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Reply to Comment by B. J. Brosilow and R. M. Ziff

In the preceding comment (*1*), Brosilow and Ziff have presented a Monte Carlo (MC) simulation of NO–CO reaction. Their work corresponds to our previous study (*2*) of this reaction when NO dissociates completely into N and O on adsorption. As we observed, they also obtain no steady reactive state (SRS) on a square surface where each site has four nearest neighbors (nn). They give a simple but convincing proof for this. On a hexagonal surface (i.e., 6 nn) they observe a SRS between two critical concentrations X_1 and X_2 of CO. For a 32 × 32 lattice, their X_1 is the same as ours for a 40 × 40 lattice. The general qualitative features are the same as in our work. The only point of discord is the value of X_2. According to our calculation $X_2 \simeq 0.338$, whereas they obtain 0.354 in C–X ensemble and 0.351 in C–θ ensemble (*1*). Since X_2 is a first-order transition critical point, it is rather difficult to estimate it. For this reason they have advanced the C–θ method, which according to their claim gives an unbiased estimation of the true transition point X_2 (*3*). In view of this discrepancy we have repeated our calculation and we still find $X_2 = 0.338$. In the following we illustrate the case.

In the C–X ensemble in MC simulation one can always obtain a poisoned state for any value of X, but in some cases the calcluation time becomes nearly indefinite. This is the case between X_1 and X_2. The X_2 is the first-order transition point where the transition from poisoned to SRS is abrupt and there is a discontinuity. Such a situation arises quite frequently (for example susceptibility versus temperature) (*4*). In such a case the physical property under investigation has a pole at the critical point. Since X_2 is also a first-order transition, it lies near a pole of t(MCS) (Monte Carlo steps) versus X curve for $X > X_2$. In Fig. 1 we present MCS to obtain a poisoned state for $0.340 \leq X \leq 0.500$ for a 64 × 64 lattice. These MCS are the average values over 10 independent runs. This curve can be represented as

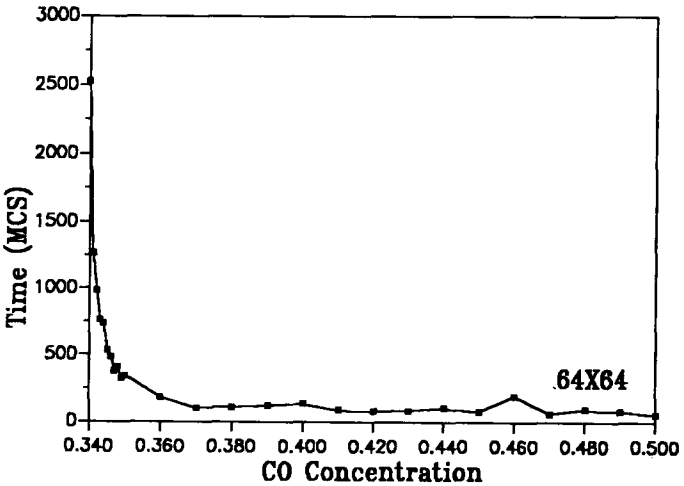

FIG. 1. Time in Monte Carlo steps (MCS) versus the CO concentration to obtain poisoned state for a hexagonal lattice (64 × 64).

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$$t = \frac{a}{X - X_c} + L, \qquad (1)$$

where X_c is the pole.

With $a \simeq 2.5$, $L = 64$, and $X_c \simeq 0.339$, a good agreement to MC curve is obtained. From this one deduces that $X = 0.340$ is the last poisoned state before the transition and $X = 0.338$, the first SRS after the transition. Thus SRS lies between $0.185 \leq X \leq 0.338$. For other lattice sizes we find the same pole position. A lattice as small as 16×16 gives the same pole $X_c \simeq 0.339$; the size effects only the constant parameters a and L.

Generally, if a critical phenomenon like a phase transition in a sample is observed, it always takes place at a fixed point irrespective of the sample size.

REFERENCES

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2. Yaldram, K., and Khan, M. A., *J. Catal.* **131,** 369 (1991).
3. Ziff, R. M., and Brosilow, B. J., *Phys. Rev. Lett.*, in press.
4. See for example Calaway, J., "Quantum Theory of the Solid State," p. 159. Academic Press, New York, 1976.

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