Monte Carlo simulation of kinetic discontinuities in hydrocarbon hydrogenation reactions

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Recent experimental studies of alkene and alkyne hydrogenation reactions have shown the presence of a transition between a reactive regime at low hydrocarbon surface coverage and a less reactive regime in which the catalyst surface is saturated with the hydrocarbon. This transition is discontinuous but reversible. Langmuir–Hinshelwood rate expressions cannot account for this discontinuity between the two regimes, indicating that the origin of the transition is related to the non-random distribution of reactants on the catalyst surface. Time-dependent Monte Carlo simulations of ethylene hydrogenation have been used to predict the presence of this transition and investigate the complex dynamics of the reaction.

Keywords: ethylene hydrogenation, Monte Carlo simulation, microkinetic model, non-ideal kinetics

1. Introduction

Experimental investigations of the hydrogenation of ethylene and ethyne have demonstrated the existence of a discontinuity separating two regimes characterised by differing kinetics. Moyes and co-workers [1] studied the hydrogenation of ethyne over alumina-supported palladium and palladium powder, and for both the supported and unsupported catalysts a sharp transition from a highly active regime to a less active regime was observed as the hydrocarbon partial pressure was increased or the temperature reduced. These results suggest that a high activity regime is associated with a low surface coverage of hydrocarbon and vice versa; for clarity these two states will be referred to as the low and high activity regimes respectively. Similar behaviour has also been observed for the hydrogenation of ethylene over a platinum catalyst [2], although in this study while the transition was observed for a dispersed silica-supported catalyst no such transitions were observed either for alumina- or molybdena-supported catalysts or for the EUROPT-1 platinum/silica reference catalyst. The existence of the transition for some catalysts but not for others is particularly surprising as ethylene hydrogenation is regarded as a clear example of a structure insensitive reaction [3] for which the rate of reaction is independent of the catalyst structure.

The nature of the transition between the two kinetic regimes is very similar for both the hydrogenation of the alkene and of the alkyne, suggesting a common origin for the onset of the transition in each reaction. In both hydrogenations the low activity regime is characterised by a high activation energy, negative kinetic order in either ethylene or ethyne and a low activity. The high activity regime is found to have a significantly lower activation energy and positive order with respect to ethylene or ethyne. The jump in activity between the two regimes is substantial, being more than two orders of magnitude in the case of ethylene hydrogenation. The transition between these two states is discontinuous and reversible. In this paper we apply a dynamic Monte Carlo (MC) algorithm to the simulation of the Horiuti–Polanyi mechanism and illustrate that the solutions obtained from the MC algorithm predict a kinetic behaviour which is in agreement with previously reported experimental data [2] and qualitatively different from that as obtained from a Langmuir–Hinshelwood type analysis of the proposed reaction mechanism.

2. Methods

2.1. General approach

The precise mechanism for the hydrogenation of ethylene over transition metals is still a matter of some debate, despite extensive surface science and kinetic studies of this reaction [4]. The Horiuti–Polanyi mechanism [5] proposed over 40 years ago has formed the basis of most models of ethylene hydrogenation. This mechanism proposes that an ethylene molecule adsorbs onto a pair of adjacent adsorption sites and reacts with a dissociated hydrogen atom forming a half hydrogenated ethyl intermediate which then can further hydrogenate to form ethane. Direct observation by in situ infrared spectroscopy [6] has suggested that the σ-bonded form of adsorbed ethylene is unstable and decomposes to form ethylidyne which is present only as an unreactive specta-

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tor species. From these infrared spectroscopy experiments it can be concluded that it is the π-bonded ethyl intermediate that is the reactive species. Although the simple Horiuti–Polanyi mechanism assumes that the indermediate is σ-bonded it does capture the main features of the hydrogenation reaction determined experimentally, namely the presence of molecularly adsorbed ethylene and the existence of a half hydrogenated intermediate. The assumption made by Horiuti and Polanyi that the adsorption of ethylene requires two surface sites is still likely to be valid even if the π-bonded ethyl group, which requires only a single adsorption site, is the stable intermediate, due to steric hindrance of a neighbouring site. In the model used in this paper the adsorption of hydrogen and ethylene is assumed to be competitive. No attempt has been made to differentiate between "activated" and "non-activated" hydrogen [7], this distinction is implicit in the MC simulation as only a fraction of the dissociated hydrogen atoms are neighbours to a hydrocarbon species [8]. The mechanism for the hydrogenation reaction is therefore assumed to be of the basic form postulated by Horiuti and Polanyi:

