A model for the catalytic oxidation of CO that includes CO desorption and diffusion, O repulsion, and impurities in the gas phase

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We present kinetic Monte Carlo simulations exploring the nonequilibrium phase diagram of a modified Ziff-Gulari-Barshad (ZGB) dynamic lattice-gas model for the catalytic oxidation of carbon monoxide (CO) on a surface. The modified model includes the simultaneous presence of contaminants in the gas phase, CO desorption, CO diffusion, and strong repulsion between adsorbed oxygen (O) atoms; all of which have been observed in experimental systems. We find that the strong O-O repulsion produces higher reaction rates, albeit in a reduced reactive pressure window. In systems with impurities, the CO$_2$ production rate is greatly reduced, but this effect is mitigated by CO desorption and diffusion. CO desorption has the effect of widening the reactive pressure window, while CO diffusion has the effect of increasing the reaction rate. In some parameter regimes the presence of impurities destroys the discontinuous transition between the reactive and high CO coverage phases.

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I. INTRODUCTION

The catalytic oxidation of CO on a surface is perhaps the most studied example of heterogeneous catalysis. Besides its obvious industrial applications, this reaction constitutes a prime example of a nonequilibrium system that exhibits a rich variety of behavioral patterns and complex irreversible critical behaviors [1, 2]. In recent years, studies based on complex lattice-gas models, combined with detailed molecular information and realistic input energetics obtained from density functional theory in combination with experiments, have provided detailed results for some aspects of this reaction [3-9]. For a recent, extensive review, see [10].

However, a comprehensive understanding of heterogeneous catalysis and the associated, nonequilibrium phase diagrams remains a challenging problem, and there is still much to be learned from simple models that can easily be manipulated to incorporate different physical features. The well-known Ziff-Gulari-Barshad (ZGB) dynamic lattice-gas model [11] is an example of such a simple model that has proved to be a fruitful laboratory for testing the effects of various processes on catalytic reactions, and for exploring out-of-equilibrium phase transitions in general [12]. The model has recently been used to test novel algorithms for studying rare events [13].

An important characteristic of this model is that it can be enriched by the inclusion of different physical processes without losing its intrinsic simplicity. In the original ZGB model, the CO-O$_2$ (or more generally the A-B$_2$) reaction occurs via a Langmuir-Hinshelwood mechanism that involves only one parameter, the relative partial pressure of CO in the gas-phase. The model exhibits two phase transitions: a continuous one at low CO pressure, between an oxygen poisoned phase and a reactive phase, and a discontinuous one, at higher CO pressure, between the reactive phase and a CO-poisoned phase. These features make the model a useful tool to explore the nature of transitions in nonequilibrium systems [14-17]. The continuous transition at low CO pressure (known to belong to the the directed percolation universality class [14]) has not been experimentally observed, but it can be easily eliminated by making minor modifications to the model [18-20], as discussed below.

With the purpose of approaching the CO-O$_2$ reaction in a somewhat more realistic way, and to understand the effects of different processes on its nonequilibrium phase diagram, our aim in this paper is to subject the ZGB model to the simultaneous influence of several perturbing processes, so that their interactions can be directly ascertained. In previous work we have studied the effects of some of these processes individually or in smaller combinations [20-22]. These include the temperature-related effect of CO desorption [20, 23, 24] and a modification that mimics experimental results that indicate that the oxygen atoms suffer a strong mutual repulsion once on the surface [18, 19].

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Several of these modifications have been studied separately and in various combinations \cite{26,28}. In order to better understand the effects of pollutants, always present in real environments, we also incorporated impurities in the gas phase \cite{21,22,29,30}. Under realistic industrial conditions the temperature and pressure can reach high values, regimes in which the validity of this simple model is limited. Nevertheless, one can still gain qualitative insight into the effects of impurities on the process and, most importantly, how they affect the nature of the nonequilibrium phase transitions. The results show that the impurities significantly affect the efficiency of the process \cite{3,21,22,31-33}. One interesting effect of adding impurities is the disappearance for low impurity desorption rate of the first-order phase transition between the reactive phase and the CO-poisoned phase \cite{21,22,29}. This result has been further confirmed for the case of quenched defects by a recent study that indicates that first-order transitions do not exist in nonequilibrium disordered systems with absorbing states \cite{34}.

