Microkinetic Models and Dynamic Monte Carlo Simulations of Nonuniform Catalytic Systems

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The combined insight gained from laboratory and computational experiments has historically provided detailed information about the complex interactions present in many heterogeneous catalytic systems. Although this information has been effectively used to interpret and explain experimental observations, it unfortunately has not, in general, been incorporated into kinetic models of the reacting systems. In particular, catalytic nonuniformity is one such phenomenon which is often ignored when kinetic models are constructed despite there being much experimental and computational evidence indicating its presence. Catalytic nonuniformity has been therefore incorporated into both microkinetic models and dynamic Monte Carlo simulations of catalytic reacting systems, and the performance and applicability of each solution method has been investigated for several model systems exhibiting different causes of nonuniform behavior.

Introduction

Quantum chemistry, molecular dynamics, and equilibrium Monte Carlo simulations have greatly improved our understanding of heterogeneous catalytic systems. The combination of experimental information and the insights gained from these computational experiments has afforded a detailed understanding of many fundamental catalytic processes. Unfortunately, these insights rarely become incorporated into kinetic models. In fact, the simplicity of kinetic models is often in stark contrast to the complexity of these systems. The past few decades have seen marked improvements in the level of detail incorporated into models of gas-phase reactions but there has not been a commensurate increase in the detail of heterogeneous catalytic models. The presence of a solid-phase catalyst increases the complexity of these systems, making models to describe them more difficult to construct than those for gas-phase systems. Nonetheless, the level of understanding achieved for many catalytic systems is capable of supporting much more sophisticated models than those which are often used. One impediment to incorporating this understanding is that the methodologies and approaches traditionally used to develop kinetic models for heterogeneous catalytic systems are insufficient. Therefore, modeling hierarchies must be developed which allow the facile and consistent incorporation of more complex interactions into kinetic models of heterogeneous catalytic reaction systems.

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An important catalytic phenomenon which is often overlooked in kinetic models is nonuniformity (Dumesic et al., 1975; Bozso et al., 1977; Bare et al., 1986; Oh et al., 1986; Zhang et al., 1996; Borodziński and Gołębiowski, 1997). Nonuniformity in reactions on surfaces may arise because of heterogeneity of the catalytic sites or because of interactions between species on the surface that result in changes in the thermodynamic and kinetic parameters as the population on the surface varies. In this article, the word nonuniformity is used for either of these phenomena. While nonuniformity is known to be present in all heterogeneous catalysts, its incorporation into kinetic models has been slowed due to the success of uniform kinetic models (Boudart, 1956). That is, models which do not account for catalytic nonuniformity often perform adequately when fitting data from systems in which nonuniformity is known to be present. However, while these models are successful at fitting data, they often fail when they are used to predict kinetic data because they do not represent the true physics of the reacting system (Dooling et al., 1999). There is evidence that incorporation of known nonuniformity into models of catalytic reaction systems can improve both their fitting and predictive capabilities (Broadbelt and Rekoske, 1996; Dooling et al., 1999; Fastrup, 1997). However, more work must be done to determine and characterize the effect of nonuniformity on kinetic models, yielding a set of heuristics for the kinetic modeler to use when applying nonuniform models to catalytic reaction systems.

One of the main difficulties in effectively studying and characterizing nonuniformity in catalytic systems is deconvoluting which macroscopic phenomena are caused by nonuniformity and which have other causes. The interaction between adsorbed species and the catalyst is very complex, with many factors determining catalyst activity and selectivity. In real catalytic systems, the effect of nonuniform phenomena, such as structure sensitivity and adsorbate-adsorbate (AA) interactions, can be indistinguishable from reactant ensemble requirements, catalyst ''hot spots,'' or even from each other. Therefore, we will focus on model systems with well-defined forms and extents of nonuniformity to facilitate the development of the methodologies required to create nonuniform kinetic models. In this way, the effect, or ''fingerprint,'' of nonuniformity on the macroscopic kinetics of the system can be unambiguously determined and studied.

Successful integration of nonuniformity into models of catalytic reaction systems requires that the kinetic models be at the same level of detail as the models of nonuniformity. For example, it is not effective to incorporate a model of AA interactions into a power-law kinetic model. Furthermore, nonuniformity can have profound effects on relative coverages of species, kinetic parameters, and reaction rates, making the traditional simplifying assumptions of a rate-determining step, most abundant reactive intermediate, and so on, inappropriate for these models. More detailed kinetic models such as microkinetic modeling (Dumesic et al., 1993; Tsai and Weinberg, 1987; Bowker et al., 1988; Stoltze and Nørskov, 1988; Dumesic and Treviño, 1989; Waugh, 1993; Aparicio, 1997) and dynamic Monte Carlo (MC) simulations (Ziff et al., 1986; Lombardo and Bell, 1991; Deem et al., 1992; Sholl and Skodje, 1995; Jansen and Lukkien, 1999) are well suited for integration with models of nonuniformity. Both approaches account for all reactions on the molecular level. The main difference between the two approaches is the model of the catalytic surface. Microkinetic modeling treats adsorbate species using the mean-field approximation, expressing reaction rates in terms of species coverages. Dynamic MC models the catalytic surface as a lattice of reaction sites, explicitly performing each reaction on the lattice. MC provides a more detailed, molecular-level approach, thereby allowing more detailed models of catalytic nonuniformity at the expense of longer solution times.

Model catalytic reaction systems exhibiting AA interactions and biographic nonuniformity were investigated using both microkinetic modeling and dynamic MC simulations. The implementation of the nonuniformity into each type of kinetic model is discussed below. The ability of microkinetic modeling and MC to capture nonuniform behavior in catalytic systems was compared. Additionally, the behavior of nonuniform systems was contrasted to uniform systems, particularly noting ''fingerprints'' of nonuniform behavior on macroscopic kinetic behavior.

