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LETTER TO THE EDITOR

Time evolution of the catalytic oxidation of carbon monoxide on a disordered substratum

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Abstract. The time evolution of the reactant concentrations, the rate of production and the concentration of vacancies around islands of the minority species, in a model for the catalytic oxidation of carbon monoxide, is studied on percolation clusters by means of Monte Carlo simulations and scaling arguments. The model exhibits two kinetic transitions and the relevant exponents for the time evolution of the above-mentioned quantities are evaluated at criticality. The influence of the fractal substratum on the behaviour of the reaction is discussed and compared with reported results for homogeneous media.

The heterogeneously catalysed oxidation of carbon monoxide is one of the most thoroughly studied reactions [1-8]. It has been established that the reaction follows the so called Langmuir-Hinshelwood mechanism, that is



where (g), (ad) and (*) denote the gas and adsorbed phases and a surface site, respectively. Recently, Ziff, Gulari and Barshad (zGB) [2] have proposed a simple model for the reaction described by (1) on the square lattice. Details of the zGB model have already been published [2-4], so we will only briefly describe their main features.

It is assumed that the surface is in contact with a reservoir containing CO and O₂, where p_{CO} is the mole fraction of CO in the reservoir. So, a molecule striking the surface could be an O₂ with probability $(1 - p_{\text{CO}})$ or a CO with probability p_{CO} . Oxygen adsorption requires two adjacent (nearest-neighbour) sites (1b) while CO adsorption needs a single site (1a). Nearest-neighbour O and CO species react to produce CO₂ which immediately desorbs leaving two empty sites on the surface (1c). During a Monte Carlo time step each site of the lattice is visited once on average. It is interesting to note that this simple model with a single parameter, i.e. p_{CO} , exhibits two kinetic (irreversible) phase transitions from a steady state with CO₂ production within the range $p_{1\text{CO}} < p_{\text{CO}} < p_{2\text{CO}}$, to off-equilibrium poisoned states with CO (for $p_{\text{CO}} \geq p_{2\text{CO}}$) and oxygen (for $p_{\text{CO}} \leq p_{1\text{CO}}$), respectively. The transition at $p_{1\text{CO}} \approx 0.389$ is of second order while the transition at $p_{2\text{CO}} \approx 0.525$ is of first order. The zGB model, originally studied on the square lattice [2], has also been simulated on hexagonal lattice and on

narrow strips by Meakin *et al* [3]. Very recently, some aspects of the time evolution of the ZGB model on the square lattice close to one critical point (p_{2CO}) have been studied by Sadiq *et al* [4]. The aim of this work is to report the study of the time evolution of the reaction on a fractal substratum. In fact, typical catalysts are constituted by small (fractal [9]) metallic clusters supported on inert (fractal [10]) substrata. Furthermore, in a recent work we have demonstrated that the behaviour of the reaction is quite different on a fractal than on a homogeneous substratum [7]. Comparing results obtained on the square lattice [2-4] and on incipient percolation clusters (IPC_s) [7], the following differences may be stressed.

(i) For IPC_s on the square lattice of size $L \times L$ with periodic boundary conditions and on the limit $L \rightarrow \infty$, a steady-state regime with CO₂ production is also found within the range $p_{1CO}^* < p_{CO} < p_{2CO}^*$ with $p_{1CO} > p_{1CO}^* = 0.314$ and $p_{2CO} > p_{2CO}^* = 0.408$. Both transitions are of second order.

(ii) The rate of CO₂ production (R_{CO_2}) exhibits a maximum close to the centre of the window, i.e. for $p_{CO}^* \approx p_{1CO}^* + p_{2CO}^*/2$, in contrast with the monotonic increment abruptly interrupted at p_{2CO} as observed on the square lattice when increasing p_{CO} from p_{1CO} to p_{2CO} .

(iii) Branches and loops of the IPC_s favour the growth of rather stable O and CO islands. So the reaction takes place at the empty sites of the border between islands of different species. In contrast, on the square lattice, CO islands only grow when very close to p_{2CO} .

Let us now discuss the time evolution of the reaction on IPC_s at criticality. Since simulations start with uncovered samples a transient period always precedes the stationary regime or the poisoned states. Let $\xi_{CO}(\xi_0)$ be the typical size of CO (O) islands on the IPC_s. At criticality we conjectured that

$$\xi_{CO} \propto t^{\alpha_{CO}} \quad p_{CO} = p_{2CO}^* \setminus L \rightarrow \infty \quad (2a)$$

$$\xi_0 \propto t^{\alpha_0} \quad p_{CO} = p_{1CO}^* \setminus L \rightarrow \infty \quad (2b)$$

where the exponents α_{CO} and α_0 have to be determined. Poisoning of IPC_s on finite lattice would occur at L -dependent times when the typical island size of the adsorbate matches the lattice size, i.e. roughly for

