

# Toward a realistic model for the kinetics of the NO + CO reaction on rhodium surfaces

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## Abstract

A model for the kinetics of NO reduction by CO on Rh(1 1 1) surfaces is proposed that takes into account recent experimental observations on the formation of an N–NO intermediate as an alternative pathway to produce N<sub>2</sub>, the formation of N-islands in the adsorbed phase, an increase of the NO dissociation probability with the number of neighboring vacant sites, and the blocking of NO dissociation due to the presence of neighboring co-adsorbed NO and CO species. When all these characteristics are taken into account, the overall behavior of the system in steady-state conditions, calculated through Monte Carlo simulations, is consistent with experimental observations. The effect and importance of each elementary process in the reaction kinetics is discussed.

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**Keywords:** NO; Monte Carlo simulations; Catalyst

## 1. Introduction

The catalytic reduction of NO to N<sub>2</sub> on metals has been intensively studied both experimental and theoretically for many years [1–21] in connection with the necessity to develop better catalysts for atmospheric pollution-control processes. Rhodium metal has proven to be one of the best catalyst for this purpose [1–3], in particular its (1 1 1) facet, which should be the one contributing largely to the activity of metal nanoclusters dispersed on the surface of the catalyst support. The key step of the NO reduction reaction has long been thought to be the breaking of the c-bond upon chemisorption on the metal. Rapid recombination of surface nitrogen atoms to form N<sub>2</sub> has been proposed to follow rapidly afterwards, and the removal of the byproduct adsorbed oxygen by the reducing agent (CO in many cases) has been assumed to be fast as well.

From the theoretical point of view, there has been a great deal of interest to establish the precise conditions under which

a reactive state can be sustained in a given system, and how such state is affected by the different steps of the reaction mechanism. Lattice-gas models studies by Monte Carlo simulations have played an important role in this by showing the effects of relevant parameters in the kinetics of the reaction and on the steady-state reached [10–21]. However, many of these theoretical studies point preferentially to the qualitative behavior of the system while keeping, at the same time, the model as simple as possible. Therefore, more realistic approaches to try to predict quantitatively experimental data have not been generally developed.

Recent molecular beam studies on the reduction of NO over Rh(1 1 1) [4,5,22–27] have indicated that the standard reaction scheme used to explain the kinetics of this reaction needs to be modified in at least two important ways. First, it was found that when a <sup>14</sup>N-covered Rh(1 1 1) surface is exposed to a <sup>15</sup>NO+CO beam, the molecular nitrogen produced always contains at least one <sup>15</sup>N atom [20,21]. This means that the nitrogen recombination step, N(ads)+N(ads)→N<sub>2</sub>(gas)+2 sites, usually assumed responsible for the formation of molecular nitrogen is in fact not fast enough under typical reaction conditions to account for

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the  $N_2$  production. Instead, an intermediate species, N–NO, appears to form on the surface, and then either decompose to  $N_2(\text{gas}) + O(\text{ads})$ , or just simply desorb.

A second important modification to the NO reduction mechanism brought about by the molecular beam work arises from the evidence that, at least on Rh(1 1 1) surfaces, atomic N forms compact islands. Indeed, it was found that the isotopic distribution of the molecular nitrogen detected in temperature programmed desorption (TPD) spectra from surfaces prepared by using isotopic mixtures of  $^{14}\text{N}$ - and  $^{15}\text{N}$ -labeled nitrogen oxide can only be explained on that basis [26,27]. The mechanism for the formation of these islands, however, has not yet been established.

The effects of the addition of the N–NO intermediate and of the formation of N-islands on the kinetics of the NO + CO reaction on Rh(1 1 1) have already been addressed through Monte Carlo simulations in previous papers [18,19]. There, the importance of several elementary processes such as the formation of the N–NO intermediate through an Eley–Rideal step and NO and CO diffusion and desorption was investigated. However, like in the majority of the former studies of this system, no attempt was made to ‘tune’ the model in order to obtain steady-state coverages for different species and reaction rates in at least qualitative concordance with experimental data.

