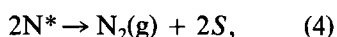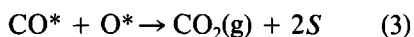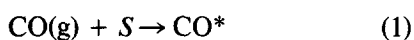# LETTERS TO THE EDITORS

Comment on "NO–CO Reaction on Square and Hexagonal Surfaces: A Monte Carlo Simulation"

Recently, Yaldram and Khan (YK) (*1*) have reported results of a Monte Carlo study of the reaction of CO and NO over a single-crystal catalyst. We have also been carrying out a study of this reaction, using a model identical to one of theirs. While our results (on a hexagonal lattice) are in qualitative agreement with theirs, we find discrepancies in the values of the transition points. For the square lattice, YK found that the system has no reactive steady state; here we provide a proof of this result.

The model that we studied corresponds to YK's for the particular case of completely dissociative adsorption of NO ($r_{NO} = 1$ in their notation). In this limit, the model is very close to that of Ziff *et al.* (*2*), the "ZGB" model, except that the O_2 is replaced by NO, and neighboring N atoms, as well as neighboring CO–O, react. The reactions' steps are

$$CO(g) + S \rightarrow CO^* \qquad (1)$$

$$NO(g) + 2S \rightarrow N^* + O^* \qquad (2)$$

$$CO^* + O^* \rightarrow CO_2(g) + 2S \qquad (3)$$

$$2N^* \rightarrow N_2(g) + 2S, \qquad (4)$$

where S represents an unoccupied site on the catalyst surface, $2S$ represents a nearest neighbor (nn) pair of such sites, (g) indicates a molecule in the gas phase, and the asterisk indicates an adsorbed molecule. The reactions in (3) and (4) are assumed to be instantaneous, while the adsorption steps (1) and (2) are rate-limiting.

When the catalyst sites are on a hexagonal (triangular) lattice, steady reactive states occur and the phase diagram is qualitatively

similar to that of the "dimer–trimer" model (*3*), with a second-order transition at X_1, a first-order transition at X_2, and an initial decrease in θ_{CO} for $X > X_2$ (Fig. 1a). YK found the transition points listed in Table 1, using the standard "constant rate" (C–X) ensemble and a lattice of size 40 × 40, initially vacant. We carried out similar C–X simulations on a 256 × 256 lattice, and our results for the transition points are also given in Table 1. To arrive at our value of X_1 for the 256 × 256 lattice, for example, we observed that at $X = 0.175$, the system remained reactive for over 4×10^6 MCS (Monte Carlo steps), while in five runs at $X = 0.170$, the surface saturated with nonreacting O^* and N^* within 3×10^4 MCS. Likewise, to determine X_2 for this lattice, we found that at $X = 0.354$ the system remained reactive after 3×10^5 MCS, while five runs at $X = 0.355$ saturated with CO^* and N^* within 2×10^4 MCS. In order to compare our results with those of YK, we repeated our simulations on a 32 × 32 lattice, and the transition values from these simulations are also shown in Table 1. Our simulation results on the smaller lattice agree with YK at X_1, but not at X_2. We could not find an explanation for this discrepancy.

When using the C–X ensemble, one generally finds a somewhat high value for X_2 because of nucleation effects that delay the formation of the new phase (*4*). In order to eliminate these interfacial effects and find X_2 without bias, we use the "constant-coverage" (C–θ) ensemble in which θ_{CO} (the fractional coverage of CO^*) is held essentially fixed while the rate of CO adsorption is allowed to vary (*4*). Whenever
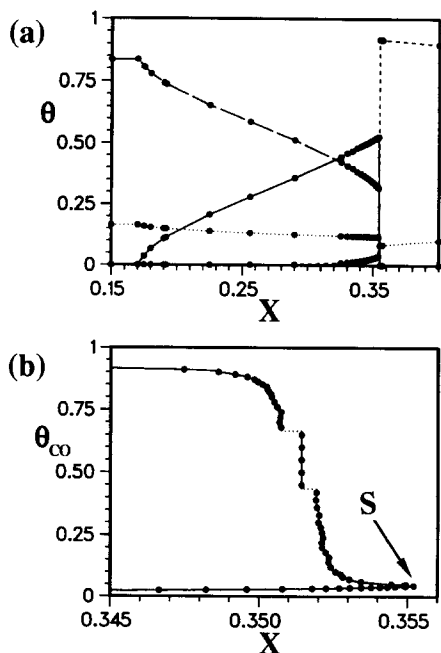
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FIG. 1. The phase diagram for the model on a 256 × 256 lattice: (a) found from the C–X ensemble and showing the reactive region; (b) found from the C–θ ensemble near the first-order transition. In (a) the curves are, from most broken to solid, θ_N, θ_{CO}, θ_O, and the coverage of unoccupied sites. In (b) only θ_{CO} is shown, and S marks the spinodal point.
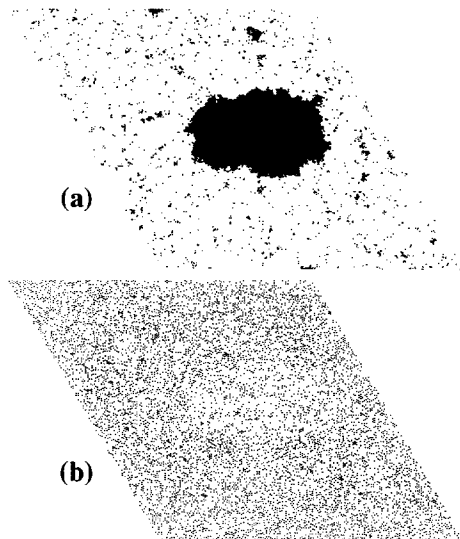