$$\xi_{CO} \approx L \approx t_2^{\alpha_{CO}}(L) \quad (3a)$$

$$\xi_0 \approx L \approx t_1^{\alpha_0}(L). \quad (3b)$$

Figure 1 shows the distribution of CO poisoning events against time for lattices of two different size. The distributions clearly exhibit finite size effects in both the time required for the onset of poisoning and the position of the maxima. A log-log plot of L against $t_2(L)$ (figure 2) allows us to roughly estimate $\alpha_{CO} \approx 0.5$. A more accurate determination of the exponents can be made using phenomenological scaling arguments. Let us analyse the behaviour of the quantities $\phi_{CO} = 1 - \theta_{CO}$ and $\phi_0 = 1 - \theta_0$, where θ_{CO} and θ_0 are the CO and O coverages of the IPC_s, respectively. One has that $\phi_{CO} \rightarrow 0$ for $t \rightarrow \infty$, $p_{CO} = p_{2CO}^*$, $L \rightarrow \infty$ and similarly for ϕ_0 . On finite lattices right at criticality one expects the following scaling approach to hold

$$\phi_{CO} = \phi_{CO}(L, \xi_{CO}) = L^D \tilde{\phi}_{CO}(\xi_{CO}/L) = L^D \tilde{\phi}_{CO}(t^{\alpha_{CO}}/L) \quad (4)$$

where $\tilde{\phi}_{CO}$ and $\tilde{\phi}_0$ are suitable scaling functions and (2a) has been used to obtain the final expression. Note that D is the exponent which dominates the critical behaviour of ϕ_{CO} . The same argument can also be applied to ϕ_0 . Figure 3 shows log-log plots

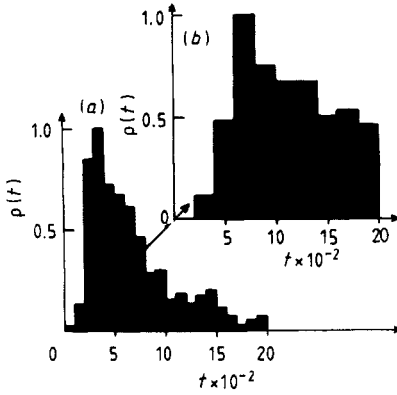


Figure 1. The normalised distribution of CO poisoning events $\{\rho(t)\}$ as a function of the Monte Carlo time, for $p_{CO} = p_{2CO}^*$ and lattices of size (a) $L = 40$ and (b) $L = 80$.

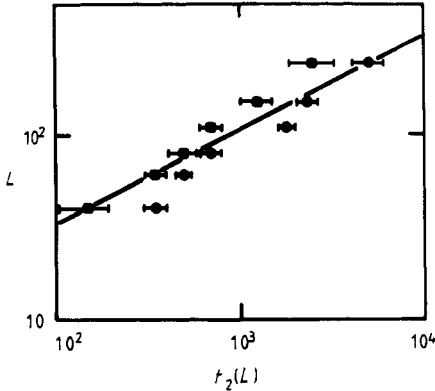


Figure 2. Log-log plot of L against $t_2(L)$ for $p_{CO} = p_{2CO}^*$ (see (3a)). \blacksquare and \bullet correspond to the onset of poisoning and the maximum of the poisoning distribution $\rho(t)$, respectively (see figure 1). The straight line with slope $\alpha_{CO} = 0.5$ is drawn for comparison.

of $\phi_i L^D$ against α_i/L ($i = O, CO$) assuming $\alpha_{CO} = 0.5$, $\alpha_O = 0.40$ and $D = 91/48 = 1.90$, i.e. the fractal dimension of the IPC since one expects the behaviour $\theta_{CO} \sim \xi_{CO}^D(p_{CO} \rightarrow p_{2CO}^*)$ and $\theta_O \sim \xi_O^D(p_{CO} \rightarrow p_{iCO}^*)$ to hold. The excellent collapsing data observed suggest that the scaling hypothesis should be correct.

