Kinetic Monte Carlo Simulation of the oscillatory catalytic CO oxidation using a modified Ziff-Gulari-Barshad model.

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Abstract. The oxidation of CO on Pt-group metal surfaces has attracted widespread attention since a long time due to its interesting oscillatory kinetics and spatiotemporal behavior. The use of STM in conjunction with other experimental data has confirmed the validity of the surface reconstruction (SR) model under low pressure and the more recent surface oxide (SO) model which is possible under sub-atmospheric pressure conditions [1]. In the SR model the surface is periodically reconstructed below a certain low critical CO-coverage and this reconstruction is lifted above a second, higher critical CO-coverage. Alternatively the SO model proposes periodic switching between a low-reactivity metallic surface and a high-reactivity oxide surface. Here we present an overview of our recent kinetic Monte Carlo (KMC) simulation studies on the oscillatory kinetics of surface catalyzed CO oxidation. Different modifications of the lattice gas Ziff-Gulari-Barshad (ZGB) model have been utilized or proposed for this purpose. First we present the effect of desorption on the ZGB reactive to poisoned irreversible phase transition in the SR model. Next we discuss our recent research on KMC simulation of the SO model. The ZGB framework is utilized to propose a new model incorporating not only the standard Langmuir-Hinshelwood (LH) mechanism, but also introducing the Mars-van Krevelen (MvK) mechanism for the surface oxide phase [5]. Phase diagrams, which are plots between long time averages of various oscillating quantities against the normalized CO pressure, show two or three transitions depending on the CO coverage critical threshold (CT) value beyond which all adsorbed oxygen atoms are converted to surface oxide.

1. Introduction

Reactions rate oscillations have been observed in the catalytic oxidation of CO on Pt-group metal surfaces. Investigations conducted with LEED, STM etc. have shown that at low pressures an adsorbate-induced phase transition, which is controlled by critical adsorbate coverages, may explain such rate oscillations [1-2]. On the other hand, at higher pressures (up to atmospheric) the "oxide model" based on the Mars–van Krevelen (MvK) mechanism has been used to explain rate oscillations [2-3].

The adsorbate-induced transition has been incorporated successfully into the ZGB simulation model by Albano to obtain periodic oscillatory behaviour, caused by transitions of the surface reconstructions coupled with reaction coverages [4-5]. On the other hand Noussiou and Provata in order to account for rate oscillations at atmospheric pressures modified the ZGB simulation model to include an additional mechanistic step of surface oxide formation along with the standard Langmuir-Hinshelwood (LH) mechanism [3].

The present authors have investigated the effect of CO desorption on the first order irreversible phase transition reported by Albano in his surface reconstruction model [6]. The authors have also carried out Monte Carlo simulation of the surface oxide model, referred to earlier, incorporating not

only the standard Langmuir-Hinshelwood (LH) mechanism, but also introducing the Mars-van Krevelen (MvK) mechanism for the surface oxide phase [7].

2. Model and Simulation Procedure

The simulation in either of the models is based on the ZGB algorithm, incorporating the Langmuir-Hinshelwood mechanism for catalytic reaction and has certain common features [8]. The model system is a two-dimensional square lattice of side $L(=100)$. Periodic boundary conditions are employed throughout the simulation. Each simulation starts from an empty lattice. The system evolves in units of Monte Carlo steps. One Monte Carlo step (MCS) of our simulation involves L^2 trials. A trial begins by choosing either CO or O_2 for adsorption attempt on the surface. Reactants CO and O_2 are adsorbed on the surface of the catalyst with normalized probabilities P_{CO} and P_{O_2} (that is $P_{CO} + P_{O_2} = 1$) proportional to the respective reactant partial pressures. If the trial selects a CO molecule from the gas phase then it may adsorb onto a vacant lattice site. On the other hand if an oxygen molecule is selected, it first dissociates into two atoms and then may get adsorbed onto two neighboring vacant sites. As per the LH mechanism, if adjacent sites are occupied by O and CO molecules, then they react to form CO_2 leaving behind two empty sites. The reaction scheme followed in the oxide model is as given below:

$$CO\,(g) + s \rightarrow CO_{ads} \qquad (1) \qquad\qquad O_2\,(g) + 2s \rightarrow 2O_{ads} \qquad\qquad (2)$$

$$O_{ads} \rightarrow ox \text{ under the condition } [\Theta_{O(ads)} > CT] \quad (3) \quad CO_{ads} + O_{ads} \rightarrow CO_2\,(g) + 2s \qquad (4)$$

$$CO\,(g) + ox \rightarrow CO_2\,(g) + s \quad (5) \qquad\qquad CO_{ads} + ox \rightarrow CO_2\,(g) + 2s \qquad\qquad (6)$$

Here the (ads) and (g) indices denote the adsorbed and gaseous species, respectively, while 's' and 'ox' denote the vacant lattice and oxide sites, respectively. In the SR model the reaction scheme consists of steps (1), (2) and (4) only.

