

# Mathematical Analysis of Physicochemical Processes on Catalytic Surfaces

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*The traditional approach followed for mathematically modeling physico-chemical processes on catalytic surfaces involves the choice of an infinitesimal surface area on the catalyst and formulation of mass balances involving adsorbate surface concentrations. Such a strategy is inadequate when the catalytic surface itself changes dynamically with respect to adsorbate-dependent surface arrangement of its catalytic atoms (and hence) its characteristic kinetics. A rigorous mathematical framework to model such processes is presented. The basic postulates of the theory are the availability of (1) a length scale over which the local infinitesimal area is of one surface type or another and (2) a time scale in which changes in fractional coverage occurring on the length scale in (1) are deterministically describable by continuous variables. A combination of probability and area-averaging is used to arrive at a deterministic set of partial differential equations for surface concentrations. The resulting equations include reaction and surface diffusion, and new terms such as dilution/augmentation of surface concentration of species brought about by phase transformation. Such terms are significant in predicting the nonlinear behavior of the system and in extracting the kinetics of surface reactions from dynamic data. An application of the theoretical framework to CO oxidation on Pt(100) is demonstrated and dilution/augmentation terms were identified in the purely temporal model. These terms are shown to be significantly important by simulation.*

## Introduction

Physicochemical processes on a catalytic surface such as adsorption, desorption, surface diffusion, and chemical reaction when coupled with an adsorbate-induced catalyst surface phase transformation give rise to nonlinear phenomena like oscillatory behavior in the macroscopic reaction rate and spatiotemporal pattern formation on the catalyst surface (Ertl, 1985; Gardner et al., 1990; Behm et al., 1983; Cox et al., 1983). Self-organization in the form of spiral waves, standing waves, and chemical turbulence have been observed during a variety of chemical reactions on the Pt(100) and Pt(110) single-crystal surfaces (Ertl, 1993; Jakubith et al., 1990; Eiswirth et al., 1989). The discovery of a rich variety of patterns as well as

successful experiments that bridged the so-called surface-science "pressure gap" have become possible as a result of the advent of advanced experimental tools such as ellipsometry for surface imaging (EMSI) and photoelectron emission microscopy (PEEM) (Rotermund, 1995; Haas et al., 1998; Rotermund et al., 1995). A widely studied reaction in this context is the CO oxidation on Pt catalysts (Slinko et al., 1994).

Various theoretical approaches have been used to model spatiotemporal dynamics on well-defined surfaces. Prominent among these have been Monte Carlo methods (Ziff et al., 1986), cellular automaton methods (Mai and von Niessen, 1991; Chavez et al., 1998), and the traditional mass-balance methods (Imbihl et al., 1985; Gruyters et al., 1996; Eiswirth et al., 1986), where reaction-diffusion models were formulated to describe the dynamics on surfaces. The formulation of mass balances to describe catalytic surface phenomena in-

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volve (a) the identification of a differential area at any spatial location on the catalytic surface, and (b) description of the dynamics of *surface* concentration (coverages) of chemical species on the area defined in (a). Such a strategy cannot be applied in a straightforward manner when formulating mass balances on transforming surfaces for reasons explained in the following.

On transforming catalytic surfaces, the physicochemical identity of any identified differential area changes dynamically *depending* on the (continuously changing) adsorbate surface concentration and the chemical nature of the adsorbed chemical species. Let us consider (without loss of generality) that the catalytic atoms that form the differential area identified earlier in (a) can exist in two different configurations. These two configurations, besides being different in their atomic arrangements, have unique and very different energetics for adsorption and desorption of reactants as well as a chemical reaction between adsorbed chemical species. The interconversion between the two catalytic surface configurations is driven *purely* by the local *configuration-specific* adsorbate concentration. Thus, any mass-balance formulation requires the dynamic description of *surface-specific* adsorbate concentrations, in addition to the fractions of the catalytic surface that exist in each of the configurations. We now address a somewhat subtle issue, connected with mass balances on surface-specific concentrations, that has not been accounted for in prior formulations. The differential area of any given surface type is itself changing continuously because of interconversion between surface types. This calls for describing dynamically changing probabilities of the differential area being of one type or another. Since the final goal is to arrive at deterministic equations for describing coverage dynamics, a suitable probability averaging is necessary, as will be seen in the mathematical development in this article.

To establish an experimental context for the preceding discussion, we briefly discuss the CO oxidation reaction on the Pt(100) catalytic surface. The Pt(100) catalyst surface atoms exhibits a hexagonal arrangement when the adsorbed CO surface concentration is lower than a certain critical value (Cox et al., 1983; Hopkinson and King, 1993; Hopkinson et al., 1993). This “hex” surface has a very low adsorption probability of oxygen (0.0001) compared to that of CO (0.78). However, during the course of the reaction, when the CO surface concentration *on the hex phase* increases above a critical concentration, the Pt(100) surface atoms dynamically rearrange to form a  $1 \times 1$  arrangement, which has comparable adsorption probabilities for CO and oxygen. Oxygen adsorption on the  $1 \times 1$  surface causes a significant chemical reaction with adsorbed CO already present on the surface producing  $\text{CO}_2$ , which is immediately desorbed. This causes adsorbate surface concentrations on the  $1 \times 1$  surface to fall below the critical value, which causes rearrangement back to the hex phase. Experimental data *specific to* the  $1 \times 1$  and the hex surfaces, such as adsorption probability dependence on surface-specific adsorbate concentrations, adsorption activation energies, chemical reaction rate constants, and desorption rate constants is abundantly available for the CO oxidation reaction on Pt(100) (Gruyters et al., 1995, 1996; Imbihl et al., 1986).

Reactions on transforming surfaces have been theoretically modeled in the literature using reaction-diffusion equations.

CO oxidation on Pt(100) was first modeled by Imbihl and coworkers (Imbihl et al., 1985). This work holds its importance in the literature because it was the first systematic attempt to predict rate oscillations on transforming surfaces. It contained considerable experimental insight, not only in using the Langmuir–Hinshelwood (LH) mechanism, but also because of the fact that it tried to use phase-transition kinetics coupled with the LH mechanism to prove the existence of oscillations as well as spatiotemporal patterns. This model has been a prototype for wide-ranging studies (Krischer et al., 1992; Bar et al., 1994; Shvartsman and Kevrekidis, 1999; Bangia et al., 1996). The model equations used by Imbihl et al. involved the definition of a *spatially* distributed  $\theta_{\text{CO}}^{1 \times 1}$ , the “global” coverage with  $\theta_{\text{CO}}^{1 \times 1} = \Theta_{\text{CO}} / \theta_{1 \times 1}$ , where  $\Theta_{\text{CO}}$  is the “local” coverage of CO on the surface. The authors do not define a differential area over which this local coverage is defined; in that sense it is not clear whether this coverage is surface-specific (the phase transformation depends on surface-specific coverages). A rational strategy would be to first identify a differential area, define the local coverage over it, and then average it over a number of areas to come up with a “global” definition. The quantity  $\theta_{\text{CO}}^{1 \times 1}$  does not really represent an area-averaged coverage; this is the local concentration normalized to the *total* area of  $1 \times 1$  on the surface, something that experiments do not measure. Hence, the motivation behind the definition of “global” coverages is ambiguous. If a correct spatial averaging was done to come up with the global coverages, it would involve the averaging of nonlinear terms (example chemical reaction) that would yield terms that would not be identical functions of the averaged physical quantity. In essence,  $\langle \theta_{\text{CO}}^{1 \times 1} \theta_{\text{O}}^{1 \times 1} \rangle \neq \langle \theta_{\text{CO}}^{1 \times 1} \rangle \langle \theta_{\text{O}}^{1 \times 1} \rangle$ . The model also does not account for dilution/augmentation terms.

Based on careful molecular beam studies, Gruyters et al. (1995) proposed and used a new power law for describing surface-phase transitions. The model by Gruyters et al. (1996) accounted for such new experimental evidence. This is a much more sophisticated model, not only because of the experimental content, but also because a term similar to dilution was included for the first time in their model. However, it is unclear why the dilution term is present in every equation, irrespective of whether the hex areas transform to  $1 \times 1$  or vice versa. As our work will prove, dilution terms cannot be present in every equation independent of the status of the transformation. Augmentation terms are missing in the equations.

In summary, we believe that past approaches to model transforming surfaces were seminal in attempting to capture the physics of adsorbate-induced phase transformation, but were ad hoc, and, hence, plagued by inconsistencies that imperil assessment of the nonlinear interaction between reaction and diffusion. Toward this, we have developed a *deterministic* framework for analyzing adsorption, reaction, desorption, and surface diffusion of gaseous species on catalytic surfaces coupled with the transformation of surfaces based on a procedure that involves *local* probability averaging as well as area averaging. While the probability averaging is to promote the deterministic framework, the area averaging is designed to produce quantities more closely related to measurement. We assume that the catalytic surface has two different types of configurations,  $\alpha$  and  $\beta$  (we do this because

Pt(100) and Pt(110), for example, can exist in two phases: the development of the theory itself is not limited by the number of configurations). By area averaging, we mean that around each spatial point on the two-dimensional surface, one can identify an averaging area, which is large enough to cover a number of “small” areas (of either type  $\alpha$  or  $\beta$ ). Each of the small areas must either be of type  $\alpha$  or  $\beta$ .

The phase transition is treated as a random event, but with a transition probability that is a strong function of coverage; hence we define the probability that the “small” area is of either type  $\alpha$  or  $\beta$ . We write master equations for relevant probability density functions, which will be defined, and suitable probability, and area averaging of these will yield a deterministic model. This development naturally gives rise to terms in the equations (for the averaged surface concentrations) that do not appear in prior mathematical treatments, which arrived at model equations by ad hoc balances. The terms in question arise out of *dilution* due to an increase in the fraction of a given surface type (following surface transformation) or *augmentation* due to a decrease in the fraction of a given surface type. We demonstrate that the phenomena represented by such terms play a significant role in determining the oscillatory behavior in surface reactions, and consequently cannot be neglected in any description of the dynamics of phenomena belonging to the generic class of surface phase transformation coupled with physicochemical processes. This is supported by simulation results of temporal oscillations in CO oxidation on Pt(100) where we evaluate the effect of the new terms.

## Theoretical Development

### Basic postulates

Consider an “infinitesimal” surface of area  $dA$  on the surface (Figure 1). This area is very small compared with the total surface. If we denote the entire catalyst surface domain by  $\Sigma_T$ , with area measure  $A_T$ , then

$$A_T = \int_{\Sigma_T} dA \quad (1)$$

There are two basic postulates associated with  $dA$ .

(1)  $dA$  is either of  $\alpha$  or  $\beta$  type, that is, it cannot accommodate both types of surface. The spatial scale of  $dA$  is small

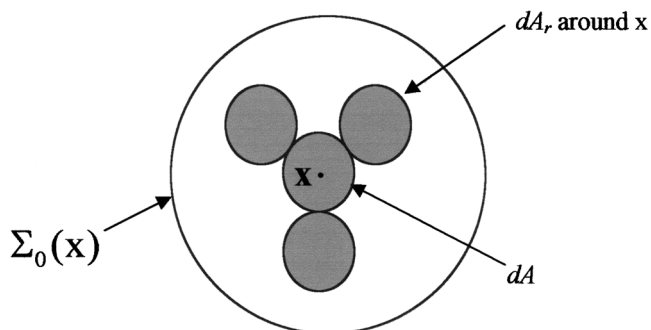


Figure 1. Area  $dA$  around a spatial point  $x$  along with the averaging area  $\Sigma_0(x)$ .

compared with the averaging area,  $\Sigma_0(x)$ , which surrounds the spatial location  $x$  (Figure 1).

(2) It is possible to find a time scale in which the changes occurring with respect to coverage of reacting species on the area  $dA$  can be described by deterministic, continuous variables. The frequency with which the reaction surfaces switch between  $\alpha$  and  $\beta$  types is comparatively smaller.