FIG. 2. A snapshot of the lattice in a simulation of the C–θ ensemble with $\theta_{CO} = 0.14$ (a) with CO* shown as black dots; (b) with N* shown as black dots. Note a slight decrease in the concentration of N* where the CO*–N* island exists, reflecting a small difference in θ_N between the two phases.

the actual value of θ_{CO} falls below its set point, only CO adsorption trials are carried out, while otherwise only NO trials are carried out. The value of X follows as the average fraction of CO adsorption attempts. This ensemble gives the same behavior of X vs θ_{CO} as shown in Fig. 1a, except near the first-order transition point,

where it gives the metastability loop shown in Fig. 1b.

This metastability loop shows that the system has a spinodal point at $X^s \approx 0.3552$, $\theta_{CO}^s \approx 0.0400$. For θ_{CO} held at a value less than θ_{CO}^s, the distribution of the surface species on the lattice remains homogeneous, while for $\theta_{CO} > \theta_{CO}^s$, the surface species separate into a reactive phase dominated by O*, N*, and vacant sites and a nonreactive phase dominated by CO* and N*, as shown in Fig. 2. When θ_{CO} is near 0.5, the two phases both wrap around the periodic boundaries and the border between the phases is on the average flat. We believe that the value of X corresponding to these states, 0.35140 ± 0.00001, gives an unbiased estimate of the true transition point X_2 for this system (4). Its value is, as expected, significantly below the value we found using the C–X ensemble, but still greater than the value found by YK.

We have also carried out a mean-field

TABLE 1

Values of the Transition Points

Study	Ensemble	Lattice size	X_1	X_2
YK	C–X	40 × 40	0.185 ± 0.002	0.338 ± 0.002
Present	C–X	32 × 32	0.185 ± 0.005	0.354 ± 0.001
Present	C–X	256 × 256	0.1725 ± 0.0025	0.3545 ± 0.0005
Present	C–θ	256 × 256	—	0.35140 ± 0.00001

Note. The underlined values are our best estimates.

analysis (5) of this model. The one-site equations are

$$\frac{d\theta_{CO}}{dt} = X\theta_V(1 - \theta_O)^z$$
$$- (1 - X)\theta_V^2[1 - (1 - \theta_{CO})^{z-1}] \quad (5)$$

$$\frac{d\theta_O}{dt} = -X\theta_V[1 - (1 - \theta_O)^z]$$
$$+ (1 - X)\theta_V^2(1 - \theta_{CO})^{z-1} \quad (6)$$

$$\frac{d\theta_N}{dt} = (1 - X)\theta_V^2[2(1 - \theta_N)^{z-1} - 1], \quad (7)$$

where $\theta_V = 1 - \theta_{CO} - \theta_O - \theta_N$, and z is the coordination number of the lattice ($z = 6$ for a hexagonal lattice). Solving these equations numerically at steady state with $z = 6$, we find $X^s = 0.3877$, $\theta_{CO}^s = 0.1172$. We also find $\theta_N = 1 - (\frac{1}{2})^{1/(1-z)}$ independent of X, and indeed, our simulations show that θ_N is only weakly dependent upon X. The one-site approximation does not predict the existence of the second-order transition, as in the ZGB model (5).

Next, we prove that the square lattice cannot support a steady reactive state for this model. We consider a square lattice of even side length and color each site alternately black and white, so that the lattice looks like a checkerboard. Define $m = b - w$, where b is the number of black sites occupied by N*, and w is the number of white sites occupied by N*. Note $0 \le b \le \nu/2$ and $0 \le w \le \nu/2$, where ν is the total number of sites on the lattice. Furthermore, $-\nu/2 \le m \le \nu/2$, with the equalities corresponding to the two nonreactive states where all the sites of one color are occupied by N* and all the sites of the other color are occupied by O* and/or CO* of any configuration. (Note, however, that these are not the only possible nonreactive states—see below.)

Each time an NO adsorbs with the N on a black site, *regardless of whether it reacts or not*, m increases by unity. Similarly, m decreases by unity each time the N lands on a white site. Because the NO adsorb on nn pairs with random orientation, these two changes in m will occur with equal probability. Thus, the value of m will perform a simple random walk, making a transition for each NO adsorption event. It follows that the reaction cannot occur forever (steady state), because one of the adsorbing states $m = \pm\nu/2$ would then be reached by this random walk after a finite number of NO adsorptions.

Note that while we used the existence of adsorbing states at $m = \pm\nu/2$ to prove that there is no reactive region for the model, these two adsorbing states are never reached in practice, because there are many other possible nonreactive states in the system. We find that the nonreactive state that is reached is typically composed of a number of separate regions, each having either virtually all its black or virtually all its white sites occupied by N*, with the other sites occupied by CO* and/or O*. Black-N* regions can never contact white-N* regions, since such contact necessitates N*–N* nn pairs. Thus the two types of regions are separated by dislocations, which are occupied by either O* or CO*.

We suspect that the time for the system to poison (become nonreactive) is independent of the lattice size for sufficiently large systems. This is because we believe that poisoning occurs when the black- and white-N* regions reach a certain average size that is independent of the system size. This contrasts with the behavior of the $A-B$ model with $X = \frac{1}{2}$ (6–8), where the time to poison grows as a power law of the system size (7, 8), and the ZGB model in the reactive region, where the time to poison grows exponentially with the system size (8).

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