Numerical Simulation of the Kinetics of the Selective Catalytic Reduction of NO by NH$_3$

J. P. Bodanese and M. Santos

Centro de Ensino de São José, Universidade do Vale do Itajaí, 88.122-000, São José, SC, Brazil

In this work we study a model of a catalytic reaction among three monomers in order to understand the kinetics of the selective catalytic reduction of NO by ammonia ($4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$). Our model takes into account the formation of the intermediate species in the global scheme of the reaction. Using the Monte Carlo method we simulated the model on a square lattice and determined its phase diagram.

1 Introduction

In the last years, severe regulations have been imposed in order to control the emissions of the nitrogen oxides from mobile and stationary sources, of these types of molecules. The principal argument to decrease the emission of nitrogen oxides is based upon the fact that these molecules have a hazardous effect on the health of the people as well as the environment [1,2]. In general, the studies to lower the emissions of nitrogen oxides only consider reduction of nitrogen monoxide, because it accounts for approximately 95% of all emitted oxides. However, as the decomposition of NO into N$_2$ and O$_2$ is thermodynamically unstable [2], the use of a catalyst is necessary to facilitate and accelerate the reaction. In this reaction, a molecule of nitrogen monoxide is adsorbed on a catalytic surface and it dissociates into O and N atoms. Then two N(O) atoms combine to form N$_2$ (O$_2$). Different types of catalysts have been used to decompose nitrogen monoxide, but all can be classified in three groups: noble metals, metallic oxides and zeolites [3]. Unfortunately, any of these catalysts is poisoned by oxygen atoms over a wide range of temperatures. An alternative to prevent the emission of nitrogen monoxides is the selective catalytic reduction (SCR) of these molecules by ammonia [2,4,5], notably when the gases are emitted by stationary sources. In this de-pollution process, NH$_3$ is used as a reducing agent to produce water and gaseous nitrogen. However, if oxygen is also added to the gaseous mixture that is adsorbed in the catalytic surface, conversion to N$_2$ and H$_2$O is enhanced [1]. Experimental and theoretical studies have been used in order to determine the kinetics of the reduction of nitrogen monoxide by ammonia on catalytic surfaces [6-8]. In both cases, there are some controversies, relative to the mechanism by which the NO molecules are decomposed. In order to provide information about the mechanisms concerned in the kinetics of the selective catalytic reduction of nitrogen monoxide by NH$_3$, we have studied, through Monte Carlo simulations [9,10], some possible paths for the overall reaction that occurs on the catalytic surface. Our approach is based on the Ziff, Gulari and Barshad model (ZGB model)[11] for the irreversible oxidation of carbon monoxide on a catalytic surface. Besides, as the gaseous reservoir contain three types of molecules (O$_2$, NH$_3$ and NO), we also used the ideas proposed by Schmidt and Santos [12] to study the poisoning of a catalytic surface when a third non-reactive monomer is present in the gaseous reservoir.
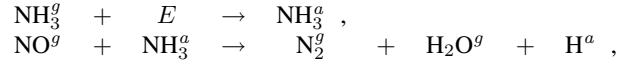
Our paper is organized as follows: in section II we present some possible paths for the reduction of NO by NH$_3$ in presence of O$_2$ as well as numerical results obtained in each case. In addition, we describe some details of the simulations. As we will see, a small modification in the reaction mechanism changes completely the dynamical behavior of the model. Finally, in section III, we address our main conclusions.
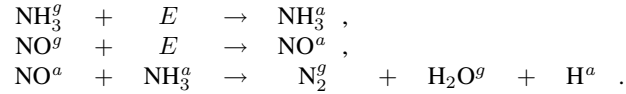
2 Models and numerical results

The process in which ammonia NH$_3$ is used to decompose nitrogen monoxide NO, on a catalytic surface to produce N$_2$ and water is called by selective catalytic reduction (SCR). The overall reaction for the reduction of NO in the presence of oxygen and ammonia is given by [3,9]