We define the local surface coverage vector on  $dA$  due to  $n$  gaseous species as follows

$$\theta = [\theta_1, \theta_2, \dots, \theta_n] \quad (2)$$

where  $\theta_i$  refers to coverage of the  $i$ th species. The area  $dA$  can transform from type  $\alpha$  to type  $\beta$  and vice versa; the transformation is a stochastic event, and the associated probability densities are strong functions of the surface coverage vector  $\theta$ . These probability densities describe the probability that the area  $dA$  is of type  $\alpha$  (or  $\beta$ ) with coverage between  $\theta$  and  $\theta + d\theta$ .

### Probability functions

The surface phase transformations between  $\alpha$  and  $\beta$  are dependent on the coverage of the chemical species adsorbed on the surface. Typically, one of the phases (say  $\alpha$ ) is stabilized by a high local coverage of the adsorbed species, while the other (say  $\beta$ ) is stabilized by low coverage of the reactants. There is in addition a spatial distribution of coverage over the surface space, meaning that the area  $dA$  around any given spatial location  $x$  has a different coverage from that at  $x + dx$ . Based on the preceding facts, and keeping in mind that the phase transition is a time-dependent process, we can introduce the following probability distribution functions:

$\pi_\alpha(x, t; \theta) d\theta \equiv$  Probability {area  $dA$  around  $x$  at time  $t$  is of the  $\alpha$  type with fractional coverages between  $\theta$  and  $\theta + d\theta$ }

$\pi_\beta(x, t; \theta) d\theta \equiv$  Probability {area  $dA$  around  $x$  at time  $t$  is of the  $\beta$  type with fractional coverages between  $\theta$  and  $\theta + d\theta$ }

In the foregoing,  $d\theta = d\theta_1 d\theta_2 d\theta_3, \dots, d\theta_n$ . We also define the probability functions

$p_\alpha(x, t) \equiv$  Probability {area  $dA$  around  $x$  at time  $t$  is of the  $\alpha$  type}

$p_\beta(x, t) \equiv$  Probability {area  $dA$  around  $x$  at time  $t$  is of the  $\beta$  type}

Then, it follows that

$$p_\alpha(x, t) = \int_{\Sigma_{\theta_i \leq 1}} d\theta \pi_\alpha(x, t; \theta)$$

$$p_\beta(x, t) = \int_{\Sigma_{\theta_i \leq 1}} d\theta \pi_\beta(x, t; \theta) \quad (3)$$

The infinitesimal area  $dA$  around  $\mathbf{x}$  must be either of type  $\alpha$  or type  $\beta$ , since it can exist only as either of the two phases. Hence

$$p_\alpha(\mathbf{x},t) + p_\beta(\mathbf{x},t) = 1 \quad (4)$$

We now define the fraction of  $\alpha$ -type area in the averaging domain  $\Sigma_0(\mathbf{x})$  at location  $\mathbf{x}$  as

$$a_\alpha(\mathbf{x},t) \equiv \frac{1}{A_0} \int_{\Sigma_0(\mathbf{x})} p_\alpha(\mathbf{x} + \mathbf{r},t) dA_r \quad (5)$$

where  $dA_r$  is an infinitesimal area around the point  $\mathbf{x} + \mathbf{r}$  and  $A_0$  is the area of  $\Sigma_0(\mathbf{x})$ . Similarly, we denote the fraction of  $\beta$ -type area in the averaging domain by

$$a_\beta(\mathbf{x},t) \equiv \frac{1}{A_0} \int_{\Sigma_0(\mathbf{x})} p_\beta(\mathbf{x} + \mathbf{r},t) dA_r \quad (6)$$

We have  $a_\alpha + a_\beta = 1$  at every point on the surface.

### Definition of probability and area-averaged quantities

Since we want to arrive at a deterministic description of coverage dynamics, we define probability-averaged coverages as follows

$$\bar{\Theta}_{i,\alpha}(\mathbf{x},t) = \frac{\int_{\Sigma_{\theta_i \leq 1}} \theta_i \pi_\alpha(\mathbf{x},t;\boldsymbol{\theta}) d\boldsymbol{\theta}}{p_\alpha(\mathbf{x},t)}$$

$$\bar{\Theta}_{i,\beta}(\mathbf{x},t) = \frac{\int_{\Sigma_{\theta_i \leq 1}} \theta_i \pi_\beta(\mathbf{x},t;\boldsymbol{\theta}) d\boldsymbol{\theta}}{p_\beta(\mathbf{x},t)} \quad (7)$$

where  $\bar{\Theta}_{i,\alpha}(\mathbf{x},t)$  is the probability-averaged coverage of species  $i$  on area  $dA$  of type  $\alpha$ . Clearly, this is a *surface-specific* definition of coverage.

The probability-averaged coverage vector on the surface of type  $\alpha$  would then be

$$\bar{\Theta}_\alpha = [\bar{\Theta}_{1,\alpha}, \bar{\Theta}_{2,\alpha}, \bar{\Theta}_{3,\alpha}, \dots, \bar{\Theta}_{n,\alpha}] \quad (8)$$

We now define local probability and area-averaged coverages as follows

$$\langle \bar{\Theta}_{i,\alpha}(\mathbf{x},t) \rangle \equiv \frac{1}{a_\alpha A_0} \int_{\Sigma_0(\mathbf{x})} \bar{\Theta}_{i,\alpha}(\mathbf{x} + \mathbf{r},t) p_\alpha(\mathbf{x} + \mathbf{r},t) dA_r \quad (9)$$

$$\langle \bar{\Theta}_{i,\beta}(\mathbf{x},t) \rangle \equiv \frac{1}{a_\beta A_0} \int_{\Sigma_0(\mathbf{x})} \bar{\Theta}_{i,\beta}(\mathbf{x} + \mathbf{r},t) p_\beta(\mathbf{x} + \mathbf{r},t) dA_r \quad (10)$$

Equations 9 and 10 define the deterministic *surface-specific* coverage of the  $i$ th species on areas of types  $\alpha$  and  $\beta$ , respectively, within the averaging domain  $\Sigma_0(\mathbf{x})$ , surrounding the point  $\mathbf{x}$  in surface space.

## Physicochemical Processes

### Processes on the catalytic surface

In a typical continuous gas-phase catalytic reaction process, physicochemical processes like adsorption, desorption, chemical reaction, and surface diffusion occur on the catalyst surface. In what follows, we discuss the representation of the kinetics of each of these processes, with special emphasis on migration processes.

We are concerned with how fractional coverage of each species changes due to various processes on the catalyst surface. Toward this, we let

$$\dot{\Theta}_i(\boldsymbol{\theta};\mathbf{x},t)$$

= Rate of change of surface coverage by the  $i$ th gas on  $dA$  as a function of prevailing surface coverage vector  $\boldsymbol{\theta}$  of the  $i$ th gas.

Hence, we have

$$\dot{\Theta}(\boldsymbol{\theta};\mathbf{x},t) \equiv \left[ \frac{d\theta_1}{dt}, \frac{d\theta_2}{dt}, \frac{d\theta_3}{dt}, \dots, \frac{d\theta_n}{dt} \right]$$

The functions  $\dot{\Theta}_i$  must be obtained by considering adsorption, desorption, reaction, and migration processes for each of the surfaces  $\alpha$  and  $\beta$ . For this purpose, we use kinetic models for the processes and the rate constants used are based on experimental values from the literature.

*Adsorption.* The rate of adsorption of the  $i$ th gas on surface type  $\alpha$  is represented by

$$r_{i,\text{ads}} = k_{i,\text{ads}}^\alpha S_i^\alpha(\boldsymbol{\theta}) P_i \quad (11)$$

where  $k_{i,\text{ads}}^\alpha$  is the rate constant for adsorption,  $S_i^\alpha(\boldsymbol{\theta})$  is the sticking probability of the  $i$ th gas onto the surface of type  $\alpha$ , and  $P_i$  is the partial pressure of the  $i$ th gas in the reactor.

*Desorption.* The rate of desorption is given by

$$r_{i,\text{des}} = k_{i,\text{des}}^\alpha \theta_i \quad (12)$$

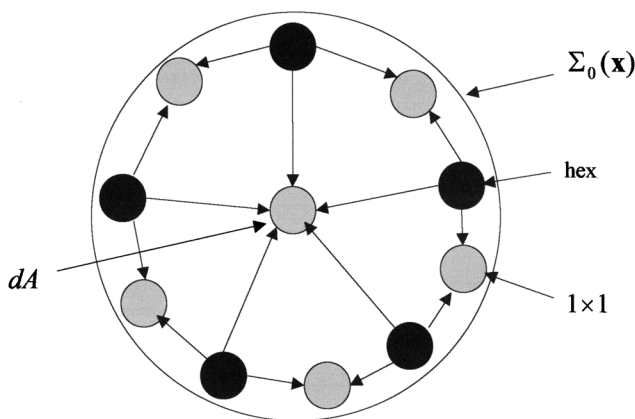
where  $k_{i,\text{des}}^\alpha$  is the desorption rate constant.

*Chemical Reaction.* Consider  $m$  chemical reactions occurring in the system. We can represent a reaction among  $s$  species in the  $j$ th reaction as

$$\sum_{i=1}^s \gamma_{ji} A_i = 0, \quad j = 1, 2, \dots, m \quad (13)$$

where  $\gamma_{ji}$  is the stoichiometric coefficient of species  $A_i$ . If  $A_i$  is a reactant,  $\gamma_{ji}$  is negative, and if  $A_i$  is a product,  $\gamma_{ji}$  is positive. If  $r_j$  is the  $j$ th (*surface-specific*) intrinsic reaction rate, then we can write the reaction rate with respect to the species  $A_i$  as

$$r_{i,\text{chem}} = \sum_{j=1}^m \gamma_{ji} r_j, \quad i = 1, 2, \dots, n \quad (14)$$



**Figure 2. Migration of CO/oxygen from neighboring areas in the averaging domain  $\Sigma_0(\mathbf{x})$  to  $dA$ .**

*Migration.* Transport along the surface occurs through diffusion where the adsorbed species move via a molecular “hopping” process. Between two catalytic surface areas, which are dissimilar with respect to the arrangement of the surface atoms, this phenomenon can be thought of as a “migration” of species from one type of area to another (Imbihl, 1985).

We represent the migration of adsorbed gas molecules between any two areas  $dA_r$  and  $dA$  in  $\Sigma_0(\mathbf{x})$ , as shown in Figure 2. Let area  $dA$  be of type  $\alpha$ . The migration of species  $i$  outward from  $dA$  is proportional to its local coverage  $\theta_i$ . Let the rate constants for migration from  $\alpha$  to  $\alpha$  and from  $\alpha$  to  $\beta$  be  $k_{\alpha-\alpha}$  and  $k_{\alpha-\beta}$ , respectively. Then the rate of migration out of  $dA$  is

$$r_{i,\text{mig}}^{\text{out}} = k_{\alpha-\alpha}\theta_i + k_{\alpha-\beta}\theta_i \quad (15)$$

The migration from all of the areas  $dA_r$  contained in  $\Sigma_0(\mathbf{x})$  into  $dA$  depends on whether  $dA_r$  is of type  $\alpha$  or type  $\beta$ . Let  $dA_r$  be of type  $\beta$ , then the migration into  $dA$  is given by

$$r_{i,\text{mig}}^{\text{in}} dA = \frac{dA}{A_0} \int_{\Sigma_0(\mathbf{x})} dA_r \int \sum_{i=1}^N \theta_i \leq 1 d\theta \frac{k_{\beta-\alpha}\theta_i\pi_\beta(\mathbf{x}+\mathbf{r},t)}{a_\alpha(\mathbf{x}+\mathbf{r},t)} \quad (16)$$

which is obtained as follows:

(1) We consider an area  $dA_r$  at  $\mathbf{x}+\mathbf{r}$ . The probability that it is of type  $\beta$  with coverage vector between  $\theta$  and  $d\theta$  is given by  $\pi_\beta(\mathbf{x}+\mathbf{r},t;\theta)d\theta$ . The rate of transfer from  $dA_r$  to surrounding areas is then given by  $k_{\beta-\alpha}\theta_i\pi_\beta d\theta$ .

