

## Domain Growth and Reaction Kinetics in Adsorbed Overlayers

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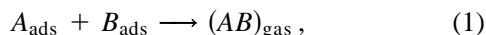
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We present the results of Monte Carlo simulations of rapid reaction between adsorbed species,  $A_{\text{ads}} + B_{\text{ads}} \rightarrow (AB)_{\text{gas}}$ , in the situation when preadsorbed  $B$  particles form domains. In the course of reaction,  $A$  particles are assumed to be supplied from the gas phase via monomolecular or dissociative adsorption. The kinetics corresponding to these two cases are essentially different from the conventional ones. To classify and explain the results obtained, the physics behind the model is discussed in detail. [S0031-9007(96)01135-0]

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Attractive or repulsive lateral interactions between particles adsorbed on single-crystal surfaces may result at relatively low temperatures in the formation of islands or domains, respectively. During the past decade, the kinetics of island or domain growth have been studied in detail [1–3]. There are also a few studies of the kinetics of heterogeneous reactions accompanied by island formation [2] (for a recent review of the theory of rate processes on solid surfaces, see Ref. [4]). On the other hand, simulations of the effect of domains on the reaction kinetics are lacking. Meanwhile, the latter problem is of considerable interest. From the theoretical point of view, it is an example illustrating limitations of the mean-field approximation (MFA). Experimentally, the scanning tunneling microscopy opens up the possibility of direct observation of shrinking islands or domains in the course of reactions [the first measurements [5] of this type exhibit evolution of the preadsorbed  $p(2 \times 1)$  oxygen and methoxy islands during the synthesis of formaldehyde from methanol on Cu(110)]. The goal of this Letter is to show the basic types of transient reaction kinetics complicated by the presence of domains on the surface. The calculations reported bridge the gap in simulations of 2D domain growth and reaction kinetics, and the results obtained might guide the experiment.

As an example, we consider the Langmuir-Hinshelwood reaction,



on a square lattice in the case when preadsorbed  $B$  particles form domains. In the course of reaction,  $A$  particles are assumed to be supplied from the gas phase. The latter process is considered to be fast compared to step (1). In turn, step (1) is assumed to be rapid compared to diffusion of  $B$  particles (i.e., these particles are considered to be immobile during reaction). [All these conditions can be met in such rapid heterogeneous reactions as CO or hydrogen oxidation on transition metals ( $A$  is for CO or hydrogen, and  $B$  is for oxygen).]

To prepare domains in the preadsorbed overlayer of  $B$  particles, we assume that one-half monolayer of these particles (with nearest-neighbor repulsion,  $\epsilon_1$ ) is quenched from high temperature in a disordered phase to a temperature below the critical one,  $T < T_c = 0.567\epsilon_1$  (we set  $k_B = 1$ ). In this case, the ground state is doubly degenerate, and the growth law for the average radius of the  $c(2 \times 2)$  domains is given [1–3] by  $R(t) \sim t^{1/2}$  for both conserved and nonconserved density. Taking into account that the domain structure is fairly insensitive with respect to details of the dynamics, we have formed domains via diffusion of  $B$  particles over nearest-neighbor sites with the standard Metropolis Monte Carlo (MC) algorithm: A site on the lattice is chosen at random. If that site is vacant, the trial ends. Otherwise, a  $B$  particle located in this site tries to diffuse. In particular, an adjacent site is randomly chosen, and, if this site is vacant, the  $B$  particle jumps to it with the probability  $W = 1$  for  $\Delta E \leq 0$  and  $W = \exp(-\Delta E/T)$  for  $\Delta E \geq 0$ , where  $\Delta E$  is the energy difference of the final and initial states. The results presented [Fig. 1(a)] have been obtained for a  $500 \times 500$  lattice (with periodic boundary conditions),  $T = \epsilon_1/3$ , and  $t = 100$  MC steps (MCS) [1 MCS corresponds by definition to  $L \times L$  attempts of diffusion ( $L$  is the lattice size)]. In this case, the average domain size is about 15 lattice spacings.

