LETTER TO THE EDITOR

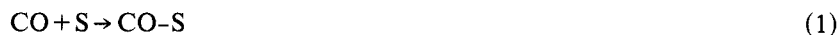# Time evolution of a catalytic surface reaction: oxidation of carbon monoxide

Khwaja Yaldram and A Sadiq

Pakistan Institute of Nuclear Science and Technology, P O Nilore, Islamabad, Pakistan

Abstract. An irreversible kinetic surface reaction based upon the oxidation of carbon monoxide exhibits both a second-order and a first-order phase transition. We study the time evolution of this reaction near and slightly above the first-order transition by Monte Carlo simulation. It is seen that oxygen concentration, for low coverages, decays exponentially with time. Near the transition the average relaxation time is found to diverge as $\tau_{CO} \propto |X_2 - X_{CO}|^\gamma$ with $\gamma = 3.54$. Here X_{CO} is the composition of carbon monoxide in the gas phase and X_2 is the value of this concentration at the transition point.

Heterogeneous catalytic reactions or reactions in which a surface plays the role of a catalyst are still not clearly understood. The reactions are irreversible and show a complicated behaviour, so their theoretical understanding is still in its infancy. It is now fairly well established that the reaction proceeds according to the following three steps [1]:

$$CO + S \rightarrow CO\text{-}S \tag{1}$$

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

$$CO\text{-}S + O\text{-}S \rightarrow CO_2 \text{ (desorbed)} + 2S \tag{3}$$

where S denotes a surface site. The oxygen dissociates on adsorption and its atoms occupy two surface sites. The carbon monoxide requires a single site for adsorption. Finally CO_2 desorbs on formation leaving behind two vacant sites.

Ziff, Gulari and Barshad [2] proposed a simple irreversible reaction model, which leaves out many important steps of the actual reaction, but is still found to exhibit interesting steady-state behaviour and two types of transitions, which occur in real systems as well. In this model the surface is represented by a square lattice. A reservoir containing oxygen and carbon monoxide is assumed to be in contact with this lattice. A choice of oxygen or carbon monoxide is made and the molecule so chosen is allowed to impinge on a randomly selected site. Carbon monoxide requires a single vacant site, while oxygen needs two adjacent sites for adsorption (steps (1) and (2)). An oxygen atom reacts with a carbon monoxide molecule to form carbon dioxide only when the two are closest neighbours. The carbon dioxide gets desorbed leaving behind two vacant sites (step (3)). In terms of X_{CO} which represents the concentration of carbon monoxide in the reservoir, the steady state exists for $X_1 \leq X_{CO} \leq X_2$. Below X_1 the surface gets poisoned with oxygen and above X_2 with carbon monoxide.

For values of X_{CO} close to but above X_1, Meakin and Scalapino [3] obtained approximate values for the exponents which describe the dependence of the steady-state densities of carbon monoxide and oxygen on $(X_{CO} - X_1)$. The values they report for carbon monoxide and oxygen are 0.69 and 0.61 respectively. Recently Sadiq and Khwaja [4] examined the time evolution of a similar but simpler catalytic reaction in which the two species are both monatomic (A, B). In such a situation the only reactive steady state exists for $X_A = X_B = 0.5$, where X_A and X_B are the compositions of the two monatomic species A and B in the reservoir. An analytical relationship for the decay of the minority species was derived. It was shown that in the mean-field approximation $\theta_A(t)$ decays exponentially with time as

$$\theta_A(t) \propto \exp[-(X_B - X_A)]t \qquad (4)$$

where $\theta_A(t)$ is the coverage of the minority species near the critical transition. In deriving the above expression it was assumed that the average cluster size is $\bar{S}(\theta_A)$ and consequently the average number of vacancies neighbouring the adsorbed A atoms $\bar{b}(\theta_A)$ can be expressed as

$$\bar{b}(\theta_A) \propto \theta^\delta. \qquad (5)$$

Computer simulation studies gave $\delta = 1$ which was consistent with expression (4).