(2) There are several other areas  $dA_r$  of type  $\alpha$  in  $\Sigma_0(\mathbf{x})$  that compete with  $dA$  of type  $\alpha$  for migrating species  $i$  from areas of type  $\beta$ . The migration is thus associated with a “hit” probability, which must be multiplied with  $k_{\beta-\alpha}\theta_i\pi_\beta d\theta$ . Assuming uniform likelihood, this hit probability is given by  $dA/(a_\alpha(\mathbf{x}+\mathbf{r},t)A_0)$ , an area ratio of the competing areas. Integration over all areas  $dA_r$  gives the form of the term in Eq. 16.

A similar term is obtained when considering migration from  $dA_r$  that are type  $\alpha$  to  $dA$

$$r_{i,\text{mig}}^{\text{in}} dA = \frac{dA}{A_0} \int_{\Sigma_0(\mathbf{x})} dA_r \int \sum_{i=1}^N \theta_i \leq 1 d\theta \frac{k_{\alpha-\alpha}\theta_i\pi_\alpha(\mathbf{x}+\mathbf{r},t)}{a_\alpha(\mathbf{x}+\mathbf{r},t)} \quad (17)$$

The net rate of change in coverage can now be written as

$$\dot{\theta}_i = r_{i,\text{ads}} - r_{i,\text{des}} + r_{i,\text{mig}}^{\text{in}} - r_{i,\text{mig}}^{\text{out}} - r_{i,\text{chem}} \quad (18)$$

We have considered the area and probability averaging of the  $\dot{\theta}_i$  function in Eq. 18, with special emphasis on migration terms in the Appendix.

### Surface transformation of the catalyst surface

The kinetics of transformation of the surface from type  $\alpha$  to type  $\beta$  and vice versa may be described by the following quantities:

$k_\alpha\phi_\alpha(\theta)dt$   
 $\equiv$  Transition probability that an  $\alpha$  surface with the surface coverage vector  $\theta$  at time  $t$  transforms to the  $\beta$  type during  $t$  to  $t+dt$  ( $k_\alpha$  is the rate constant describing the process).

$k_\beta\phi_\beta(\theta)dt$   
 $\equiv$  Transition probability that a  $\beta$  surface with the surface coverage vector  $\theta$  at time  $t$  transforms to the  $\alpha$  type during  $t$  to  $t+dt$  ( $k_\beta$  is the rate constant describing the process).

### Differential Equations for $\pi_\alpha(\mathbf{x},t;\theta)$ and $\pi_\beta(\mathbf{x},t;\theta)$

We can now identify the differential equations for  $\pi_\alpha(\mathbf{x},t;\theta)$  and  $\pi_\beta(\mathbf{x},t;\theta)$  as follows: Let us consider the area  $dA$  at time  $t$  and let it be of type  $\alpha$ . This is a result of the situation at time  $t-dt$  when the area  $dA$  could be of type  $\alpha$  or type  $\beta$ . The coverage on  $dA$  changes in this time interval,  $dt$ , from  $\theta'$  at time  $t-dt$  to  $\theta$  at time  $t$ . Area  $dA$  in this interval can either remain type  $\alpha$  or transform to type  $\beta$ . Thus

$$\pi_\alpha(\mathbf{x},t;\theta)d\theta$$

[Probability that at time  $t$ ,  $dA$  is of the type  $\alpha$  and has coverage between  $\theta$  and  $\theta+d\theta$ ]

$$= \pi_\alpha(\mathbf{x},t-dt;\theta')d\theta'$$

[Probability that at time  $t-dt$ ,  $dA$  is of the type  $\alpha$  and has coverage between  $\theta'$  and  $\theta'+d\theta'$ ]

$$\times [1 - k_\alpha\Phi_\alpha dt]$$

[Probability that during  $t-dt$  to  $t$ , the area  $dA$  does not transform to type  $\beta$ ]

$$+ \pi_\beta(\mathbf{x},t-dt;\theta')d\theta'$$

[Probability that during  $t - dt$  to  $t$ , the area  $dA$  was of type

$$\beta] \\ \times k_\beta \Phi_\beta dt$$

[Probability that during the time interval  $dt$ , the area transforms from type  $\beta$  to type  $\alpha$ ]

Transposing the first term on the righthand side of the preceding equation to the left, dividing by  $dt$  and  $d\theta'$ , and letting  $dt \rightarrow 0$ , we get

$$[d\theta]^{-1} \lim_{dt \rightarrow 0} \frac{\pi_\alpha(\mathbf{x}, t; \boldsymbol{\theta}) d\boldsymbol{\theta} - \pi_\alpha(\mathbf{x}, t - dt; \boldsymbol{\theta}') d\boldsymbol{\theta}'}{dt} \\ = -k_\alpha \phi_\alpha \pi_\alpha(\mathbf{x}, t; \boldsymbol{\theta}) + k_\beta \phi_\beta \pi_\beta(\mathbf{x}, t; \boldsymbol{\theta}) \quad (19)$$

where we have used the fact that  $\lim_{dt \rightarrow 0} \boldsymbol{\theta}' = \boldsymbol{\theta}$  and  $\lim_{dt \rightarrow 0} d\boldsymbol{\theta}' = d\boldsymbol{\theta}$ . It follows from Eq. 19 that

$$[d\theta]^{-1} \frac{d}{dt} [\pi_\alpha(\mathbf{x}, t; \boldsymbol{\theta}) d\boldsymbol{\theta}] = -k_\alpha \phi_\alpha \pi_\alpha(\mathbf{x}, t; \boldsymbol{\theta}) \\ + k_\beta \phi_\beta \pi_\beta(\mathbf{x}, t; \boldsymbol{\theta}) \quad (20)$$

where

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{j=1}^n \dot{\theta}_{j,\alpha}(\boldsymbol{\theta}) \frac{\partial}{\partial \theta_j} \quad (21)$$

Note, in particular, the volume  $d\boldsymbol{\theta}$  contained within the differentiation with respect to time on the lefthand side of Eq. 20. Thus, the derivative (Eq. 21) must be applied to  $d\boldsymbol{\theta}$  using the relationship, which is obtained in a manner similar to that in fluid mechanics (Aris, 1962), relating the rate of volume strain to the divergence of the straining field, which in this case is given by  $\dot{\theta}_{i,\alpha}$  ( $\dot{\theta}_{i,\alpha}$  is the time rate of change of the coverage of the  $i$ th species on  $dA$  [see Eq. 18]). Thus, we have

$$[d\theta]^{-1} \frac{d[d\theta]}{dt} = \sum_{i=1}^n \frac{\partial}{\partial \theta_i} [\dot{\theta}_{i,\alpha}(\boldsymbol{\theta})] \quad (22)$$

Combining Eqs. 20, 21, and 22 gives

$$\frac{d\pi_\alpha}{dt} + \sum_{i=1}^n \frac{\partial \dot{\theta}_{i,\alpha}}{\partial \theta_i} \pi_\alpha = -k_\alpha \phi_\alpha \pi_\alpha + k_\beta \phi_\beta \pi_\beta \quad (23)$$

Using Eq. 21 and rearranging, we can arrive at

$$\frac{\partial \pi_\alpha}{\partial t} + \sum_{i=1}^n \frac{\partial}{\partial \theta_i} [\dot{\theta}_{i,\alpha} \pi_\alpha] = -k_\alpha \phi_\alpha \pi_\alpha + k_\beta \phi_\beta \pi_\beta \quad (24)$$

Similarly

$$\frac{\partial \pi_\beta}{\partial t} + \sum_{i=1}^n \frac{\partial}{\partial \theta_i} [\dot{\theta}_{i,\alpha} \pi_\beta] = k_\alpha \phi_\alpha \pi_\alpha - k_\beta \phi_\beta \pi_\beta \quad (25)$$

The preceding Eqs. 24 and 25 are the *master equations* in the sense that all other averaged equations must be obtained from them. For example, we can derive equations for the area probability that  $dA$  at any time is of type  $\alpha$  or  $\beta$ .

## Probability Averaging

In this section, we demonstrate the probability and area-averaging process applied to Eqs. 24 and 25.

### Equations for $p_\alpha(\mathbf{x}, t)$ and $p_\beta(\mathbf{x}, t)$

We obtain the equations for  $p_\alpha(\mathbf{x}, t)$  and  $p_\beta(\mathbf{x}, t)$  by integrating the previous equations over the region  $0 \leq \sum_{i=1}^n \theta_i \leq 1$ .

This is equivalent to taking the zeroth moment. The result is given by

$$\frac{\partial p_\alpha}{\partial t} + \sum_{j=1}^n \int \sum_{\theta_i \leq 1} \prod_{k=1, j}^n d\theta_k \left[ \pi_\alpha \left( \mathbf{x}, t; 1 - \sum_{i=1, j}^n \theta_i, (\theta_l)_{l=1, j}^n \right) \right. \\ \left. \times \dot{\theta}_{j,\alpha} \left( 1 - \sum_{i=1, j}^n \theta_i, (\theta_l)_{l=1, j}^n \right) - \pi_\alpha(\mathbf{x}, t; \boldsymbol{\theta}) \dot{\theta}_{j,\alpha}(\mathbf{0}) \right] \\ = -k_\alpha \bar{\Phi}_\alpha p_\alpha + k_\beta \bar{\Phi}_\beta p_\beta \quad (26)$$

where

$$\bar{\Phi}_\alpha p_\alpha = \int_{\sum \theta_i \leq 1} d\boldsymbol{\theta} \phi_\alpha \pi_\alpha, \quad \bar{\Phi}_\beta p_\beta = \int_{\sum \theta_i \leq 1} d\boldsymbol{\theta} \phi_\beta \pi_\beta \quad (27)$$

Similarly, we obtain

$$\frac{\partial p_\beta}{\partial t} + \sum_{j=1}^n \int \sum_{\theta_i \leq 1} \prod_{k=1, j}^n d\theta_k \left[ \pi_\beta \left( \mathbf{x}, t; 1 - \sum_{i=1, j}^n \theta_i, (\theta_l)_{l=1, j}^n \right) \right. \\ \left. \times \dot{\theta}_{j,\beta} \left( 1 - \sum_{i=1, j}^n \theta_i, (\theta_l)_{l=1, j}^n \right) - \pi_\beta(\mathbf{x}, t; \boldsymbol{\theta}) \dot{\theta}_{j,\beta}(\mathbf{0}) \right] \\ = k_\alpha \bar{\Phi}_\alpha p_\alpha - k_\beta \bar{\Phi}_\beta p_\beta \quad (28)$$

In the preceding equations, the integral terms on the lefthand side must vanish because the rate of change of the probability that the area  $dA$  is of type  $\alpha$  or the  $\beta$  type must depend only on the transition rates on the righthand side. Also, since we have used a continuous differential equation to describe the dynamics of coverage, even the shortest time must cause a change on the surface with respect to coverage, making it impossible to maintain for any length of time the situation at the *boundary* of the region  $0 \leq \sum_{i=1}^n \theta_i \leq 1$ , that is,

along  $\theta_1 = 0, \theta_2 = 0, \dots, \theta_n = 0$  and  $\sum_{i=1}^n \theta_i = 1$ . For example,

along  $\sum_{i=1}^n \theta_i = 1$ , the coverage is total, which will definitely result in "instantaneous" removal of the gas. Similarly on  $\theta_i$

= 0, there must be an immediate addition of the  $i$ th gas, making it impossible to maintain a condition of zero coverage by the  $i$ th gas. Thus we must impose the boundary conditions that

$$\pi_\alpha, \pi_\beta = 0 \left( \text{along } \theta_1 = 0, \theta_2 = 0, \dots, \theta_n = 0 \text{ and } \sum_{i=1}^n \theta_i = 1 \right) \quad (29)$$

We have thus the differential equations

$$\frac{\partial p_\alpha}{\partial t} = -\frac{\partial p_\beta}{\partial t} = -k_\alpha \bar{\Theta}_\alpha p_\alpha + k_\beta \bar{\Theta}_\beta p_\beta \quad (30)$$