$$H_2 + 2* \rightarrow 2H^* \tag{a}$$

$$2H^* \rightarrow H_2 + 2* \tag{b}$$

$$C_2H_4 + 2* \rightarrow C_2H_4^* \tag{c}$$

$$C_2H_4^* \rightarrow C_2H_4 + 2* \tag{d}$$

$$C_2H_4^* + H^* \rightarrow C_2H_5^* + * \tag{e}$$

$$C_2H_5^* + * \rightarrow C_2H_4^* + H^* \tag{f}$$

$$C_2H_5^* + H^* \rightarrow C_2H_6 + 3* \tag{g}$$

The $*$ denotes a vacant adsorption site and the * superscript an adsorbed species. The desorption of ethane has been assumed to be irreversible. The kinetic parameters for each of the above reaction steps were estimated from a previous study [7] and are detailed in table 1. These parameters were estimated from a non-linear regression analysis based on the assumptions of an ideal adsorbed overlayer. While part of the aim of the present work is to demonstrate that the presence of a discontinuity implies that these assumptions do not hold, an algebraic set of equations is required to obtain estimates of the kinetic parameters from experimental data.

Table 1
Kinetic parameters for the Horiuti–Polanyi mechanism. Pre-exponential factors have units of Torr^{-1} s^{-1} for adsorption steps and of s^{-1} for surface reactions; 1 Torr = 133.3 Pa. Activation energies have units of kJ/mol. Data are taken from the study of Rekoske et al. [7]

Step	A	E_a	Step	A	E_a
a	1.50×10^5	0.00	e	1.39×10^9	25.12
b	4.00×10^5	0.00	f	1.25×10^7	37.68
c	3.40×10^{10}	39.48	g	3.58×10^9	44.80
d	3.60×10^{15}	37.68			

The MC method for simulating catalytic reactions on surfaces has been described previously in detail for several systems. In particular the oxidation of CO has attracted much attention [9] due to the formation of complex spatio-temporal patterns and the oscillatory kinetic behaviour of the reaction. Numerous hypothetical diffusion-limited reactions which cannot be represented adequately by simple algebraic equations that assume ideal mixing of the adsorbed overlayer have also been the subject of a great deal of previous work [10]. Recently, these statistical simulations have been extended and applied to the more complex ethylene hydrogenation reaction [8].

In the MC method the catalyst surface is considered to be composed of a regular square lattice of discrete adsorption sites representing the (100) face of the platinum particles on the catalyst surface. These sites can either be vacant or occupied by one of the hydrocarbon species or dissociated hydrogen atoms. Reactants adsorb from the gas phase, which can be considered to be an infinite reservoir of constant composition, and occupy a randomly selected vacant surface site subject to geometric constraints imposed by the size and shape of the molecule. Once adsorbed onto the catalyst surface the molecule may desorb back into the bulk gas phase or react with a neighbouring molecule. The reaction mechanism is represented as a series of discrete time steps, each leading to a change in the arrangement of the adsorbed species on the lattice. The steps of the Horiuti–Polanyi mechanism are represented by the transformations of a small section of the lattice shown in fig. 1. Adsorbed species that form nearest neighbour pairs may react with each other with a rate constant, r_α, where $\alpha = \{a, b, \ldots, g\}$ and denotes one of the elementary steps of the Horiuti–Polanyi mechanism.

2.2. Details of the simulation

A modified MC method based on the table method

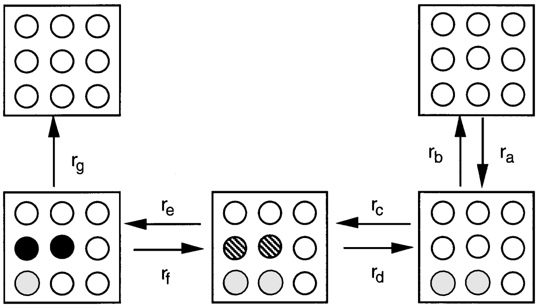


Fig. 1. The transformations of the lattice in a Monte Carlo simulation that represent the steps a–g of the Horiuti–Polanyi mechanism. Empty circles represent unoccupied lattice sites. Shaded circles represent (▨) ethylene, (○) hydrogen and (●) ethyl.

[11] has been used to simulate the hydrogenation reaction. In this method all the possible reactions that can occur on the lattice representing the catalyst surface are placed on individual lists, with one list for each of the reaction steps a–g. An event is picked from one of these lists, the lattice updated accordingly and time incremented assuming that the occurrence of reaction events corresponds to a Poission process.

