Yaldram-Khan model with CO and N desorption

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Abstract. We present kinetic Monte Carlo simulations of a modified Yaldram-Khan (YK) model for the catalytic reduction of NO on a surface. The model includes the individual desorption of CO molecules and N atoms, associated with temperature effects. We find that the combined desorption of these species produces a reactive phase that is absent in the original YK model on a square lattice. In this reactive phase, N checkerboard structures are reduced in size and reactive zones between them can be established.

1. Introduction

The catalytic reduction of NO has received a great deal of attention because of the key role it plays in the control of vehicle exhaust emissions \cite{1, 2}, and the variety of non-equilibrium phenomena it can exhibit \cite{3, 4, 5, 6}. A simple lattice-gas model, based on the Langmuir-Hinshelwood mechanism, was proposed by Yaldram and Khan (YK) \cite{7} to study this reaction. In this model, inspired by the Ziff-Gulari-Barshad model for the catalytic oxidation of CO \cite{8}, CO and NO molecules in a gas phase, can be adsorbed on a catalytic surface and once there react. The adsorption probability depends on the partial pressure of the compound in the gas mixture, \( y \) for CO and \( 1 - y \) for NO. CO molecules are adsorbed on single sites, while NO molecules are dissociatively adsorbed on nearest-neighbor (nn) sites. When CO and O or a pair of N atoms are located on nn sites, they react, liberating CO\textsubscript{2} or N\textsubscript{2}, respectively, and leaving behind two empty sites. On a square lattice, the formation of checkerboard structures of N atoms prevents the existence of a reactive state \cite{9}. Several authors have tried to eliminate this “checkerboarding” process on a square lattice, by modifying the original reaction by the inclusion of CO desorption or adding an Eley-Rideal mechanism \cite{10, 11, 12, 13, 14, 15}.

Other approaches to the NO reduction are provided by more elaborate lattice-gas models that explicitly take into account energetic effects \cite{16, 17, 18}. Still, we consider that there is much to learn from a simple model such as the YK that can be easily modified to include many relevant processes. In this paper we study the individual desorption of CO molecules and N atoms in the YK model on a square lattice. We are not aware of previous studies that take into account the desorption of N atoms in the CO+NO reaction.

2. Model and Simulations

The model is simulated on a square lattice that represents the catalytic surface. A Monte Carlo simulation generates a sequence of trials: CO or NO adsorption, or CO or N desorption. A
A schematic representation of the process is given by the following equations:

\[
\begin{align*}
\text{CO}(g) + S & \rightarrow \text{CO}(a) \\
\text{NO} + 2S & \rightarrow \text{N}(a) + \text{O}(a) \\
\text{CO}(a) + \text{O}(a) & \rightarrow \text{CO}_2(g) + 2S \\
\text{N}(a) + \text{N}(a) & \rightarrow \text{N}_2(g) + 2S
\end{align*}
\]  

(1)

Here S represents an empty site on the surface, g means gas phase and a means adsorbed. The first four steps correspond to the Langmuir-Hinshelwood mechanism that defines the YK model. The last two correspond to the desorption processes that we are including. Coverage is defined as the fraction of sites on the surface occupied by an adsorbate. We calculate the CO, O and N coverages, and the rate of production of CO$_2$ and N$_2$. $\theta_X$ stands for the coverage of species X.

### 3. Results

We first fix the value of $k_N$ and vary $k_{CO}$. In Fig. 1 and Fig. 2 we present the coverages and reaction rates, respectively, for $k_N = 0.1$ and different $k_{CO}$ values. For small values of y the behavior of the system is practically independent of $k_{CO}$. In this low y region, the coverage of CO is very low, so its desorption is not relevant. For $k_{CO} = 0$, there is a discontinuous transition from a reactive state to a CO poisoned one. As $k_{CO}$ increases, the transition becomes smoother and there is no CO poisoning. For large enough values of $k_{CO}$, the transition seems to be continuous, $\theta_{CO}$ increases almost linearly with y while $\theta_O$ correspondingly decreases in a linear way. $\theta_N$ reaches a maximum and then decreases smoothly toward zero. $\theta_{CO}$ decreases with $k_{CO}$ in favor of $\theta_N$ and $\theta_O$ in such a way that now a reactive state is possible.

CO desorption clearly favors the reactivity of the system, increasing with $k_{CO}$ as seen in Fig. 2. This is expected since now the lattice cannot be poisoned with CO. There is an interval of y within the reactive window for which the CO coverage is almost zero, indicating that in that region most of the CO atoms once adsorbed react immediately with O atoms. Analogously, there is an interval, for higher values of y, for which the O coverage is almost zero. In this region the O atoms are the ones that react immediately with CO molecules. In this fashion, particularly for high values of y, O atoms are depleted from the surface, while some N atoms still remain.

When $k_{CO}$ increases, the production rates increase as well, in spite of the fact that the N structures tend to grow in size. The production takes place in the regions between such structures. Within these reactive regions, a larger CO desorption rate favors the reactivity because there are more empty sites available where NO molecules can adsorb. At the same time, this favors the creation of N structures but the inclusion of $k_N$ keeps them from covering the lattice and establishing a non-reactive state.