### Equations for $\bar{\Theta}_{i,\alpha}(x,t)$ and $\bar{\Theta}_{i,\beta}(x,t)$

Equations for  $\bar{\Theta}_{i,\alpha}(x,t)$  and  $\bar{\Theta}_{i,\beta}(x,t)$  must be obtained by taking the first moment of Eqs. 24 and 25. We will derive equations only for the quantities specific to the alpha phase; equations for the beta phase can be similarly derived. The first moment of Eq. 24 yields

$$\begin{aligned} \frac{\partial}{\partial t} [\bar{\Theta}_{i,\alpha} p_\alpha] + \int \sum_{\theta_i \leq 1}^n d\theta \left\{ \sum_{i=1}^n \frac{\partial}{\partial \theta_i} [\dot{\Theta}_{i,\alpha} \pi_\alpha] \right\} \\ = -k_\alpha \int \sum_{\theta_i \leq 1}^n \theta_i \phi_\alpha \pi_\alpha d\theta + k_\beta \int \sum_{\theta_i \leq 1}^n \theta_i \phi_\beta \pi_\beta d\theta \end{aligned} \quad (31)$$

Integrating by parts one obtains, using the divergence theorem and the boundary conditions in Eq. 29

$$\begin{aligned} \frac{\partial}{\partial t} [\bar{\Theta}_{i,\alpha} p_\alpha] = \int \sum_{\theta_i \leq 1}^n \dot{\Theta}_{i,\alpha} \pi_\alpha d\theta - k_\alpha \int \sum_{\theta_i \leq 1}^n \theta_i \phi_\alpha \pi_\alpha d\theta \\ + k_\beta \int \sum_{\theta_i \leq 1}^n \theta_i \phi_\beta \pi_\beta d\theta \end{aligned} \quad (32)$$

Since it will be of importance in the sequel (see the following section), we also take the second moments of Eq. 24

$$\begin{aligned} \frac{\partial}{\partial t} [\bar{\Theta}_{i,\alpha}^2 p_\alpha] = \int \sum_{\theta_i \leq 1}^n 2\theta_i \pi_\alpha \dot{\Theta}_{i,\alpha} d\theta - k_\alpha \int \sum_{\theta_i \leq 1}^n \theta_i^2 \phi_\alpha \pi_\alpha d\theta \\ + k_\beta \int \sum_{\theta_i \leq 1}^n \theta_i^2 \phi_\beta \pi_\beta d\theta + \sum_{i=1,j}^n \left( \langle \bar{\Theta}_i \bar{\Theta}_j \rangle - \langle \bar{\Theta}_i \rangle \langle \bar{\Theta}_j \rangle \right) \frac{\partial^2}{\partial \theta_i \partial \theta_j} \left\} f(\langle \bar{\Theta} \rangle) + H.O.T. \end{aligned} \quad (37)$$

$$\begin{aligned} \frac{\partial}{\partial t} [\bar{\Theta}_{i,\alpha} \bar{\Theta}_{j,\alpha} p_\alpha] = \int \sum_{\theta_i \leq 1}^n \left[ \theta_i \dot{\Theta}_{j,\alpha} + \theta_j \dot{\Theta}_{i,\alpha} \right] \pi_\alpha d\theta \\ - k_\alpha \int \sum_{\theta_i \leq 1}^n \theta_i \theta_j \phi_\alpha \pi_\alpha d\theta + k_\beta \int \sum_{\theta_i \leq 1}^n \theta_i \theta_j \phi_\beta \pi_\beta d\theta \end{aligned} \quad (34)$$

Area averaging of Eqs. 32 through 34 based on the definitions in Eqs. 9 and 10 will give rise to deterministic, spatiotemporal differential equations for describing the dynamics on the surface. This is described in the next section.

## Area Averaging

### Probability and area averaging of any arbitrary nonlinear function

In general,  $\dot{\Theta}_{i,\alpha}$  and  $\dot{\Theta}_{i,\beta}$  in Eqs. 32 through 34 will be nonlinear functions of  $\theta$ , the coverage vector (see Eq. 18). Hence, we demonstrate the area and probability averaging of any arbitrary nonlinear function  $f(\theta)$ . For statistically averaging  $f(\theta)$ , we can write

$$\bar{F}(x,t) = \frac{\int_{\sum \theta_i \leq 1} d\theta f(\theta) \pi(x,t; \theta)}{p(x,t)} \quad (35)$$

For the present we do not need to distinguish between surface type, so we can drop the subscript on the master probability function. It is necessary to take the local area-average of this quantity. Before we do this, we expand  $f(\theta)$  by Taylor series about the area-averaged quantity  $\langle \bar{\Theta}(x,t) \rangle$  at the point  $x$

$$\begin{aligned} f(\theta) = f(\langle \bar{\Theta} \rangle) + \sum_{i=1}^n (\theta_i - \langle \bar{\Theta}_i \rangle) \frac{\partial}{\partial \theta_i} f(\langle \bar{\Theta} \rangle) \\ + \frac{1}{2} \left[ \sum_{i=1}^n (\theta_i - \langle \bar{\Theta}_i \rangle)^2 \frac{\partial^2}{\partial \theta_i^2} + \sum_{i=1,j}^n (\theta_i - \langle \bar{\Theta}_i \rangle) \right. \\ \left. \times (\theta_j - \langle \bar{\Theta}_j \rangle) \frac{\partial^2}{\partial \theta_i \partial \theta_j} \right] f(\langle \bar{\Theta} \rangle) + H.O.T. \end{aligned} \quad (36)$$

Thus, the local area-averaged expression for any arbitrary nonlinear function of coverage can be written as

$$\langle \bar{F}(x,t) \rangle = \left\{ 1 + \frac{1}{2} \left[ \sum_{i=1}^n (\langle \bar{\Theta}_i^2 \rangle - \langle \bar{\Theta}_i \rangle^2) \frac{\partial^2}{\partial \theta_i^2} \right. \right.$$

No subscript has been included on the area-averaged or probability-averaged quantities in the preceding for generality. We notice that the righthand side contains only moments of second order. In using this formula, it must be borne in

mind that

$$\begin{aligned} \langle \bar{F}(\mathbf{x}, t) \rangle &= \int_{\Sigma_o(\mathbf{x})} p(\mathbf{x} + \mathbf{r}, t) dA_r \\ &= \int_{\Sigma_o(\mathbf{x})} dA_r \int_{\sum_{i=1}^n \theta_i \leq 1} d\boldsymbol{\theta} f(\boldsymbol{\theta}) \pi(\mathbf{x} + \mathbf{r}, t; \boldsymbol{\theta}) \quad (38) \end{aligned}$$

so that

$$\begin{aligned} \langle \bar{F}(\mathbf{x}, t) \rangle &= \frac{1}{A_0 a(\mathbf{x}, t)} \int_{\Sigma_o(\mathbf{x})} dA_r \int_{\sum_{i=1}^n \theta_i \leq 1} d\boldsymbol{\theta} f(\boldsymbol{\theta}) \pi(\mathbf{x} + \mathbf{r}, t; \boldsymbol{\theta}) \\ &= \frac{1}{A_0 a(\mathbf{x}, t)} \int_{\Sigma_o(\mathbf{x})} dA_r \bar{F}(\mathbf{x} + \mathbf{r}, t) p(\mathbf{x} + \mathbf{r}, t) \quad (39) \end{aligned}$$

where  $a$  will earn the subscript  $\alpha$  or  $\beta$  on  $\pi$ .

### Surface diffusion

The average coverage  $\langle \bar{\Theta} \rangle$  is distributed in space, and, hence, spatial gradients can be thought of as giving rise to a macroscopic diffusion term. This term arises from the area averaging of the migration term, which is a local phenomenon occurring on the scale of  $dA$ . In that respect, it can be thought of as a macroscopic interpretation of migration. Consider the time rate of change of coverage on an area  $dA_r$  of type  $\alpha$  surrounding a point  $\mathbf{x} + \mathbf{r}$  in physical space. We can write (see Eq. 18)

$$\begin{aligned} \dot{\Theta}_i(\boldsymbol{\theta}; \mathbf{x} + \mathbf{r}, t) &= \gamma_i(\boldsymbol{\theta}; \mathbf{x} + \mathbf{r}, t) + \frac{k_{\beta-\alpha}}{A_0} \int_{\Sigma_o(\mathbf{r})} dA_r \int_{\sum_{i=1}^N \theta_i \leq 1} \\ &\times d\boldsymbol{\theta} \frac{\theta_i \pi_\beta(\mathbf{x} + \mathbf{r}, t; \boldsymbol{\theta})}{a_\alpha(\mathbf{x} + \mathbf{r}, t)} + \frac{k_{\alpha-\alpha}}{A_0} \int_{\Sigma_o(\mathbf{r})} \\ &dA_r \int_{\sum_{i=1}^N \theta_i \leq 1} d\boldsymbol{\theta} \frac{\theta_i \pi_\alpha(\mathbf{x} + \mathbf{r}, t; \boldsymbol{\theta})}{a_\alpha(\mathbf{x} + \mathbf{r}, t)} \quad (40) \end{aligned}$$

where  $\gamma_i = (r_{i,\text{ads}} - r_{i,\text{des}} - r_{i,\text{mig}}^{\text{out}} - r_{i,\text{chem}})$  is the net change of coverage as a result of adsorption, desorption, chemical reaction, and migration out of  $dA$ , and the other two terms describe the rate of migration into  $dA_r$  (refer to Eqs. 16 and 17). Consider the substitution of  $\dot{\Theta}_i$  in Eq. 32. The term in question here is the first term on the righthand side of Eq. 32. The area averaging of this term yields the following

$$\begin{aligned} \int_{\Sigma_o(\mathbf{x})} dA_r \int_{\sum_{i=1}^n \theta_i \leq 1} d\boldsymbol{\theta} \dot{\Theta}_i \pi_\alpha &= \int_{\Sigma_o(\mathbf{x})} dA_r \int_{\sum_{i=1}^n \theta_i \leq 1} \\ &\times d\boldsymbol{\theta} \left( \gamma_i + \frac{k_{\beta-\alpha}}{A_0} \int_{\Sigma_o(\mathbf{r})} dA_r \int_{\sum_{i=1}^N \theta_i \leq 1} d\boldsymbol{\theta} \frac{\theta_i \pi_\beta}{a_\alpha}(\mathbf{x} + \mathbf{r}, t) \right. \\ &\left. + \frac{k_{\alpha-\alpha}}{A_0} \int_{\Sigma_o(\mathbf{r})} dA_r \int_{\sum_{i=1}^N \theta_i \leq 1} d\boldsymbol{\theta} \frac{\theta_i \pi_\alpha}{a_\alpha}(\mathbf{x} + \mathbf{r}, t) \right) \pi_\alpha \quad (41) \end{aligned}$$

We consider the third term *inside* the brackets on the righthand side (a similar analysis applies to the second term inside the brackets as well). Assuming  $a_\alpha(\mathbf{x} + \mathbf{r}, t) = a_\alpha(\mathbf{x}, t)$  for simplicity, we have

$$\begin{aligned} \frac{k_{\alpha-\alpha}}{a_\alpha(\mathbf{x}, t) A_0} \int_{\Sigma_o(\mathbf{r})} dA_r \int_{\sum_{i=1}^N \theta_i \leq 1} d\boldsymbol{\theta} \theta_i \pi_\alpha(\mathbf{x} + \mathbf{r}, t; \boldsymbol{\theta}) \\ = k_{\alpha-\alpha} \langle \bar{\Theta}_{i,\alpha} \rangle(\mathbf{x} + \mathbf{r}, t) \quad (42) \end{aligned}$$

We expand the area-averaged coverage on  $dA_r$  surrounding any point  $\mathbf{x} + \mathbf{r}$  as

$$\begin{aligned} \langle \bar{\Theta}_{i,\alpha} \rangle(\mathbf{x} + \mathbf{r}, t) &= \langle \bar{\Theta}_{i,\alpha} \rangle(\mathbf{x}, t) + \mathbf{r} \cdot \nabla \langle \bar{\Theta}_{i,\alpha} \rangle(\mathbf{x}, t) \\ &+ \frac{1}{2} \mathbf{r} \mathbf{r} : \nabla \nabla \langle \bar{\Theta}_{i,\alpha} \rangle(\mathbf{x}, t) + o(r^2) \quad (43) \end{aligned}$$