A very general characteristic common to almost any model for the NO + CO reaction is the prediction that the surface becomes mainly poisoned with oxygen at low CO gas phase concentrations. Then, as that CO concentration increases, the coverage of atomic oxygen on the surface decreases steadily and then drops rapidly to almost zero. In contrast, the observed behavior for the reaction on Rh(1 1 1) [23] as CO concentration in the gas phase increases is such that oxygen coverage is first negligible at low CO concentrations but then increases suddenly as the reaction sets up and finally decreases again slowly. Significantly, a similar behavior is followed by the reaction rate. Our previous experience in simulating this reaction suggests that the high oxygen coverage at low CO concentrations is due to an excess of NO dissociation. However a simple general reduction in NO dissociation rate leads to a complete closing of the reaction window. The only possible way to overcome this difficulty seems to be to take into account the fact that the NO dissociation rate not only depends on the availability of vacant sites, but also on the energetic changes on the surface induced by adsorbed NO and CO. This effect is such that NO dissociation is further inhibited by the presence of other neighboring adsorbed NO and CO molecules. Indeed NO dissociation appears to be a quite complex process, as indicated by the extensive experiments of Niemantsverdriet and coworkers [28]. Their results clearly show that the NO dissociation rate decreases as the number of nearest-neighbor vacant sites decreases and, in particular, with the presence of nearest-neighbor co-adsorbed NO and CO molecules.

Another important experimental observation, which should be reproduced by the model is the behavior of ad-

sorbed atomic nitrogen. As the CO concentration in the gas phase increases, the coverage of atomic nitrogen on the surface increases steadily from relatively low values to intermediate ones, crossing the O coverage curve in the reactive region [23]. This could probably be controlled by choosing an appropriate balance between the two possible processes leading to  $N_2$  production: N–NO formation and N–N recombination steps. It has been recently shown experimentally [29] that both steps are operational in the catalytic NO reduction by CO on Rh(1 1 1) but that the second one is much slower than the first. As a complementary result arising from the same experimental study, it was also shown that the formation and decay of the intermediate N–NO species is facilitated by the presence of neighboring co-adsorbed molecules.

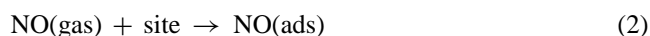
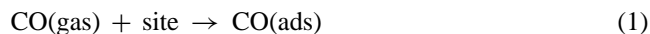
The purpose of the present work is to propose a reaction model that takes into account all the above experimental observations and to test it through Monte Carlo simulations against experimental data on reaction rates and O and N coverages. In Section 2 we describe the lattice-gas model and the reaction scheme used in this work to incorporate the new features suggested by the experimental evidence, and the Monte Carlo simulation method to follow the kinetics of the system. The results from those simulations are then presented, discussed and compared with experimental data in Section 3, and the conclusions are given in Section 4.

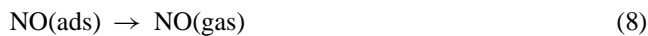
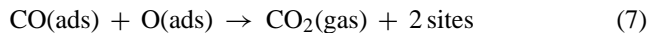
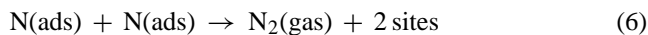
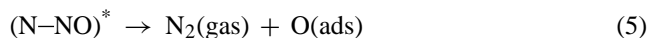
## 2. Model and simulation method

In our simulations, the surface of a Rh(1 1 1) single crystal is represented as a triangular lattice of  $L \times L$  sites with periodic boundary conditions. The gas phase is assumed to be a mixture of NO and CO molecules with molar fractions  $Y_{\text{NO}}$  and  $Y_{\text{CO}}$  adding up to a total value of one. Our reaction scheme takes into account:

- The formation of an N–NO intermediate as the key step for the formation of  $N_2$ .
- The formation of N-islands on the surface.
- The inhibition of NO dissociation due to the presence of neighboring adsorbed particles.
- The desorption of NO and CO species.
- The surface diffusion of NO and CO species.

