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Computer Simulation of Competitive Adsorption on Ideal Surfaces

Adsorption inhibition due to the unavailability of a specific geometrical arrangement of adsorption sites has been examined by a Monte Carlo simulation. When two species having different site requirements for chemisorption compete for available empty sites, there is a reduction in the ratio of their concentrations on the fully covered lattice. This reduction increases as the interaction strength between adsorbates increases. We apply this premise to the competitive adsorption of dual- and single-site species. This example might find application in the understanding of the mechanism for methanation: Hydrogen (dual) + carbon monoxide (single) → CH_4.

BACKGROUND

In the past Monte Carlo calculations have been successful in modeling the selectivity and activity patterns for surface reactions (*1–5*). In those studies a reaction mechanism was proposed and simulation of the surface reaction was based on the results of an examination of the configurations of the adsorbate layer after chemisorption according to the Monte Carlo calculation, which is concerned only with placing the chemisorbing species randomly on the adsorption sites. From the proposed mechanisms it was seen that certain configurations of adsorbate species need to exist before chemical bonds could be broken or formed. Surface reaction was then determined by the number of such proper configurations which had resulted from random chemisorption. These calculations, like the ones we will describe below, are devoid of any energetic considerations. However, unlike our simulations, these previous computer experiments have not addressed the question of specific geometric requirements for surface adsorbed species and how such requirements can constrain the available pool of surface intermediates.

The question of excluding energetics is valid to raise. Little, if any, direct experimental data are available. However, in two of the three cases considered, we have included some simple modeling of energetics. These cases only treat energetics through possible descriptions of interactions between adsorbates.

Our approach to the problem of obtaining a better understanding of the mechanisms of surface reactions is to view the surface as a reservoir which collects adsorbing reactants, intermediates, and adsorbed products. The premise presented in this work is that each adsorbed species requires a specific geometrical arrangement of sites. If these site requirements cannot be met because random selection of a series of surface atoms shows they are occupied, then the species cannot exist in the pool of species collected in the surface reservoir. For a given situation we then can evaluate the ratio of species having one type of site requirement, to a species with another type of site requirement. Since the probability that a reaction channel is available to the elements in this pool is proportional to their concentration, we may, through these simple ideas, obtain information on the activity or selectivity of the surface reaction.

THE BASIC MODEL

Our current interest in trying to understand the mechanism of the methanation reaction ($3H_2 + CO \rightarrow CH_4 + H_2O$) has prompted us to apply the above concepts to the competitive adsorption of species requiring (i) a dual site (hydrogen), and (ii) a single site (carbon monoxide).

The activity of a good methanation cata-

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lyst has been attributed to the hydrogenation capacity of the catalyst. Since four hydrogens per carbon atom are necessary to produce a methane molecule, the higher the hydrogen surface concentration under reaction conditions (hydrogenation capacity), the higher the methanation activity.

The question of the involvement of hydrogen in the rate-limiting step (*6*) has been recently reinvestigated (*7*). The conclusions of Wilson (*7*) support our own experimental measurements (*8*) and suggest that even the simple modeling we propose here can be useful in examining possible factors that might limit the surface concentration of hydrogen. We have examined how the site requirements for hydrogen (dual) and carbon monoxide (single) might limit the ratio of H/C on an ideal square lattice. The computer simulation has been carried out over a large number of lattice points (10^4) many times (10^2) to determine the surface concentration of dual- and single-site adsorbing species in this competitive adsorption scheme. In this model a dual-site species requires two empty nearest-neighbor sites; a single-site species requires an empty lattice site.

The computer simulates the processes that are involved in chemisorption. A "gas phase" consisting of duals and singles in a particular ratio is established. Random selection from this collection is made, and an adsorption attempt is made. We might view in this part of the sequence that the molecule is in a precursor state. In this precursor state the adsorption requirements which would guarantee a chemisorption event are tested. Three cases have been considered and for each case the "strength" of the interaction between the adsorbates has been increased as discussed below. If the event is successful the concentration on the surface is incremented by 1 (single) or 2 (dual). The process is repeated a large number of times ($\sim 5 \times 10^4$) until ~80–85% of the surface is covered. The dual/single ratio is determined after a large enough number of attempts have been made to insure essentially saturation values. After we discuss the algorithms for the three cases we have considered we will present the results of the simulation. The dual/single ratio on the ideal square lattice has been studied as a function of the potentially available dual/single concentrations available in the "gas phase."

Case I: Geometry

Case I requires only that a specific geometry be available for the adsorbing species. A single-site candidate tests a randomly chosen lattice site to determine its occupancy. If empty, the attempt is registered as a success. A dual species first selects a lattice site. If empty, it randomly tests a nearest-neighbor site. If both attempts are successful, the adsorption takes place. To simulate dissociative mobile adsorption, the concentration of any other two randomly chosen lattice sites (not necessarily adjacent) is incremented by 2.