Evaluating now the third term on the righthand side of Eq. 41, using Eq. 43, we finally get

$$\begin{aligned} k_{\alpha-\alpha} \int_{\Sigma_o(\mathbf{r})} dA_r \int_{\sum_{i=1}^N \theta_i \leq 1} d\boldsymbol{\theta} \langle \bar{\Theta}_{i,\alpha} \rangle(\mathbf{x} + \mathbf{r}, t) \pi_\alpha &= k_{\alpha-\alpha} \int_{\Sigma_o(\mathbf{r})} \\ &\times dA_r \langle \bar{\Theta}_{i,\alpha} \rangle(\mathbf{x} + \mathbf{r}, t) \int_{\sum_{i=1}^N \theta_i \leq 1} d\boldsymbol{\theta} \pi_\alpha \\ &= k_{\alpha-\alpha} \langle \bar{\Theta}_{i,\alpha} \rangle(\mathbf{x}, t) \int_{\Sigma_o(\mathbf{r})} dA_r p_\alpha(\mathbf{x} + \mathbf{r}, t) + k_{\alpha-\alpha} \int_{\Sigma_o(\mathbf{r})} \\ &\times dA_r p_\alpha(\mathbf{x} + \mathbf{r}, t) \mathbf{r} \cdot \nabla \langle \bar{\Theta}_{i,\alpha} \rangle(\mathbf{x}, t) \\ &+ \frac{k_{\alpha-\alpha}}{2} \int_{\Sigma_o(\mathbf{r})} dA_r p_\alpha(\mathbf{x} + \mathbf{r}, t) \mathbf{r} \mathbf{r} : \nabla \nabla \langle \bar{\Theta}_{i,\alpha} \rangle(\mathbf{x}, t) + o(r^2) \quad (44) \end{aligned}$$

From Eq. 44, we see that the coefficients associated with  $\nabla \langle \bar{\Theta}_{i,\alpha} \rangle$  and  $\nabla \nabla \langle \bar{\Theta}_{i,\alpha} \rangle$  can be interpreted as representing “surface motion” as well as “surface” diffusion that occur with velocity

$$\mathbf{v} \equiv k' \int_{\Sigma_o(\mathbf{r})} dA_r p_\alpha(\mathbf{x} + \mathbf{r}, t) \mathbf{r} \quad (45)$$

and diffusion coefficient as

$$\mathbf{D} \equiv k' \int_{\Sigma_o(\mathbf{r})} dA_r p_\alpha(\mathbf{x} + \mathbf{r}, t) \mathbf{r} \mathbf{r} \quad (46)$$

It is likely that the velocity just defined is negligible because of the fact that

$$\int_{\Sigma_o(\mathbf{r})} dA_r \mathbf{r} = \mathbf{0} \quad (47)$$



### Dilution and augmentation terms

*Area and Probability Averaging.* We establish here terms in the averaged equations, which are of crucial importance to the framework of this article. They arise because phase transformation changes the fraction of a specific phase, say  $\alpha$ , in the averaging area. The concentrations specific to the  $\alpha$  phase will then be either increased when the  $\alpha$  area fraction decreases, or decreased when the  $\alpha$  area fraction increases. We therefore refer to these terms as augmentation and dilution terms, respectively. These terms naturally arise from the probability and area-averaging process, as demonstrated below.

Consider the area averaging of the probability-averaged equation (Eq. 30)

$$\int_{\Sigma_o(x)} dA_r \frac{\partial p_\alpha}{\partial t} = -k_\alpha \int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} d\theta \phi_\alpha \pi_\alpha + k_\beta \int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} d\theta \phi_\beta \pi_\beta \quad (48)$$

where  $\theta_\alpha(\boldsymbol{\theta})$  is a nonlinear function of  $\boldsymbol{\theta}$  in general. Following the treatment in the subsection on surface diffusion, we expand  $\theta_\alpha(\boldsymbol{\theta})$  by Taylor series about the area-averaged quantity  $\langle \bar{\Theta}(\mathbf{x}, t) \rangle$  at the point  $\mathbf{x}$  (see Eq. 36). Using only the zeroth-order term in the expansion for simplicity

$$\int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} d\theta \phi_\alpha(\boldsymbol{\theta}) \pi_\alpha(\boldsymbol{\theta}; \mathbf{x} + \mathbf{r}, t) = \phi_\alpha(\langle \bar{\Theta} \rangle) \int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} d\theta \phi_\alpha(\boldsymbol{\theta}) \pi_\alpha(\boldsymbol{\theta}; \mathbf{x} + \mathbf{r}, t) = \phi_\alpha(\langle \bar{\Theta}_\alpha \rangle) a_\alpha(\mathbf{x}, t) A_0 \quad (49)$$

Similarly

$$\int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} d\theta \phi_\beta(\boldsymbol{\theta}) \pi_\beta(\boldsymbol{\theta}; \mathbf{x} + \mathbf{r}, t) = \phi_\beta(\langle \bar{\Theta}_\beta \rangle) a_\beta(\mathbf{x}, t) A_0 \quad (50)$$

Using Eqs. 49 and 50 in Eq. 48 and using the definition in Eq. 5, we get

$$\frac{\partial a_\alpha}{\partial t} = k_\alpha \phi_\alpha a_\alpha + k_\beta \phi_\beta a_\beta \quad (51)$$

Typically, the kinetics of the phase transformation have been experimentally observed to be such that at any given instant, we have

$$k_\alpha \phi_\alpha = 0 \quad \text{for } c < 1; \quad k_\beta \phi_\beta = 0 \quad \text{for } c \geq 1 \quad (52)$$

where  $c = f(\boldsymbol{\theta}, \boldsymbol{\theta}_{\text{crit}})$ ;  $\boldsymbol{\theta}_{\text{crit}} = (\theta_{1,\text{crit}}, \theta_{2,\text{crit}}, \theta_{3,\text{crit}}, \dots, \theta_{n,\text{crit}})$  being a critical coverage vector governing the transformation determined experimentally (Imbihl et al., 1986; Gruyters et al., 1995). Thus for  $c < 1$ , areas of type  $\beta$  transform to that of type  $\alpha$ , while for  $c \geq 1$ , the areas of type  $\alpha$  transform to type

$\beta$ . For  $c \geq 1$ , Eq. 51 becomes

$$\frac{\partial a_\alpha}{\partial t} = k_\beta \phi_\beta a_\beta \quad (53)$$

Next, we consider the area averaging of the probability-averaged Eq. 32

$$\begin{aligned} \int_{\Sigma_o(x)} dA_r \frac{\partial}{\partial t} [\bar{\Theta}_{i,\alpha} p_\alpha] - \int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} \dot{\Theta}_{i,\alpha} \pi_\alpha d\boldsymbol{\theta} \\ = -k_\alpha \int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} \theta_i \phi_\alpha \pi_\alpha d\boldsymbol{\theta} \\ + k_\beta \int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} \theta_i \phi_\beta \pi_\beta d\boldsymbol{\theta} \quad (54) \end{aligned}$$

We represent  $\theta_i \phi_\alpha(\boldsymbol{\theta})$  using the Taylor series expansion about  $\langle \bar{\Theta}(\mathbf{x}, t) \rangle$  as before, and using only the zeroth-order term, we have

$$\theta_i \phi_\alpha(\boldsymbol{\theta}) = \langle \bar{\Theta}_i \rangle \phi_\alpha(\langle \bar{\Theta} \rangle) \quad (55)$$

Substituting Eq. 55 in the first term on the righthand side of Eq. 54, we have

$$\begin{aligned} k_\alpha \int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} \theta_i \phi_\alpha \pi_\alpha d\boldsymbol{\theta} \\ = k_\alpha \langle \bar{\Theta}_{i,\alpha} \rangle \phi_\alpha(\langle \bar{\Theta}_\alpha \rangle) \int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} \pi_\alpha d\boldsymbol{\theta} \\ = k_\alpha \langle \bar{\Theta}_{i,\alpha} \rangle \phi_\alpha a_\alpha A_0 \quad (56) \end{aligned}$$

Similarly, the second term on the righthand side of Eq. 54 is

$$\begin{aligned} k_\beta \int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} \theta_i \phi_\beta \pi_\beta d\boldsymbol{\theta} \\ = k_\beta \langle \bar{\Theta}_{i,\beta} \rangle \phi_\beta(\langle \bar{\Theta}_\beta \rangle) \int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} \pi_\beta d\boldsymbol{\theta} \\ = k_\beta \langle \bar{\Theta}_{i,\beta} \rangle \phi_\beta a_\beta A_0 \quad (57) \end{aligned}$$

Substituting Eqs. 56 and 57 in Eq. 54, and using the definition of area-averaged coverage in Eq. 9 and rearranging, we have

$$\begin{aligned} a_\alpha \frac{\partial \langle \bar{\Theta}_{i,\alpha} \rangle}{\partial t} - \frac{1}{A_0} \int_{\Sigma_o(x)} dA_r \int_{\Sigma_{\theta_i \leq 1}} \dot{\Theta}_{i,\alpha} \pi_\alpha d\boldsymbol{\theta} \\ = -\langle \bar{\Theta}_{i,\alpha} \rangle \frac{\partial a_\alpha}{\partial t} - k_\alpha \langle \bar{\Theta}_{i,\alpha} \rangle \phi_\alpha a_\alpha + k_\beta \langle \bar{\Theta}_{i,\beta} \rangle \phi_\beta a_\beta \quad (58) \end{aligned}$$

For  $c < 1$ , where  $k_\alpha \phi_\alpha = 0$ , using Eq. 53 and rearranging, we get

$$\begin{aligned} \frac{\partial \langle \bar{\Theta}_{i,\alpha} \rangle}{\partial t} - \frac{1}{A_0 a_\alpha} \int_{\Sigma_0(x)} dA_r \int_{\sum_{i=1}^n \theta_i \leq 1} \dot{\Theta}_{i,\alpha} \pi_\alpha d\theta \\ = - \frac{\langle \bar{\Theta}_{i,\alpha} \rangle}{a_\alpha} \frac{\partial a_\alpha}{\partial t} + \frac{\langle \bar{\Theta}_{i,\beta} \rangle}{a_\alpha} \frac{\partial a_\alpha}{\partial t} = \frac{\langle \bar{\Theta}_{i,\beta} \rangle - \langle \bar{\Theta}_{i,\alpha} \rangle}{a_\alpha} \frac{\partial a_\alpha}{\partial t} \end{aligned} \quad (59)$$

For  $c < 1$ , areas of type  $\beta$  transform to an area of type  $\alpha$ , hence  $\partial a_\alpha / \partial t$  will be positive. The term  $(\langle \bar{\Theta}_{i,\beta} \rangle / a_\alpha) (\partial a_\alpha / \partial t)$  increases the coverage,  $\langle \bar{\Theta}_{i,\alpha} \rangle$ , by adding to it the coverage  $\langle \bar{\Theta}_{i,\beta} \rangle$ ; this term will be called ‘‘augmentation.’’ At the same time, owing to the increase in the area fraction of type  $\alpha$ , there is a decrease in the area-averaged coverage, described by  $(\langle \bar{\Theta}_{i,\alpha} \rangle / a_\alpha) (\partial a_\alpha / \partial t)$  on the righthand side; we call this term ‘‘dilution.’’ It is seen that these terms arise naturally as a consequence of the area and probability-averaging process. If we carry out a similar area averaging for coverage on the  $\beta$  surface, we have

$$\begin{aligned} \frac{\partial}{\partial t} [\langle \bar{\Theta}_{i,\beta} \rangle a_\beta] - \frac{1}{A_0} \int_{\Sigma_0(x)} dA_r \int_{\sum_{i=1}^n \theta_i \leq 1} \dot{\Theta}_{i,\beta} \pi_\beta d\theta \\ = k_\alpha \langle \bar{\Theta}_{i,\alpha} \rangle \phi_\alpha a_\alpha - k_\beta \langle \bar{\Theta}_{i,\beta} \rangle \phi_\beta a_\beta \end{aligned} \quad (60)$$

For the  $c < 1$  case, using Eq. 53 in the preceding equation and rearranging, we have

$$\begin{aligned} \frac{\partial \langle \bar{\Theta}_{i,\beta} \rangle}{\partial t} - \frac{1}{A_0 a_\beta} \int_{\Sigma_0(x)} dA_r \int_{\sum_{i=1}^n \theta_i \leq 1} \dot{\Theta}_{i,\beta} \pi_\beta d\theta \\ = \frac{\langle \bar{\Theta}_{i,\beta} \rangle}{a_\beta} \frac{\partial a_\beta}{\partial t} - \frac{\langle \bar{\Theta}_{i,\beta} \rangle}{a_\beta} \frac{\partial a_\beta}{\partial t} = 0 \end{aligned} \quad (61)$$

We do not have dilution/augmentation terms appearing on the righthand side of the previous equation; this is expected, since the areas of type  $\alpha$  do not transform to those of type  $\beta$  for the  $c < 1$  case. For the  $c \geq 1$  case, these terms would be present in the equations for  $\langle \bar{\Theta}_{i,\beta}(x,t) \rangle$ , and *not*  $\langle \bar{\Theta}_{i,\alpha}(x,t) \rangle$ .