We exclude in this simulation the Eley–Rideal step,  $\text{NO}(\text{gas}) + \text{N}(\text{ads}) \rightarrow (\text{N–NO})^*$ , considered in previous studies [18,19], due to the fact that it was found that when this step is active no N-islands are observed, contradicting experimental observations [26,27]. The proposed reaction scheme is then as follows:





A few step probability parameters also need to be introduced in our model in order to control some of the most relevant quantities, such as the extent of NO dissociation, NO and CO desorption and diffusion, the relative extent of step (6) compared to step (4), and the path for the consumption of the intermediate species. To this end,  $p_{\text{ads}}$  is defined as the probability of an adsorption event taking place (versus  $1 - p_{\text{ads}} = p_{\text{dif}}$  for a diffusion event),  $p_{\text{dis}}$  as the probability for NO dissociation, step (3) (so  $1 - p_{\text{dis}}$  is the probability that NO remain adsorbed as a monomer),  $p_{\text{des}}(\text{NO})$  and  $p_{\text{des}}(\text{CO})$  as the probabilities for NO and CO desorption, respectively,  $p_{\text{N+N}}$  as the probability for  $\text{N}_2$  formation through step (6) when an adsorbed N is chosen on the surface (so  $1 - p_{\text{N+N}}$  is the probability for step (4) under the same conditions. Note that if NO is chosen on the surface then step (4) is attempted for the formation of  $\text{N}_2$ ), and  $p_{\text{N-NO}}$  as the probability for the formation and decay of the N–NO intermediate species.

The dissociation of NO, being a complex and the most important process, deserves separate consideration. The following must be taken into account: (a) the formation of N-islands, by considering that NO dissociation is facilitated by the presence of neighboring co-adsorbed N atoms; (b) the dissociation probability increase with increasing number of vacant neighboring sites; and (c) the blocking effect on the dissociation probability by the presence of neighboring co-adsorbed NO and CO molecules. Therefore, the following expression is proposed for the dissociation probability for an NO molecule located at a given site:

$$p_{\text{dis}} = \frac{c_{\text{N}}n_{\text{N}} + c_{\text{V}}n_{\text{V}} - c_{\text{N-O}}(n_{\text{NO}} + n_{\text{CO}})}{6} \quad (12)$$

where  $n_{\text{N}}$ ,  $n_{\text{V}}$ ,  $n_{\text{NO}}$  and  $n_{\text{CO}}$  are the number of nearest-neighbor sites occupied by N, vacant and occupied by NO and CO, respectively, and the coefficients  $c$  are the corresponding weight factors. These weight factors represent the relative importance of the three effects (a–c), described above, and are used as fitting parameters in our model.

Finally, the experimental observation that the formation and decay of the N–NO intermediate is facilitated by the presence of neighbor co-adsorbed NO and CO [29] must be taken into account. This can be achieved by considering that:

$$p_{\text{N-NO}} = \frac{c_{\text{N-NO}}(n_{\text{NO}} + n_{\text{CO}})}{8} \quad (13)$$

where the new variables have significance similar to those in Eq. (12).

We now briefly describe the simulation method; the details, with the obvious modifications due to the particularities of the present model, can be found in Ref. [19].

A Monte Carlo trial begins by deciding which of two processes, an adsorption step with probability  $p_{\text{ads}}$  or a diffusion step with probability  $1 - p_{\text{ads}}$ , is to be executed. After that, the algorithm can be described as follows:

- **Adsorption:** A molecule from the gas phase, CO or NO, is chosen. The chance of selecting one or the other is given by  $Y_{\text{CO}}$  and  $Y_{\text{NO}} = 1 - Y_{\text{CO}}$ , respectively. Then a site is chosen at random and, if vacant, the chosen molecule is adsorbed and the reaction chain is followed until no more reaction steps are possible. If the chosen site is occupied, then the trial ends.
- **Diffusion:** A site on the surface is chosen at random. If it is either occupied by NO or CO, and if one or more nearest-neighbor vacant sites are available, then the particle is moved to one of the vacant sites, chosen at random, otherwise the trial ends.
- **Desorption:** After any successful adsorption step is executed, a desorption step is attempted. A site is chosen at random and, if it is occupied either by NO or CO, the desorption is attempted with the corresponding probability,  $p_{\text{des}}(\text{NO})$  or  $p_{\text{des}}(\text{CO})$ .

It must be kept in mind that, whenever a new vacant site is generated on the surface as a consequence of any of the above processes, this vacant site must be treated as a species, which can participate in a NO dissociation reaction.