In the present letter we have extended the above treatment to a more realistic system consisting of oxygen and carbon monoxide. The arguments presented for the derivation of expressions (4) and (5) still hold for the present case. A simple replacement of A by O and B by CO in the two expressions is enough to give an expression for the decay of the minority oxygen atoms (O) for X_{CO} slightly greater than X_2. Simulations were carried out on a (40×40) square lattice. Starting with an initially
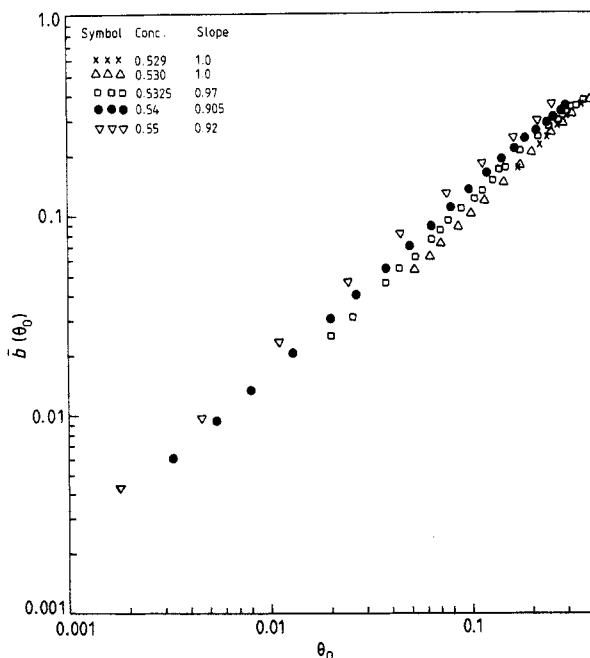

Figure 1. Average number of vacancies $b(\theta_O)$ surrounding the adsorbed oxygen atoms plotted against the coverage θ_O of the minority oxygen species on a log-log scale for different concentrations.

empty lattice and using periodic boundary conditions the average number of vacancies surrounding the oxygen atoms $b(\theta_0)$ was determined as a function of the oxygen coverage θ_0. The results for X_{CO} slightly above X_2 are shown in figure 1. The value of δ, determined by the slope of the curves, is very close to 1 and in fact becomes 1 for $X_2 \lesssim X_{CO} \lesssim 0.532$. This is true for oxygen coverages $\theta_0 \lesssim 0.4$. To see the effect of higher coverages we started with a lattice which is initially 75% covered with oxygen atoms. It is found that $b(\theta_0)$ reaches a maximum and then decays with further increase in θ_0. The results for the oxygen coverage θ_O plotted in figure 2 as a function of time (expressed in Monte Carlo cycles) confirms the exponential decay of the coverage for intermediate and long times. As X_{CO} tends towards X_2 the approach towards the steady state ($\theta_O = 0$) clearly becomes slower. The inverse of the slopes of these curves gives us the relaxation time. To see the behaviour of the relaxation time near the poisoning transition, it is important to obtain an exact value for the critical composition X_2. In figure 3 we have plotted the reciprocal of the relaxation time against X_{CO}. From this figure as well as the fact that runs taken at $X_{CO} = 0.526$ invariably lead to a poisoned state, while for $X_{CO} = 0.525$ the steady state is a non-poisoned one, we conclude that the critical value of X_{CO} for which the transition takes place is 0.5255 ± 0.0005. Ziff *et al* [2] working with a (128×256) lattice quote a value of 0.525 ± 0.0001, while Meakin *et al* [3] quote a value of 0.5277 ± 0.0002 for a (512×512) lattice. Our earlier experience with the (A, B) system [4] showed that the critical concentration at which the transition takes place is not affected by increasing the size of the lattice from (40×40) to (80×80). We have therefore restricted ourselves to (40×40) lattices, in
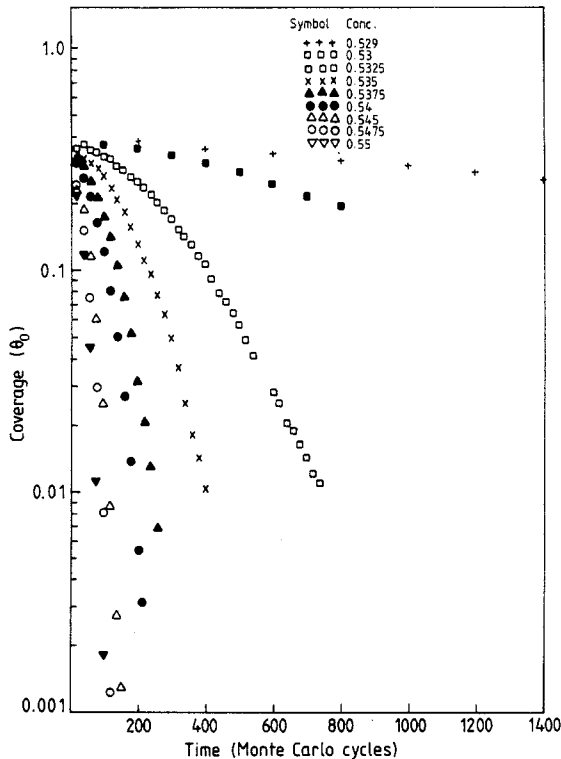