## Application to CO Oxidation on Pt(100)

### Assumptions in the formulation of the temporal model

Rate oscillations have been experimentally observed during CO oxidation on Pt(100), but often in the absence of spatiotemporal pattern formation (Imbihl et al., 1986; Lauterbach and Rotermund, 1994; Lele et al., 2001; Lele and Lauterbach, 2002). Hence, we can assume that for certain control parameters, the areas on the surface are similar to well-mixed reactors; there are no large spatial gradients in coverage. This has also been the approach followed in other modeling efforts (Imbihl et al., 1985; Gruyters et al., 1996). Uniform coverage implies that there is no spatial distribution

of  $\langle \bar{\Theta}_i \rangle(x,t)$ . Hence, the local coverage on  $dA$  must be equal to the average coverage, that is

$$\theta_i \equiv \langle \bar{\Theta}_i \rangle \quad (62)$$

There are two important implications of the preceding equation.

1. There is no ‘‘macroscopic’’ diffusion term.
2. The area and probability averaging of any arbitrary nonlinear function  $f(\theta)$  defined on any area  $dA_r$  in  $\Sigma_0(x)$  (here  $f(\theta)$  could represent a nonlinear reaction rate term, or a nonlinear adsorption term), reduces to

$$\begin{aligned} \int_{\Sigma_0(x)} dA_r \int_{\sum_{i=1}^n \theta_i \leq 1} d\theta f(\theta) \pi(x,t;\theta) \\ = f(\langle \bar{\Theta} \rangle) \int_{\Sigma_0(x)} p(x+r,t) dA_r = f(\langle \bar{\Theta} \rangle) a A_0 \end{aligned} \quad (63)$$

Thus, the average of a nonlinear function is now the function of the average. The two previous statements eliminate the presence of second moments in the model.

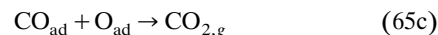
### Steps in the formulation of the model

We outline here a systematic application of the framework in the formulation of a spatiotemporal model for CO oxidation on Pt(100); suitable assumptions then lead to a temporal model. The same steps can be used to model any other reaction of interest, on any type of transforming surface.

The expression for the net rate of change of coverage on  $dA$  of the  $i$ th species can be written as

$$\dot{\Theta}_i(\theta, x, t) = r_{i,ads} - r_{i,des} + r_{i,mig}^{in} - r_{i,mig}^{out} - r_{i,chem} \quad (64)$$

The kinetic expressions are based on a suitable mechanism for the reaction; CO oxidation on Pt(100) follows the LH mechanism, which is as follows



The  $*$  denotes the type of site, which for Pt(100) can be either hex or  $1 \times 1$ . If  $dA$  is of type  $1 \times 1$ , the rate of adsorption of the  $i$ th species from  $dA$  is given by

$$r_{i,ads} = k_{i,ads}^{1 \times 1} S_i^{1 \times 1}(\theta_{\text{CO}}, \theta_{\text{O}}) P_i \quad (66)$$

where the subscript  $i$  stands for adsorbed CO and oxygen.  $S_i^{1 \times 1}$  thus represents the adsorption probability of the  $i$ th gas on the surface of type  $1 \times 1$ . The rate of desorption of CO from  $dA$  is given by

$$r_{i,des} = k_{i,des}^{1 \times 1} \theta_{\text{CO}} \quad (67)$$

The dependence of the adsorption probabilities of CO and oxygen on the surface coverage have been obtained by fitting experimental data from the literature (Gruyters et al., 1996). The rate constants for adsorption, desorption, migration, and the phase transformation kinetics have also been obtained from the literature (Gruyters et al., 1996). The rate of migration into  $dA$  of type  $1 \times 1$  from neighboring areas  $dA_r$  that are of type hex can be written as

$$r_{i,\text{mig}}^{\text{in}} = dA \int dA_r \int \sum_{i=1}^N \theta_i \leq 1 \frac{d\theta k_{\text{hex}-1 \times 1} \theta_i \pi_{\text{hex}}(\mathbf{x} + \mathbf{r}, t)}{a_{1 \times 1}(\mathbf{x} + \mathbf{r}, t)} \quad (68)$$

Using the definition of area and probability-averaged coverage, and the assumption that the area fraction  $a_{1 \times 1}$  is not a function of the spatial location  $\mathbf{x}$  for the well-mixed case, the rate of migration into  $dA$  that is type  $1 \times 1$  from the neighboring areas that are type hex can be written as

$$r_{i,\text{mig}}^{\text{in}} = \int dA_r \int \sum_{i=1}^N \theta_i \leq 1 \frac{d\theta k_{\text{hex}-1 \times 1} \theta_i \pi_{\text{hex}}(\mathbf{x} + \mathbf{r}, t)}{a_{1 \times 1}(\mathbf{x} + \mathbf{r}, t)} = \frac{k_{\text{hex}-1 \times 1} \langle \Theta_i^{\text{hex}} \rangle a_{\text{hex}} A_0}{a_{1 \times 1}} \quad (69)$$

The rate of reaction is given by

$$r_{i,\text{chem}} = k \theta_{\text{CO}} \theta_{\text{O}} \quad (70)$$

We can now arrive at an expression for  $\dot{\theta}_i$  as a function of the local coverage on  $dA$  using Eqs. 66 through 70. Substitution of  $\Theta_i$  into the area and probability averaged Eqs. 58 and 60, along with the assumption that the surface behaves homogeneously with respect to coverage during reaction rate oscillations yields the model equations.

### The temporal model

On applying the steps outlined above, we arrive at the following ordinary differential equations

For  $c = (\langle \Theta_{\text{CO}}^{1 \times 1} \rangle / \theta_{\text{crit}}^{\text{CO}}) + (\langle \Theta_{\text{O}}^{1 \times 1} \rangle / \theta_{\text{crit}}^{\text{O}}) < 1$

$$\frac{d\Theta_{1 \times 1}}{dt} = -k_9 \theta_{1 \times 1} \left( 1 - \frac{\langle \Theta_{\text{CO}}^{1 \times 1} \rangle}{\theta_{\text{crit}}^{\text{CO}}} - \frac{\langle \Theta_{\text{O}}^{1 \times 1} \rangle}{\theta_{\text{crit}}^{\text{O}}} \right) \quad (71)$$

$$\frac{d\Theta_{\text{hex}}}{dt} = -\frac{d\Theta_{1 \times 1}}{dt}$$

$$\frac{d\langle \Theta_{\text{CO}}^{1 \times 1} \rangle}{dt} = k_1 p_{\text{CO}} S_{\text{CO}}^{1 \times 1} - k_3 \langle \Theta_{\text{CO}}^{1 \times 1} \rangle - k_5 \langle \Theta_{\text{CO}}^{1 \times 1} \rangle + k_4 \langle \Theta_{\text{CO}}^{\text{hex}} \rangle \frac{\Theta_{\text{hex}}}{\Theta_{1 \times 1}} - k_7 \langle \Theta_{\text{CO}}^{1 \times 1} \rangle \langle \Theta_{\text{O}}^{1 \times 1} \rangle \quad (72)$$

$$\frac{d\langle \Theta_{\text{O}}^{1 \times 1} \rangle}{dt} = k_6 S_{\text{O}_2}^{1 \times 1} p_{\text{O}_2} - k_7 \langle \Theta_{\text{CO}}^{1 \times 1} \rangle \langle \Theta_{\text{O}}^{1 \times 1} \rangle \quad (73)$$

$$\frac{d\langle \Theta_{\text{CO}}^{\text{hex}} \rangle}{dt} = k_1 S_{\text{CO}}^{\text{hex}} p_{\text{CO}} - k_2 \langle \Theta_{\text{CO}}^{\text{hex}} \rangle - k_4 \langle \Theta_{\text{CO}}^{\text{hex}} \rangle + k_5 \langle \Theta_{\text{CO}}^{1 \times 1} \rangle \frac{\Theta_{1 \times 1}}{\Theta_{\text{hex}}} - k_7 \langle \Theta_{\text{CO}}^{\text{hex}} \rangle \langle \Theta_{\text{O}}^{\text{hex}} \rangle + \frac{\langle \Theta_{\text{CO}}^{1 \times 1} \rangle - \langle \Theta_{\text{CO}}^{\text{hex}} \rangle}{\Theta_{\text{hex}}} \frac{d\Theta_{\text{hex}}}{dt} \quad (74)$$

$$\frac{d\langle \Theta_{\text{O}}^{\text{hex}} \rangle}{dt} = k_6 S_{\text{O}_2}^{\text{hex}} p_{\text{O}_2} - k_7 \langle \Theta_{\text{CO}}^{\text{hex}} \rangle \langle \Theta_{\text{O}}^{\text{hex}} \rangle + \frac{\langle \Theta_{\text{O}}^{1 \times 1} \rangle - \langle \Theta_{\text{O}}^{\text{hex}} \rangle}{\Theta_{\text{hex}}} \frac{d\Theta_{\text{hex}}}{dt} \quad (75)$$

$$c = \frac{\langle \Theta_{\text{CO}}^{1 \times 1} \rangle}{\theta_{\text{crit}}^{\text{CO}}} + \frac{\langle \Theta_{\text{O}}^{1 \times 1} \rangle}{\theta_{\text{crit}}^{\text{O}}} \geq 1$$

$$\frac{d\Theta_{1 \times 1}}{dt} = k_8 \Theta_{\text{hex}} \langle \Theta_{\text{CO}}^{\text{hex}} \rangle^n \quad (76)$$

$$\frac{d\Theta_{\text{hex}}}{dt} = \frac{d\Theta_{1 \times 1}}{dt}$$

$$\frac{d\langle \Theta_{\text{CO}}^{1 \times 1} \rangle}{dt} = k_1 p_{\text{CO}} S_{\text{CO}}^{1 \times 1} - k_3 \langle \Theta_{\text{CO}}^{1 \times 1} \rangle - k_5 \langle \Theta_{\text{CO}}^{1 \times 1} \rangle + k_4 \langle \Theta_{\text{CO}}^{\text{hex}} \rangle \frac{\Theta_{\text{hex}}}{\Theta_{1 \times 1}} - k_7 \langle \Theta_{\text{CO}}^{1 \times 1} \rangle \langle \Theta_{\text{O}}^{1 \times 1} \rangle + \frac{\langle \Theta_{\text{CO}}^{\text{hex}} \rangle - \langle \Theta_{\text{CO}}^{1 \times 1} \rangle}{\Theta_{1 \times 1}} \frac{d\Theta_{1 \times 1}}{dt} \quad (77)$$

$$\frac{d\langle \Theta_{\text{O}}^{1 \times 1} \rangle}{dt} = k_6 S_{\text{O}_2}^{1 \times 1} p_{\text{O}_2} - k_7 \langle \Theta_{\text{CO}}^{1 \times 1} \rangle \langle \Theta_{\text{O}}^{1 \times 1} \rangle + \frac{\langle \Theta_{\text{O}}^{\text{hex}} \rangle - \langle \Theta_{\text{O}}^{1 \times 1} \rangle}{\Theta_{1 \times 1}} \frac{d\Theta_{1 \times 1}}{dt} \quad (78)$$