A Monte Carlo step (MCS) is chosen to consist of  $L \times L$  trials, so, on average, every site on the lattice is visited for adsorption or diffusion. A lattice size of  $L = 100$  was picked so to make finite size effects negligible (a fact verified by independent simulations). For a given value of  $Y_{\text{CO}}$ , and starting with an initial empty surface, the process was deemed to have reached steady-state when the total surface coverage  $\theta = \theta_{\text{N}} + \theta_{\text{O}} + \theta_{\text{NO}} + \theta_{\text{CO}}$  stopped changing appreciably over the last  $10^3$  MCS. In all cases, stabilization was achieved before  $7 \times 10^4$  MCS. After the simulation was considered finished, plots of the coverages of each species as well as of the reaction rates  $R_{\text{N}_2}$ ,  $R_{\text{CO}_2}$ ,  $R_{\text{N}_2\text{O}}$  versus  $Y_{\text{CO}}$  were obtained. Reaction rates were calculated as the number of molecules produced divided by the number of Monte Carlo trials performed.

### 3. Results and discussion

A large amount of calculations were performed in order to understand the effect of each of the parameters of the model. Here we present only a subset stressing the most important results.

Fig. 1 shows the steady-state phase diagram (a), the  $\text{N}_2$  and  $\text{CO}_2$  overall reaction rates (b), and the rate for several

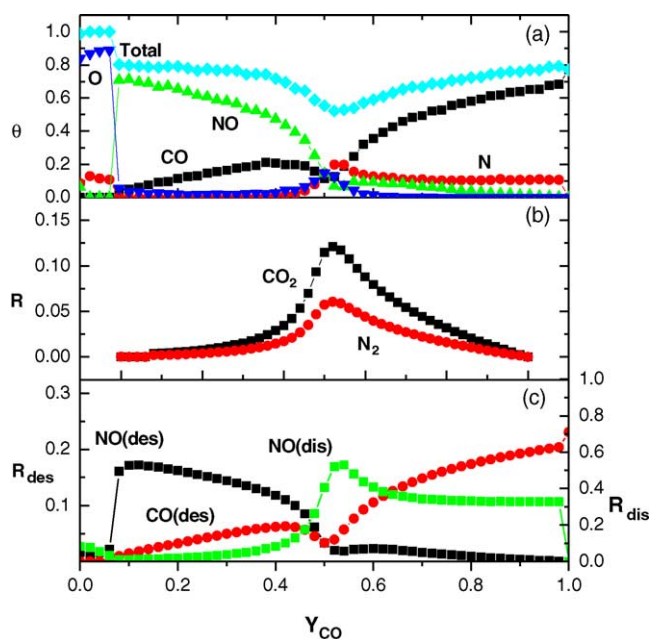


Fig. 1. Steady-state coverages (a),  $N_2$  and  $CO_2$  reaction rates (b), and elementary step rates (c), as a function of CO concentration in the gas phase,  $Y_{CO}$ , for the following set of parameters producing a satisfactory behavior:  $p_{ads} = 0.9$  ( $p_{dif} = 0.1$ ),  $p_{des}(NO) = 0.25$ ,  $p_{des}(CO) = 0.3$ ,  $c_N = 0.7$ ,  $c_V = 0.7$ ,  $c_{N-O} = 1.5$ ,  $p_{N+N} = 0.3$ ,  $c_{N-NO} = 3.0$ .

elementary steps (c), obtained for a combination of parameter values leading to a satisfactory behavior of the system:  $p_{ads} = 0.9$  ( $p_{dif} = 0.1$ ),  $p_{des}(NO) = 0.25$ ,  $p_{des}(CO) = 0.3$ ,  $c_N = 0.7$ ,  $c_V = 0.7$ ,  $c_{N-O} = 1.5$ ,  $p_{N+N} = 0.3$ ,  $c_{N-NO} = 3.0$ . This set of parameters indicates that there is an important amount of surface diffusion and desorption of NO and CO species, that NO dissociation increases moderately with the presence of neighboring vacant sites and co-adsorbed N atoms (there is some N-islands formation) and is strongly depressed by the presence of neighboring co-adsorbed NO or CO species, that reaction step (6) is operational to some extent (30%), and that the formation and decay of the N–NO intermediate is moderately facilitated by neighboring co-adsorbed NO or CO species. The following characteristics are observed which qualitatively reproduce experimental observations: (a) the reaction window, manifested by measurable  $N_2$  and  $CO_2$  production rates, extends from low values of CO concentrations in the gas phase up to almost CO saturation; (b) the reaction rate increases rapidly with  $Y_{CO}$ , passes through a maximum near  $Y_{CO} = 0.5$ , and then decays slowly toward zero; (c) the coverage of adsorbed O atoms is very low at low CO concentrations in the gas phase, then peaks near 0.5, and goes back to zero at higher CO concentrations; (d) the coverage of adsorbed N atoms is practically zero at low  $Y_{CO}$ , then crosses the curve of O coverage near 0.5, and stabilizes around  $\theta_N = 0.1$  at higher values of  $Y_{CO}$ .

