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Dimer–dimer surface reaction of Albano's type: a cellular automaton approach

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Abstract. The dimer–dimer catalytic surface reaction of Albano's type ($\frac{1}{2}A_2 + B_2 \rightarrow B_2A$) is studied with the aid of the cellular automaton model of Chopard and Droz, as modified by Ziff, Fichtorn and Gulari. A mean-field analysis is given, with results indicating that the reaction proceeds only at $p = p_c$ (p is the partial pressure of species B_2 in the gaseous phase), when no recombination reaction of adsorbed B-species is considered, and a reaction window with B_2A production occurs for $p > p_c$, when the recombination mentioned above is taken into account. Our mean-field results are qualitatively in agreement with Albano's Monte Carlo simulations on a square lattice, and are valid in general, independent of the type of the lattice (square, hexagonal, etc).

1. Introduction

There has been a great deal of interest in the study of kinetic models for catalytic surface reactions, since the monomer–dimer model or AB_2 model was first proposed by Ziff, Gulari and Barshad in 1986 [1]. In contrast to the traditional method using rate equations, kinetic models take into account local fluctuations and spatial correlations in the concentrations of the surface reaction species, and hence they exhibit the complicated dynamic behaviour of the reaction system. Because of the lack of a general theory based on first principles, the kinetic model, in conjunction with computer simulations, provides a powerful method for investigating the dynamics of catalytic surface reaction. Up to now various models (monomer–dimer, dimer–dimer, dimer–trimer, etc) have been studied [2, 3] and different simulation methods have been proposed [4, 5].

Somewhat later the monomer–dimer model of Ziff *et al* was recast in the formalism of the cellular automaton (CA) model by Chopard and Droz [6], and the CA model so obtained has in addition the merit of being capable of following the time evolution of all its microscopic degrees of freedom and amenable to theoretical analyses. In the CA formalism the catalytic surface is modelled as a lattice, each site of which is endowed with a finite number of states, and its time evolution is determined by a set of local rules. With proper stoichiometry taken into account [7], this model yields qualitatively the same results as those of Ziff *et al* [1].

In this paper we use the CA model to investigate the dimer–dimer reaction of the type $\frac{1}{2}A_2 + B_2 \rightarrow B_2A$. Although inspired by the catalytic oxidation of hydrogen on

a platinum surface, Albano [8] proposed this type of dimer–dimer reaction to simulate a generic bimolecular Langmuir–Hinshelwood reaction, carrying out Monte Carlo simulations and finite-size analysis on a square lattice with a view to investigating the effect of different surface processes on the promotion of a steady reactive state. In this paper we give mean-field analyses [7, 9] of this model and draw the conclusion that the recombination reaction of adsorbed B species is crucial to the existence of a reactive regime with finite extent, in accordance with Albano’s Monte Carlo simulations. Furthermore, we show that the above conclusion is valid in general, independent of the type of the lattice (square, hexagonal, etc). In section 2, the reaction mechanism is briefly reviewed and the corresponding CA rules are formulated and discussed. In section 3, a mean-field analyses are given for the cases of no recombination and recombination of adsorbed B species, and in the latter case the occurrence of a steady reactive state with finite extent is established. Finally, in section 4, some general remarks are made.

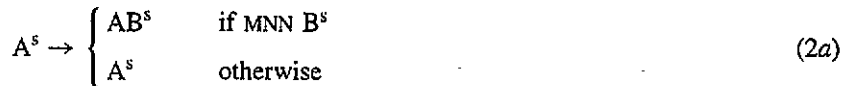
2. The model

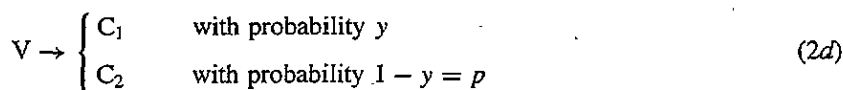
Inspired by the catalytic oxidation of hydrogen on platinum surface, Albano supposed that the dimer–dimer reaction of the type $\frac{1}{2}A_2 + B_2 \rightarrow B_2A$ proceeds according to the Langmuir–Hinshelwood mechanism as follows [8]:



where s and $2s$ represent a vacant site and a pair of nearest-neighbour vacant sites, respectively; (g) refers to the gaseous phase and the superscript s denotes the adsorbed state. It is assumed that there exists an intermediate species AB^s corresponding to hydroxyl groups and an AB group is adsorbed through the A atom with the B atom pointing away from the surface. Furthermore, both diffusion of B^s and recombination of a pair of nearest-neighbour adsorbed B’s are allowed.