Method

To allow for rapid and efficient creation of nonuniform kinetic models, software was developed which allows facile development and solution of a wide variety of complex reaction mechanisms. Rather than hard-coding mechanistic information into the software, the software is capable of interpreting mechanisms input in human-readable format and converting the mechanistic information into a form appropriate for a model solution. Additionally, kinetic parameters and reactor configurations can also be interpreted dynamically by the software. This allows many different mechanisms, nonuniform models, rate parameters, and reactor configurations to be investigated quickly and easily.

The microkinetic modeling component of the software is based upon the approach of Dumesic et al. (1993). A separate program which converts the human-readable reaction mechanisms into machine-compilable species balance equations was written and extended to allow nonuniform model information to be input. The output from this program is then linked with methods which combine the species balance equations with reactor design equations, resulting in a set of coupled ordinary differential equations. The system of equations is solved using standard techniques (Brenan et al., 1996). Currently, ideal constant-volume batch, constant-pressure plug flow, and transient constant-pressure continuous stirred-tank reactor design equations are implemented in the software for both microkinetic analysis and noncatalytic kinetic modeling approaches. Additionally, biographic nonuniformity and AA interaction models of nonuniformity are available for use.

All MC simulations were performed with a dynamic MC algorithm described previously (Dooling and Broadbelt, 2000). One of the main advantages of this MC implementation is its ability to perform MC simulations on complex reaction mechanisms defined by the user. In addition, the MC algorithm, which is based on the work of Gillespie (1976), maps each MC step into real time, so the solution can be performed in coordination with reactor design equations and the results compared with experiment. The conversion between human-readable reaction mechanisms and information needed by the MC engine to perform the simulation is handled internally by the software. This is in contrast to traditional MC simulation tools, which were designed for a single system and required adjustment to handle different mechanisms or reactor configurations. Because mechanisms are parsed dynamically, arbitrary reactant and product ensembles can be used during lattice simulations. As will be shown below, this allows straightforward implementation of complex nonuniform models into kinetic models.

Adsorbate-Adsorbate Interaction Model

Adsorbate-adsorbate interactions are common in heterogeneous reaction systems. Most often, these interactions are due to short-range, repulsive forces between neighboring adsorbates. This leads to a decrease in the enthalpy of adsorption as the surface becomes more crowded and the adsorbates are forced to interact with each other. While these interactions are thought to be present in many systems, very few kinetic models have attempted to incorporate this phenomenon. Fastrup (1997) incorporated AA interactions into a microkinetic model of ammonia synthesis in a self-consistent manner. Tavares et al. (1996) implemented AA interactions between carbon monoxide and hydrogen in a microkinetic model of carbon formation on nickel surfaces. In this model, the enthalpy of adsorption of carbon monoxide was assumed to decrease linearly with the coverage of hydrogen.

Vlachos (1997) compared linear mean-field and MC AA interaction models for a simple surface reaction. Lombardo and Bell (1991) used bond-order conservation techniques to incorporate AA interactions into desorption activation energies. The effect of lateral interactions were shown to significantly influence the reactivity of different adsorbed states in ethylene hydrogenation (Pallassana and Neurock, 1999; Neurock and Hansen, 1998). Masel (1996) demonstrated that the commonly used Elovich equation could not capture temperature programmed desorption from ordered adsorbate layers. While these and other models, which have incorporated AA interactions, have been successful, little is known about how to accurately incorporate AA interactions into kinetic models.

To begin to answer questions such as this, we have generated nonuniform temperature-programmed desorption (TPD) data for a simple desorption mechanism using MC simulations. The mechanism investigated in this study was

$$A + * \rightleftharpoons *A \tag{1}$$

where $*$ is an empty site and $*A$ represents an adsorbed molecule of A. It is advantageous to use TPD to study AA interactions, because the entire range of surface coverage is probed. Additionally, since the mechanism only involves adsorption and desorption steps, the effect of the AA interactions on the kinetics can be easily extracted. MC simulations were used to generate the data, because they allow for exact incorporation of the short-range interactions characteristic of AA interactions. Because the state of the surface is known at all times during the simulation, the interactions between adsorbates can be incorporated into the local rate of desorption for each individual adsorbate. The MC simulations modeled the catalyst as a periodic square lattice, and only nearest-neighbor (NN) AA interactions were considered. All possible desorption events, desorption of an isolated adsorbate, an adsorbate having one NN, two NN, and so on, were represented as different reactions in the mechanism, each having its own rate constant for desorption. More specifically, the preexponential factor for all desorption events was held constant and the enthalpy of adsorption varied. Adsorption was specified to be unactivated, so the activation energy for desorption was equal to the negative of the enthalpy of adsorption. The activation energy for desorption E_d was decreased by a fixed amount ΔE_d for each NN of the adsorbate desorbing

$$E_d = E_d^0 - n\Delta E_d \tag{2}$$

where E_d^0 is the activation energy for desorption of an isolated adsorbate and n is the number of neighbors. For a square lattice with only NN interactions, n can range from zero to four.

In contrast to MC lattice simulations, models using mean-field coverage information can only account for lateral interactions using either an infinite set of equations or some approximation (Sholl and Skodje, 1995). Several investigators have developed detailed modeling approaches for nonuniform TPD spectra (Tovbin and Votyakov, 1997; Rudzinski et al., 2000). While these approaches have been successful at modeling TPD spectra, they are inherently complex, still introduce a degree of approximation, and are not readily extendable to arbitrary catalytic reaction systems. Although microkinetic models also use mean-field coverage information, they are simpler to implement and more generally applicable than these approaches. Further, microkinetic modeling is much more computationally efficient than MC simulations. These advantages provide the impetus to develop accurate nonuniform models that are compatible with microkinetic modeling. To this end, several models which relate enthalpy of adsorption to surface coverage were assessed. Only relationships between enthalpy of adsorption and coverage were investigated to maintain consistency with the MC simulations. Additionally, experimental information on the variation of enthalpy of adsorption with coverage is more readily available through microcalorimetry than is information on the variation of the entropic contribution to the rate with coverage.

