



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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HIGHLIGHTS

- We present Monte Carlo simulations of a modified ZGB model for CO oxidation.
- The model includes CO desorption, diffusion, lateral O–O repulsion, and impurities.
- CO diffusion and strong O–O repulsion give increased reaction rate.
- Impurities give reduced reaction rate and may destroy discontinuous CO poisoning.
- The various processes influence the critical CO desorption rate in different ways.

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ABSTRACT

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 CO₂ 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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1. 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 Ref. [10].

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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–O₂ (or more generally the A–B₂) reaction occurs via a Langmuir–Hinshelwood mechanism that involves only one parameter, the relative partial pressure of CO in the gas phase, y . 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 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–O₂ 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 [23–25,20] and a modification that mimics experimental results that indicate that the oxygen atoms suffer a strong mutual repulsion once on the surface [18,19]. Several of these modifications have been studied separately and in various combinations [26–28]. In order to better understand the effects of pollutants, always present in real environments, we also incorporated impurities in the gas phase [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 [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 [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 [34].

CO desorption prevents the formation of a CO-poisoned absorbing state, and consequently the abrupt transition from the reactive state to the low reactivity state becomes reversible [12,15–17,23–25]. 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 [12,21,25], where it terminates at a critical point that belongs to the two-dimensional Ising universality class [15]. 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 [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 [35], and that it synchronizes oscillations in models that include surface reconstruction [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 [37,38]. The wide range of time scales makes computer simulation of this rapid diffusion very challenging. Several approaches have been proposed, including coarse-grained methods, generalized Metropolis simulations, and even hydrodynamics based algorithms [10]. An interesting approach is to treat the diffusion by a mean field and the reaction with Monte Carlo [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 Section 2 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 Section 3 we present our numerical results for the modified model, and in Section 4 we present our conclusions.

2. 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, O₂, and inert impurities, X, in different proportions. As in the original ZGB model, CO and O₂ can be adsorbed on the surface, and once there they react to produce CO₂ 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

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