The distribution of  $B$  particles described above have been employed to simulate the reaction. First, we have studied the case when the second reactant ( $A$  particles) is supplied from the gas phase via monomolecular adsorption,  $A_{\text{gas}} \rightarrow A_{\text{ads}}$ . Assuming the  $A$  impingement rate to be high, we consider that during reaction all the non- $B$  sites are occupied by  $A$ .

To calculate the reaction rate, we need in general to introduce the  $A$ - $A$ ,  $A$ - $B$ , and  $B$ - $B$  adsorbate-adsorbate interactions in the ground and activated states [2] (the terms “ground” and “activated” correspond to the transition state theory). To emphasize the physics behind the MC simulations, we take into account only the  $B$ - $B$  interaction in the ground and activated states,  $\epsilon_1$  and  $\epsilon_1^*$ . The  $A$ - $A$  and  $A$ - $B$

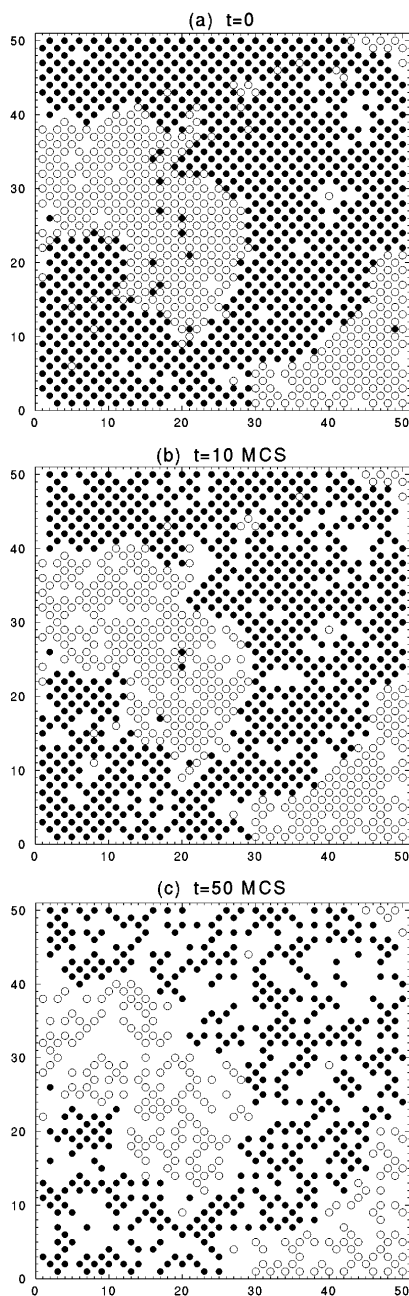


FIG. 1. A  $50 \times 50$  fragment of the  $500 \times 500$  lattice in the course of reaction between adsorbed  $A$  and  $B$  particles at  $T = \epsilon_1/3$ . Filled and open circles indicate  $B$  particles located on two sublattices corresponding to the  $c(2 \times 2)$  structure. All the other sites are occupied by  $A$  particles (not shown). Panel (a) exhibits the initial distribution of  $B$  particles (after 100 MCS for diffusion). The initial  $B$  coverage is 0.5 monolayer. Panels (b) and (c) show the surface after 10 and 50 MCS for reaction. In the latter cases, the  $B$  coverage is 0.42 and 0.26 monolayer, respectively.

interactions are ignored because these interactions do not affect the domain structure and, accordingly, do not change the special features of the reaction kinetics under consideration. The *apparent* rate constants in the equations describing the reaction [e.g., in Eqs. (2) and (3) below] are,

of course, dependent on the  $A$ - $A$  and  $A$ - $B$  interactions, but this dependence is of minor importance for understanding of the reaction kinetics. If necessary, the  $A$ - $A$  and  $A$ - $B$  interactions can be easily incorporated into the model.

With our choice of lateral interactions, the reaction rate of a given pair of nearest-neighbor  $A$  and  $B$  particles is, as usual [2], proportional to  $\exp(-n\Delta\epsilon/T)$ , where  $\Delta\epsilon = \epsilon_1^* - \epsilon_1$ , and  $n \leq 3$  is the number of  $B$  particles adjacent to a  $B$  particle from the pair under consideration. As a rule [2], the interaction in the activated state is lower than that in the ground state. In our simulations, we have used  $\epsilon_1^* = \epsilon_1/2$ .