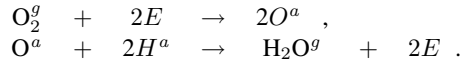$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \ . \qquad (1)$$
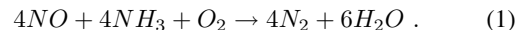
The first problem that appears in the study of this reaction is related to the mechanism that control the reaction scheme. In fact, several kinetic studies have been reported where the rate equations for this reaction is based on either the Eley-Rideal (ER)[13,14] or Langmuir-Hinshelwood (LH)[15,16] mechanisms. More recently, in an extensive review about the current state of research on NO$_x$ catalysis, Fritz and Pitchon [3] presented two possible reaction schemes for nitrogen monoxide reduction by NH$_3$. The ER mechanism involves a NO molecule in the gas phase directly reacting with an ammonia-adsorbed species, that is,

$$
\begin{array}{rcll}
NH_3^g & + & E & \rightarrow & NH_3^a \ , \\
NO^g & + & NH_3^a & \rightarrow & N_2^g \quad + \quad H_2O^g \quad + \quad H^a \ ,
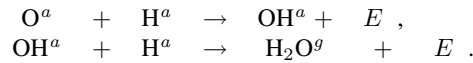\end{array}
$$

where the index a indicates that the molecules are adsorbed on the surface, g that the molecules are in the gas-phase and E indicates an empty site. On the other hand, for the LH mechanism, the particles of nitrogen monoxide must also be adsorbed on the catalytic surface to react with ammonia. In this case we have

$$
\begin{array}{rcll}
NH_3^g & + & E & \rightarrow & NH_3^a \ , \\
NO^g & + & E & \rightarrow & NO^a \ , \\
NO^a & + & NH_3^a & \rightarrow & N_2^g \quad + \quad H_2O^g \quad + \quad H^a \ .
\end{array}
$$

We observe that, in both reaction schemes, the catalytic surface is poisoned by the intermediate species H. To regenerate the surface, the oxygen gas is added to the gaseous reservoir, and two new reactions can occur on the catalytic surface

$$
\begin{array}{rcll}
O_2^g & + & 2E & \rightarrow & 2O^a \ , \\
O^a & + & 2H^a & \rightarrow & H_2O^g \quad + \quad 2E \ .
\end{array}
$$

This last reaction occurs by two steps

$$
\begin{array}{rcll}
O^a & + & H^a & \rightarrow & OH^a + & E \ , \\
OH^a & + & H^a & \rightarrow & H_2O^g & + \quad E \ .
\end{array}
$$

Here, we note the presence of other intermediate species. We assume that the reactions among the adsorbed species are instantaneous, and that the rates of collisions of the gaseous oxygen, nitrogen monoxide and ammonia with the catalytic surface, here denoted by Y_O, Y_{NO}, and Y_{NH_3}, respectively, depend on their mole fractions in the gas phase. They are related by

$$
Y_O + Y_{NO} + Y_{NH_3} = 1 \ . \tag{2}
$$

In order to perform Monte Carlo simulations for the two mechanisms (ER and LH) we use a square lattice of linear size L with periodic boundary conditions. The unit of time in the simulations is the Monte Carlo step (MCs), in which $N = L^2$ adsorption steps occur. We start our simulation for the ER mechanism with an empty lattice, for fixed values of Y_{NH_3} and Y_{NO}. At random, we choose a site on the catalytic surface and a particle (NO, NH$_3$, or O$_2$) to react on it. If NO is chosen, and the site is occupied by ammonia, the two molecules react to yield the intermediate species H on that site. After this, we scan its neighborhood in order to verify the possible reactions of H with OH and O, respectively. Otherwise, if the chosen site is empty or occupied by any other species, the trial ends. If the chosen particle is ammonia the simulation proceeds as follows: first we verify if the site is empty or occupied. If it is occupied, the trial ends again, but if it is empty, the NH$_3$ particle is immediately adsorbed. As the molecule of ammonia does not react, we pass to the next trial of adsorption. Now, if the chosen particle to hit on the catalytic surface is O$_2$, and if the chosen site is occupied, we stop the adsorption step. On the other hand, if it is empty, the following procedure is adopted: we check the neighborhood of the chosen site. If one of the four first neighbor sites is empty, this site, and the chosen one, are occupied by the two oxygen atoms. If there are two or more first neighbor sites that are empty, the adsorption site is randomly chosen. After the adsorption, we scan the neighborhood of the two oxygen atoms in order to see the possible reactions of O with H to yield OH. After this, we chek the possibility that the last molecule reacts, in its neighborhood, with another H to yield a water molecule.