Two different approaches were employed to investigate the ability of microkinetic models to capture the effect of AA interactions on adsorption/desorption kinetics. Previous investigations suggest that incorrect kinetic models are sometimes able to fit nonuniform data, but the kinetic parameters required to fit the data often lack physical significance (Dooling et al., 1999). Therefore, the first approach fixed all kinetic and nonuniform parameters in the microkinetic models to values consistent with those used to generate the data, that is, the values used in the MC simulations. Several different simple relationships between enthalpy of adsorption and coverage commonly used in the literature (Tavares et al., 1996; Fastrup, 1997; Vlachos, 1997; Dooling et al., 1999) were compared to the results from the MC simulations. This approach tested the ability of commonly used, mean-field models of nonuniformity to accurately capture molecular-level interactions using the appropriate kinetic parameters. Thus, any failure of the model indicates a failure of the functional form of the model rather than a failure of a parameter fit. The second approach fit a simple polynomial to enthalpy of adsorption vs. coverage data obtained from MC simulations. The resulting function was used as the mean-field nonuniform model in the microkinetic analysis. This approach was used to determine if microcalorimetry data can be used to parameterize nonuniform microkinetic models. The predictions of all of the different nonuniform microkinetic models were compared with those from the MC simulations to determine which, if any, of the mean-field models are able to adequately describe AA interactions.

Both the MC and microkinetic modeling simulations modeled a constant pressure continuous stirred-tank reactor with a total pressure of 10^5 Pa and a volume of 10^{-5} m^3. The feed was a pure inert diluent flowing at a rate of 10^{20} molecules/s. Since the MC time steps are discrete, the flow of molecules in and out of the reactor must also be discretized. If the input flow rate of species i is F_i, $F_i\Delta t$ molecules of species i are added to the CSTR during the time step Δt. After the flow in and reaction have been performed, the amount of each species which needs to exit the reactor to maintain a constant pressure is calculated and removed. The temperature was ramped at a rate of 0.25 K/s. Uniform TPD both with and without readsorption were studied first to ensure the accuracy of both the microkinetic and MC methods. The

uniform TPD data were generated using a preexponential factor for desorption of 10^{13} molecule/site/s and an activation energy for desorption (negative of the enthalpy of adsorption) of 110 kJ/mol. The agreement between the two methods was excellent in all cases for square lattices with sides of either length 50 (L = 50) or 100 (L = 100) in the MC simulations. Typical solution times of the microkinetic models were less than a second, while those for the MC simulations ranged from a few seconds (uniform desorption without diffusion) to several days (nonuniform desorption with both readsorption and diffusion) on a GNU/Linux PC with an AMD K6-2 400 MHz processor.

The introduction of AA interactions creates a more complicated situation in which the rate of desorption is dependent on the local environment of the adsorbate. There are many possible functional forms one can use to approximately incorporate AA interactions into rate constants. Three different equations which relate the activation energy to coverage were investigated: linear, isolated, and hyperbolic tangent. As outlined above, the parameters for each of these equations were set to be consistent with the parameters used for the MC simulations. The linear form expresses the activation energy for desorption as a linearly decreasing function of coverage

$$E_d = E_d^0 - n_{\max}\theta\Delta E_d \tag{3}$$

where θ is the coverage of the desorbing species, $n_{\max}$ is the maximum number of neighbor interactions for the lattice used in the MC lattice simulations, and ΔE_d is the same here as in Eq. 2. For square lattices with only NN interactions, $n_{\max} = 4$. The isolated form assumes adsorbates are isolated at coverages below some threshold coverage θ_{iso} and, beyond that point, a linear dependence is used

$$E_d = \begin{cases} E_d^0 & \text{if } \theta < \theta_{\text{iso}} \\ E_d^0 - n_{\max}\left(\dfrac{\theta - \theta_{\text{iso}}}{1-\theta_{\text{iso}}}\right)\Delta E_d & \text{otherwise} \end{cases} \tag{4}$$

where all symbols have the same meaning as above. The final model investigated uses a hyperbolic tangent function centered at $\theta = 0.5$ to describe the variation of activation energy with coverage

$$E_d = E_d^{0.5} - \frac{n_{\max}}{2}\Delta E_d \tanh\left[\alpha(\theta - 0.5)\right] \tag{5}$$

where $E_d^{0.5}$ is the activation energy for desorption when $\theta = 0.5$ and α is a measure of the curvature of the hyperbolic tangent curve. As α increases, the enthalpy of adsorption vs. coverage curve becomes less of a linear decrease and more of a step from the maximum to the minimum enthalpy of adsorption value. All nonuniform TPD spectra discussed below were generated using $\Delta E_d = 10$ kJ/mol. If attractive rather than repulsive NN interactions were of interest, a negative value of ΔE_d could be used.

Each of the above models for incorporating AA interactions into microkinetic models represents a reasonable approximation of the actual physical system. In all of these models, the activation energy for desorption is greatest at low coverages where it would be expected that there will be few adsorbates in close proximity to each other, resulting in few repulsive AA interactions. As coverage, and, therefore, AA interactions, increase, the activation energy decreases monotonically. For TPD, this varying activation energy for desorption means that initially, at high coverage, the activation energy for desorption is low, leading to desorption at lower temperatures. As desorption occurs and the coverage decreases, the activation energy for desorption increases, resulting in an increase in the temperature required for desorption. The overall result is a widening of the temperature range over which desorption takes place as compared to TPD from a uniform surface. This widening of the temperature range is observed in both experimental and theoretical investigations (Tovbin and Votyakov, 1997), indicating all of these models provide the correct general behavior.