It is clear from Fig. 1c that NO dissociation plays a fundamental role in the overall NO reduction reaction, as it is

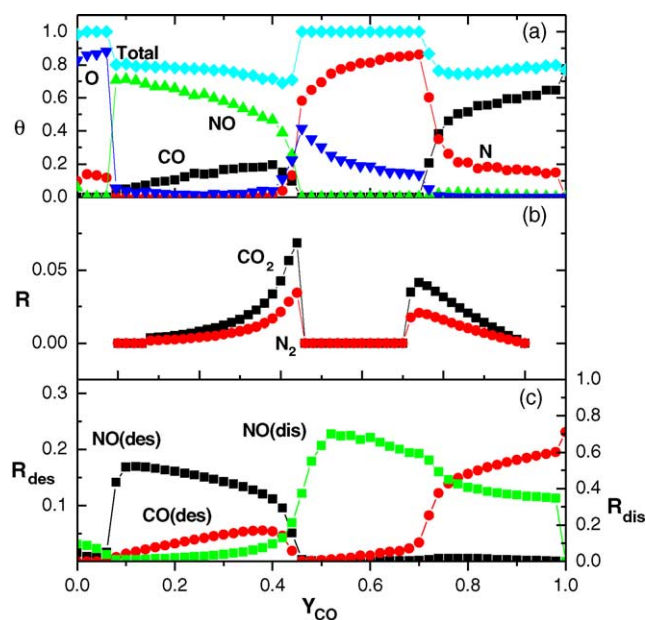


Fig. 2. Effect of neglecting the N+N recombination step for the formation of  $N_2$ . The same as Fig. 1 except that  $p_{N+N} = 0$ .

seen that the NO dissociation rate is depressed at low values of  $Y_{CO}$ , increases abruptly near 0.5, passes through a peak, and then stabilizes at higher values of  $Y_{CO}$ . This behavior is similar to that seen for the overall reaction rate. However, as we shall see below, several other processes are also important to obtain the right balance between different effects leading to the satisfactory behavior presented in Fig. 1. We will try to understand the effects of the most relevant processes by observing what happens when we suppress each one of them in the general scheme corresponding to the set of parameter values given above.

First, we consider the suppression of reaction step (6), the classical step for the formation of  $N_2$ . Thus, we make  $p_{N+N} = 0$  while keeping the same values as above for all other parameters. The results are given in Fig. 2, where drastic change is seen in spite of the fact that the behavior of NO dissociation is quite similar to that of Fig. 1. In particular, the reaction window disappears in the region of intermediate  $Y_{CO}$  values, where the surface becomes poisoned with adsorbed O and N, the latter showing a very high coverage. It can then be said that, when the dissociation of NO starts to accelerate, which is the condition for the reaction rate to reach its maximum, the formation and decay of the N–NO intermediate species is not enough to consume adsorbed N on its own, because NO disappears simultaneously from the surface and the reaction dies out. It has been shown in our previous work [19] that it is possible to maintain the reaction without step (6), but at the cost of introducing some unlikely process such as an Eley–Rideal step between NO(gas) and N(ads). We therefore conclude that step (6) must be considered in the mechanism of NO reduction, even if it is not the fastest way of producing  $N_2$ .