Results for the time evolution of the rate of CO_2 production (R_{CO_2}) at criticality are plotted in figure 4 against $(1 - \theta_T)$, with $\theta_T = \theta_O + \theta_{CO}$. The obtained straight lines for $2 \times 10^1 \leq t \leq 5 \times 10^3$ strongly suggest that

$$R_{CO_2} \propto (1 - \theta_O - \theta_{CO}) \tag{5}$$

in contrast to mean field predictions for homogeneous substrata, that is $R \propto \theta_O \theta_{CO}$ if both absorbates do not form islands [5, 6], $R \propto \theta_O \sqrt{\theta_{CO}}$ if only CO forms islands [5, 6], and corrected versions of these equations [6]. It should be stressed that (5) not only holds during the transient period at criticality but also in the steady-state regime. Therefore, on IPCs, R_{CO_2} is proportional to the concentration of empty sites of the fractal and the reaction takes place mainly in the border between islands of CO and O. These islands are rather stable because, due to the heterogeneity of the substratum,

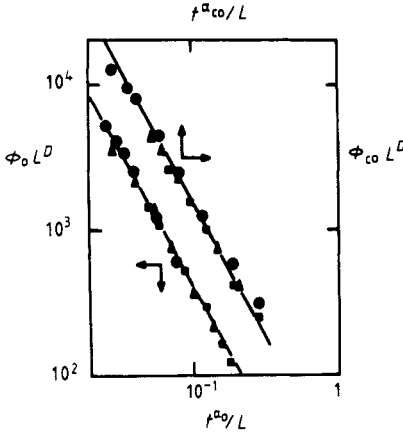


Figure 3. Log-log plots of $\phi_O L^D$ against t^{α_O}/L with $\alpha_O = 0.4$ and $\phi_{CO} L^D$ against $t^{\alpha_{CO}}/L$ with $\alpha_{CO} = 0.5$. The straight lines with slope $D = -1.90$ are drawn for comparison. ● $L = 240$, ▲ $L = 150$, and ■ $L = 105$.

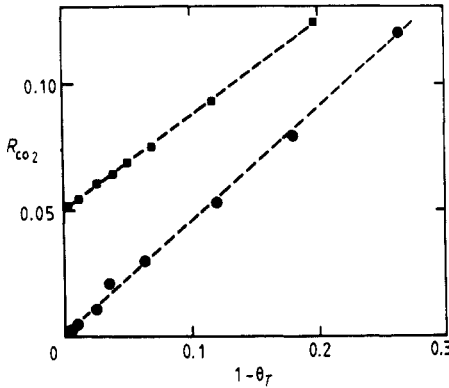


Figure 4. Plots of the rate of CO_2 production (R_{CO_2}) against $1 - \theta_T$ during the transient period at criticality, $L = 240$. (●) $p_{CO} = p_{2CO}^*$ and (■) $p_{CO} = p_{1CO}^*$. Full squares are shifted up 0.05 units for the sake of clarity.

they are mostly surrounded by inactive sites of the lattice, i.e. those sites which do not belong to the IPCs.

For a simpler catalytic reaction in which both species are monoatomic (A, B), Sadiq *et al* [11] have shown that the average number of vacancies neighbouring the adsorbed atoms of the minority species of type A denoted by $\bar{b}(\theta_A)$ can be expressed as $\bar{b}(\theta_A) \sim \theta_A^\delta$, $\delta = 1$. Very recently, Sadiq *et al* [4] have reported that this conjecture may also hold for the ZGB model on the square lattice close to p_{2CO} , after replacing A by O and B by CO . In fact, they obtained $\delta \approx 1$ for $p_{2CO} \leq p_{CO} \leq 0.532$ [4]. We have tested the conjecture on IPCs at criticality assuming $\bar{b}(\theta_A) \sim (1 - \theta_T)$ as shown in figure 5. For $p_{CO} = p_{2CO}^*$ a straight line with slope $\delta \approx 1$ is obtained within the whole time interval ($2 \times 10^1 \leq t \leq 4 \times 10^3$). On the other hand, for $p_{CO} = p_{1CO}^*$ one gets $\delta \approx 1.5$. The value of δ in the square lattice for $p_{CO} = p_{1CO}$ is not available for comparison.

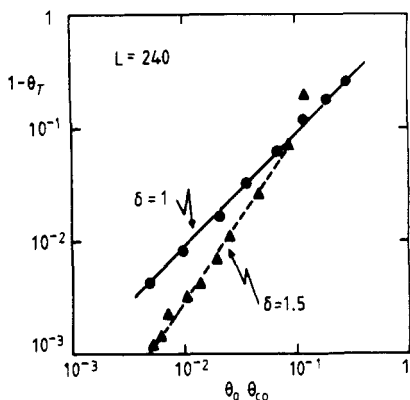


Figure 5. Average number of empty sites on the IPC plotted against the coverage of the minority species during the transient period: θ_{CO} for $p_{CO} = p_{CO}^*$ (\blacktriangle) and θ_O for $p_{CO} = p_{CO}^*$ (\bullet).

Summing up, using the ZGB model for the catalytic oxidation of CO on IPCs, we have studied and evaluated the relevant exponents for the time evolution at criticality of:

- (i) the convergence with the reactants;
- (ii) the rate of CO_2 production and
- (iii) the concentration of vacancies surrounding islands of the minority species.

We hope that this study will contribute to the understanding of poisoning transitions observed in real systems [3, 8].

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