A comparison between the linear nonuniform microkinetic model and several different MC simulations is shown in Figure 1 for TPD in which readsorption of species *A* was not allowed. Comparison of the uniform model results (not shown) and the nonuniform spectra (Figure 1) revealed that, for all nonuniform simulations, the range of temperatures over which desorption occurs was increased by over a factor of two. In fact, nonuniformity makes the range of desorption for the TPD without readsorption in Figure 1 wider than that for the uniform TPD with readsorption. Three different MC simulations are shown in Figure 1. The simulations carried out using lattices with sides of length 50 and 100 are in good agreement with each other, indicating the L = 50 lattice provides a sufficient number of sites for these simulations which is consistent with results in the literature for other simple adsorption models (Binder and Landau, 1981). The MC simulation labeled ''diffusion'' was performed allowing the ad-

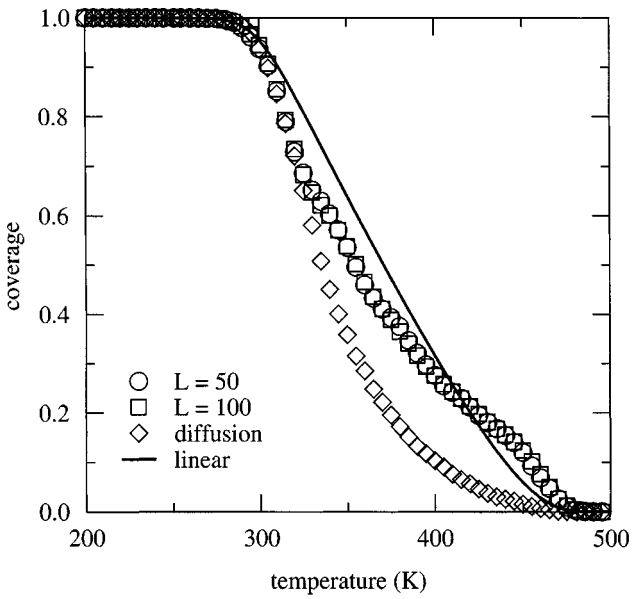

Figure 1. Coverage of species $*A$ as a function of temperature for MC simulations and linear nonuniform model of adsorbate-adsorbate repulsion for TPD without readsorption.

sorbate to diffuse around on the surface. The diffusion was incorporated into the model as a random walk with a preexponential factor of 10^9 molecules/site/s and an activation energy of 60 kJ/mol. The figure shows diffusion increased the rate of desorption at coverages below 0.7. At this point, the number of adsorbates with four NN is low, and the rate of desorption for adsorbates with three NN becomes comparable due to the higher number of these types of adsorbates. Diffusion allows the creation of more adsorbates with four NN, thereby increasing the overall rate of desorption. This same effect occurs at lower coverages when adsorbates with three NN and two NN are created when they would have otherwise been previously depleted through desorption events.

The linear nonuniform microkinetic model shown in Figure 1 adequately captures the variation of the coverage with temperature from the MC simulations without diffusion over the entire temperature range. While the prediction of the linear model is unable to capture all of the features of the MC data, it does accurately predict the breadth of the TPD data. Figure 2 contains the predictions of the isolated nonuniform model for values of θ_{iso} ranging from 0.05 to 0.25. The $\theta_{iso} = 0.05$ curve most closely approximates the MC data, with the agreement worsening with increasing θ_{iso}. In fact, the overall agreement of the linear model is better than any of the isolated models. Nevertheless, the curves with low values of θ_{iso} are in reasonable agreement with the MC data. Figure 3 shows the prediction of the hyperbolic tangent model for several values of the curvature parameter α. The shape of the coverage vs. temperature curves depends strongly on the value of α. As α increases the coverage curve goes from a curve similar to those in the linear model to one which displays two distinct desorption regions at low and high temperature. The best agreement between the MC data and the hyperbolic tangent model occurs when $\alpha = 2.5$. This model has comparable acuracy to the linear model and the best isolated model.

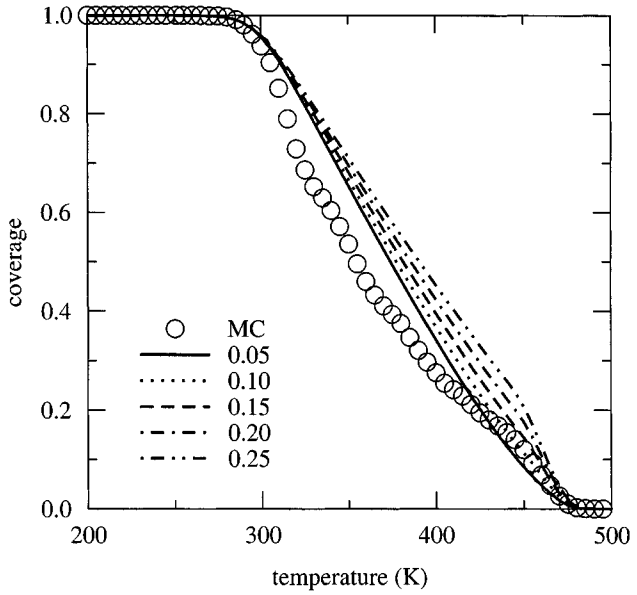

Figure 2. Coverage of species $*A$ as a function of temperature for MC simulations and isolated nonuniform model of adsorbate-adsorbate repulsion for TPD without readsorption.

The predicted curves for several values of the isolated coverage limit θ_{iso} are shown.

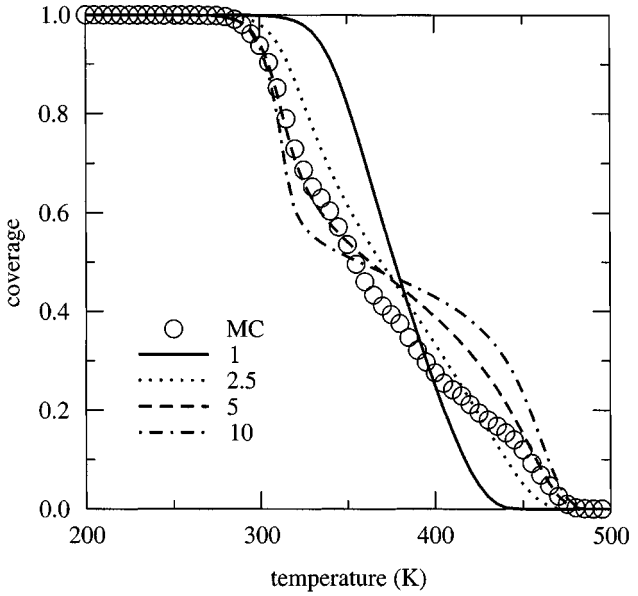

Figure 3. Coverage of species $*A$ as a function of temperature for MC simulations and hyperbolic tangent nonuniform model of adsorbate-adsorbate repulsion for TPD without readsorption.

