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Kinetic Phase Transitions in an Irreversible Surface-Reaction Model

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An irreversible kinetic surface-reaction model, based upon the reaction of carbon monoxide and oxygen on a catalyst surface, is presented. It is found by computer simulation that the adsorbed molecules on the surface undergo both first- and second-order *kinetic* phase transitions. These transitions correspond to the "poisoning" phenomenon seen on catalysts. Interesting transient and periodic behavior is also seen.

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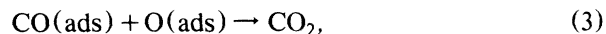
Irreversible dynamical systems are known to show complicated behavior, including dissipative structures, oscillations, kinetic phase transitions, etc., and because these systems are outside classical statistical mechanics, there is no general theory to describe them. At this stage of understanding, it is useful to examine specific dynamical models and study their behavior. In this Letter, we describe a simple irreversible reaction model based upon some of the known steps of the CO-O₂ reaction on a single-crystal catalyst surface. While the model leaves out many important steps of the actual system, it is found to exhibit interesting steady-state off-equilibrium behavior and two types of phase transitions, which occur in real systems.

The basic steps in heterogeneous catalysis of a chemical reaction are (1) the adsorption of the reacting species on the surface, (2) their reaction, and (3) the desorption of the product (the Langmuir-Hinshelwood process).¹ Adsorption on the catalyst causes a change in the state of the reactants, possibly including disassociation, which allows the reaction to take place. Before the reaction actually occurs, there may also be substantial diffusion and possibly reassociation and desorption of unreacted species. The final desorption step (3) is necessary for the product to be recovered and for the catalyst to be regenerated.

The classical approach for the kinetics of these processes is to consider only average concentrations of the adsorbed species, and to write systems of differential equations of varying complexity with multiple

parameters (the adsorption-desorption model).¹ However, such models, besides being sometimes unwieldy, have difficulty explaining some of the unusual observed behavior, such as the observations² that the reaction properties are history dependent and that operation under periodic conditions can lead to enhanced operation.³ Clearly, what is needed is a more microscopic picture, which takes into account fluctuations in density or spatial correlations of the positions of the adsorbed species.

The oxidation of carbon monoxide is one of the most extensively studied heterogeneous catalysis reactions, being important in automobile-emission control, among other applications. It is well established that the reaction occurs by the following three steps⁴:



where (ads) indicates that the molecule is adsorbed on the surface. Upon adsorption, the O₂ disassociates into two O atoms, each residing on a *separate* surface site, while the CO requires only a single site. In the third step, the CO₂ desorbs after it is produced.

In our model, we replace the surface of the catalyst, which may have various crystal planes exposed, by a simple square two-dimensional lattice of active sites. We assume that when gas-phase molecules of CO or O₂ collide with blank sites, they absorb immediately,

and when the O and CO occupy adjacent (nearest neighbor) sites, they react immediately. The CO_2 that is produced desorbs instantly and does not interact further with the system. The composition in the gas phase is not changed by the reaction; the gas volume is assumed to be very large, or to be continually replenished by a fresh feed. We do not consider any of the other mechanisms which may be important, such as finite reaction rates, diffusion of the species about the surface, reassociation and desorption of the O atoms, desorption of unreacted CO molecules (except in some of the simulations described briefly below), or multiple crystal planes. Thus we have made a very idealized model of the reaction that basically retains just the adsorption selectivity rules. One virtue of having such a simplified model is that there are *no energy parameters* (in this regard it is analogous to a hard-particle gas), and the only independent variable is the gas-phase composition—the relative amounts of O_2 and CO. The rate-limiting step is the collision of a gas molecule with an active site on the surface of the catalyst.

This model is intrinsically irreversible because the molecules stick to the site that they hit (if there is no reaction) and remain stationary until removed by a reaction. Thus, we assume that the surface impingement rate is much greater than the surface diffusion rate. The other extreme case is where the molecules diffuse so quickly, and react so slowly, that the surface is essentially a two-dimensional equilibrium gas (and thus reversible). Further work needs to be done to see under what conditions our model is valid for the CO-O_2 system.