The critical threshold value in the SO model is defined as the adsorbed oxygen coverage above which all adsorbed oxygen atoms convert into surface oxide sites (step 3). After the formation of the above oxide sites the production of CO_2 may take place by any of the three mechanisms (steps (4)-(6)), including the Mars-van Krevelen (MvK) mechanism (step 5). In the SR model once CO coverage Θ_{CO} exceeds ≥ 0.485, all sites in the model catalyst surface transform to the non-reconstructed phase. The sticking coefficient of oxygen becomes 1, the normal ZGB algorithm is initiated and Θ_{CO} decreases because of reactions between neighboring adsorbed CO and O. Whenever the condition $\Theta_{CO} \leq 0.1$ is achieved, all sites in the system are assumed to transform to the reconstructed phase. Thereafter, as mentioned earlier, only CO adsorption occurs at a rate proportional to P_{CO} until the condition $\Theta_{CO} \geq 0.485$ is achieved again. This completes one cycle of the adsorbate coverage induced transition.

3. Results and Discussion
3.1. Surface reconstruction Model

In order to understand the effect of desorption on this discontinuous transition, we now present results for systems with k > 0 [6]. It is found that for smaller sizes (L=60) with increase in k

there is broadening in the bimodal distribution to such an extent, that for k = 0.04, a unimodal distribution sweeps across smoothly from the reactive side to the partially poisoned side as P_{CO} is increased (Fig 1). Focusing only on the distribution at the finite size coexistence point $P_{CO}^c(L)$ for systems at different desorption rates, it is observed that for a given large enough system size (L=230), the transition retains the bimodal distribution character (Fig. 2) even at high desorption rates (k=0.04). This suggests that the phase transition remains first-order and only becomes weaker with increase in desorption rates. For a given desorption rate the strength of first-order phase transition increases with size.
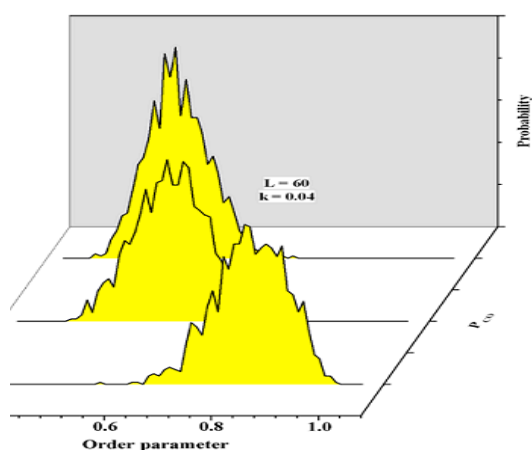

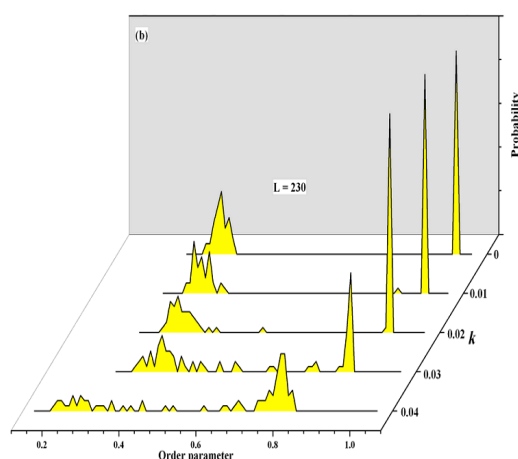Fig 1 Order parameter probability distribution $\overline{\Theta}_{CO}$ for L=60 and desorption rate k = 0.04

Fig 2 Order parameter probability distribution $\overline{\Theta}_{CO}$ for L= 230 at increasing desorption rates