After the specification above, the MC algorithm for describing the reaction is as follows. Two adjacent sites are chosen at random. If the occupation of those sites is  $AA$  or  $BB$ , the trial ends. If, however, the occupation is  $AB$ , this pair tries to react with the probability  $W = \exp[(3-n)\Delta\epsilon/T]$  (note that the reaction probability is maximum,  $W = 1$ , in the case when a given  $B$  particle has three adjacent  $B$  particles).

The reaction kinetics obtained (Fig. 2) for monomolecular adsorption ( $A_{\text{gas}} \rightarrow A_{\text{ads}}$ ) is exponential,

$$\theta_B(t) \approx \theta_B(0) \exp(-kt), \quad (2)$$

where  $\theta_B$  is the  $B$  coverage. Minor deviations from the exponential law are observed only in the beginning. To rationalize Eq. (2), one can note that at  $t = 0$  the high-reactive  $B$  particles (with one, two, or three adjacent  $B$  particles) are located primarily in the domain boundaries [Fig. 1(a)]. The fraction of such particles is low, and they are rapidly consumed on the early stage of the reaction [Fig. 1(b)]. The main bulk of  $B$  particles located inside domains reacts afterwards. In the latter case, the nearest-neighbor  $B$ - $B$  pairs are, in fact, absent, and, accordingly, the kinetics is exponential with the rate constant given by  $k = \exp(3\Delta\epsilon/T)$  [with the parameters  $\epsilon_1 = 3T$  and  $\epsilon_1^* = \epsilon_1/2$  corresponding to Fig. 2, we have  $k = \exp(-9/2) = 0.011$ ]. Thus, with increasing time, the global domain structure is preserved, but the fine details of the domain boundaries are smeared, and the domains become “diluted” due to consumption of  $B$  particles [Fig. 1(c)].

The results shown in Fig. 2 correspond to preadsorption of one-half monolayer of  $B$  particles [ $\theta_B(0) = 0.5$ ]. This case is of particular interest from the point of view of the theory of domain growth because the critical temperature of the order-disorder  $c(2 \times 2)$  phase transition is maximum at  $\theta_B = 0.5$ . With decreasing or increasing coverage,  $T_c$  drops rapidly [1,2]. The special features of the reaction kinetics at  $\theta_B(0) \neq 0.5$  can be understood by employing the same qualitative analysis as above. In particular, it is clear that at  $\theta_B(0) < 0.5$  the reaction kinetics will also be exponential [because in this case almost all the  $B$  particles will (due to repulsion) have no  $B$  neighbors at  $t = 0$ ]. At  $\theta_B(0) > 0.5$ , the fraction of

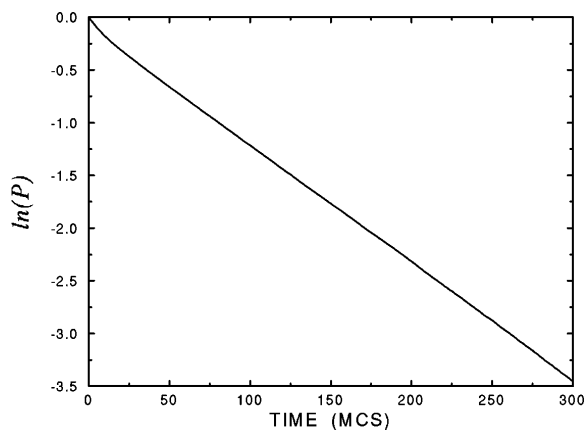


FIG. 2. Probability,  $P$ , to find a  $B$  particle on the surface as a function of time for the reaction accompanied by rapid monomolecular adsorption of  $A$  particles at  $T = \epsilon_1/3$ .

high-reactive  $B$  particles will, at  $t = 0$ , be higher than for  $\theta_B(0) = 0.5$ , and, accordingly, the deviations from the exponential regime in the beginning will be stronger compared to Fig. 2.

