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STUDY OF THE KINETIC PHASE TRANSITIONS IN THE CATALYTIC OXIDATION OF CARBON MONOXIDE

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ABSTRACT

Catalytic oxidation of carbon monoxide on a platinum (111)-surface was simulated by the Monte Carlo technique using a model based on the simplified one proposed by Ziff, Gulari and Barshad (ZGB). Our simulation which will take into account desorption and diffusion among other processes such as adsorption and reactions, has given an extend overview to physical processes on the oxidation kinetics of carbon monoxide. A plot of the average coverage of O, CO and the CO_2 production rate as a function of the normalized CO partial pressure (p_{co}), shows clearly two kinetic phase transitions, at $p_{co} = y_1$ and $p_{co}= y_2$ for a steady state configuration. For $y_1<p_{co}<y_2$ a reactive steady state (continuous CO_2 production) is found. Outside of the interval, the only steady state is characterized by a pure CO or O poisoned surface.

INTRODUCTION

Oxidation of CO is one of the most extensively studied heterogeneous catalysis reactions, being important in automobile-emission control [1-13]. This reaction is also interesting because serves as a pattern for many important industrial oxidation processes heterogeneously catalyzed by transition metals. The most known computer simulation model of this reaction was presented by Ziff et al [1] and it is based on the Langmuir-Hinshelwood mechanism [14]. ZGB-model reproduces some of the main features showed by the experiments: i) a reactive steady-state region between CO partial pressures $y_1=P_{CO}=0.39$ and $y_2=P_{CO}=0.53$, and ii) outside of the interval (y_1, y_2), the steady state is characterized by the poisoning of the catalyst with O ($P_{CO}<y_1$) and CO ($P_{CO}>y_2$). At $P_{CO}=0.39$ a second order phase transition of the CO_2 rate is clearly observed. If P_{CO} increases a first order kinetic phase transition when $P_{CO}=y_2$ can also be seen. In this work another surface processes such as diffusion and desorption was taken into account, and the kinematics of the reaction was studied through Monte-Carlo simulation via a extended-ZGB model.

THE MODEL

In the Monte Carlo simulation, catalyst surface is replaced by a two dimensional lattice of active sites. Gas phase is assumed to be composed by CO and O_2 and total pressure is normalized to unity. P_{CO} and P_{O2} represent the partial pressure of CO and O_2, respectively. Because of on Pt surfaces the O_2 molecule adsorbs dissociatively, two empty nearest neighbor sites on the lattice are required for O_2 adsorption. On the contrary, only a empty lattice site is necessary for CO adsorption.

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Simulation begins with a randomly selected gas-phase molecule (CO or O_2) that interacts with the surface. P_{CO} and P_{O2} are the probabilities for a CO or O_2 molecule to be selected. One or two nearest neighbor sites in the lattice are randomly chosen depending on if the selected molecule is CO or O_2. Molecule adsorbs if the sites are empty. Otherwise, it is reflected and the adsorption step ends. When a molecule adsorbs on a surface site, the corresponding four nearest neighbors are randomly checked for reactants of opposite type. Reaction occurs with a probability P_R which is assumed to be greater than in gas phase. If reaction is successful, the formed CO_2 molecule desorbs immediately and both sites on the lattice become empty.

Adsorption step is usually reversible. However, desorption of atomic oxygen is not considered because this process is thermodynamically unfavorable. In this model CO can be removed from the surface and return to the gas phase with a probability P_{DS}. The number of molecules that will be removed from the surface is determined using a binomial distribution.

Surface diffusion is a strongly surface temperature depend process. According to experimental evidence, in this model only the CO phase is considered significatively mobile. CO diffusion probability is P_{DF}. Like in the previous step, a binomial distribution defines the number of randomly chosen CO molecules to be moved. After each cycle, the nearest neighbor sites are checked for the possibility of the reaction.

To determine the convergence to a steady state, the mean and the variance of CO_2 reaction rate (R), and both CO and oxygen coverage (θ_{CO}, θ_O) are calculated. In this work a 100x100 lattice was used. The simulation was allowed to continue until all observables, θ_{CO}, θ_O had variances less than $1x10^{-3}$.

RESULTS AND DISCUSIÓN

Figures 1 and 2 show results of the simulations using the extended-ZGB model described in the previous section, i.e., taking into account both, desorption and diffusion of randomly selected CO molecules. In this figures the variation of CO_2 rate , θ_{CO} and θ_O as a function of P_{CO} are shown. Pronounced differences with the results obtained using the ZGB model can easily observed and will be described in the next section . Our results also reproduces the general behavior of the reaction experimentally observed on Pt(111) surfaces [2].

