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Ziff–Gulari–Barshad model with CO desorption under oscillating reactant pressure

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ABSTRACT

We study the Ziff–Gulari–Barshad (ZGB) model subjected to periodic variation of reactant pressure, without desorption as well as at different desorption rates. Keeping the time period of oscillation fixed at a small value, Monte Carlo simulations are carried out at different amplitudes. With increase in the amplitude of oscillation, a transition occurs from the reactive state to the (partially) poisoned state. The reactant pressure oscillation is periodic cosine and symmetric about the ZGB discontinuous phase transition. Even for the model with no desorption, the numerical data for the fourth-order cumulant and the finite size scaling analysis suggest that the system does not undergo any phase transition but only a smooth crossover from the reactive to the poisoned state.

1. Introduction

In heterogeneous catalysis, periodic forcing of control parameters leads to significant increase in reaction rates, selectivity or both. Reactions, which play a role in the automotive catalytic converter, have mostly been subjected to such a periodic forcing. Thus, several periodic forcing experiments have been reported on the catalytic CO oxidation reaction. For instance, the periodic switching of the feed of CO and O_2 on Pt or Pd supported catalysts, results in considerable increase of the reaction rate [1,2]. Such cases have also been studied for single crystal catalyst surfaces and for reactions under high-pressure conditions [3–5]. Eiswirth et al. [6] found that the periodic forcing of self-sustained oscillations during catalytic oxidation of CO causes harmonic to chaotic response. Recent studies on catalytic CO oxidation have concentrated on a variety of complex spatiotemporal reaction–diffusion patterns due to different resonant periodic forcing [7–9] conditions.

Monte Carlo simulations, using the Ziff–Gulari–Barshad (ZGB) model [10] for CO oxidation on a catalyst surface, have enhanced our understanding of the dynamic response of the system to such a periodic forcing. Lopez et al. reported increase in catalytic activity for the ZGB model when the system is perturbed by a periodic CO partial pressure (P_{CO}) that drives it briefly into the CO poisoned state [11]. In this model, CO partial pressure is a periodic cosine function of time. Subsequently, other workers have investigated the effect of CO pressure as a square wave function of time [12,13] for ZGB models that include CO desorption and diffusion. Recently, we published our results for a modified ZGB model that includes the Eley–Rideal step (ERZGB) with the CO partial pressure perturbed by periodic cosine function of time [14]. Except for ZGB model with CO diffusion [13], in all other cases increase in catalytic activity is observed when compared to systems subjected to steady state CO pressure.

The ZGB model considers the catalytic oxidation of CO on a crystal surface. The reaction is assumed to proceed by the Langmuir–Hinshelwood mechanism [15]:

$$CO(g) + S \rightarrow CO(S) \tag{1}$$

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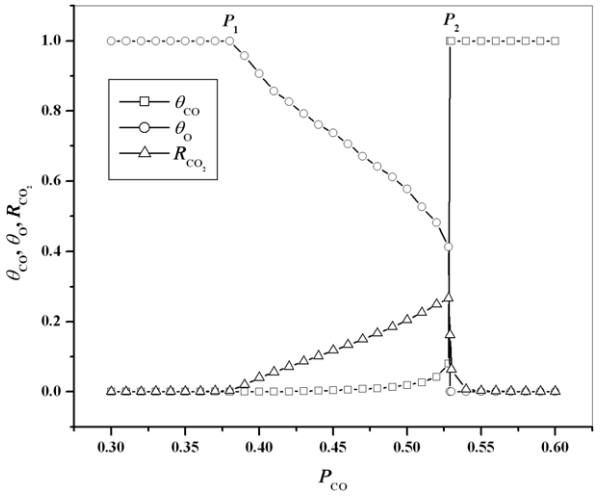

Fig. 1. Plots of R_{CO_2}, θ_{CO} and θ_O against steady state P_{CO} for the ZGB model, showing irreversible phase transitions at P_1 and P_2.