Figure 2. Oxygen coverage θ_O plotted against time on a semilog scale for different concentrations of CO.
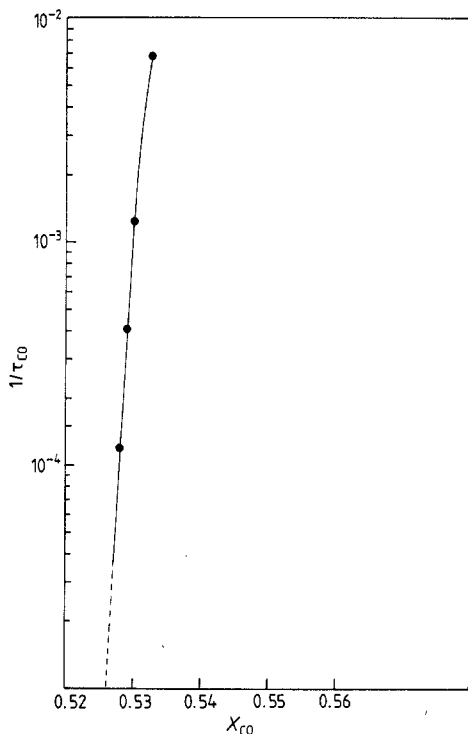
Figure 3. Inverse of the relaxation time plotted against the CO concentration. The line is drawn as an aid to the eye.

order to get reasonable statistics. We expect that increasing the size of the lattice will not affect the results in any appreciable way.

Finally in figure 4 we have plotted the relaxation times as a function of $|X_2 - X_{CO}|$. Close enough to the poisoning transition we get a straight line with a slope of 3.54. This is consistent with a power-law behaviour

$$\tau_{CO} \propto 1/|X_{2-}X_{CO}|^\gamma \qquad \text{where} \qquad \gamma = 3.54.$$

It is seen that γ depends on the critical concentration X_2. Within the quoted error in X_2, the power law holds, with γ increasing with the increase in X_2.

The (CO, O_2) system shows the same general behaviour near the transition X_2 as that exhibited by the (A, B) system [4]. The decay of the oxygen coverage for X_{CO} slightly greater than X_2 follows an exponential behaviour. The relaxation time for this decay slows down as we approach the critical transition X_2. The dependence of the relaxation time on the difference of the composition $|X_{CO} - X_2|$ follows a power-law behaviour, with an exponent which is much higher for the (CO, O_2) system ($\gamma = 3.54$) as compared with the (A, B) system ($\gamma = 1.3$). This slowing down of the system's approach to equilibrium is a consequence of the two-site rule for the adsorption of oxygen, which requires that oxygen only be adsorbed when two adjacent sites are available to it. Although each successful attempt for oxygen adsorption means that two oxygen atoms are accommodated on the surface, with time the availability of two empty adjacent sites decreases. The fluctuations take long to die off, giving longer relaxation times.
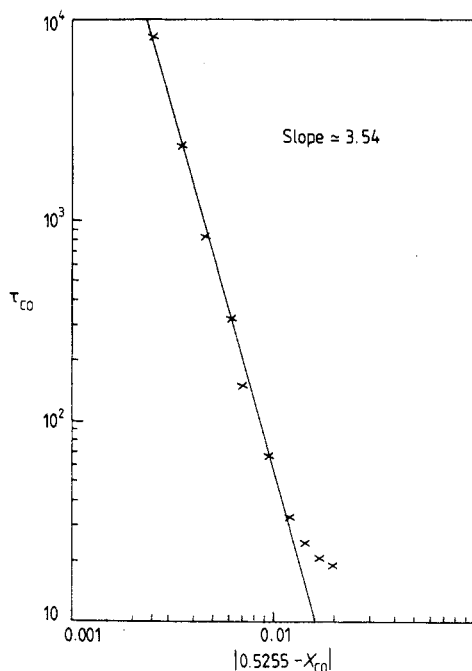
Figure 4. Relaxation time τ_{CO} plotted against the difference in composition $|X_2 - X_{CO}|$.

Meakin *et al* [3] in a similar work on the (CO, O_2) system investigated the behaviour of the system near the other transition at X_1. The transition at X_1 is continuous and of second order. They studied the steady-state coverages of both oxygen and carbon monoxide for values of X_{CO} near to but slightly greater than X_1. These steady-state coverages show a power-law behaviour on the difference $|X_{CO} - X_1|$, with exponents that are almost the same for the two species (about 0.69).

Our simulations were performed near the first-order discontinuous transition that takes place at X_2. Since we investigated the region slightly above X_2 our steady state is always a CO-poisoned surface. As opposed to the steady-state work of Meakin *et al* we investigated the time dependence of the decay of the oxygen coverage.

We hope to carry out a further simulation for X_{CO} slightly less than X_2. In this case we are in the region where we get a steady reactive state; we can thus obtain steady-state values for the oxygen and CO coverages. The results could then be compared with those of Meakin *et al*, who explored the region near the transition X_1.

References

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[3] Meakin P and Scalapino J 1987 *J. Chem. Phys.* **87** 731
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