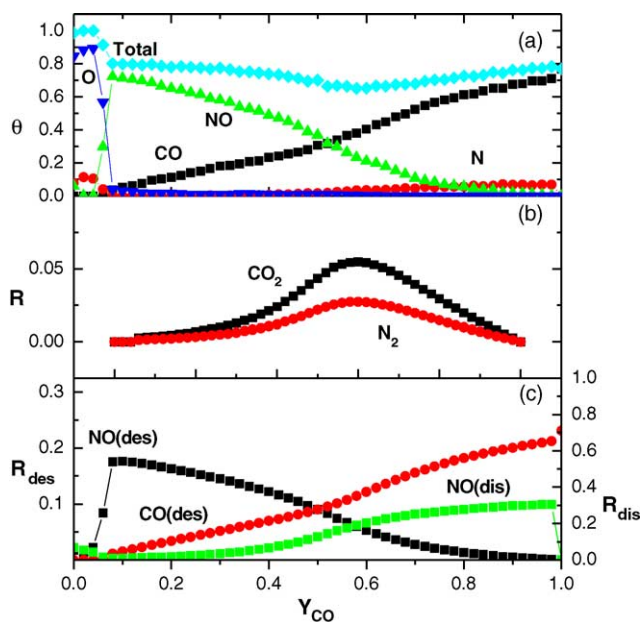


Fig. 3. Effect of neglecting the N–NO pathway for the formation of  $N_2$ . The same as Fig. 1 except that  $p_{N+N} = 1$ .

Next, the suppression of reaction steps (4) and (5) is considered, assuming that the only way to produce  $N_2$  is through the classical  $N + N$  recombination step (6). Fig. 3 shows the resulting behavior of the system: the overall reaction rate is depressed, strongly smoothed, and the maximum shifted to higher  $Y_{CO}$  values. Also, the N and O coverages almost disappear, in contradiction with experimental observations. This indicates that the formation of the N–NO intermediate is an important reaction step in the mechanism of NO conversion, and cannot be neglected. Even more, combining this result with the one above, it can be said that the two ways of producing  $N_2$  must be included in any quantitative description of this system, even if the N–NO formation process is dominant.

It is interesting to find out what the effect of N-islands formation is on the behavior of the system. By making  $c_N = 0$ , NO dissociation is no longer facilitated in the presence of neighboring co-adsorbed N atoms, and therefore the N-islands formation mechanism is shut down. Results using this assumption are shown in Fig. 4, where it can be seen that the increase in the reaction rate before reaching the maximum becomes smoother, the peak is shifted to higher CO concentrations in the gas phase, and N and O coverages become quite depressed. Therefore the N-islands formation also seems to be a necessary process to reproduce the experimental observations.

Next, we analyze the influence of NO and CO surface diffusion. Suppressing surface diffusion of these species, the behavior represented in Fig. 5 is obtained. The increase of the reaction rate before reaching the maximum becomes smoother, and the behavior of O and N coverages is not in good concordance with experimental observations. On the

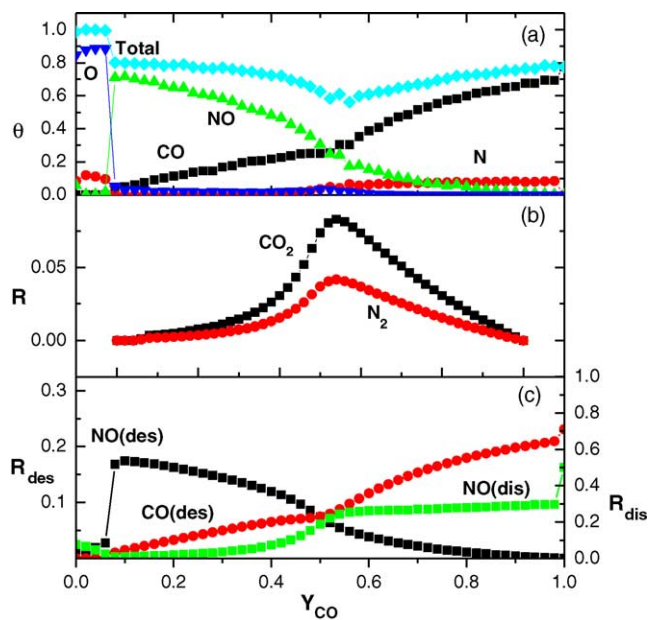


Fig. 4. Effect of neglecting the process of formation of N-islands. The same as Fig. 1 except that  $c_N = 0$ .

other hand, the NO dissociation rate becomes appreciably depressed near  $Y_{CO} = 0.5$ . The correct general behavior could be recovered, but at the cost of introducing a much higher desorption probability for CO than for NO, which would be unrealistic. Therefore, we conclude that the mobility of adsorbed NO and CO species is important to keep the appropriate behavior of NO dissociation and the overall behavior of the system.