CO desorption prevents the formation of a CO-poisoned absorbing state, and consequently the abrupt transition from the reactive state to the low reactive state becomes reversible \cite{12,13,15,17,23,25}. A totally CO-poisoned state cannot be achieved experimentally due to the nonvanishing CO desorption. The first-order nature of the transition only remains up to a critical value of the CO desorption rate \cite{12,21,22}, where it terminates at a critical point that belongs to the two-dimensional Ising universality class \cite{13}. Our previous studies indicate that CO desorption can counteract the negative effect of the impurities by widening the region where the system remains catalytically active \cite{22}.

In the present work we are particularly interested in studying how CO diffusion, when added to the other effects (O-O repulsion, CO desorption, and gas-phase impurities), alters the behavior of the system. It is well known that the mobility of the adsorbates plays an important role in the overall reactivity of the surface. Kinetic Monte Carlo studies indicate that CO diffusion is the key to the qualitative differences between the CO electrooxidation dynamics on rhodium and platinum \cite{35}, and that it synchronizes oscillations in models that include surface reconstruction \cite{36}.

Real diffusion is usually very fast, especially in systems at low pressure, with very large diffusion lengths that determine the characteristic length scale of spatial patterns and the propagation of reaction fronts \cite{37,38}. The wide range of time scales makes computer simulation of this rapid diffusion very challenging. Several approaches have been proposed, from coarse-grained methods, generalized Metropolis simulations, even hydrodynamics based algorithms \cite{10}. An interesting approach is to treat the diffusion by a mean field and the reaction with Monte Carlo \cite{39}. In the present work we treat diffusion as a relatively slow process. Even in this limit, diffusion proves to have significant effects on the nonequilibrium phase diagram of the model.

The rest of this paper is organized as follows. In Sec. II we describe in detail how the ZGB model is modified to eliminate the unphysical continuous phase transition at low CO pressure by including strong repulsion between adsorbed O atoms, how we incorporate CO desorption and add diffusion to the processes included in our previous studies, and how we take into account the impurities in the gas phase. In Sec. III we present our numerical results for the modified model, and in Sec. IV we present our conclusions.

## II. MODEL AND SIMULATIONS

In this work we study the catalytic oxidation of CO on a surface immersed in a gas phase that consists of a mixture of CO, O$_2$, and inert impurities, X, in different proportions. As in the original ZGB model, CO and O$_2$ can be adsorbed on the surface, and once there they react to produce CO$_2$ that is immediately desorbed. The impurities can be adsorbed or desorbed at single lattice sites on the surface, where they do not react with the other adsorbates. (Several common catalytic poisons, such as sulfur and lead, adsorb at single lattice sites, although the chemistry of the reaction inhibition can be more complicated than the simple site blocking we consider here.) This model differs from the original ZGB model in the presence of impurities in the gas phase, in the entrance mechanism for the O atoms, and in the existence of CO desorption and diffusion. The modification of the entrance mechanism is inspired by experimental results that indicate that the O atoms tend to repel each other once on the surface \cite{15,40}. Recently, quite sophisticated models amenable to analytic treatment have been introduced for the dissociative adsorption of O$_2$. Some of these also incorporate exclusion of nn pairs of adsorbed O, and successfully reproduce experimental results that describe the behavior of the sticking coefficient versus the coverage \cite{10}.

We impose the condition that an O$_2$ molecule can be adsorbed on two next-nearest-neighbor (nnn) vacant sites (separated by $\sqrt{2}$ lattice constants) only if the six nearest neighbors (nn) to these sites contain no O. In the original ZGB model the O atoms are adsorbed on nn empty sites. Thus, in the modified model, the adsorption of an O$_2$ molecule requires the existence of eight sites that do not contain O. Clearly, this requirement eliminates the unphysical O-poisoned phase that appears in the standard ZGB model. In the literature this adsorption prescription is known as the eight-site rule \cite{13,41,42}. Previous work shows that just requiring that the O atoms enter nn sites is sufficient to ensure that the O-poisoned phase disappears \cite{21,22,43}. The mechanism is essentially that, at low values of $y$ the surface is mostly covered by O. The few isolated empty sites can only be filled with CO that will react with one of its
nn O and leave two nn empty sites. In the original ZGB model these empty nn sites would, with very high probability, be filled by O, eventually poisoning the surface. With the requirement of nn O adsorption, they can be filled only with CO that will continue reacting with their O neighbors, preventing the buildup of a complete O coverage [21].