In the corresponding CA model each lattice site has six different states A^s , B^s , AB^s , V , C_1 and C_2 , where V is the vacant state, and C_1 and C_2 are the conditional occupation states by an atom A and B, respectively, The time evolution of the CA is given by the following set of rules, which determine the state of a site at time $t + 1$ according to the states of this site and its nearest neighbours at time t [6, 7]:





where MNN denotes 'matching nearest neighbour', a notion invoked by Ziff *et al* to take into account proper stoichiometry for two-site processes, such as dimer adsorption and $A^s - B^s$ reaction. It should be noted that rules (2a)–(2f) are not strictly equivalent to the reaction mechanism (1a)–(1d); in these rules dimer adsorption and monomer–monomer reaction occur with much lower effective probabilities due to the requirement of MNN, which only leads to a rescaling of transition points without substantial change in the phase diagram, as shown by Ziff *et al* for the monomer–dimer model [7]. In addition, the surface diffusion of adsorbed species is ignored, just in order to investigate the influence of recombination in reaction step (1b) on the occurrence of a reactive regime with finite extent.

3. Mean-field analysis

As is well known, much can be learned from mean-field analyses [9] of kinetic models for catalytic surface reactions: even one-site approximations may be used to predict, e.g., the existence of a steady reactive state. From the CA rules (2a)–(2f), we get one-site equations for coverages of various adsorbed species (including V, C_1 and C_2) as follows:

$$\frac{d\theta_A}{dt} = \frac{1}{n}\theta_{C_1}^2 - \frac{1}{n}\theta_A\theta_B \quad (3a)$$

$$\frac{d\theta_B}{dt} = \frac{1}{n}\theta_{C_2}^2 - \frac{1}{n}\theta_B\theta_B - \frac{1}{n}\theta_B\theta_A - \frac{1}{n}\theta_B\theta_{AB} \quad (3b)$$

$$\frac{d\theta_{AB}}{dt} = \frac{1}{n}\theta_A\theta_B - \frac{1}{n}\theta_{AB}\theta_B \quad (3c)$$

$$\frac{d\theta_{C_1}}{dt} = y\theta_V - \theta_{C_1} \quad (3d)$$

$$\frac{d\theta_{C_2}}{dt} = (1 - y)\theta_V - \theta_{C_2} \quad (3e)$$

$$\theta_V = 1 - \theta_A - \theta_B - \theta_{AB} - \theta_{C_1} - \theta_{C_2} \quad (3f)$$

where, for generality, we consider a lattice with coordination number n , e.g. $n = 4$ for a square lattice.

Setting the time derivatives of θ_i equal to zero, we get from (3a)–(3f) a set of equations to determine steady states. It should be noted that the coordination number n does not appear in these equations, hence solutions obtained from them are valid for lattices of any type (square, hexagonal, etc).

In order to highlight the crucial role of the recombination of adsorbed B species in the promotion of a reactive state, we consider two models.

Model 1. No recombination of adsorbed B species is considered, hence the term $\theta_B\theta_B$ disappears from equation (3b). There are three sets of solutions corresponding to three different phases.

Set 1. $\theta_B = 0$, so that $\theta_{C_1} = \theta_{C_2} = \theta_V = 0$ and $\theta_A + \theta_{AB} = 1$. That is, the reaction system has an A^s - AB^s poisoned phase, or concretely, an O^s - OH^s poisoned phase.

Sets 2,3. $\theta_B \neq 0$, so that $\theta_A = \theta_{AB}$. If $\theta_A = 0$, it follows that $\theta_{C_1} = \theta_{C_2} = \theta_{AB} = \theta_V = 0$ and $\theta_B = 1$, i.e. the reaction system has a B^s poisoned phase, or concretely, a H^s poisoned phase. If $\theta_A \neq 0$, it follows that $\theta_{C_1} \neq 0$, $\theta_{C_2} = \sqrt{2}\theta_{C_1}$, $\theta_V \neq 0$ and $y_c = -1 + \sqrt{2} \simeq 0.4142$, i.e. the system has a reactive phase, which occurs only at $p_c = 1 - y_c = 0.5858$, p is the partial pressure of B_2 in the gaseous phase.

By and large, the model with no recombination has a reactive phase at $p < p_c$ and a B^s poisoned phase for $p > p_c$, qualitatively in agreement with Albano's simulations (see Albano's figure 1).