We note that there has recently been substantial interest in related “scavenger” reactions, such as $A + B \rightarrow 0$ (inert), in which diffusion is the essential process and the rate-limiting step.⁵⁻¹⁰ The present model differs substantially from these because here the surface is constantly being replenished and no diffusion is allowed.

In the simulation of our model, a trial begins with the random collision of a gas molecule on a square lattice, which represents the surface. The colliding molecule is chosen to be CO with a given probability y_{CO} and O_2 with probability $1 - y_{\text{CO}}$, where y_{CO} is determined by the mole fraction of CO in the gas phase. Then, *if the colliding molecule is a CO*, the following happens: (1) A site on the lattice is randomly chosen. (2) If that site is already occupied, then the

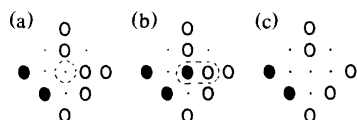


FIG. 1. A CO molecule (a) strikes the blank site in the center, adsorbs, (b) sees a neighbor O, and (c) the two react and desorb. Open symbols denote oxygen and closed symbols, carbon monoxide.

trial ends (the CO bounces off the surface); (3) otherwise, the CO adsorbs, and (4) the four nearest neighbors (nn) are checked in random order. (5) If an O is found in any of the nn sites, both sites are vacated (the molecules react and the CO_2 desorbs). *If the colliding gas molecule is an O_2* , the following occurs: (1) Two adjacent sites are randomly chosen on the surface. (2) If either site is occupied, the trial ends; (3) otherwise, the O_2 disassociates and adsorbs on the two sites, and (4) all six nn sites are checked randomly for CO. (5) If any of the six nn sites has a CO, it is reacted with the adjacent O atom, and the two sites are vacated.

Illustrations of this model are shown in Figs. 1 and 2.

Figure 3 shows a typical steady-state configuration produced by this simulation. Here we started with a blank lattice of 128×256 sites (using periodic boundary conditions), with $y_{\text{CO}} = 0.5$, and waited until apparent steady state was reached. About 55% of the sites are occupied by O atoms, 2% by CO molecules, and the rest blank. It can be seen that blank sites occur commonly among the O atoms as well as at the boundary around the few CO clusters (dark islands). These blank sites allow additional molecules to adsorb, and are thus necessary for reaction to proceed. Note that very few CO molecules remain on the lattice at this value of y_{CO} .

We found that a reactive steady state like that in Fig. 3 occurs only for $y_1 < y_{\text{CO}} < y_2$, where $y_1 = 0.389 \pm 0.005$, and $y_2 = 0.525 \pm 0.001$. Outside of the interval, the only steady state is a “poisoned” catalyst of pure CO or pure O. The steady-state coverage fractions of CO and O as a function of y_{CO} are shown in Fig. 4. The CO_2 production rate or activity (defined as the number of CO_2 molecules produced per collision or trial) is also plotted in that figure.

As can be seen in Fig. 4, when y_{CO} is increased toward y_2 the activity increases, but when y_2 is reached large clusters of CO suddenly grow and cover every lattice site. For $y_{\text{CO}} > y_2$, the only steady state is this nonreactive, solid CO state. The transition occurs abruptly, with discontinuities of the coverage fractions and the activity, implying that this is a first-order *kinetic* transition. Likewise, when y_{CO} is lowered to y_1 , the

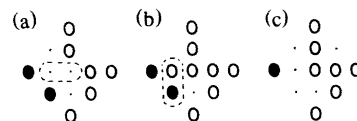


FIG. 2. (a) An O_2 molecule strikes the two blank sites, indicated by dotted lines, and adsorbs. (b) One of the O atoms sees a neighboring CO; (c) the two react, and desorb. Open symbols denote oxygen and closed symbols, carbon monoxide.

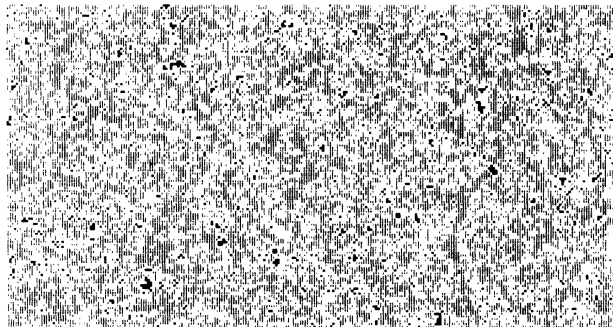


FIG. 3. A view of the catalyst surface under steady-state conditions with $y_{\text{CO}}=0.5$. The dark areas represent CO and the light (mostly here) represents O.

system poisons with oxygen. This transition is continuous, and therefore it is of second order. These are *kinetic* phase transitions in an intrinsically nonequilibrium, non-Hamiltonian system, not to be confused with the usual phase transitions in an equilibrium system.