$$\frac{d\langle \Theta_{\text{CO}}^{\text{hex}} \rangle}{dt} = k_1 S_{\text{CO}}^{\text{hex}} p_{\text{CO}} - k_2 \langle \Theta_{\text{CO}}^{\text{hex}} \rangle - k_4 \langle \Theta_{\text{CO}}^{\text{hex}} \rangle + k_5 \langle \Theta_{\text{CO}}^{1 \times 1} \rangle \frac{\Theta_{1 \times 1}}{\Theta_{\text{hex}}} - k_7 \langle \Theta_{\text{CO}}^{\text{hex}} \rangle \langle \Theta_{\text{O}}^{\text{hex}} \rangle \quad (79)$$

$$\frac{d\langle \Theta_{\text{O}}^{\text{hex}} \rangle}{dt} = k_6 S_{\text{O}_2}^{\text{hex}} p_{\text{O}_2} - k_7 \langle \Theta_{\text{CO}}^{\text{hex}} \rangle \langle \Theta_{\text{O}}^{\text{hex}} \rangle \quad (80)$$

where  $\langle \Theta_{\text{CO}}^{1 \times 1} \rangle$ ,  $\langle \Theta_{\text{O}}^{1 \times 1} \rangle$  represent the area and probability-averaged coverage of CO and oxygen on  $1 \times 1$  areas, respectively;  $\langle \Theta_{\text{CO}}^{\text{hex}} \rangle$ ,  $\langle \Theta_{\text{O}}^{\text{hex}} \rangle$  represent the area and probability-averaged coverage of CO and oxygen on the hex areas, respectively;  $\Theta_{1 \times 1}$  represents the area fraction of  $1 \times 1$  on the surface. The rate constants are available in the literature (Imbühl et al., 1985; Gruyters et al., 1995, 1996). The value of the parameter  $c$  decides whether the areas will transform from type  $1 \times 1$  to hex and vice versa; for  $c < 1$ ,  $1 \times 1$  areas transform to hex, while for  $c > 1$ , the hex areas transform to

**Table 1. Dilution/Augmentation Terms in the Model Equations**

Term. No.	Term in the Model	Eq.	Parameter $c$
1	$\frac{\langle \Theta_{CO}^{1 \times 1} \rangle - \langle \Theta_{CO}^{hex} \rangle}{\Theta_{hex}} \frac{d\Theta_{hex}}{dt}$	22	$c < 1$
2	$\frac{\langle \Theta_O^{1 \times 1} \rangle - \langle \Theta_O^{hex} \rangle}{\Theta_{hex}} \frac{d\Theta_{hex}}{dt}$	23	$c < 1$
3	$\frac{\langle \Theta_{CO}^{hex} \rangle - \langle \Theta_{CO}^{1 \times 1} \rangle}{\Theta_{1 \times 1}} \frac{d\Theta_{1 \times 1}}{dt}$	25	$c > 1$
4	$\frac{\langle \Theta_O^{hex} \rangle - \langle \Theta_O^{1 \times 1} \rangle}{\Theta_{1 \times 1}} \frac{d\Theta_{1 \times 1}}{dt}$	26	$c > 1$

$1 \times 1$ . Of special note are the form of the migration terms and the dilution/augmentation terms (see Table 1). For  $c < 1$ , the  $1 \times 1$  area transforms to hex, since the total adsorbate coverage is not enough to stabilize the  $1 \times 1$  area. The average coverage of CO on hex in Eq. 74 will be reduced by this increase in the hex area, as represented by  $-\langle \Theta_{CO}^{hex} \rangle / \Theta_{hex} (d\Theta_{hex} / dt)$  ( $d\Theta_{hex} / dt$  is positive for  $c < 1$ ). This is the *dilution* effect. The transforming  $1 \times 1$  areas also add their adsorbed CO molecules to the hex phase. This is represented by the term  $(\langle \Theta_{CO}^{1 \times 1} \rangle / \Theta_{hex}) (d\Theta_{hex} / dt)$ , and is the *augmentation* effect, because it results in an increase in CO coverage on hex. These effects can be easily understood by considering Figure 3. The shaded areas are of type  $1 \times 1$ , the lighter areas are of type hex, with black dots representing CO coverage on  $1 \times 1$  and white dots CO coverage on hex. When a part of the  $1 \times 1$  area transforms to hex, it increases the hex area, thus reducing the average CO coverage on hex (dilution); at the same time the transforming  $1 \times 1$  area adds its coverage to that on the hex area, increasing coverage on hex

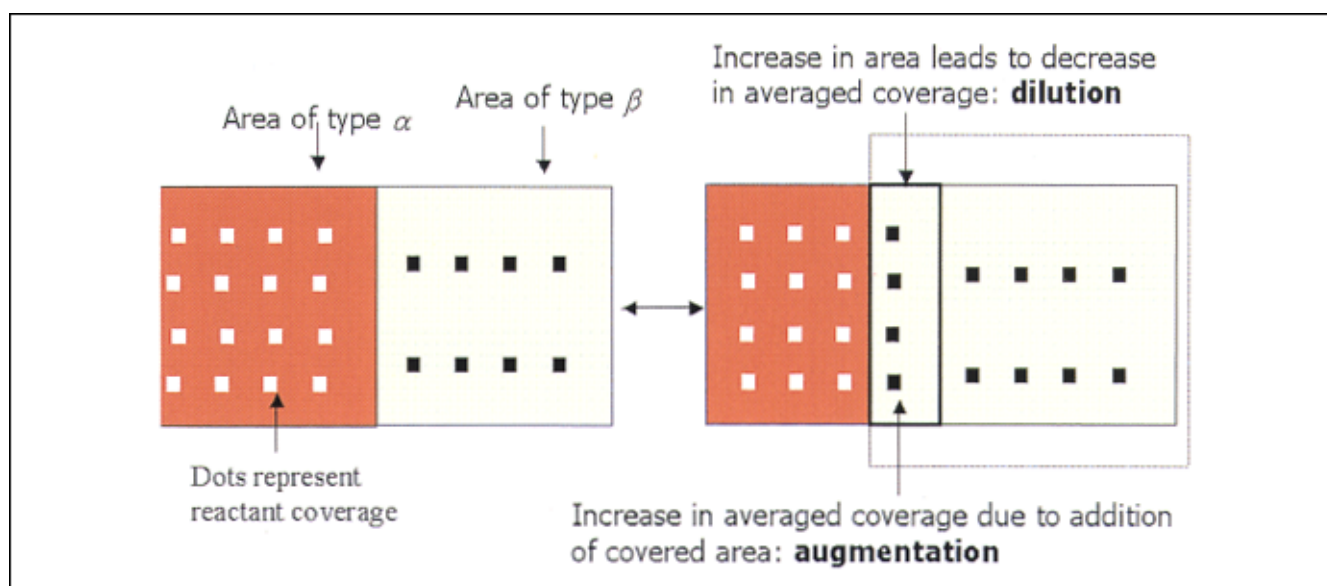
(augmentation). The average coverage on the  $1 \times 1$  areas does not change by dilution and augmentation (these terms are absent in Eqs. 72 and 73), since for  $c < 1$  there is no transformation of hex areas to  $1 \times 1$ . A similar explanation applies for the presence of the term

$$\frac{\langle \Theta_O^{hex} \rangle - \langle \Theta_O^{1 \times 1} \rangle}{\Theta_{hex}} \frac{d\Theta_{hex}}{dt}$$

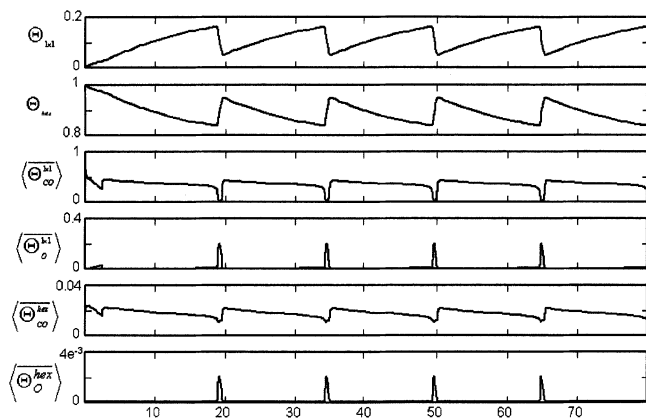
in Eq. 75, which describes the rate of change of oxygen coverage on the hex area. For  $c > 1$ , the hex areas transform to the  $1 \times 1$  area. The average coverage of CO on the  $1 \times 1$  phase in Eq. 77 will now be reduced by dilution, resulting from the increase in the  $1 \times 1$  area, as represented by  $(-\langle \Theta_{CO}^{1 \times 1} \rangle / \Theta_{1 \times 1}) (d\Theta_{1 \times 1} / dt)$ . The coverage will be increased by an augmentation resulting from a direct addition of adsorbed molecules on the transforming hex being directly to the  $1 \times 1$  phase as represented by  $(\langle \Theta_{CO}^{hex} \rangle / \Theta_{1 \times 1}) (d\Theta_{1 \times 1} / dt)$ .

### Simulation

Figure 4 shows the result of integrating the model for fixed reaction conditions of  $T = 510$  K,  $p_{CO} = 1 \times 10^{-5}$  mbar, and  $p_{O_2} = 2.5 \times 10^{-5}$  mbar, where  $p_{CO}$  and  $p_{O_2}$  are the partial pressures of the reactant gases CO and oxygen, and  $T$  is the catalyst temperature. Shown are the area and probability-averaged surface-specific coverages, as well as the area fractions as a function of time. There is a perfect anticorrelation between simulated CO and oxygen coverages during an oscillatory cycle, on either type of surface; this has been observed experimentally (Lauterbach and Rotermund, 1994; Lele and Lauterbach, 2001). When the transformation from the hex phase to the  $1 \times 1$  phase is underway, the  $1 \times 1$  surface is predicted to be poisoned by CO at a coverage of approximately 0.5. This has been experimentally confirmed by Imbihl et al. (1986), who observed that  $1 \times 1$  areas grew in size with a con-

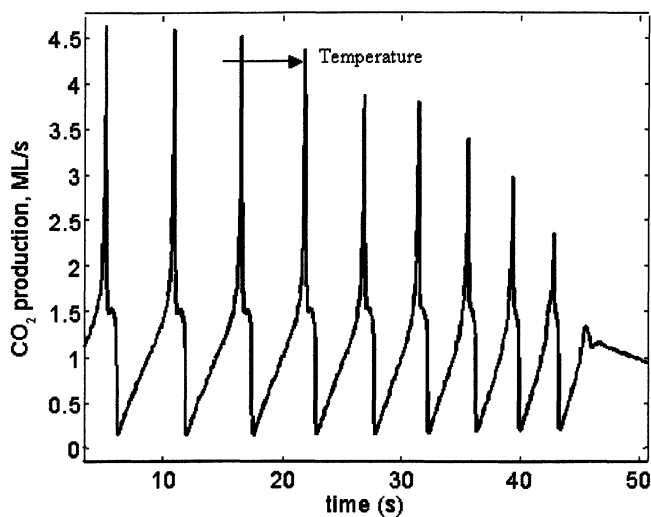


**Figure 3. Dilution and augmentation effect.**

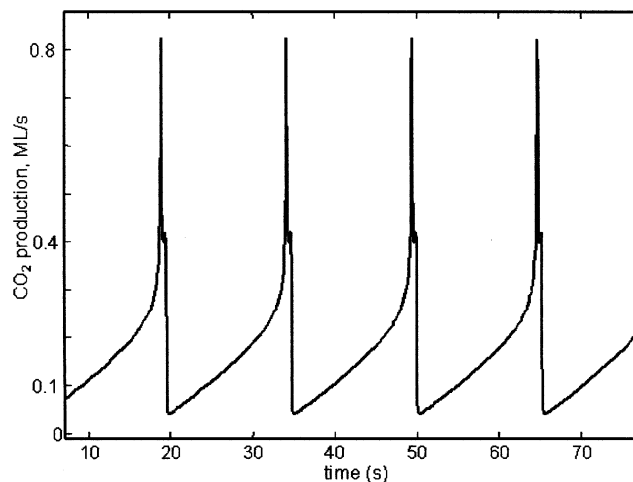


**Figure 4.** Simulation of rate oscillations using the ordinary differential Eqs. 19–28 for reaction conditions of  $T = 510$  K,  $p_{\text{CO}} = 1 \times 10^{-5}$  mbar and  $p_{\text{O}_2} = 2.5 \times 10^{-5}$  mbar.