$$O_2(g) + 2S \rightarrow 2O(S) \tag{2}$$

$$CO(S) + O(S) \rightarrow CO_2(g). \tag{3}$$

'S' denotes a vacant site on the surface. The catalytic surface is assumed to be a two-dimensional square lattice with periodic boundary conditions. Reactant molecules CO and O_2 are selected for adsorption on the surface of the catalyst with probabilities P_{CO} and $1-P_{CO}$. These probabilities are proportional to the reactant partial pressures of CO (P_{CO}) and O_2 (P_{O_2}). In case CO molecule is selected, it irreversibly adsorbs onto a randomly chosen vacant site. The oxygen molecule dissociates into atoms and undergoes irreversible adsorption on two adjacent vacant sites on the catalyst surface. No adsorption happens if the site selected is already occupied. Adjacent O and CO molecules react to form CO_2 and desorb leaving behind two empty sites. The model shows two kinetic (or irreversible) phase transitions (Fig. 1). For low values of gas phase partial pressure of CO($P_{CO} < P_1$), the surface is oxygen poisoned, while for higher values of the partial pressure ($P_{CO} > P_2$), the surface is CO poisoned. A reactive phase exists only in a narrow window of CO partial pressures ($P_2 > P_{CO} > P_1$). The phase transition at P_1 is second order, whereas the second transition at P_2 is first order. Experimental studies of CO oxidation on transition metals do not show the second-order transition to an oxygen-poisoned state because oxygen does not impede the adsorption of CO. However, transitions between states of low and high CO coverage have been observed experimentally [16].

When desorption is included in the ZGB model, the discontinuous, non-equilibrium phase transition occurs from a low to a high CO coverage phase. Following earlier literature, we call the ZGB model including desorption as ZGB-k model. The difference between high and low CO coverage phases disappears for desorption rate k above a critical value, k_c (=0.0406) [17,18]. Further, the non-equilibrium phase transition at k_c is in the same universality class as the two-dimensional kinetic Ising model at equilibrium [17]. Recently, the effect of inclusion of the Eley–Rideal step on the discontinuous ZGB-k phase transition has also been studied [19].

Lopez et al. [20] used epidemic simulations for studying ZGB systems with the reactant pressure undergoing square wave oscillations between $P_2 > P_{CO} > P_1$ and $P_{CO} > P_2$. They found such systems get trapped into the poisoned (or absorbing) state, for long enough (square wave) oscillation periods or large amplitudes. Keeping in view that the time scale for poisoning ($P_{CO} > P_2$) is shorter than the time required for depoisoning ($P_{CO} < P_2$), Machado et al. studied the effect of reactant pressure as an asymmetric square wave function of time on the ZGB-k model [12]. For fixed amplitude of oscillation and poisoning time period, Monte Carlo simulations were done at increasing reactive time periods. They found for low values of the desorption rate; at a critical reactive time period value, this driven non-equilibrium system undergoes a second-order phase transition between high CO_2 production and a nonproductive phase. Using finite size scaling analysis, the authors demonstrated that the observed non-equilibrium dynamic phase transition belongs to the two-dimensional Ising model universality class.

In this paper we investigate the effect of the reactant pressure as a cosine function of time on the above-mentioned transition from the reactive to the poisoned state in the ZGB model. In contrast to work of Machado et al. [12], the applied perturbation is symmetric about the ZGB-k discontinuous phase transition. Models with desorption as well as that with no desorption are considered. Monte Carlo simulations are done at different amplitudes of oscillation. At a given desorption rate; the amplitude regime at which transition occurs from a low CO coverage phase to a high CO coverage phase is found and the transition is analyzed. In this study we are interested in ascertaining the nature of this transition. To the best of our knowledge such an analysis has not been done for this model system. Through kinetic Monte Carlo simulations, we determine the nature of the fourth-order cumulants and carry out the finite size scaling analysis of the data at these transitions. It must be mentioned that Lopez et al. also studied the dynamic response of the ZGB model with the reactant