The rate at which each step in the reaction mechanism occurs depends on the configuration of the lattice and on the intrinsic rate at which each step proceeds. Ignoring the influence of substrate heterogeneity and assuming a random distribution of the reactants over the catalytic surface, the rate of reaction for each fundamental step in the reaction mechanism can be written as a simple analytical function of the rate constant and mean surface coverage of each species. If the distribution of the adsorbates is not random, which will be the case if the diffusion of each species is not much more rapid than the rate of the reaction steps, then the reaction rate will not be constant at all locations on the catalyst surface and will differ according to the environment in which each adsorbed molecule resides. This leads to a general expression for the rate of an elementary reaction step, r_α, of the form

$$r_\alpha = k_\alpha f(\sigma)\,, \tag{1}$$

where $f(\sigma)$ is a function describing the probability of a group of lattice sites occurring that will permit reaction α to occur. The configuration of the lattice is described by the state vector, σ. For a lattice consisting of N sites

$$f(\sigma) = \frac{n_\alpha}{N}\,, \tag{2}$$

given n_α is the number of possible events of type α that exist for a given configuration of the lattice. The function $f(\sigma)$ will not in general be a simple expression involving the mean surface coverages and so cannot be written exactly in a simple, closed algebraic form. The MC method, however, intrinsically accounts for the form of $f(\sigma)$ as this is determined by the distribution of the reactants on the lattice, all that is required by the MC model are the values of the rate coefficients.

The probability, Pr, of a particular event occurring with respect to the other possible reaction, adsorption or desorption events is written as

$$\Pr\{\alpha\} = \frac{r_\alpha}{\sum r_\alpha}\,. \tag{3}$$

Each possible single event of a given type that can occur is assigned to a separate list containing all the possible reactions of that type that exist for the lattice in a given configuration. The probability of choosing a particular list is therefore the probability of choosing one of the seven possible reaction steps and is proportional to the number of these transitions that are possible for a given lattice configuration and the rate constant of the elementary reaction step, hence

$$\Pr\{\alpha\} = \frac{k_\alpha n_\alpha}{\sum k_\alpha n_\alpha}\,. \tag{4}$$

Once a list has been selected then one of the possible events from that list must be chosen. All events of the same type are considered equivalent, implicit in this assumption is that molecular interactions and surface energetic heterogeneity are neglected. One event is then selected at random from the list with a probability given by $1/n_\alpha$. The event is then carried out and the lattice configuration altered as required and the number of events in each list updated.

The correlation between each event and real time was considered by Gillespie who demonstrated that the occurrence of each reaction can be considered as a Poission process [12]. Adopting this approach we consider an arbitrarily small time interval, dt, in which only one reaction is likely to occur. The time until this reaction occurs has an exponential distribution and is given by

$$\Pr\left\{\begin{array}{l}\text{no reaction occurs in}\\ \text{time interval } (t, t+\mathrm{d}t)\end{array}\right\} = \exp\left[-\sum_\alpha n_\alpha k_\alpha \mathrm{d}t\right]. \tag{5}$$

Each time a reaction is selected from the list of all possible reactions time is advanced by an amount given by

$$\mathrm{d}t = -\frac{1}{\sum_\alpha n_\alpha k_\alpha}\ln(R)\,, \tag{6}$$

R being a uniformly distributed random number between 0 and 1. Once the time step has been calculated the total simulation time is updated and the process repeated until convergence to a steady state has been achieved. Turnover numbers are defined in terms of the simulation time and number of lattice locations:

$$R = \frac{N_\mathrm{g}}{Nt}\,, \tag{7}$$

where N_g is the total number of reactions of type g that have occurred up to time t.

A typical simulation was conducted for 1×10^7 events corresponding to approximately 1–10 s of real time. It should be pointed out that this does not correspond to only $(1 \times 10^7)/128^2 \approx 610$ Monte Carlo steps (MCS), as a single MCS corresponds to one *attempted* event per lattice location per time step. As every event that is attempted in this approach is successful it is a great deal more efficient than traditional importance sampling methods [11,13]. A further consideration is the influence of size effects imposed by the use of a finite lattice. Simulations over a range of lattice sizes demonstrated that a large lattice composed of 128 × 128 locations was required to avoid correlations between subsequent events occurring on the lattice; below this value the hydrogenation rate was found to be influenced by the lattice size. Correlations between events can also occur from the use of an inadequate random number generator. In this work L'Ecuyer's method was used [14], a routine that has a period of 2×10^{18}, which is several orders of magnitude greater than the number of random numbers needed for each simulation. The simulations were implemented using FORTRAN and C++ subroutines on a Silicon Graphics Indigo2 R4000 workstation. Approximately 2 h of dedicated CPU time were required for each simulation.