If  $A$  particles are supplied from the gas phase via dissociative adsorption,  $(A_2)_{\text{gas}} \rightarrow 2A_{\text{ads}}$ , an arriving  $A_2$  molecule needs *two* vacant sites for adsorption. Simulating this process, we assume (in analogy with monomolecular adsorption) that the impingement rate of  $A_2$  molecules is high compared to the reaction rate. In addition, we consider that adsorbed  $A$  particles rapidly diffuse by jumping to nearest-neighbor vacant sites. In this case,  $A_2$  adsorption can be imitated simply by filling by  $A$  particles all the non- $B$  site clusters (by definition, a cluster contains two or more adjacent sites). Thus, a non- $B$  site is considered to be vacant only if it is surrounded by *four*  $B$  particles. (This prescription simplifying simulations is reasonable because it is precise for the clusters containing even number of sites and rather accurate for the odd clusters.) Then, the reaction kinetics can be calculated by employing the MC algorithm similar to that described above. In particular, Fig. 3 shows shrinkage of domains in the course of reaction. The dependence of  $B$  coverage on time (Fig. 4) exhibits in this case a crossover from the linear regime,

$$\theta_B(t) \approx \theta_B(0) - \kappa t, \quad (3)$$

at appreciable coverages to the exponential regime at low coverages. The physics behind this behavior is as follows. The reaction starts on the domain boundaries. Later on, the reaction continues to occur on the boundaries of shrinking domains because dissociative adsorption of  $A_2$  molecules inside perfect  $c(2 \times 2)$  domains is impossible. The transition from the linear to the exponential regime takes place when the average domain size becomes small. From this analysis, it is clear that the *effective* rate constant  $\kappa$  [Eq. (3)] will decrease with increasing the average initial domain radius. An analytical expression for this rate constant can hardly be derived. We can, however, note

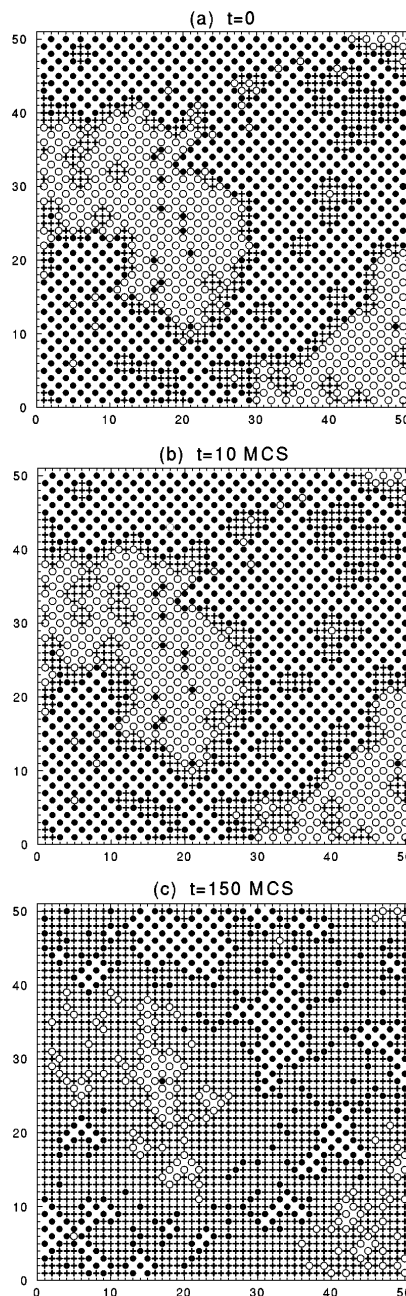


FIG. 3. A  $50 \times 50$  fragment of the  $500 \times 500$  lattice during reaction between adsorbed  $A$  and  $B$  particles at  $T = \epsilon_1/3$ . Filled and open circles indicate  $B$  particles located on two  $c(2 \times 2)$  sublattices. Plus signs show sites occupied by  $A$  particles (due to rapid dissociative adsorption of  $A_2$  molecules). Vacant sites are not shown. Panel (a) exhibits the initial distribution of reactants (after 100 MCS for  $B$  diffusion followed by  $A_2$  adsorption). The initial  $B$  coverage is 0.5 monolayer. Panels (b) and (c) show the surface after 10 and 150 MCS for reaction. In the latter cases, the  $B$  coverage is 0.48 and 0.27 monolayer, respectively.