Case II: Geometry plus Local Concentration

Adsorbate–adsorbate interactions in the adlayer are known to weaken the surface–adsorbate bond. To fold this possibility into the simulation we test the local environment of the chemisorbing species. If the local concentration is high, we reduce the adsorption probability proportionally. For example, once the geometrical requirements specified in Case I are met the following additional requirements are imposed:

1. Single site. The occupancy of the ensemble of five lattice sites including the single and four nearest neighbors is tallied. The adsorption probability is reduced from unity by Σ (nearest-neighbor occupancy)/5.

2. Dual site. The occupancy of the ensemble of eight lattice sites including the two dual sites and six nearest neighbors is tallied and the adsorption probability in this case is reduced by Σ (nearest-neighbor occupancy)/8.

Case III: Displacement

Case III retains all of the features of Cases I and II and allows the potential displacement from previously occupied sites. Such displacement interactions are well known. In this case a single adsorbing on a site occupied by a dual can displace the dual if there exists a nearest-neighbor dual. Thus two dual elements (a dual species) are removed and replaced by single.

RESULTS

Table 1 summarizes the results of this simulation. In Table 1 we show the dual to single ratio on the square lattice after enough attempts have been made to insure ~80% occupancy of the 10^4 lattice points. Each of the three cases has been tested for three dual/single concentrations in the "gas phase" adsorbing pool of reactants. Since each successful dual adsorption increases the concentration on the lattice by 2 and each single by 1, we may compare the potentially available dual to single ratio shown in Column 2 with that actually obtained for the three cases. In each case considered the actual concentration ratio on the surface is less than would be expected from the "gas phase" concentrations, and this quantity decreases as the stringency of the site requirments increases. Increasing the dual to single ratio in Cases I–III does not offset this decrease. Furthermore, for Case I the critical 4 hydrogen/1 carbon concentration is not met until the "gas phase" ratio is greater than the stoichiometric ratio of 3/1. When displacement is considered, even a 15/1 ratio does not afford the proper surface stoichiometry.

TABLE 1

Summary of Results of Simulation

Dual/single ratio	Dual/single ratio			
	Max	Case I[a]	Case II[a]	Case III[a]
1/1	2/1	0.99	0.82	0.25
3/1	6/1	2.69	1.95	0.43
15/1	30/1	12.9	11.37	2.9

[a] At ≈80% total coverage.

One might argue that these results are to be expected. This is true, but the magnitude of the effect of site requirements on the surface concentrations in this competitive adsorption process is significant: less than half of the hydrogen supplied to the surface actually becomes available in the reactant pool.

There are obviously many limitations to the model proposed here. However, the concepts do permit a relatively simple way of evaluating selectivity and possibly activity patterns in complex systems. We are currently examining and will soon report the effects of inert overlayers, the lattice symmetry, and the effect of more complicated site requirements on the surface concentrations of intermediates. Such data might then be related to the catalytically important questions of the effect of alloying or the influence of poisons in systems of commercial interest.

During the revision of this note, a report by Rostrup-Nielsen and Pedersen appeared in this journal (*9*). They concluded that the effect of sulfur (a poison) on the methanation reaction over nickel was geometric. This conclusion does support the ideas we have presented here in that sulfur is proposed to modify the necessary ensemble of nickel atom adsorption sites. However, recent experimental work showing the influence of sulfur on the chemisorption of hydrogen and carbon monoxide on ruthenium (*10, 11*), and extensions of the simulations presented here, would suggest that the sharp decrease in the methanation activity was due mainly to the strong suppression of hydrogen chemisorption (requiring an empty dual site) and not the effect of sulfur on carbon monoxide adsorption.

REFERENCES

1. Callahan, J. L., and Grasselli, R. K., *AIChE J.* **9**, 755 (1963).

2. Dabrowski, J. E., Butt, J. B., and Bliss, H., *J. Catal.* **18,** 297 (1970).
3. Welsch, R. J., and Butt, J. B., *Chem. Eng. Commun.* **1,** 155 (1973).
4. Butt, J. B., and Starzec, L. T., *J. Catal.* **32,** 99 (1974).
5. Peri, J. B., *J. Phys. Chem.* **69,** 220 (1965).
6. Dalla Betta, R. A., and Shelef, M., *J. Catal.* **44,** 439 (1976).
7. Wilson, T. P., *J. Catal.* **60,** 167 (1979).
8. Polizzotti, R. S., and Schwarz, J. A., to be submitted.
9. Rostrup-Nielsen, J. R., and Pedersen, K., *J. Catal.* **59,** 395 (1979).
10. Schwarz, J. A., and Kelemen, S. R., *Surface Sci.* **87,** 510 (1979).
11. Schwarz, J. A., *Surface Sci.* **97,** 525 (1979).

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