In Fig. 5 we show the surface in the process of being poisoned by CO, with $y_{\text{CO}}=0.527$. Because this value of y_{CO} is only slightly greater than y_2 , the poisoning occurs very slowly. In this figure, 10 000 units of time have passed since the initial blank state, where a unit of time is defined such that each site is visited once, on the average (or 32 768 trials for this size lattice). Complete poisoning in this simulation did not occur until about 4000 more units of time passed. For y_{CO} even slightly higher, such as 0.53, the CO poisoning occurs much more rapidly (1856 units of time in one run). Exactly at $y_{\text{CO}}=y_2$, we expect that the two phases (an oxygen-rich phase, and a solid CO phase) coexist, similar to what is seen in Fig. 5.

We used this hypothesis of the coexistence of phases to find an accurate value of y_2 as follows. A periodic lattice of 80×25 sites was initially half covered with CO and half blank, which is equivalent to a series of bands of CO and blank sites in an infinite system. The simulation was carried out with different values of y_{CO} until the solid CO phase was found to spread over the whole system, or to disappear, with equal probability. This gave $y_2 = 0.525 \pm 0.001$.

Interestingly, when we went back to the larger lattice, initially blank, we did not see the CO transition until $y_{\text{CO}}=0.527$ (this is, in fact, the simulation of Fig. 5). This small but significant increase reflects the difficulty of nucleating a CO island when no CO phase exists, and shows that there is an effective surface tension in the system. Presumably, if we had waited long enough at $y_{\text{CO}}=0.525$, we would have seen a transition. The band simulation eliminates the effect of the critical curvature because it starts with a flat interface between the phases.

To find the value of y_1 , the band initial condition does not work well because there is no interface, since

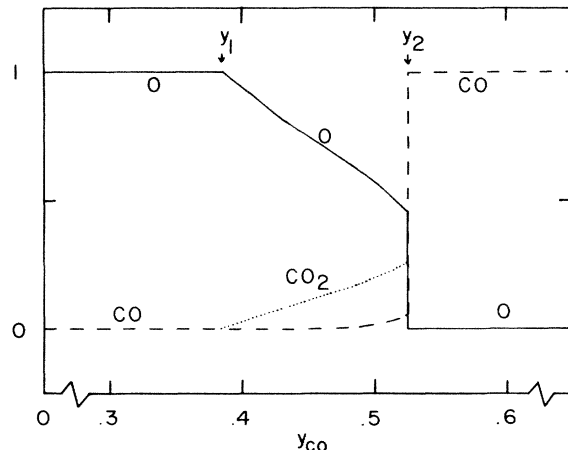


FIG. 4. The average coverage fractions of O (solid lines) and CO (dashed lines), and the CO_2 production rates (dotted lines) for steady-state operation, as a function of y_{CO} . Transitions occur at y_1 and y_2 .

the coverage of O(ads) goes to unity continuously as $y_{\text{CO}} \rightarrow y_1^+$. Instead, we used a lattice (of 200×640 sites) initially covered with O except for a single blank site in the center. The reaction simulation was carried out with different values of y_{CO} until a reacting phase containing many vacant sites was found to appear after a reasonable number of attempts (10^3 – 10^5). Note that these vacant sites were not in the form of a compact cluster, but were scattered over the lattice (no distinct phases). This simulation gave $y_1 = 0.389 \pm 0.005$.

Thus, we find that the simple surface model shows the main features of the CO-O₂ system: a region of steady-state reaction, and regions where poisoning occurs, as seen experimentally.²⁻⁴ Note that in the experimental systems, the poisoning is reversible because of desorption, and so when the atmosphere is returned to a composition that allows steady-state operation, the reactivity is seen to go back to normal after an induction time.