Following the procedure outlined above, we performed Monte Carlo simulations for $L = 256$ and for fixed values of the collision rates. We find that the densities of the various types of molecules on the surface reach a stationary state. Moreover, these values depend on the values of the collision rates. For instance, in Fig. 1, we plot the density of empty sites and also the coverages of the other species versus the normalized collision rate of the NO molecules for $Y_{NH_3} = 0.3$. $Y_{max} = 1.0 - Y_{NH_3}$ is the maximum value assumed by Y_{NO} (in this case $Y_{max} = 0.7$). As we can see, all the types of molecules can coexist on the surface depending on the value of the collision rates. After a critical value of this parameter, the catalytic surface is poisoned and the only species remaining on the surface is H. In addition, for values of Y_{NO}/Y_{max} smaller than the critical one, the density of empty sites is different from zero, characterizing an active phase for this catalytic model. However, this quantity can not be used to characterize the transition between the active and inactive phases. In fact, while the density of ammonia on the catalytic surface is different from zero, it is possible to produce N$_2$ and H$_2$O. Therefore, we use the density of ammonia as the relevant parameter to characterize the transition between the active and inactive phases. In Fig. 2 we show how the density of ammonia changes with Y_{NO}/Y_{max} for some values of Y_{NH_3}. We note that the increase in the collision rate of ammonia corresponds
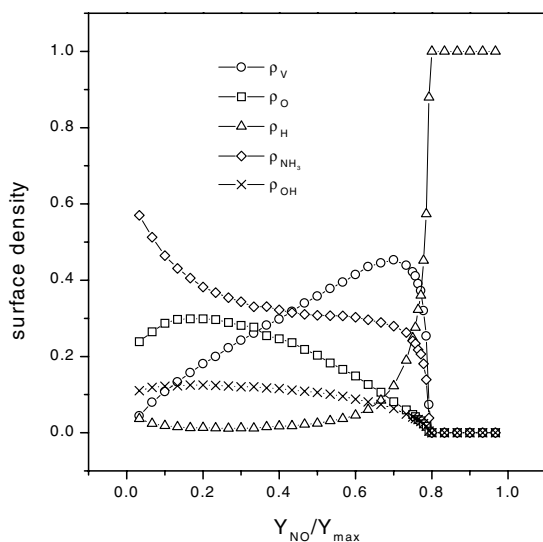
to

Figure 1. Plot of the stationary value of the surface density versus the normalized collision rate of nitrogen monoxide for $Y_{NH_3} = 0.3$ and $L = 256$. Y_{max} is the maximum value of Y_{NO} for each value of Y_{NH_3}. The maximum occurs when $Y_O = 0.0$ and, in this case, $Y_{max} = 0.7$.
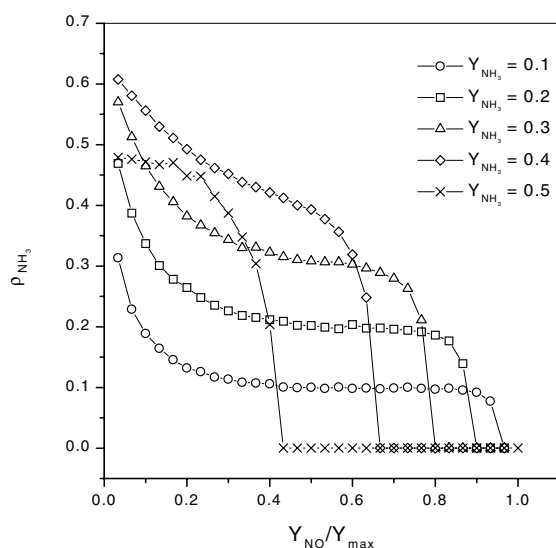