3. Results and discussion

Turnover rates from the simulation of the hydrogenation of ethylene to ethane are given in fig. 2 over a range of temperatures and hydrocarbon pressures. A clear discontinuity in the reaction rate isotherm is predicted by the MC model. In agreement with experimental results this transition between the high activity and low activity regimes is displaced to higher ethylene pressures as the temperature increases. In accordance with experimental observations it is found that the apparent activation energies obtained from an Arrhenius plot differ significantly in each of these regimes. An Arrhenius plot obtained from simulation data is given in fig. 3 using the same reaction conditions as investigated experimentally by Jackson et al. [2], the apparent activation energy for the reaction in the low activity regime is found to be 39.7 kJ/mol compared to 15.9 kJ/mol for the high activity regime. These compare to values of between 37 and 51 kJ/mol typically reported from experimental studies [4]. The study of Rekoske et al. [7], from which the kinetic parameters used in this work are taken, reported an activation energy of 36 kJ/mol. The turnover numbers obtained in the experimental study were of the order of 0.01–1, which is in good agreement with the present simulation results.

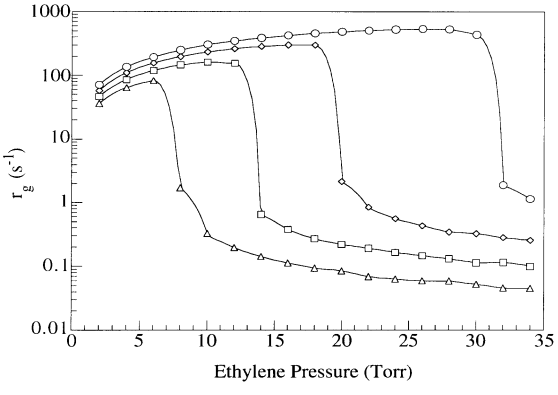


Fig. 2. Monte Carlo simulation of a kinetic discontinuity in the hydrogenation of ethylene. The order of magnitude of the ethane formation turnover number, r_g, declines from 10^2 s^{-1} in the high activity regime to 10^{-2} s^{-1} in the low activity regime. A constant hydrogen pressure of 100 Torr was used to simulate the reaction isotherms. (△) 260 K, (◇) 270 K, (□) 280 K, (○) 290 K.

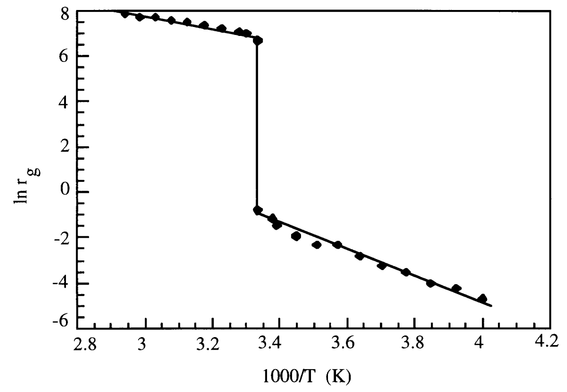
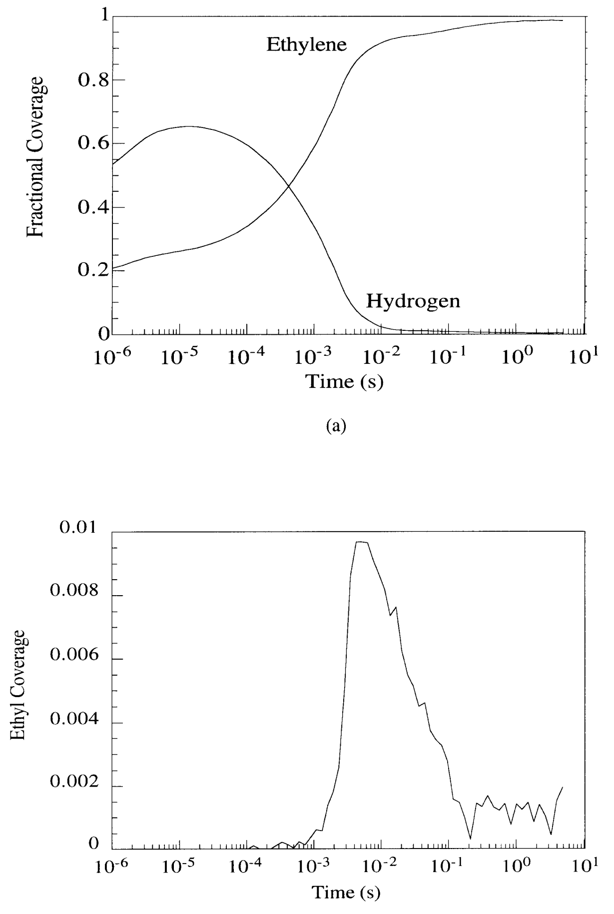