We note that next-nearest-neighbor O adsorption is not the only mechanism that can remove the unphysical O-poisoned phase. Another possibility is an Eley-Rideal mechanism that allows reaction between CO molecules in the gas phase and adsorbed O atoms [20]. The incorporation of CO desorption and diffusion has the purpose to emulate temperature effects that are known to be very important in the catalytic process. In contrast, O atoms are relatively immobile at temperatures below 400 K [44], and in general O typically has a significantly higher diffusion barrier than CO [10, 45, 46]. We therefore choose to neglect O diffusion in our model. The impurities in the gas-phase are added to study the system under somewhat more realistic industrial conditions.

The model is simulated on a square lattice of linear size $L$ that represents the catalytic surface. A Monte Carlo simulation generates a sequence of trials: CO, X, or O$_2$ adsorption, CO or X desorption, or CO diffusion. A site $i$ is selected at random. If it is occupied by CO, we attempt desorption with probability $k_{co}$ and diffusion with probability $d$. ($k_{co} + d \leq 1$.) For the diffusion step we randomly choose one of the nn of $i$. If it is empty, we move the CO to the new site. If $i$ is occupied by an X, we attempt desorption with probability $k_x$. If $i$ is empty, we attempt adsorption: CO with probability $y$, X with probability $y_x$, or O$_2$ with probability $1 - y - y_x$. These probabilities are the relative impingement rates of the molecules and are proportional to the amounts of the different species in the gas phase. The dissociative adsorption of an O$_2$ molecule requires the existence of a pair of vacant nn sites and that the six nn to the pair do not contain an O atom. A nn of site $i$ is selected at random; if it is occupied the trial ends, if not, the six nn of the pair are checked, if none of them contains an O molecule, the adsorption proceeds and the O$_2$ molecule is adsorbed and dissociates into two O atoms. After CO adsorption or diffusion or O$_2$ adsorption, all nn pairs are checked in random order. Pairs consisting of a nn CO and O react: a CO$_2$ molecule is released, and two nn sites are vacated. A schematic representation of this algorithm is given by the equations,

\[
\begin{align*}
CO(g) + S \rightarrow CO(a) \\
O_2 + 2S \rightarrow 2O(a) \\
CO(a) + O(a) \rightarrow CO_2(g) + 2S \\
X(g) + S \rightarrow X(a) \\
X(a) \rightarrow X(g) + S \\
CO(a) \rightarrow CO(g) + S \\
CO(a)_S + S' \rightarrow CO(a)_{S'} + S
\end{align*}
\] (1)

Here, S and S' represent empty sites on the surface, g means gas phase, and a means adsorbed. CO(a)$_S$ means an adsorbed CO at the S site. The first three steps correspond to a Langmuir-Hinshelwood mechanism. The fourth and fifth terms represent the adsorption and desorption of an impurity, respectively. The sixth term represents CO desorption, and the seventh represents diffusion of a CO molecule from site S to its nearest neighbor site S'.

In our simulations the surface is represented by a lattice of size 120×120 with periodic boundary conditions. (Additional results for a 200×200 system are included in Fig. 5) The time unit is one Monte Carlo Step per Site (MCSS), during which each site is visited once on average. Averages are taken over $10^5$ MCSS after $10^5$ MCSS that are used to achieve a stationary state.

Coverage is defined in the usual way as the fraction of sites on the surface occupied by an adsorbate. We calculate the CO, O, and X coverages and the rate of production of CO$_2$. For each value of $y$ and $y_x$ we start from an empty lattice and let the system reach a steady state before taking measurements.