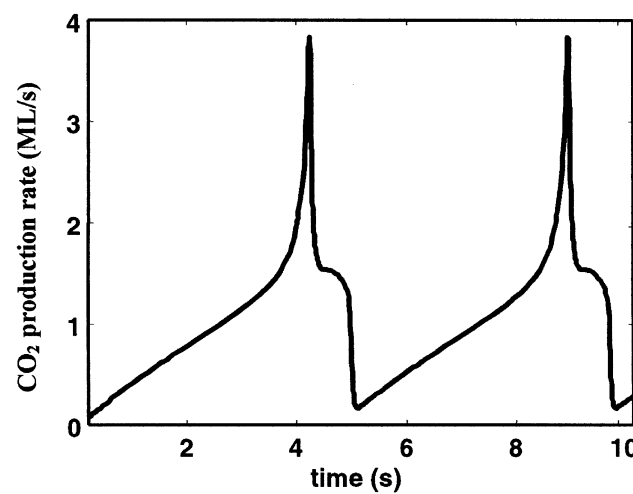
stant coverage of approximately 0.45. The oscillations are of a relaxation type, revealing the multi-time-scale behavior that is characteristic of the difference in the kinetics of the phase transformation, as compared to adsorption, desorption, and chemical reaction. The period of oscillation of 15–20 s is close to experimentally observed values. Figure 5 shows a simulation in which the differential equations were integrated for a slow temperature ramp, without allowing steady state. This is an analog of experiments, which are often performed in this manner to access qualitative information about the system. The simulated reaction rate is seen to be sensitive and decreasing with increasing temperature, as expected (Lele and Lauterbach, 2001). Figure 6a and 6b show the changing shape of the oscillation under different temperature conditions. To demonstrate the effect of terms like dilution, augmentation,



**Figure 5.** Effect of temperature ramp on reaction rate (the model was integrated for a temperature increase from 490 K to 515 K, at fixed,  $p_{\text{CO}} = 1 \times 10^{-5}$  mbar and  $p_{\text{O}_2} = 2.5 \times 10^{-5}$  mbar).



(a)



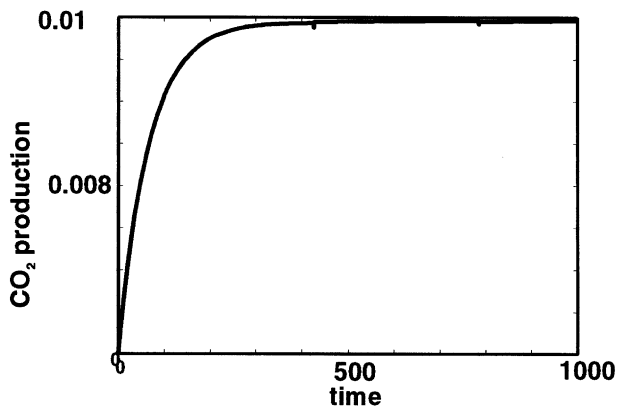
(b)

**Figure 6.** (a) Simulation of oscillatory  $\text{CO}_2$  rate at  $T = 500$  K; (b) oscillatory  $\text{CO}_2$  production at  $T = 510$  K, for  $p_{\text{CO}} = 1 \times 10^{-5}$  mbar and  $p_{\text{O}_2} = 2.5 \times 10^{-5}$  mbar.

and migration, we strip the foregoing model equations of such terms and examine their dynamic behavior (as shown in Figure 7) relative to that of the proper equations (as shown in Figure 6b). With the terms present, the reaction-rate oscillates, with a high average reactivity, as seen in Figure 6b. Without the terms, the surface goes into a low reactivity steady state.

## Summary

We have developed a general mathematical framework for analyzing adsorption, desorption, reaction, and surface diffusion of gaseous species on catalytic surfaces, coupled with catalytic surface-phase transformation based on a procedure that involves both local probability and area averaging. While the probability averaging is to promote the deterministic



**Figure 7. Dynamic behavior in the absence of terms in the model equations at  $T = 510$  K, for  $p_{\text{CO}} = 1 \times 10^{-5}$  mbar and  $p_{\text{O}_2} = 2.5 \times 10^{-5}$  mbar (compare with Figure 6b).**

framework, the area averaging is designed to produce quantities more closely related to measurement. This development naturally gives rise to terms such as dilution/augmentation in the equations for averaged surface concentrations that do not appear in prior mathematical treatments that arrived at model equations by ad hoc balances. Such terms are of significance to predicting the nonlinear behavior of the system and in extracting the kinetics of surface reactions from dynamic data. We have demonstrated an application of the theoretical framework to CO oxidation on Pt(100) by deriving a purely temporal model for CO oxidation on Pt(100). Dilution/augmentation terms were identified in the temporal model and shown to be significantly important by simulation.

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### Appendix

In the absence of all kinetic terms, that is, adsorption, desorption, and chemical reaction, the net rate of change of coverage of species  $i$  on the total surface area (including surfaces of either type) should be zero. This implies that the form of the dilution/augmentation and migration terms, which evolve out of the framework, must be consistent with conservation of mass balance. That this is indeed the case is shown below.

Consider the *total* rate of change of coverage of CO for  $c < 1$ . The equation for the total rate of change of CO cover-

age is

$$\frac{d\langle\overline{\Theta_{CO}^{total}}\rangle}{dt} = \frac{d}{dt} \left( \Theta_{1 \times 1} \langle\overline{\Theta_{CO}^{1 \times 1}}\rangle + \Theta_{hex} \langle\overline{\Theta_{CO}^{hex}}\rangle \right) = \Theta_{1 \times 1} \frac{d\langle\overline{\Theta_{CO}^{1 \times 1}}\rangle}{dt} + \Theta_{hex} \frac{d\langle\overline{\Theta_{CO}^{hex}}\rangle}{dt} + \langle\overline{\Theta_{CO}^{1 \times 1}}\rangle \frac{d\Theta_{1 \times 1}}{dt} + \langle\overline{\Theta_{CO}^{hex}}\rangle \frac{d\Theta_{hex}}{dt} \quad (A1)$$

Using the model equations (Eqs. 71 through 80), we have in the absence of adsorption, desorption, and chemical reaction

$$\begin{aligned} \frac{d\langle\overline{\Theta_{CO}^{total}}\rangle}{dt} &= \Theta_{1 \times 1} \frac{d\langle\overline{\Theta_{CO}^{1 \times 1}}\rangle}{dt} + \Theta_{hex} \frac{d\langle\overline{\Theta_{CO}^{hex}}\rangle}{dt} + \langle\overline{\Theta_{CO}^{1 \times 1}}\rangle \frac{d\Theta_{1 \times 1}}{dt} + \langle\overline{\Theta_{CO}^{hex}}\rangle \frac{d\Theta_{hex}}{dt} \\ &= \Theta_{1 \times 1} \left( -k_5 \langle\overline{\Theta_{CO}^{1 \times 1}}\rangle + k_4 \langle\overline{\Theta_{CO}^{hex}}\rangle \frac{\Theta_{hex}}{\Theta_{1 \times 1}} + \frac{\langle\overline{\Theta_{CO}^{hex}}\rangle - \langle\overline{\Theta_{CO}^{1 \times 1}}\rangle}{\Theta_{1 \times 1}} \frac{d\Theta_{1 \times 1}}{dt} \right) \\ &\quad + \Theta_{hex} \left( -k_4 \langle\overline{\Theta_{CO}^{hex}}\rangle + k_5 \langle\overline{\Theta_{CO}^{1 \times 1}}\rangle \frac{\Theta_{1 \times 1}}{\Theta_{hex}} \right) + \langle\overline{\Theta_{CO}^{1 \times 1}}\rangle \frac{d\Theta_{1 \times 1}}{dt} + \langle\overline{\Theta_{CO}^{hex}}\rangle \frac{d\Theta_{hex}}{dt} \\ &= 0 \end{aligned} \quad (A2)$$

It is instructive to consider the substitution of Eq. 18 into the first term of the probability-averaged Eq. 32. Let  $dA$  be of type  $\alpha$ , then the migration terms take the form of Eqs. 16 and 17, then

$$\int_{\sum_{i=1}^n \theta_i \leq 1} \dot{\Theta}_{1,\alpha} \pi_\alpha d\theta = \int_{\sum_{i=1}^n \theta_i \leq 1} \left( r_{i,ads} - r_{i,des} + r_{i,mig}^{in} - r_{i,mig}^{out} - r_{i,chem} \right) \pi_\alpha d\theta \quad (A3)$$

Considering only the migration terms in the preceding equation and assuming  $a(\mathbf{x} + \mathbf{r}, t) = a(\mathbf{x}, t)$  as before, for simplifying the analysis, we have

$$\begin{aligned} \int_{\sum_{i=1}^n \theta_i \leq 1} (r_{i,mig}^{in} - r_{i,mig}^{out}) \pi_\alpha d\theta &= \int_{\sum_{i=1}^n \theta_i \leq 1} \left( \frac{1}{A_0} \int_{\Sigma_o(r)} dA_r \int_{\sum_{i=1}^N \theta_i \leq 1} d\theta \frac{k_{\beta-\alpha} \theta_i \pi_\beta}{a_\alpha} \right. \\ &\quad \left. + \frac{1}{A_0} \int_{\Sigma_o(r)} dA_r \int_{\sum_{i=1}^N \theta_i \leq 1} d\theta \frac{k_{\alpha-\alpha} \theta_i \pi_\alpha - k_{\alpha-\alpha} \theta_i - k_{\alpha-\beta} \theta_i}{a_\alpha} \right) \pi_\alpha d\theta \\ &= k_{\beta-\alpha} \langle\overline{\Theta_{i,\beta}}\rangle P_\alpha \frac{a_\beta}{a_\alpha} + k_{\alpha-\alpha} \langle\overline{\Theta_{i,\alpha}}\rangle P_\alpha - k_{\alpha-\alpha} \overline{\Theta_{i,\alpha}} P_\alpha - k_{\alpha-\beta} \overline{\Theta_{i,\alpha}} P_\alpha \end{aligned} \quad (A4)$$

Area averaging this equation yields

$$\begin{aligned} \int_{\Sigma_o(r)} dA_r \int_{\sum_{i=1}^N \theta_i \leq 1} (r_{i,mig}^{in} - r_{i,mig}^{out}) \pi_\alpha d\theta &= \int_{\Sigma_o(r)} dA_r \left( k_{\beta-\alpha} \langle\overline{\Theta_{i,\beta}}\rangle P_\alpha \frac{a_\beta}{a_\alpha} + k_{\alpha-\alpha} \langle\overline{\Theta_{i,\alpha}}\rangle P_\alpha - k_{\alpha-\alpha} \overline{\Theta_{i,\alpha}} P_\alpha + k_{\alpha-\beta} \overline{\Theta_{i,\alpha}} P_\alpha \right) \\ &= \left( k_{\beta-\alpha} \langle\overline{\Theta_{i,\beta}}\rangle \frac{a_\beta}{a_\alpha} + k_{\alpha-\alpha} \langle\overline{\Theta_{i,\alpha}}\rangle - k_{\alpha-\alpha} \langle\overline{\Theta_{i,\alpha}}\rangle - k_{\alpha-\beta} \langle\overline{\Theta_{i,\alpha}}\rangle \right) a_\alpha A_0 = -k_{\alpha-\beta} \langle\overline{\Theta_{i,\alpha}}\rangle a_\alpha A_0 + k_{\beta-\alpha} \langle\overline{\Theta_{i,\beta}}\rangle a_\beta A_0 \end{aligned} \quad (A5)$$

It is seen that the migration into and out of  $dA$  between areas of type  $\alpha$  compensates for each other exactly under the assumption that  $a_\alpha(\mathbf{x} + \mathbf{r}, t) = a_\alpha(\mathbf{x}, t)$ .

Manuscript received Feb. 4, 2002, revision received Nov. 27, 2002, and final revision received Mar. 17, 2003.