DESORPTION

The effect of non zero P_{DS} on the CO_2 production rate are shown in figure 1. Values of P_{DS} in the range 0 to 1 were take into account. In all studied cases the first phase transition begins at y_I=0.39. However, as P_{DS} increases, the maximum of CO_2 rate shifts to higher P_{CO} and at this P_{CO} value, the phase transition changes from a first order transition to a second order one.

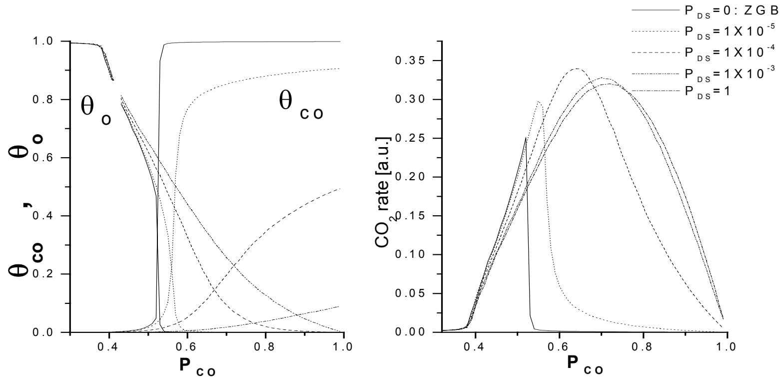

Figure No. 1.Simulation including desorption.The left graph indicate the CO and O surface coverage. The values of PDS are:0,1x10^{-5} 1x10^{-4}, 1x10^{-3} and 1.

Other results not pointed out in this graph, show that with P_{DF} values over 0.01 the curve of reaction is almost the same. The value of the maximum increases with P_{DS} until P_{DS}=0.0001, after which the maximum downs to reach a constant value close to 0.32.

The rate reaction, including a CO desorption probability, causes empty sites within the CO clusters, then, an increase in P_{DS} lowers the CO surface coverage. Also, to compensate for the desorption, higher CO concentrations are required, and phase diagram shows larger width reactive-steady-state regions. The rate reaction maximum does not increase continuously with P_{DS}, because the number of CO molecules on surface with a reaction probability is reduced. This theoretical results are in agreement to experimental behaviour observed with Pt(111).

DIFFUSION

Figure 2 shows the CO_2 reaction rate for different probabilities of CO diffusion, P_{DF}. It is observed that an increase in P_{DF} does not affect the overall qualitative behavior of the phase diagram . Two transitions points, y_1 and y_2 between which the system reach a steady –reactive-state with continuous production of CO_2 is also observed. Critical CO pressure y_2 slightly changes, while y_1 does not. Nature of this transitions are second and first order, respectively. Rate production of CO_2 increases with diffusion. In this case, poisoning of the surface with CO require a higher CO concentrations. CO_2 rate is proportional to P_{CO} until a sharp (first order) transition occurs at the maximum reaction rate. The reaction rate slope is slightly lower if P_{DF} is higher.

CONCLUSIONS

The extended ZGB-model described in this work can be used to reproduce the qualitative experimental results on the catalytic oxidation of CO. The simulations allows us to understand the influence of the, both, CO desorption and diffusion rates on the physical behavior of the catalytic reaction studied.

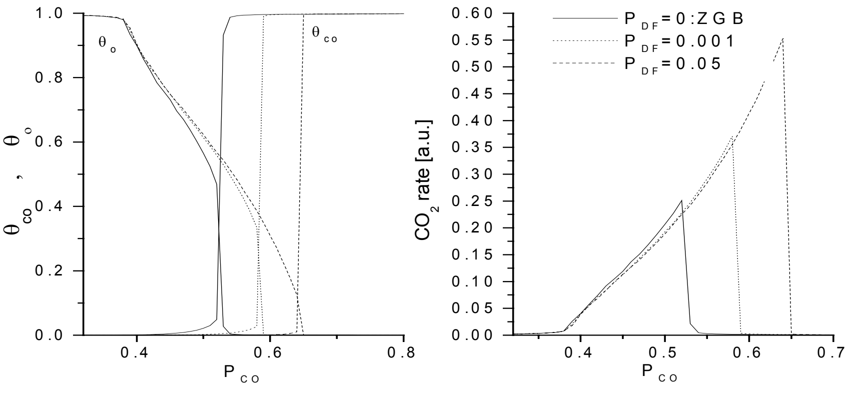

Figure2. Simulation including diffusion.The left graph indicate the CO and O surface coverage.The values of PDS are:0, 1x10^{-3}, and 5 x10^{-2}

Introduction of desorption and diffusion in ZGB model adds some interesting features in the phase diagram. Width of the reactive region increases with P_{DF} or P_{DS}. A noticeable increment in CO_2 reaction rate is observed when P_{DF} increases. Non zero values of P_{DS} causes a slightly increase in CO_2 rate and destroy the first order transition observed in the ZGB model.

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