### III. RESULTS

To understand the effects of the strong repulsion between adsorbed O and the presence of CO diffusion and desorption, in Sec. IIIA we first present the case in which there are no impurities and compare the results with those obtained by a previous model [22] that does not include CO diffusion or the new entrance mechanism for O. Then, in Sec. IIIB we present the results for the full model described in Sec. II which includes impurities.

#### A. Without impurities, $y_x = 0$

In this subsection we introduce CO diffusion in two models that both include CO desorption, but differ in the entrance mechanism for oxygen. In one model, that for simplicity will be labeled A in this subsection, the O atoms
enter a pair of nnn sites without any other requirement \[22\]. In the second model (in this subsection labeled B), the entrance of the O atoms at a pair of vacant nnn sites occurs only if the six nn of the pair are free of oxygen. Thus, the dissociative adsorption of O in model A requires two empty sites, while in model B it requires two empty sites and six additional sites free of O. In this subsection, neither model includes impurities.

In Fig. \[1\] and Fig. \[2\] we compare the coverages and reaction rates of the two models, for a small CO desorption rate, \(k_{co} = 0.01\), and for a larger one, \(k_{co} = 0.05\), respectively. In each case we plot the results for the case without CO diffusion \((d = 0)\), and with a high diffusion rate \((d = 0.9)\). The first effect associated with the new entrance mechanism for oxygen, is that the transition to the CO poisoned state is smoother for model B, and that it occurs at a lower value of \(y\). The latter effect is due to the higher CO coverage in the active phase in model B, as observed in Fig. \[1(a)\] and Fig. \[2(a)\]. As expected, the O coverage, Fig. \[1(b)\] and Fig. \[2(b)\], is much smaller in model B. It is well known that the O poisoned phase that characterizes the standard ZGB model is not present in these models, in which the O enter at nnn sites \[21, 22, 13\]. As expected, the coverage of empty sites, which can be trivially calculated from the CO and O coverages, is much larger in model B. The reaction rate behaves quite differently in the two models, Fig. \[1(c)\] and Fig. \[2(c)\]. In model A it starts growing very slowly but increases quite rapidly as the transition point \(y_\ast\) is reached. In model B it increases at an almost constant rate until it reaches its maximum. As a result, below the transition point (which depends on the model), for the same value of \(y\), the reaction rate is much higher in model B. As has also been observed in other models, the reaction rate increases with \(k_{co}\). It is generally expected that diffusion increases the reaction rates, since the mobility of the adsorbates facilitates the number of encounters between the reactants. However this effect is only relevant when the lattice has a significant number of empty sites that allow diffusion to take place, and a high coverage of the diffusing species. In the reactive region model B has a larger number of empty sites and also a larger CO coverage. This explains why the reaction rates, Fig. \[1(c)\] and Fig. \[2(c)\], show a marked increase with \(d\). In contrast, in model A the CO coverage and the number of empty sites below the transition point is very small. Therefore, the diffusion effects are almost negligible. These results indicate that the system behaves quite differently when a strong repulsion effect between the O atoms is taken into account, and in this case the mobility of the CO is quite relevant. Notice in Fig. \[2\] that, when \(d = 0\), model A has a sharp transition to the CO rich phase, even for \(k_{co} = 0.05\), larger than \(k_{co}^{crit} \lessapprox 0.04\) for the original ZGB model with CO desorption \[13, 17, 24, 17\]. This is consistent with previous results \[13\] that indicate that the critical value of \(k_{co}\) is increased in model A. On the other hand, in model B, which includes the eight-site rule, it appears that the critical value of \(k_{co}\) is reduced relative to the ZGB model with CO desorption, leading to the smooth maxima in the reaction rate.

Diffusion increases the spatial reaction range, leading to an increase in the critical value of \(k_{co}\) \[47, 48\]. In Fig. \[1\] this has the effect that the transition in Model B is continuous for \(d = 0\), but discontinuous for \(d = 0.9\). At the higher value of \(k_{co}\) shown in Fig. \[2\] however, the transition is continuous both with and without diffusion. In Model A, the size of the discontinuity is seen to increase with \(d\) in both Fig. \[1\]and Fig. \[2\].