(cf. Figs. 2 and 4) that  $\kappa$  for dimers [Eq. (3)] is much lower than  $k$  for monomers [Eq. (2)] because in the latter case the reaction occurs not only on the domain boundaries but also inside domains.

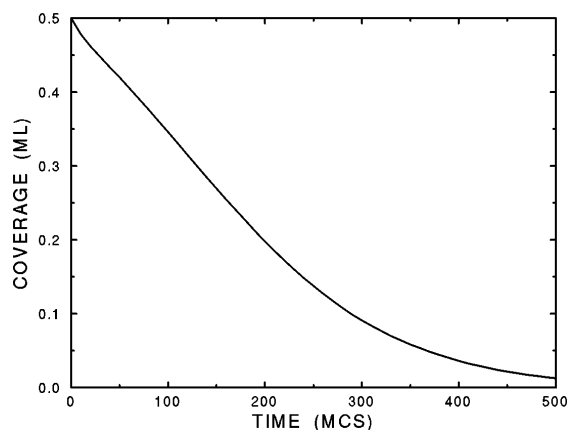


FIG. 4.  $B$  coverage as a function of time for the reaction accompanied by rapid dissociative adsorption of  $A_2$  molecules at  $T = \epsilon_1/3$ .

The arguments presented in the paragraph above are applicable at  $\theta_B(0) \approx 0.5$ . Thus, the special features of the reaction kinetics shown in Fig. 4 will hold at all the coverages where the  $c(2 \times 2)$  phase transition takes place. Beyond the  $c(2 \times 2)$  region, the reaction kinetics will be different. In particular, it will be close to exponential at  $\theta_B(0) < 0.3$  (in analogy with monomolecular adsorption) because in this case almost all the  $B$  particles are surrounded by  $A$  particles. At  $\theta_B(0) > 0.8$ , dissociative adsorption of  $A_2$  molecules is strongly suppressed. It will start on pairs of vacant nearest-neighbor sites (the pairs are located at random and the average distance between them is large). Accordingly, the reaction kinetics will be of the same type as that predicted by the Avrami equation (see below).

The kinetics presented in Figs. 2 and 4 are different from the conventional ones. For example, the MFA equation for describing reaction (1) with nearest-neighbor interactions between  $B$  particles is [2]

$$d\theta_B/dt = -k_0 \exp(-3\Delta\epsilon \theta_B/T)\theta_A\theta_B, \quad (4)$$

where  $k_0$  is the reaction rate constant at low coverages. Replacing  $\theta_A$  in Eq. (4) by  $(1 - \theta_B)$  (this step corresponds to the high impingement rate of  $A$  or  $A_2$  molecules), one can easily show that this equation, predicting rapid decrease of the reaction rate with decreasing coverage, does not reproduce the kinetics exhibited in Figs. 2 and 4. The quasichemical approximation [2] fails also. The phenomenological Avrami equation [6] describing a reaction which starts from the “active” centers located at random and then occurs on the boundaries of spots around these centers,

$$\theta_B(t) = \theta_B(0) \exp[-\pi N_0(vt)^2], \quad (5)$$

( $N_0$  and  $vt$  are the concentration of centers and the spot radius, respectively) does not fit the kinetics obtained either. In addition, it is reasonable to mention that the problem under consideration does not seem to be connected with percolation theory or with “epidemic” models. The standard site and bond percolation problems [7], based on the assumption that particles are located at random, are irrelevant because in our case local correlations are very strong. In addition, the reaction kinetics is obviously independent of the global “conductivity” of domains because adsorption from the gas phase is possible even below the percolation threshold (the percolation theory is more appropriate for describing the reaction kinetics in porous solids [8]). The epidemic models [9] might be applicable if the kinetics are dependent on competition between different processes (e.g., “reproduction” and “death”). In our case, however, there is no competition of adsorption and reaction (these steps are rather consequent).

In summary, our study identifies a class of surface kinetics dependent on the domain growth of one of the reactants. Such kinetics, sensitive with respect to the mechanism of adsorption (monomolecular or dissociative) of another reactant, are shown to be essentially different compared to the conventional ones.

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