The predicted curves for several values of the curvature parameter α are shown.

The comparisons between the MC simulations and the nonuniform microkinetic models for TPD with readsorption are shown in Figures 4–6. Readsorption was unactivated and was assigned a rate constant of 1 molecule/Pa/site/s. Its rate was directly proportional to the number of unoccupied sites and the partial pressure of A in the gas phase. The inclusion of surface diffusion in the MC simulation again increases the overall rate of desorption at lower coverages, but the difference is much less pronounced when readsorption is allowed because both readsorption and surface diffusion have a similar effect on the adsorbates. Both phenomena redistribute the adsorbates on the surface, creating adsorbates with a greater number of NN than on a surface without their influence.

The agreement between the MC simulations and microkinetic models for TPD with readsorption is slightly better than for the TPD without readsorption. The coverage vs. temperature curves for all of the nonuniform models capture the increased range of desorption due to both the nonuniformity and the readsorption. The temperature range over which desorption occurs has widened to over twice that in the uniform TPD with readsorption. The linear model does an adequate job of matching the MC simulations throughout the entire range of coverage. The dependence of the predicted curves for the isolated and hyperbolic tangent models on their adjustable parameters was less for the TPD with readsorption than for the TPD without readsorption, but the trends as

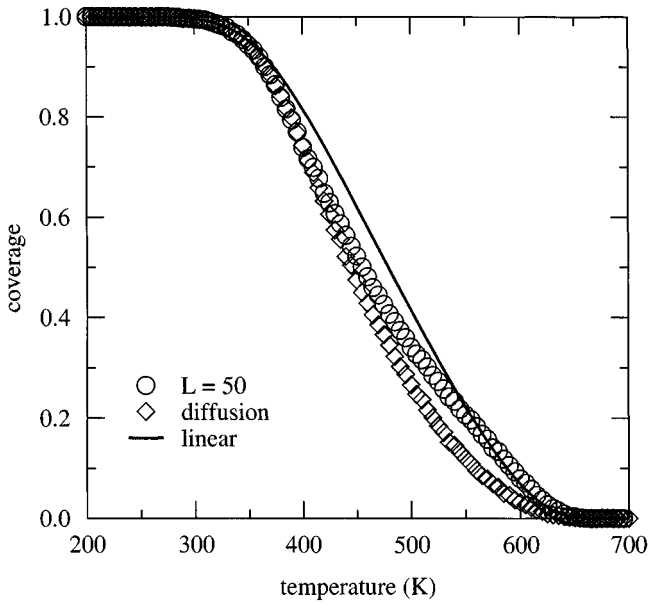

Figure 4. Coverage of species $*A$ as a function of temperature for MC simulations and linear nonuniform model of adsorbate-adsorbate repulsion for TPD with readsorption.

the parameters changed were similar. As was the case for the TPD without readsorption, the isolated model with $\theta = 0.05$ and the hyperbolic tangent model with $\alpha = 2.5$ were in best agreement with the MC simulations.

The models discussed above demonstrate that the nonuniform models which are often used in kinetic models do an

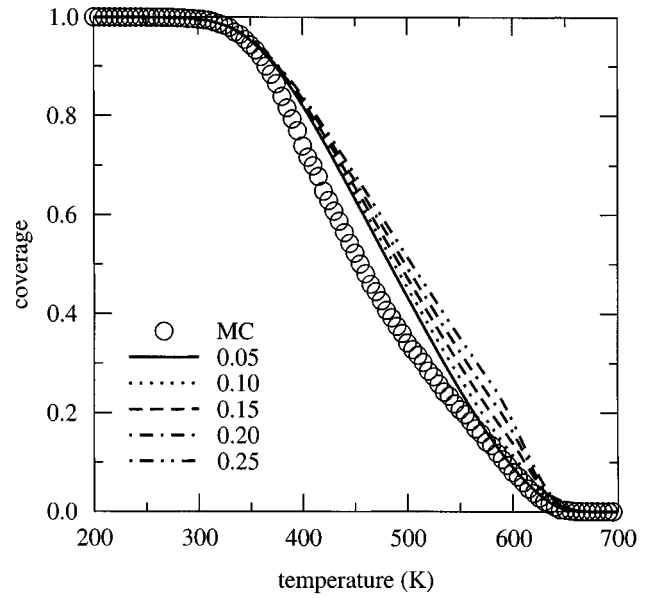

Figure 5. Coverage of species $*A$ as a function of temperature for MC simulations and isolated nonuniform model of adsorbate-adsorbate repulsion for TPD with readsorption.

The predicted curves for several values of the isolated coverage limit, θ_{iso}, are shown.

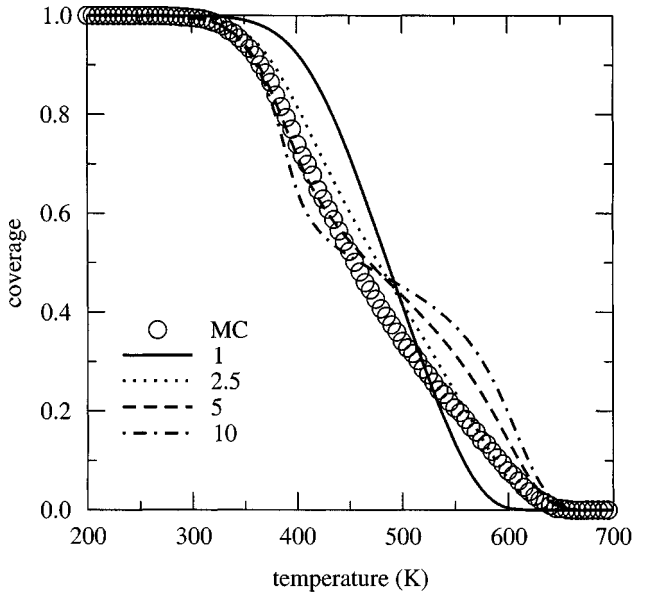

Figure 6. Coverage of species $*A$ as a function of temperature for MC simulations and hyperbolic tangent nonuniform model of adsorbate-adsorbate repulsion for TPD with readsorption.

