordinate chosen. This dependence is similar

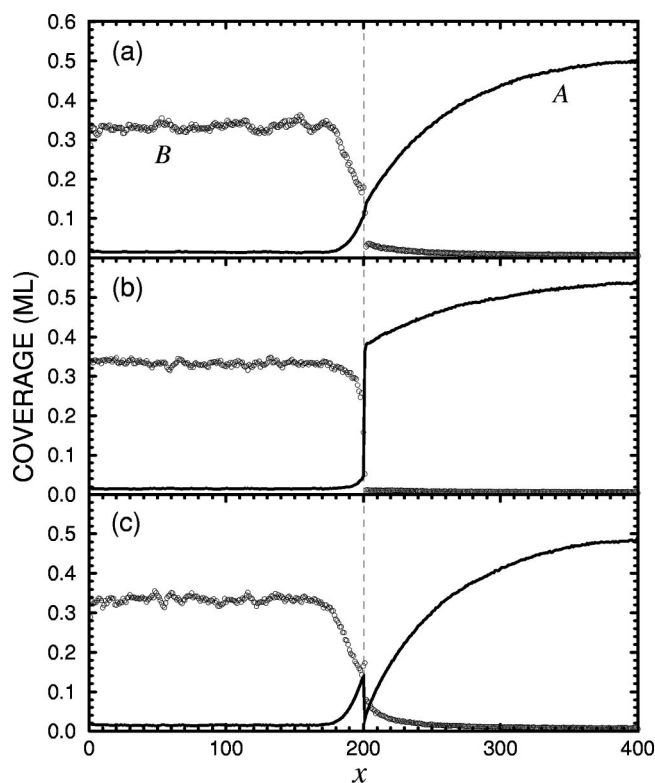


FIG. 1. A and B coverage along the coordinate perpendicular to the boundary between the two 200×400 sublattices of the 400×400 lattice in the cases when (a) there is no preference for A adsorption on the sublattices, (b) A adsorption is preferable on the right sublattice, and (c) A adsorption is preferable on the left sublattice. The dashed line shows the position of the boundary between the sublattices.

to that predicted by the MFRD equations with the boundary condition (4). The decrease of the B coverage is abrupt. This deviation from the MFRD prediction is connected with the fact that the B particles are immobile in our model.

If A adsorption is energetically preferable on the right sublattice [Figs. 1(b) and 2(b)], the stepwise changes in the A and B coverages are dramatic, because both thermodynamics and kinetics favor separation of A and B particles.

If A adsorption is preferable on the left sublattice [Figs. 1(c) and 2(c)], the thermodynamics drives A particles to the left sublattice. The “downhill” (energetically) flux of A from right to left causes A enrichment on the left-hand side. This A accumulation is counteracted by the $A + B$ reaction. In other words, the reaction prevents propagation of the reaction front far inside this sublattice. For this reason, the dependences of both coverages on the coordinate along the surface are nonmonotonous. For B particles, this effect is minor, but for A particles the changes are appreciable.

The total reaction rate on the composite catalyst is higher (in all three cases) compared to that calculated for the separate counterparts.

In summary, we have shown the types of standing fronts which can be realized in bistable reactions on composite catalytic surfaces. The moving reaction fronts with stepwise changes of coverages [as in cases (a) and (b)] were earlier

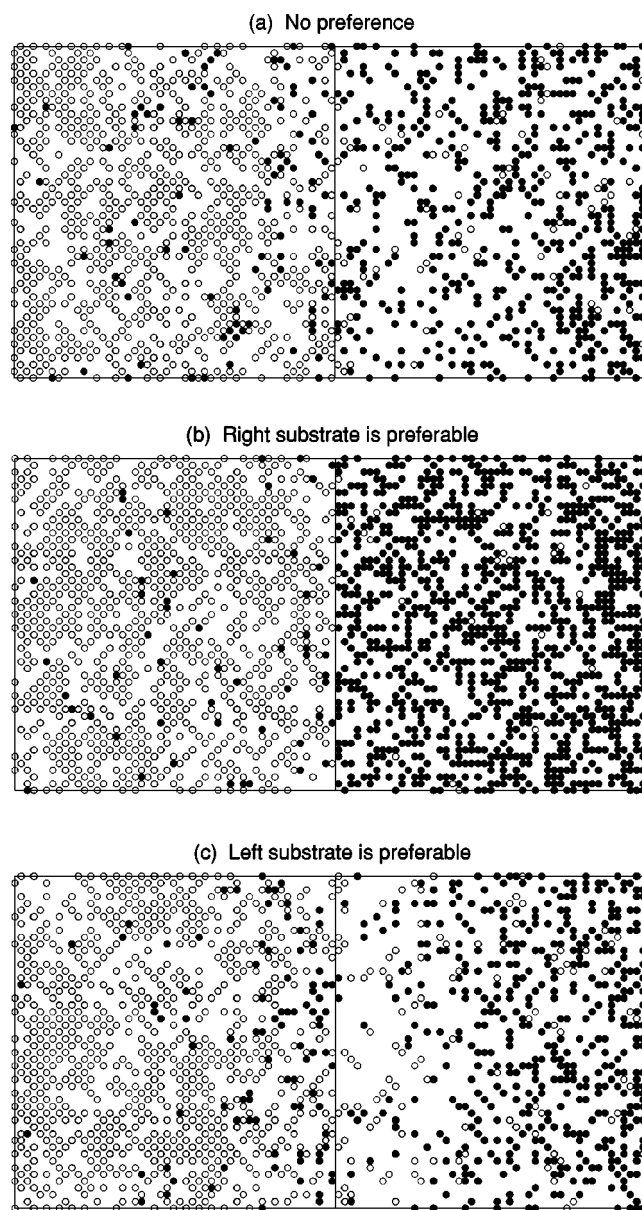


FIG. 2. Central 50×100 fragments of the 400×400 lattice for cases (a), (b), and (c) in Fig. 1. Filled and open circles indicate A and B particles. The vacant sites are not shown. The thin line indicates the boundary between the two sublattices. Note that B particles form small $c(2 \times 2)$ domains, because B_2 adsorption occurs on nnn sites.

found⁸ in the situations when propagation of chemical waves is accompanied by adsorbate-induced surface restructuring. The fronts of type (c) are inherent for composite catalysts and can hardly be observed on uniform surfaces.

Finally, it is appropriate to note that the results obtained in our study can be used for optimization of performance of composite catalysts. In case (c), for example, the reaction front is much wider than in case (b). The optimum catalyst size (perpendicular to the boundary) in the former case should accordingly be larger.

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