Next, we fix the value of $k_{CO}$ and vary $k_N$. In Fig. 3 and Fig. 4 we present the coverages and reaction rates, respectively, for $k_{CO} = 0.3$ and different $k_N$ values. $\theta_{CO}$ increases with $k_N$ mainly to the detriment of $\theta_N$. $\theta_O$ remains rather unaltered. In this case a reactive state also appears, and the reactive window increases its area as $k_N$ increases. These observations suggest that desorbing N atoms, adjacent to O atoms, leave individual empty sites where CO molecules can adsorb and react. For high values of y this leads to a lattice almost covered with CO. In contrast to the case with $k_N$ fixed, the positions of the maxima of production are almost independent of $k_N$.

N$_2$ production increases initially with $k_N$ but, unlike CO$_2$ production, it reaches a saturation value. This happens rather quickly and the reaction rates of N$_2$ are almost the same from
Figure 1. Coverages vs $y$ when there is CO and N desorption with $k_N = 0.1$ fixed. (a) CO (b) O and (c) N. The values of $k_{CO}$ are indicated in (b).

Figure 2. Reaction rates vs $y$ when there is CO and N desorption with $k_N = 0.1$ fixed. The values of $k_{CO}$ are indicated in (a).

$k_N = 0.05$ onward. This happens because the number of N atoms capable of reacting on the lattice is reduced by N desorption. The curves with $k_N = 0$ are not very smooth, because the system with only $k_{CO}$ presents large fluctuations associated with the growth of N structures that may or may not cover the entire lattice [19].

Snapshots of the lattice show, as expected, that the formation of N structures is hampered by the inclusion of N desorption. For low $k_N$ values, some N structures remain and the production
Figure 3. Coverages vs $y$ when there is CO and N desorption with $k_{CO} = 0.3$ fixed. (a) CO (b) O and (c) N. The values of $k_N$ are indicated in (b).

takes place in the regions between them. For high $k_N$ values, the N structures disappear almost completely, and the production of CO$_2$ and N$_2$ occurs uniformly over the lattice. When N desorption is present, the production of N$_2$ depends on two competing effects: the reduction of the N structures that favors the reactivity of the lattice, and the reduction of the number of N atoms capable of reacting that minimizes the N$_2$ reaction rate.

Figure 4. Reaction rates vs $y$ when there is CO and N desorption with $k_{CO} = 0.3$ fixed. The values of $k_N$ are indicated in (a).
4. Conclusions
In this work we studied the catalytic reduction of NO on a surface by kinetic Monte Carlo simulations of a modified YK model that includes CO and NO desorption rates, $k_{CO}$ and $k_N$, respectively. We found that, contrary to what happens in the standard YK model on a square lattice, our modified model presents a reactive window where CO$_2$ and N$_2$ are produced. For a fixed value of $k_N$, an increment of $k_{CO}$ impedes the formation of a CO poisoned state and favors the formation of N structures. The reactivity is enhanced because larger $k_{CO}$ values benefit the reactivity since more empty sites are available where NO molecules can adsorb, the N desorption stops the N structures from taking over the lattice, and reactive zones between such structures can be established. For a fixed value of $k_{CO}$, both the production of CO$_2$ and N$_2$ are favored by increasing $k_N$ but not in the same proportion. This is in contrast to the case with $k_N$ fixed, where the increase of $k_{CO}$ favors both reaction rates equally.

References
[1] Taylor K C 1993 Catal. Rev. Sci. Eng. 35 457
[2] Liu G and Gao P 2011 Catal. Sci. Technol. 1 552
[3] Marro J and Dickman R 1999 Nonequilibrium phase transitions in lattice models (New York: Cambridge University Press).
[4] Christmann K 1991 Introduction to Surface Physical Chemistry (Darmstadt: Steinkopff Verlag).
[5] Bond G C 1987 Catalysis: Principles and Applications (Oxford: Clarendon Press).
[6] Imbihl R and Ertl G 1995 Chem. Rev. 95 697
[7] Yaldram K and Khan M A 1991 J. Catal. 131 369
[8] Ziff R M, Gulani E and Barshad Y 1986 Phys. Rev. Lett. 56 2553
[9] Brosilow B J and Ziff R M 1992 J. Catal. 136 275
[10] Meng B, Weinberg W H and Evans J W 1993 Phys. Rev. E 48 3577
[11] Meng B, Weinberg W H and Evans J W 1994 J. Chem. Phys. 101 3234
[12] Kortlůk O and von Niessen W 1996 J. Chem. Phys. 105 4764
[13] Khan M A, Yaldram K, Khalil G K and Khan K M 1994 Phys. Rev. E 50 2156
[14] Khan M A and Ahmad W 2002 J. Phys. A: Math. Gen. 35 2713
[15] Bustos V, Uñac R, Zaera F and Zgrablich G 2003 J. Chem. Phys. 118 9372
[16] Luque J J, Gómez A and Córdoba A 2004 Physica A 31 505
[17] Cortés J and Valencia E 2008 Bull. Chem. Soc. Jpn. 81 1267
[18] Mei D H, Du J C and Neurock M 2010 Ind. Eng. Chem. Res. 49 10364
[19] Díaz J J, and Buendía G M 2017 Submitted