Figure 2. Plot of the stationary value of the density of ammonia as a function of the normalized collision rate of nitrogen monoxide for $L = 256$ and various values of Y_{NH_3}.

the decrease of the critical value Y_{NO}/Y_{max} at which the transition occurs. The phase transition is continuous for any values of Y_{NO} and Y_{NH_3}. Taking all these results we can construct the phase diagram for the model of the SCR of NO by ammonia when the kinetics of the reaction is governed by the ER mechanism. In Fig. 3, we show the phase diagram for this model. As we can see, it contains a set of points separating an active phase from an inactive one. A final result for this model is related to the production of the N_2

and H_2O gases. As we can see in Fig. 4, the production rates of these gases, in the stationary regime, exhibit a maximum value as a function of Y_{NO}/Y_{max}. As we expected from the kinetics of the reaction, the quantity of water produced is larger than the production of N_2. A maximum value of this production rate also depends on the collision rate of ammonia, as shown in Fig. 5, in which we plot the N_2 production rate versus Y_{NO}/Y_{max} for some values of YNH_3.
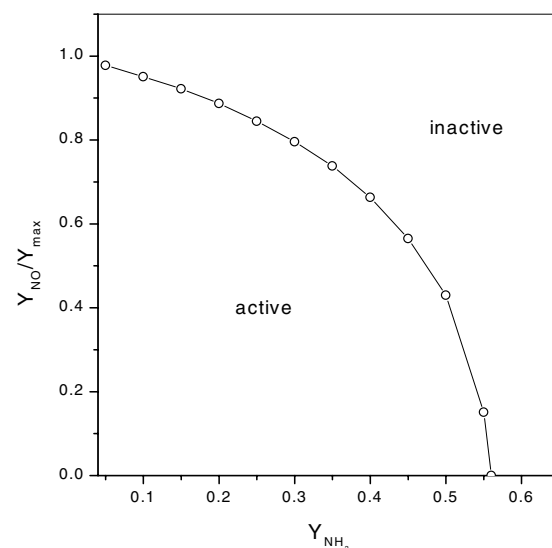

Figure 3. Phase diagram in the plane normalized adsorption rate of nitrogen monoxide versus Y_{NH_3}. The points indicate the phase transition between the active and inactive phases. The line is a guide to eyes.
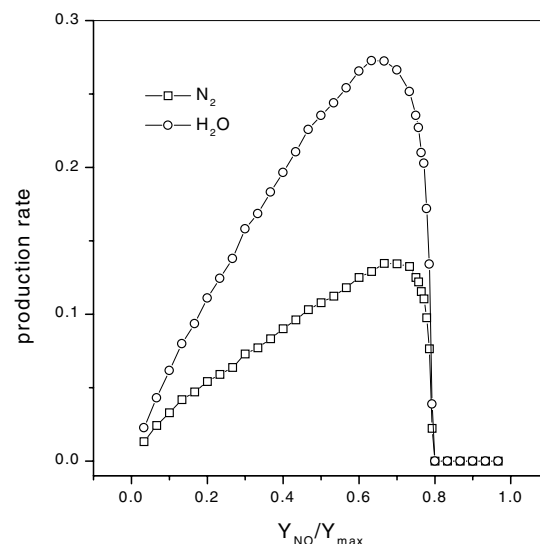

Figure 4. Plots of the production rates of the N_2 and H_2O gases, in the stationary regime, as a function of Y_{NO}/Y_{max} for $Y_{NH_3} = 0.3$ and $L = 256$.
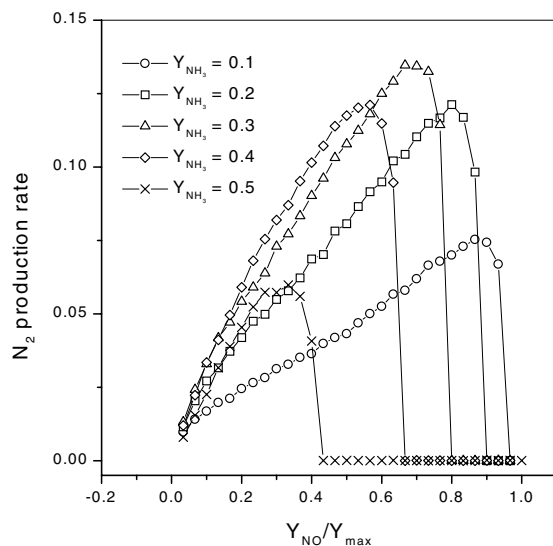
Figure 5. Plot of the stationary value of the production rate of N_2 as a function of the normalized collision rate of nitrogen monoxide for $L = 256$ and various values of Y_{NH_3}.

