ENHANCED REACTION RATE IN HETEROGENEOUSLY CATALYZED CO OXIDATION UNDER OSCILLATING CO PRESSURE

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Introduction

Heterogeneously catalyzed oxidation of CO to CO_2 is important in a number of industrial and scientific applications. Because of its simplicity, it is also important as a benchmark model system. In this project we used kinetic Monte Carlo simulations to study the Ziff-Gulari-Barshad (ZGB) model with CO desorption. This model describes the oxidation process as a Langmuir-Hinschelwood process,

$$\begin{aligned} &CO(g)+v \leftrightarrow CO(a) \\ O_2(g) + 2v &\rightarrow 2O(a) \\ &CO(a) + O(a) \rightarrow CO_2(g) + 2v, \end{aligned} \qquad (1)$$

where g stands for gaseous, a for adsorbed, and v for a vacant surface site. As a function of the partial CO pressure *y*, the model has two nonequilibrium phase transitions [1]. The first separates a phase of high O coverage at low *y* from a phase in which both reactants are present on the surface at intermediate *y*. The second transition separates the intermediate-*y* phase from an oxygen-poisoned phase, in which the surface is totally covered in O and the oxidation reaction is consequently blocked. When CO can also desorb from the surface, the oxygen-poisoned phase can be decontaminated by decreasing *y* back into the intermediate-*y* region. For sufficiently high rate of CO desorption, the line of phase transitions terminates in a nonequilibrium critical point [2]. In the present study we subjected the system to periodically oscillating CO pressure.

Results and Discussion

The periodically oscillating CO pressure was found to enhance the CO_2 production rate, compared to the maximum rate attainable at constant pressure [3-5]. The oscillating pressure and the corresponding oxidation rate are shown in Fig. 1.

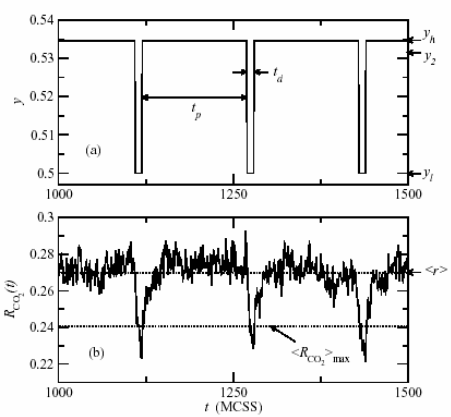

Figure 1. (a) The periodically oscillating partial CO pressure *y*. (b) The CO_2 production rate under oscillating CO pressure and its average value (upper dashed horizontal line), compared with the maximum value attainable under constant *y* (lower horizontal line).

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References

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