Fig. 3. Arrhenius plot showing the transition between the high activity and low activity regimes, illustrated by the discontinuity in the turnover number for ethane production, r_g. The activation energies for the low and high activity regimes are 37.9 and 15.9 kJ/mol respectively. Results are shown for an ethylene pressure of 50.9 Torr and a hydrogen pressure of 111.7 Torr. The data are at the same conditions as used in the experimental work of Jackson et al. [2].

In a previous MC study of the ethylene hydrogenation reaction [8] no observation of such a discontinuity was made. There are two principal reasons why the current model predicts the existence of this phase transition that the previous model did not show. Firstly, the previous study assumed that, due to steric hindrance, no neighbouring pairs of ethylene molecules could exist on the surface, this prevented the existence of the low activity regime where the ethylene coverage approaches unity. Secondly, the small, but significant concentration of the ethyl half-hydrogenated state was neglected in this previous study.

A study of the reaction dynamics shows the reason for the transition between the two states clearly. The onset of the transition between the high activity state, where the predominant surface species is dissociated hydrogen, and low activity state in which the surface is saturated with the hydrocarbon is shown in fig. 4a. As hydrogen adsorption and desorption are rapid processes the hydrogen coverage rapidly approaches an equilibrium value. However, the adsorption of the hydrocarbon is almost irreversible, and so if the influence of steric hindrance on the adsorption of the hydrocarbon is assumed to be insignificant then the hydrocarbon will eventually displace adsorbed hydrogen from the surface. The time taken for the ethylene to displace the hydrogen from the surface will depend on the relative rates of desorption of the two species. Since the desorption of ethylene from the surface has a higher activation energy than that of hydrogen desorption, it is expected that the rate of desorption of the hydrocarbon will decrease more quickly than that of hydrogen as the reaction temperature is reduced. As a consequence, adsorption of the hydrocarbon becomes favoured as the temperature is reduced and displacement of the equilibrated hydrogen



(a)

(b)

Fig. 4. Surface coverage of (a) adsorbed hydrogen and ethylene and (b) of the ethyl intermediate as a function of reaction time. The 280 K isotherm is shown using the reaction conditions as specified for fig. 3.

layer becomes more rapid. The corresponding coverage of the ethyl intermediate is given in fig. 4b, the statistical "noise" which is present is due to the finite size of the lattice. As the number of the ethyl species is so low a large lattice is required to represent the concentration of this species accurately, it was for this reason that a 128 × 128 lattice was required.

The reason the reaction rate declines so dramatically at the discontinuity shown in figs. 2 and 3 is illustrated by fig. 5. As the number of dissociated hydrogen atoms on the surface declines the proportion of hydrogen atoms that are isolated from other hydrogens increases rapidly. These isolated hydrogens cannot desorb, and can only react with the predominant adsorbed ethylene to form the ethyl intermediate; this mechanism is shown in fig. 6. The hydrogenation of ethylene creates a vacancy next to the ethyl species, as a consequence the number of possible vacancy–ethyl pairs is much greater than the mean field value given by $\theta_* \theta_{C_2H_5}$. The dissociation of the ethyl back to ethylene and hydrogen therefore becomes much more rapid at low hydrogen coverages

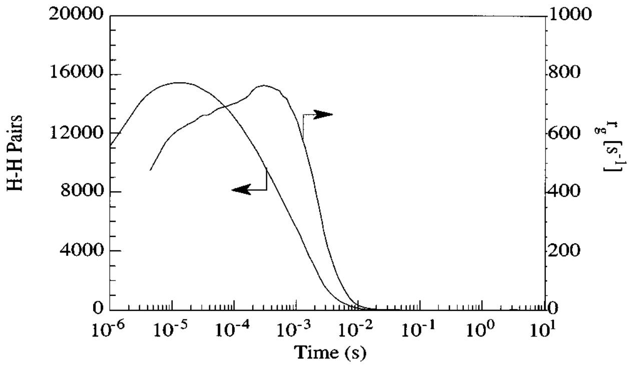


Fig. 5. The rapid decline in hydrogenation rate at the point of transition, and the correspondingly rapid decline in the number of nearest-neighbour hydrogen pairs that can form molecular hydrogen and desorb is shown. The 280 K isotherm is shown using the reaction conditions as specified for fig. 3.