We also investigated some other aspects of this system, which we briefly describe below:



FIG. 5. With $y_{\text{CO}}=0.527$, slightly above y_2 , CO poisoning is slowly occurring (non-steady-state).

(1) *Desorption*.—In most systems, CO desorption is common at the operating temperature. Adding a probability of desorption (now there is a parameter), we found that the two transitions remain, but are shifted to higher values of y_{CO} . Of course, the CO phase is no longer solid but contains fluctuating holes. These holes allow the reversibility in the system mentioned above: One can poison the lattice with CO, and then renew it by making the atmosphere high in O, although this process is very slow because of the two-site requirement for O₂ to desorb.

(2) *O annealing*.—While CO poisoning can occur rapidly, the O poisoning occurs very slowly. When the O₂ adsorb, they generally leave single blank sites, reminiscent of the “parking car” problem.¹¹ These holes must be enlarged first by a CO reaction before they can possibly be filled up with O. Simulations at low y_{CO} show that the O slowly “anneals” and that O poisoning is a slow process.

(3) *The $A + B \rightarrow AB \rightarrow 0$ model*.—To investigate the importance of the two-site rule for oxygen adsorption, we considered the reaction $A + B$ where neither A nor B disassociates upon adsorption. Neighboring A - B adsorbed sites immediately react, and the AB that is formed desorbs immediately. We find that when $y_A > 0.5$, the catalyst poisons with A , and when $y_A < 0.5$, it poisons with B . A reactive steady state occurs only at the *single point* $y_A = 0.5$. From this we conclude that the two-site rule for O₂ is very important, as it leads to a whole *region* $y_1 < y_{\text{CO}} < y_2$, where the system reacts in steady state. Note that a related $A + B \rightarrow AB \rightarrow 0$ reaction model has been studied by Wicke *et al.*¹² They assumed that the adsorption occurs rapidly, while the reaction rate was the limiting step. As in our $A + B$ model, their model leads to poisoning whenever $y_A \neq 0.5$.

(4) *Transient behavior*.—By running the system at $y_{\text{CO}} > y_2$, a higher activity can be produced for a while until CO poisoning begins. If the atmosphere is then switched to low CO, the activity again jumps, until oxygen poisoning begins. In both cases, there is an induction time before the high reactivity occurs.

(5) *Periodic operation*.—The procedure described above can be repeated to produce *periodic* operation of

the reactor. We carried out such simulations in which the gas was alternately switched between pure O to pure CO. With proper choice of the cycle time, we were able to find an increase net production rate over optimum steady-state operation (which occurs at y_{CO} just below y_2), although so far not the order-of-magnitude increase seen experimentally.³ The kinetic model provides a simple explanation for the increase: The periodic operation keeps the cluster sizes under control, and allows the catalyst to operate under very optimum conditions, at least during parts of the cycle.

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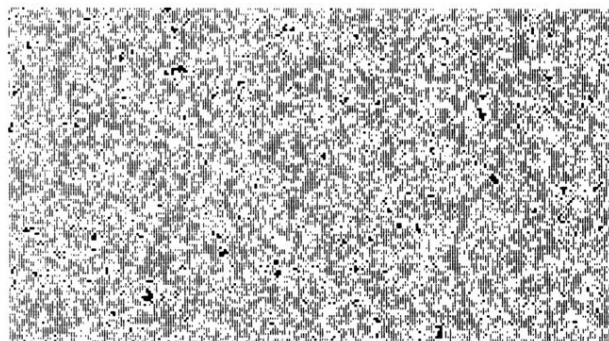


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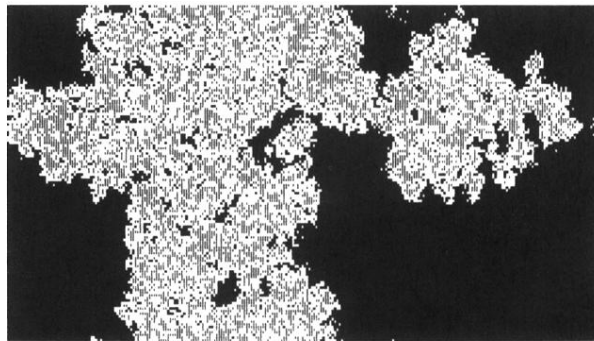


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