The predicted curves for several values of the curvature parameter α are shown.

adequate job of approximating the effect of AA intereactions on TPD spectra. For catalyst systems which have been studied by microcalorimetry, however, more information is available than simply the breadth of the nonuniformity. Microcalorimetry data provide the actual functional dependence of the enthalpy of adsorption on coverage. These data can be fit to an appropriate functional form, which can then be embedded into kinetic models as carried out for the nonuniform models above. The result of a simulated microcalorimetry experiment on the MC surface is shown in Figure 7. First, a nonequilibrium TPD without diffusion of a surface that is initially fully covered was carried out with ΔE_d in Eq. 2 equal to 10 kJ/mol. The enthalpy of adsorption as a function of coverage was then back-calculated from the known values of the rate of desorption, the preexponential factor for desorption and the coverage. At low coverages, the data exhibits a constant enthalpy of adsorption of E_d^0 equal to 130 kJ/mol, after which the enthalpy of adsorption decreases monotonically. Because of the discontinuity in the slope of the microcalorimetry data, the function chosen to fit the data was similar in form to the isolated model discussed above. Below a coverage of 0.15, the enthalpy of adsorption was taken to be 130 kJ/mol. Above a coverage of 0.15, a sixth-order polynomial was fit to the microcalorimetry data. The fit of this model to the microcalorimetry data is also shown in Figure 7. A sixth-order polynomial was used to accurately capture the features of the microcalorimetry data and provide a contrast to the other nonuniform models investigated above. Of course, any function could be used which adequately fits the data.

The predictions of the polynomial fit to the microcalorimetry data for TPD without and with readsorption are shown in Figure 8. The polynomial model outperforms any of the other

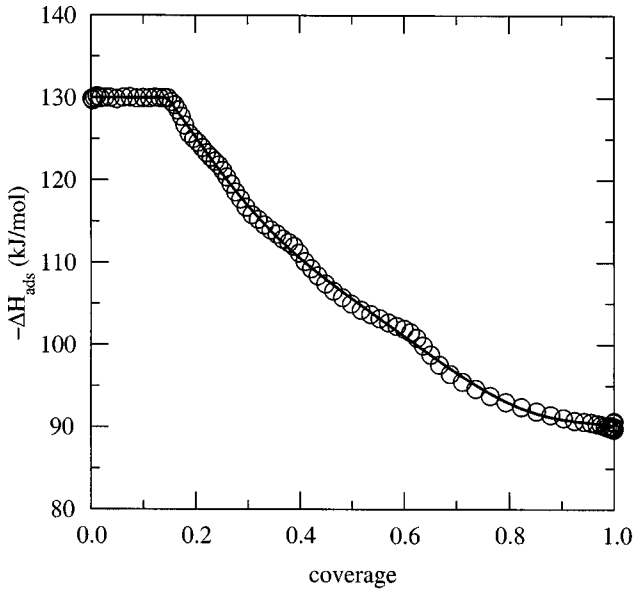

Figure 7. Simulated microcalorimetry experiments for adsorbate-adsorbate repulsion model of nonuniformity (symbols) and the polynomial model fit (line).

models investigated, matching the MC data nearly perfectly. This indicates that when the appropriate functional form is used to describe the change in enthalpy of adsorption vs. coverage, mean-field models are capable of capturing the effect of AA interactions. Given the tremendous decrease in the required solution time for microkinetic models compared to MC simulations, the microkinetic model must be the preferred solution method for these systems Of course, microcalorimetry data are not available for all systems. When this information is not available, Figures 1–6 show that all of the approximate models are able to adequately capture the change in coverage vs. temperature data from the MC simulations. These predictions are not ideal, but if microcalorimetry data is not available, the information required to accurately capture the interactions using MC simulations is most likely not available either. Thus, these simple models provide a good starting point for the incorporation of nonuniformity into kinetic models when only limited information on the system is available.

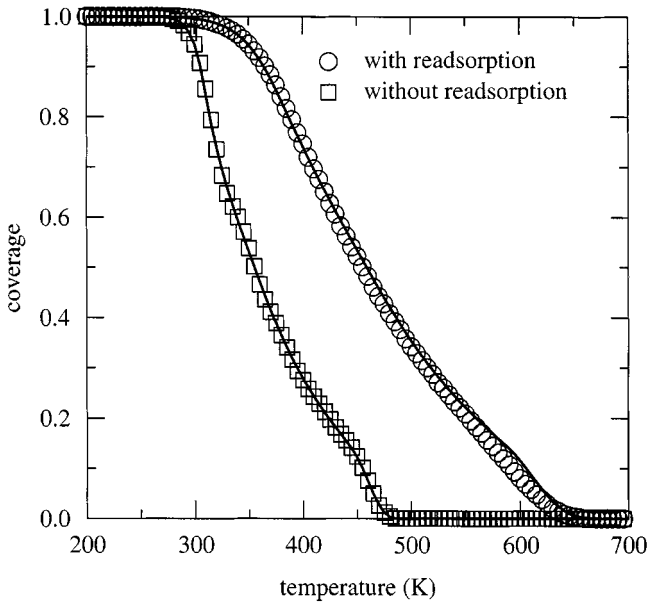

Figure 8. Comparison of the coverage of species $*A$ as a function of temperature from MC simulations (symbols) and microkinetic model using the polynomial fit to the microcalorimetry data model of nonuniformity (lines) for TPD with and without readsorption.