We now turn our attention to study the model when the LH mechanism defines the kinetics of the overall reaction of the SCR of nitrogen monoxide by ammonia. According to the kinetics above mentioned, we have simulated the model as follows. First we choose, at random, the particle to be adsorbed as well as the site where the adsorption step occurs. If the chosen site is occupied, the trial ends. Otherwise, the chosen particle is adsorbed. If the chosen particle to be adsorbed is the oxygen gas, an additional first neighbor site, also empty, is needed. In this case, the O_2 molecule dissociates on these two sites of the catalytic surface. After the adsorption, we scan the neighborhood of the adsorbed species in order to see the possible reactions. Then, according to this algorithm, we perform Monte Carlo simulations on the square lattice of linear size LxL with $L = 256$. Surprisingly, we observed that the stationary states of this model are always poisoned for any values of the collision rates of the molecules NO, NH_3 and O_2. Besides, all the species that can be on the catalytic surface can coexist on the surface in the poisoned regime. Thus, despite the great similarity between the two reaction schemes, we find a very different dynamical behavior for the densities on the catalytic surface. To avoid the poisoning of the catalytic surface we changed the reaction scheme of the LH mechanism to include dissociation of both ammonia and nitrogen monoxide but, unfortunately, the inactive stationary state is always reached.

3 Conclusions

We have studied two heterogenous catalytic reaction models among three monomers on a square lattice in order to understand the kinetics of the selective catalytic reduction of NO by ammonia. Using Monte Carlo simulations we have shown that, while the Eley-Riedel mechanism provides an active regime for the system, the Langmuir-Hinshelwood mechanism always leaves the surface completely poisoned for any values of the collision rates.

References

[1]   M. Chiron, Stud. Surf. Sci. Catal. **30**, 1 (1987).

[2]   H. Bosch and F. Janssen, Catal. Today **2**, 369 (1988).

[3]   A. Fritz and V. Pitchon, Appl. Catal. B **13**, 1 (1997).

[4]   F. Nakashjima and I. Hamada, Catal. Today **29**, 109 (1996).

[5]   P. Forzatti and L. Lietti, Heter. Chem. Rev. **3**, 33 (1996).

[6]   F. Janssen, F. van den Kerkhof, H. Bosch, and T. J. R. Ross, J. Phys. Chem. **91**, 5921 (1987).

[7]   V. Tufano and M. Turco, Appl. Catal. B **2**, 9 (1993).

[8]   W. S. Kijlstra, D. S. Brands, E. K. Poels, and A. Bliek, Catal. Today **50**, 133 (1999).

[9]   P. Forzatti, Catal. Today, **62**, 51 (2000).

[10] D. P. Landau and K. Binder, *A guide to Monte Carlo Simulations in Statistical Physics*. Cambridge, Cambridge University Press (2000).

[11] R. M. Ziff, E. Gulari, and Y. Barshad, Phys. Rev. Lett. **56**, 2553 (1986).

[12] D. H. Schmidt and M. Santos, Phys. Stat. Sol. (a) **187**, 305 (2001).

[13] C. U. I. Odenbrand, A. Bahamonde, P. Avilla, and J. Blanco, Appl. Catal. B **5**, 117 (1994).

[14] J. A. Dumesic, N. -Y. Topsøe, H. Topsøe, Y. Chen, and T. Slabiak, J. Catal. **163**, 409, (1996).

[15] H. -G. Lintz and T. Turek, Appl. Catal. A **85**, 13 (1992).

[16] M. Turco, L. Lisi, R. Pirone, and P. Ciambelli, Appl. Catal. B **3**, 133 (1994).