Monte Carlo simulations on nanocatalysts: effect of active sites location in the CO-NO surface reaction

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Computer simulation in heterogeneous catalysis has shown as a powerful tool in the understanding of the kinetics of catalyzed reactions. Monte Carlo simulations has been especially important to avoid the problems found in mean field models, due to spatial correlations under nonequilibrium conditions. The fast development of computers in the last decades, together with the lack of knowledge of the intimate details of the reaction mechanisms on catalysts, has enhanced the importance of simulations, providing a useful method to model new catalysts with improved performance.

Actual catalysts [1] are usually constituted by nanometer-sized metallic particles placed on an surface of an inert porous support. Current technology allows an accurate design of the placement of such particles. Therefore it is possible to improve the performance of a catalyst without increasing the cost associated with the use of higher amounts of raw material (usually very expansive). To this end, we have conducted kinetic Monte Carlo simulations of the CO+NO reaction, based on the mechanism proposed by Belton et al. [2], on square and hexagonal lattices. The elemental reaction steps involved in this model [3] are:

1. $CO(g) + *\ \rightarrow CO(a)$
2. $NO(g) + 2*\ \rightarrow NO(a)$
3. $NO(a) + *\ \rightarrow N(a) + O(a)$
4. $N(a)\ + N(a) \rightarrow N_2(g) + 2*$
5. $NO(a) + N(a) \rightarrow N_2O(g) + 2*$
6. $CO(a) + O(a) \rightarrow CO_2(g) + 2*$

where (g) and (a) indicate if the molecule is in gaseous phase or adsorbed onto the surface, and * stands for an vacant site on the surface. Diffusion of N monomers is allowed. Monomers can react only if one of them occupies a so-called active site. To take into account the effect of the active sites distribution on the lattice, three different ways of placing a x_{active} fraction of active particles. These are:

1. Random distribution. The active particles are randomly distributed on the surface.
2. Regular distribution. The active particles are placed holding the maximum distance between them.
3. Nucleated distribution. The active particles occupy randomly connected sites.

The size of the lattice used was $L \times L = 128 \times 128$ sites. Figure 1 shows the fraction of vacant sites on the lattice versus the control parameter y_{CO} (equals to the partial pressure of CO in the gas phase, i.e., the probability of CO adsorbtion onto the surface) obtained from the simulations for two different values of x_{active} ($x_{active}=0.4$, $x_{active}=0.7$) for each of the distributions mentioned above, as well as for the completely active surface (see references [3,4]) in a hexagonal lattice.

The curves displayed resemble those obtained for Luque et al. [5] for the CO+NO reaction using the Yaldram [6] mechanism, with a well defined steady reactive window (SRW) $y_1 < y_{CO} < y_2$ surrounded by two inactive regions in which the surface is mainly covered by O

($y_{CO}<y_1$) or CO ($y_{CO}>y_2$). The regular distribution gives a higher reactivity for any value of x_{active}, and also a broader SRW than the obtained for random a nucleated distributions if x_{active} is large enough, otherwise SRW for the nucleated distribution is the widest. Random distribution provides higher reactivity than nucleated, consistently with the larger number of pairs of sites on the lattice with at least one of them active. It is also remarkable that for $x_{active} \approx 0.5$ and smaller, the nature of the phase transition in y_2 changes from a continuous type to a first order type, probably due to a displacement of the spinoidal point to smaller values of y_{CO}.

References:

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Figure 1: Fraction of vacant sites versus control parameter for different active site distributions in a hexagonal lattice.