3.2. Oxide Model

The phase diagram obtained in our "oxide" model, which includes the Mars-van Krevelen (MvK) mechanism, is shown in figure 3 for critical threshold (CT) = 0.4. It is observed from the curve that the reactive state undergoes a continuous transition from one reactive state to another at T_1. Above T_1 the nature of rate oscillations changes gradually with P_{CO}. The continuous transition (T_1) in terms of $\overline{\Theta}_{O(ad)}$ is indicative of the change in mechanism of CO oxidation. In this regime the mechanism of CO oxidation oscillates between the MvK + LH mechanism exhibited by the oxide phase and the LH only mechanism of adsorbed CO with adsorbed oxygen. It is found that for $CT \geq 0.5$ the phase diagram shows another transition T_2 (before T_3) where $\overline{\Theta}_{ox}$ decreases to zero (ig 4). If $\overline{\Theta}_{ox}$ is considered the order parameter then T_2 appears to be a continuous transition. With increase in CT, the maximum P_{CO} at which the oxide phase transition (T_2) can happen, decreases, that is T_2 shifts leftwards with CT. The change in nature of CO_2 rate oscillations with increase in P_{CO} at CT = 0.55 is depicted in figure 5. With increase in CT the transition T_2 shifts to the left, therefore the distance between P_{CO} = 0.45 and T_2 decreases. In other words, with increase in CT, at a given P_{CO} value the probability of surface oxide formation decreases. We observe from the figure that the amplitude and

period of the rate oscillations increase as P_{CO} is increased gradually from 0.45 to 0.5 and the rate oscillations die out or become negligible at P_{CO} = 0.52, since this is above the transition T$_2$.
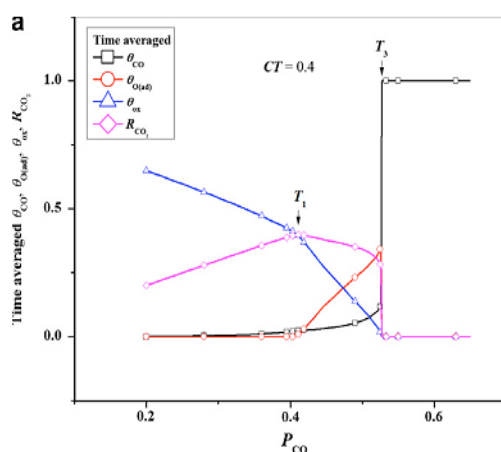

Fig 3 Phase diagram showing plots of $\overline{R_{CO_2}}$, $\overline{\Theta_{CO}}$, $\overline{\Theta_{O_2(ad)}}$, $\overline{\Theta_{Ox}}$ vs. P_{CO} at $CT = 0.4$
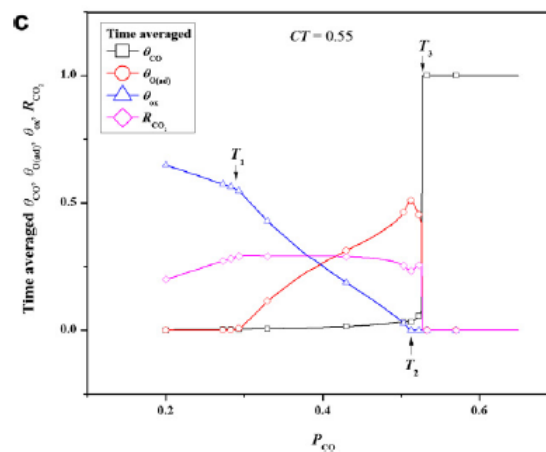

Fig 4 Phase diagram showing plots of $\overline{R_{CO_2}}$, $\overline{\Theta_{CO}}$, $\overline{\Theta_{O_2(ad)}}$, $\overline{\Theta_{Ox}}$ vs. P_{CO} at $CT = 0.55$
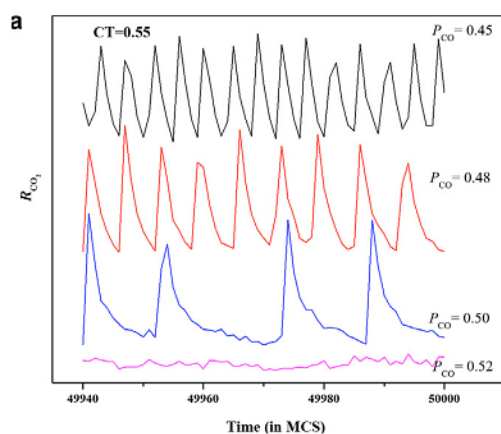

Fig 5. Change in R_{CO_2} oscillatory behaviour with increase in P_{CO} at $CT = 0.55$

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