Biographic Nonuniformity Model

Another common cause of nonuniformity in catalytic systems is inherent activity differences between sites. Differing atomic configurations, catalyst-support interactions, catalytic activity of the support, and so on, can lead to vastly different chemical environments at different points on the catalyst. These differing chemical environments can lead to different reactivities and selectivities, yielding a nonuniform distribution of catalytic sites. For example, the rate of ammonia synthesis over iron catalysts is strongly dependent on the configuration of surface iron atoms and iron particle size (Ertl, 1980). The hydrogenation of acetylene-ethylene mixtures is thought to proceed over three types of sites, two of which are selective for the hydrogenation of acetylene to ethylene and one which hydrogenates ethylene (Borodziński and Gołębiowski, 1997). Several kinetic modeling approaches, including microkinetic modeling, have been applied to these and other systems where inherent, biographic nonuniformity is present. For example, Duca et al. (1999) noted the importance of a small amount of hydrogen occupying lower coordinated lattice sites in their description of the kinetics of ethylene hydrogenation. As was the case for AA interactions, even though these models have been used, it is not clear how to best implement these complex interactions into mathematical models of the reacting systems. To investigate the effectiveness of microkinetic models at capturing biographic nonuniformity, the predictions of a microkinetic model were compared to MC simulation results for the following model hydrogenation system

$$H_2 + 2* \rightleftharpoons 2*\mathrm{H} \tag{6}$$

$$A + * \rightleftharpoons *A \tag{7}$$

$$*A + *H \rightleftharpoons *B + * \tag{8}$$

$$*B + *H \rightleftharpoons *C + * \tag{9}$$

$$*C \rightleftharpoons C + * \tag{10}$$

The rate constant parameters for the above reactions can be found in Table 1. Biographic nonuniformity was incorporated into the system by setting aside a fraction of the sites as ''support'' sites. These sites were only able to adsorb hydrogen, but the hydrogen adsorbed on these sites was still able to react with the species on the ''catalyst'' sites. Additionally,

Table 1. Arrhenius Kinetic Parameters for Biographic Nonuniformity Model System

Reaction	Forward A	Forward E_A kJ/mol	Reverse A	Reverse E_A kJ/mol
6	5*	0	10^{12}**	110
7	10*	0	10^{13}**	105
8	10^{10}**	80	10^{11}**	90
9	10^{9}**	77	10^{11}**	95
10	10^{13}**	80	1*	0
11	10^{7}**	50	10^{7}**	50
MC diffusion	10^{9}**	50		

*Molecules/Pa/site/s.
**Molecules/site/s.

hydrogen adatoms were allowed to diffuse between the two types of sites

$$* H + *_s \rightleftharpoons * + *_s H \qquad (11)$$

where $*_s$ represents a support site. The simulations were performed in a batch reactor at a temperature of 500 K. MC simulations modeled the catalyst as a periodic square lattice having 250 lattice points per side. The lattice results were automatically scaled to a reaction volume of 10^{-4} m^3 with the total number of catalytic sites equal to 10^{19}. The reactor was initially charged with a 90/10 mixture of H_2 and A at a total pressure of 10^5 Pa. All adsorbates were allowed to diffuse in the MC simulations using the rate parameters found in Table 1.

The results of modeling the above system without any support sites using both MC simulations and microkinetic modeling are shown in Figure 9. The results from the two approaches are in good agreement over the entire reaction time. Close inspection of the early time behavior in Figure 9 reveals that the initial slope of the partial pressure vs. time curve for species C is much greater at short times than at longer times. Both the microkinetic model and MC simulation capture this change in slope and indicate that the decrease in the rate of production of species C is due to the self-poisoning of the surface. The slow net rate of surface hydrogenation as compared to adsorption causes the surface to be almost completely covered with adsorbates. Initially, the surface is covered with hydrogen due to the higher rate of adsorption, as compared to species A. As the surface fills, the rate of hydrogen adsorption decreases much faster than the rate of adsorption of species A due to the requirement of two sites for adsorption. Very quickly, the surface becomes depleted of the hydrogen needed for reaction, and the overall rate of production of C decreases.

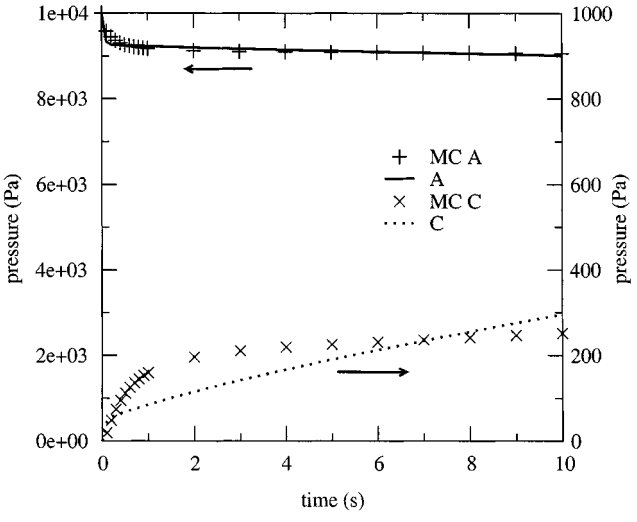

Figure 9. Comparison of MC simulation and microkinetic modeling results for biographic nonuniformity models without any contribution from the support.

One method to combat self-poisoning catalysts is to disperse the catalyst on a support which can dissociatively adsorb hydrogen. If the support does not adsorb the other reacting species, it would not poison and would act as a source of hydrogen adatoms for the catalytic sites. For the MC simulations, these support sites were located randomly on the surface lattice. Figure 10 shows the ratio of the final (at 10 s) partial pressure of species C from the MC and microkinetic simulations to the final partial pressure of species C for the MC simulation without support sites as the fraction of support sites θ_s ranges from 0 to 0.5. For this set of results, the rate constants used for hydrogenation involving hydrogen from the support sites were equivalent to those on the catalyst sites (Table 1). The final partial pressure of species C was greater for all simulations with support sites than it was for the simulations without support sites. The figure shows, however, that the predictions of the microkinetic model and the MC simulations are very different. While the MC simulations predict only modest improvement in the production of

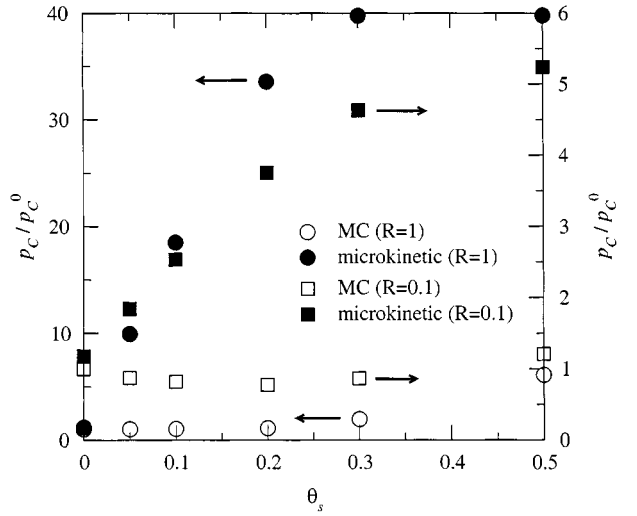

Figure 10. Ratio of the final partial pressure of species C, p_C, for microkinetic models and MC simulations to the final partial pressure of species C for the MC simulation with no support sites p_C^0 as a function of the fraction of support sites θ_s.