### B. With impurities, \(y_x > 0\)

In this subsection we study the effects of impurities in the gas phase, considering only the model labeled in the previous subsection as B, which includes the new mechanism for the entrance of oxygen, as well as CO diffusion and desorption. Since this is the only model we consider in this subsection, we drop the label B. The effects of impurities in the gas phase in the model without CO diffusion and without the strong repulsion between adsorbed O, were discussed in Ref \[22\]. The impurities can be desorbed from the surface with probability \(k_x > 0\). Previous studies \[21, 22\] indicate that when non-desorbing impurities, \(k_x = 0\), are present, the steady state of the system has reaction rate zero. We verified that this is also the case in the model described here; the existence of CO diffusion does not alter this behavior. We fix the partial pressure of impurities to \(y_x = 0.005\). To analyze the effects of \(k_{co}\), \(d\), and \(k_x\), we start by fixing \(k_x\) and study the dependence of the system on \(d\) for different values of \(k_{co}\). As an example, in Fig. \[3\] we present the coverages and the reaction rates with \(k_{co} = 0.001\) and \(k_{co} = 0.01\). For larger values of \(d\) as \(d\) increases, the CO coverage decreases and the O and X coverages increase. The reaction rate increases considerably with \(d\). Notice that when \(d\) reaches a limiting value of about 0.9, further increase does not affect the coverages or the reaction rate. This can be seen in Fig. \[4\] where we plot the reaction rate vs \(y\) for several values of \(d\) for \(k_{co} = 0.01\) (a) and \(k_{co} = 0.05\) (b). Since, for the same value of \(y\), the CO coverage becomes smaller as \(d\) increases (see Fig. \[3(a)\]) and the number of empty sites remains almost the same above a certain value of \(d\), it is easy to see why increasing \(d\) beyond a certain point does not have any effect on the behavior of the system. In our algorithm the maximum value that \(d\) can take is \(1 - k_{co}\). Comparing Fig. \[1(c)\] and Fig. \[2(c)\] with Fig. \[4(a)\] and Fig. \[4(b)\], respectively, we see that the presence of impurities substantially reduces the reaction rate of the system. Comparing, Fig. 4(d) with Fig. 4 we see that, as expected, the reaction rate increases when \(k_{co}\) increases, however this effect seems to be only significant when \(d\) is small. Comparing Fig. 4(a) and Fig. 4(b), it is evident that the most relevant effect is that the reactive
window increases considerably when $k_{\text{co}}$ increases.

To further understand the effect of the CO diffusion, in Fig. 5 we plot the reaction rates for the model with fixed $k_{\text{co}}$ and different values of $k_x$, when there is no diffusion ($d = 0$), Fig. 5(a), and with a high diffusion attempt rate ($d = 0.9$), Fig. 5(b). Clearly, the diffusion term greatly increases the reaction rate of the system. Notice that for the higher value of $d$, the range of $y$, for which the system produces CO$_2$, is slightly larger. For very small values of $k_x$, the reaction rate is almost zero and almost totally insensitive to $d$. This is expected because, as we already mentioned, when the impurities do not desorb, or have a very low desorption rate, in the steady state the reaction rate is close to zero. The non-desorbing impurities take over the empty spaces, creating a barrier between the adsorbed O and CO (see Fig. 3 of Ref. [21]), such that they cannot react. Since there are no empty sites available, the rate of attempted diffusion moves has no effect in this case. Comparing Fig. 5(a) and (b), we again see that the reaction rate increases with $k_x$ and $d$.