Model 2. The recombination is taken into account, hence the term $\theta_B\theta_B$ is retained in equation (3b). There are two sets of solutions corresponding to two different phases.

Set 1. $\theta_B = 0$, an A^s - AB^s poisoned phase occurs, just as in model 1, where no recombination is considered.

Set 2. $\theta_B \neq 0$, so that $\theta_A = \theta_{AB}$, and all the coverages θ_i may be expressed as functions of θ_V :

$$\theta_{C_1} = y\theta_V \quad (4a)$$

$$\theta_{C_2} = (1 - y)\theta_V \quad (4b)$$

$$\theta_A = \theta_{AB} = \frac{y^2}{(1 - y)^2}(1 - 2\theta_V) \quad (4c)$$

$$\theta_B = \frac{(1 - y)^2\theta_V^2}{(1 - 2\theta_V)} \quad (4d)$$

and θ_V satisfies the following equation:

$$(y^4 - 4y^3 + 10y^2 + 4y - 3)\theta_V^2 - 4(y^2 + 2y - 1)\theta_V + (y^2 + 2y - 1) = 0$$

which yields

$$\theta_V = \frac{2(y^2 + 2y - 1) + (y - 1)^2(1 - 2y - y^2)^{1/2}}{y^4 - 4y^3 + 10y^2 + 4y - 3} \quad (4e)$$

The negative root should not be taken into account, otherwise some θ_i 's would take unreasonable values. The set of solutions (4a)-(4e) corresponds to a reactive phase if and only if $1 - 2y - y^2 > 0$, i.e. $y < y_c$ (or $p > p_c = 1 - y_c$), where $y_c = -1 + \sqrt{2} = 0.4142$ ($p_c = 0.5858$) is a solution of the equation $1 - 2y - y^2 = 0$.

As a whole, the model with recombination has an A^s - AB^s poisoned phase for $p \leq p_c = 0.5858$ and has a reactive phase for $p > p_c = 0.5858$. This conclusion is also qualitatively in agreement with Albano's simulation results (see Albano's figure 3). A careful comparison of the above results (4a)-(4e) with Albano's simulations reveals an interesting discrepancy. In Albano's simulation as y tends to zero or p tends to unity, nearly all lattice sites turn out to be vacant, e.g. for $p = 0.90$, about 90% of lattice sites are vacant. In contrast, if we let y tend to zero in equations (4a)-(4e), we get $\theta_V = \theta_{C_2} = \theta_B = \frac{1}{2}$ and $\theta_A = \theta_{AB} = \theta_{C_1} = 0$.

This discrepancy is due to the appearance of C states and the 'matching' requirement in the CA model: under the strike of a B₂ dimer a vacant site becomes a C₂ state at the first time step; on the other hand, the two nearest adsorbed B's cannot recombine and desorb immediately, these leading to finite coverages of C₂ and B^s.

4. Conclusions and remarks

Finally, we give some general conclusions and remarks.

(i) One-site mean-field analyses of the CA model may be used to study the characteristics of the reactive phase for a surface reaction system [6, 7, 10, 11, 12, 13], especially for the dimer-dimer reaction of Albano's type; these analyses even provide valuable results for the phase diagram as a whole, although it cannot predict the existence of the second-order transition or yield results for the relevant universal quantities such as critical exponents.

(ii) In model 1 with no recombination of adsorbed B species, there exists a reactive phase at $p = p_c = 0.5858$, an A^s-AB^s poisoned phase for $p < p_c$ and a B^s poisoned phase for $p > p_c$, similar to the phase diagram of the monomer-monomer model, but with a somewhat larger p_c value [10] due to the formation of the intermediate AB^s species.

(iii) In model 2 with the recombination taken into account, there exists a reactive phase for $p > p_c = 0.5858$ and an A^s-AB^s poisoned phase for $p \leq p_c$, formally very similar to the phase diagram of the monomer-dimer model with the Eley-Rideal mechanism considered, in both cases one poisoned phase disappears due to the recombination of adsorbed B species (dimer-dimer model) or the Eley-Rideal mechanism (monomer-dimer model) [14, 5].

(iv) Conclusions (ii) and (iii) obtained with one-site mean-field analyses of a CA model are qualitatively in agreement with Albano's simulation results, and our conclusions are valid in general, independent of the type of the lattice, while Albano's simulations are carried out only on a square lattice [3, 10, 11].

Acknowledgments

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