The preexponential factors of the rate constants for the hydrogenation reactions involving the support sites were either equivalent to (R = 1) or 10% of (R = 0.1) those on the catalytic sites.

species C below a support site fraction of 0.5, the microkinetic model results predict an increase in the production of species C by as much as a factor of 40. This overestimation is due to the mean-field description of the surface used in microkinetic modeling. The MC simulations explicitly model the connectivity of the surface lattice points (catalytic sites), thereby only allowing reactions between NN sites. By expressing reaction rates in terms of species' coverages, microkinetic modeling implicitly assumes that all adsorbates are accessible to all other adsorbates. Thus, even when the fraction of support sites is very small, they are assumed to be accessible to all other sites. For systems where surface diffusion is rapid, this is a good assumption. The agreement between mean-field models and MC simulations in the limit of rapid surface diffusion was also noted by McLeod and Gladden (1997) when adsorbate-adsorbate interactions were the origin of nonuniformity. However, the catalytic surface in this system is almost completely covered with adsorbates, greatly reducing the overall rate of surface diffusion since adsorbates can only diffuse onto sites which are unoccupied. This causes the assumptions of the microkinetic model to break down and leads to the poor predictive performance of the model.

The above simulations assumed the rate constants for hydrogenation involving either type of site were equivalent. Given the differing chemical environments of the support and catalyst, it is likely that the rate constants for hydrogenation from a support site will be different than those corresponding to the native catalyst site. This effect was investigated by reducing the preexponential factors of the rate constants for hydrogenation from the support sites to 10% of the values on the catalyst sites (Table 1). Figure 10 compares the results for microkinetic modeling and the MC simulations as a function of the fraction of support sites. As was the case when the rate constants were identical, the microkinetic model predicts an increase in the production of species C even at the lowest fraction of support sites. The MC simulations actually predict a decrease in the production of species C at low fractions, with the production reaching a minimum at $\theta_s = 0.2$. This decrease is due to the reduction in sites available for hydrogenation without an offsetting degree of hydrogenation from the support sites. As stated above, the total number of sites was held constant through all the simulations. At a fraction of 0.5, the MC simulations predict a modest improvement in the production of species C, but it is far less than that predicted by the microkinetic model. The discrepancy between the two approaches again arises due to a failure of the assumptions of microkinetic modeling.

The vast difference between the predictions of the MC and microkinetic simulations for this model hydrogenation system indicates the microkinetic approach is insufficient for these systems. Specifically, systems in which the catalyst surface is nearly completely covered with adsorbates cannot be adequately described by a mean-field approach when different sites perform different chemistries. The connectivity between the different types of sites cannot be captured without the addition of a spatial variable, so the rates of intersite reaction are overestimated. To accurately capture the kinetics of the system, a microkinetic model would require that the reaction rates for the intersite hydrogenation reactions have a much stronger (higher-order) dependence on species' coverages or much lower preexponential factors. This indicates that for systems such as these, MC simulations must be used to accurately capture the physics of the system.

Conclusion

Nonuniformity is often neglected when models are developed for heterogeneous catalytic reaction systems. This neglect has resulted in a dearth of available information on how to best incorporate nonuniformity into kinetic models. While there have been some attempts to incorporate nonuniformity into MC simulations and microkinetic models, there has not been a systematic study to determine when microkinetic models are sufficiently accurate to model nonuniform systems and what are the best methods to incorporate nonuniformity into microkinetic models. The results from the two model systems above begin to answer some of these questions. The TPD system shows that microkinetic models can be used to effectively capture repulsive AA interactions. Although the simple nonuniform models investigated failed to capture the exact behavior of the coverage vs. temperature curves, they all did an adequate job of matching the MC data over the entire range of temperatures. Furthermore, when information is available about the change in enthalpy of adsorption vs. coverage from methods such as microcalorimetry, mean-field models are capable of capturing the effect of adsorbate-adsorbate interactions. Conversely, the agreement was poor between the MC simulations and the microkinetic model of biographic nonuniformity. The high total surface coverage caused the mobility of the adsorbates to be greatly reduced in the MC simulations. This caused the assumptions of the microkinetic modeling approach to fail, resulting in large overpredictions in product evolution.

As experimental and computational investigations are able to provide more and more detailed information about the phenomena in catalytic reaction systems, so too must models attempt to incorporate this detailed information. For this to be successful, methodologies must be developed to guide researchers in the effort to effectively model these complex systems. The software used in the above investigations provides the tools required to model these systems, but a set of heuristics for modeling nonuniformity must be developed as well. Results from the above model systems provide some guidelines for identifying nonuniformity and determining what methods should be used to model it. Further investigations are needed to gain a deeper understanding of the effect of nonuniformity on reaction kinetics and the effectiveness of different models at capturing nonuniform fingerprints. Facile and rational incorporation of nonuniformity into kinetic models will allow researchers the opportunity to develop accurate, predictive models which provide unparalleled insight into the controlling reaction rates and species' coverages of these complex systems.

Acknowledgments

The support of the Chemical Reaction Processes Program of the National Science Foundation (CTS-9705238) is gratefully acknowledged.

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Manuscript received May 4, 2000, and revision received Oct. 23, 2000.