than at higher coverages where the ethyl could easily react with a neighbouring hydrogen atom formed by the dissociative adsorption of H_2. The relative rates of steps f and g, as compared to the rate of formation of the ethyl intermediate, are shown in fig. 7. In the high activity regime the rates of steps e and g are almost equal, as a consequence the ratio r_g/r_e is almost unity and most of the ethyl intermediate is further hydrogenated to ethane. However in the low activity regime the opposite is true, and the rate of step f increases rapidly leading to a decline in the ethane production rate as r_f/r_e approaches 1. The defining characteristic of these two states is therefore the distribution of the hydrogen. In the low temperature and unreactive state the hydrogen is present mainly as isolated atoms while in the high activity regime most hydrogen is present as a dissociated nearest-neighbour pair. There is, therefore, a change in the rate controlling mechanism from step e, the formation of the ethyl group, to step g, the formation of the final product. This would explain the drop in activation energy observed in the Arrhenius plot, as step e has an activation energy of only 25.1 kJ/mol compared to 44.8 kJ/mol for step g. This analysis assumes negligible surface diffusion, however, in the limit of rapid surface diffusion we simply have the mean field solution which can be obtained from the solution of the differential balance

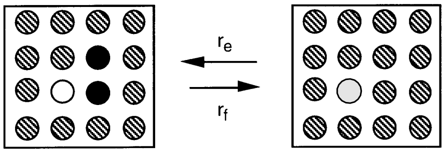


Fig. 6. Formation of a "trapped" hydrogen atom on a lattice saturated with hydrocarbon. Unable to associatively desorb the hydrogen atom can only repeatedly hydrogenate one of the neighbouring ethylene molecules. The rate of dehydrogenation of the intermediate is enhanced due to the presence of the newly vacated lattice site. The symbols are as defined in fig. 1.

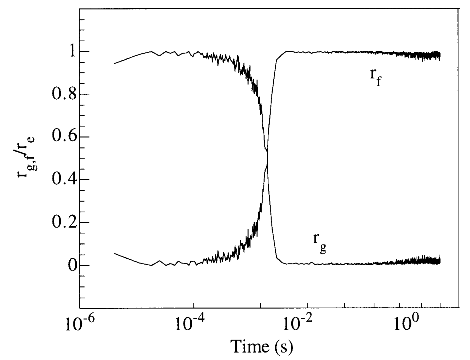


Fig. 7. The effect of the existence of mainly isolated hydrogen atoms on the reaction mechanism as a result of diffusion limitation. r_g/r_e represents the fraction of ethyl formed that is further hydrogenated to ethane. r_f/r_e is the fraction that dissociates back to ethylene and hydrogen.

equations and a MC approach is not required. The inclusion of surface diffusion has been considered previously [8] and, as expected, no phase transition was observed. It can be concluded from this work that the existence of a transition implies diffusion limitation to some extent.

4. Conclusions

A dynamic model of a simple hydrogenation reaction has shown that the use of Langmuir–Hinshelwood type rate equations to model the kinetics of hydrocarbon reactions fails to predict the qualitative characteristics of the reaction. It has been shown that stochastic models based on MC methods can address these limitations and provide an insight into the mechanism of complex surface reactions that cannot be obtained from simple analytical models. Due to the computational limitations imposed by MC simulations, however, the benefit of using such "brute force" stochastic simulations in extending the microkinetic analysis of surface reactions [15] is limited. Those cases in which anomalous kinetic behaviour cannot be explained in terms of simple algebraic rate expressions are the preferred candidates for a more rigorous simulation of the surface reaction. Even in this case previous studies of this reaction have successfully modelled the reaction using the assumptions of Langmuir–Hinshelwood methodology, but the validity of such simplified models is constrained to a limited range of physical conditions.

Further work is currently being undertaken to investigate the influence of both energetic and geometric surface heterogeneity on a series of simple hydrogenation reactions and extend the current work on MC simulations to the use of lattice gas models and coupled systems of differential equations in the modelling of surface reactions. These methods will address in detail the limitations imposed by the Langmuir–Hinshelwood approach.

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