IV. CONCLUSIONS

In this work a modified version of the ZGB model for the reaction CO+O $\rightarrow$ CO$_2$ on a catalytic surface has been analyzed. With the aim to make the model richer and more amenable to present interesting nonequilibrium behaviors, and also to make it somewhat more realistic, we consider the simultaneous action of several processes that are present in real situations. We change the mechanism for the dissociative adsorption of O$_2$ to incorporate experimental results that indicate that, once on the surface, the O atoms experience a strong mutual repulsion. In our model, the dissociative adsorption of O$_2$ requires two empty nnn sites and occurs only if the six nm of the entrance sites are not occupied by O. This mechanism is known as the eight-site rule [19, 41, 42]. The model also incorporates CO desorption and diffusion that in real systems are related to temperature effects. To further understand what happens in experimental conditions, particularly in industrial environments, we also study the effect of impurities (X) in the gas phase. Once adsorbed on the surface, the impurities do not react with the other species and can only be desorbed. Then, besides the variable $y$, proportional to the partial pressure of CO in the gas, that defines the ZGB model, our model has several other variables: $y_x$, proportional to the partial pressure of X in the gas; $k_{\text{co}}$ and $k_x$, the desorption rates of CO and X, respectively; and $d$, the attempt rate for CO diffusion. An evident consequence of the modification of the entrance mechanism for oxygen is that the non-physical oxygen poisoned phase of the original ZGB model disappears [21, 22]. Another consequence of the strong O repulsion is a considerable increase of the CO$_2$ production rate for values of $y < y_c$, where $y_c$ is the value of $y$ at which the system becomes filled mostly with CO. $y_c$ is smaller for the system with strong O repulsion, such that the range of values of $y$ for which the system remains reactive is significantly reduced for these systems. We also find that the transition to the CO rich phase is smoother for the system with strong O repulsion, and the dependence of $y_c$ on the CO desorption rate is more accentuated: $y_c$ increases with increasing values of $k_{\text{co}}$. Beyond a critical value of $k_{\text{co}}$, the discontinuous transition at $y_c$ is replaced by a smooth crossover. These results can be explained by the fact that the strong repulsion between the O atoms, represented by the eight-site rule, hinders their entrance, thus favoring the entrance of the other species. If there are no impurities, the empty sites are filled with CO such that the CO poisoning occurs at lower values of $y$. When impurities are added to the gas-mixture, the sites that cannot be filled with O can be filled with CO or X. Since the adsorbed X do not react, they form a barrier between domains of CO and O impeding their reaction, and unless the X desorption rate is high, their presence greatly diminishes the CO$_2$ production and eliminates the first-order transition between the productive and CO-poisoned phases [21, 22, 23, 43]. In this scenario, where the strong O repulsion favors the existence of a larger number of empty sites and the adsorption of the other species, the diffusion of CO also plays an important role in increasing the reaction rate. This study shows that CO desorption and diffusion can in certain ways counteract the negative effect of the presence of impurities on the reaction rates. This effect may explain why systems with impurities increase or recover their catalytic productivity with increased temperature.

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FIG. 1: Coverages and reaction rate vs $y$ in the case that there are no impurities ($y_x = 0$) for models A (empty symbols) and B (filled symbols) with the values of the diffusion probability $d$ indicated in the figures. (a) CO coverage, (b) O coverage, (c) CO$_2$ production rate. $k_{co} = 0.01$, below the critical value for the original ZGB model with CO desorption. The results in this and subsequent figures are for systems of size $120 \times 120$ lattice sites.
FIG. 2: Coverages and reaction rate vs $y$ in the case that there are no impurities ($y_z = 0$) for models A and B with the values of the diffusion probability $d$ indicated in the figures. (a) CO coverage, (b) O coverage, (c) CO$_2$ production rate. $k_{CO} = 0.05$, above the critical value for the original ZGB model with CO desorption.
FIG. 3: Coverages and reaction rate vs $y$ when the partial pressure of impurities is $y_x = 0.005$, (model B) with the values of $d$ indicated in the figures. (a) CO coverage, (b) O coverage, (c) X coverage and (d) CO$_2$ production rate. $k_{CO} = 0.001$ and $k_x = 0.01$. 
FIG. 4: Reaction rates vs $y$ when the pressure of impurities is $y_x = 0.005$ (model B), at $k_x = 0.01$ with the values of $d$ indicated in the figures. (a) $k_{co} = 0.01$. (b) $k_{co} = 0.05$. Notice that for the latter value of $k_{co}$, the phase transition is replaced by a smooth crossover.
FIG. 5: Reaction rates vs $y$ when the partial pressure of impurities is $y_A = 0.005$, (model B) with the values of $k_A$ indicated in the figures. (a) $d = 0$. (b) $d = 0.9$. $k_{co}=0.01$. Additional data for a $200 \times 200$ system show that finite-size effects are negligible.