We have already shown in previous work [19] the importance of the NO and CO desorption processes for the

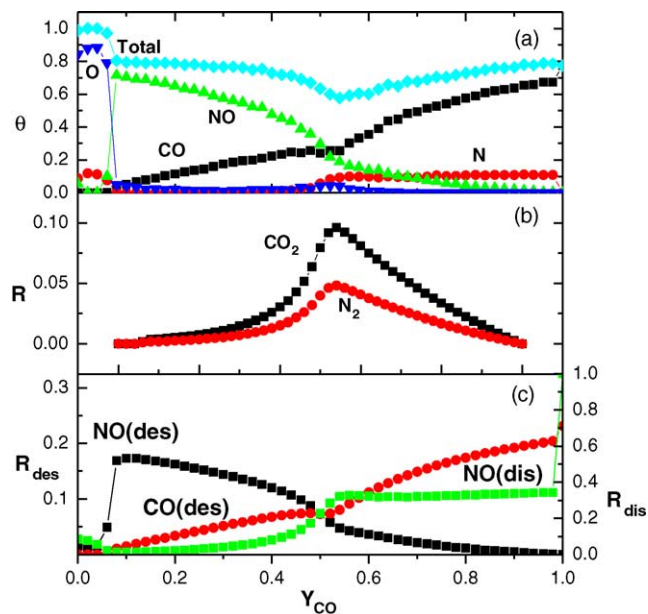


Fig. 5. Effect of neglecting NO and CO surface diffusion. The same as Fig. 1 except that  $p_{ads} = 1$ .

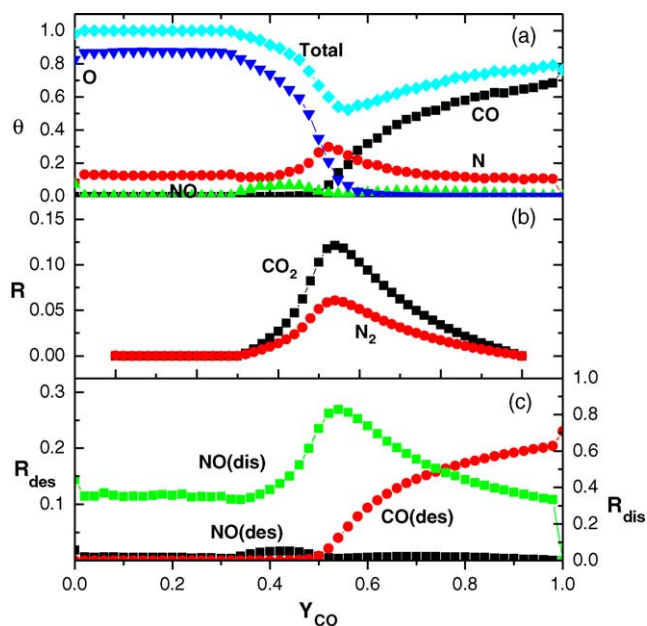


Fig. 6. The effect of neglecting the blocking of NO dissociation due to the presence of neighbor co-adsorbed NO and CO species. The same as Fig. 1 except that  $c_{N-O} = 0$ .

proper kinetics of NO reduction. If these are suppressed the reaction window disappears unless an Eley–Rideal reaction step is included, which we discarded as already discussed.

We now turn to another very important effect, the depression of NO dissociation by the presence of neighboring co-adsorbed NO or CO species. If this effect is suppressed by choosing  $c_{N-O} = 0$ , the results shown in Fig. 6 are obtained, where even though the behavior of reaction rates is correct, the behavior of adsorbed O is completely changed, with a high value of  $\theta_O$  at low CO concentration in the gas phase, which is in contradiction with experimental observations. No combination of parameter values could be found to recover the correct behavior in this case, because there are no other processes available to depress the high NO dissociation rate at low and intermediate  $Y_{CO}$  values.

Finally, the importance of the facilitating effect of the presence of neighboring co-adsorbed NO and CO on the formation and decay of the N–NO intermediate species is analyzed. By making  $c_{N-NO} = 0$ , a behavior (not shown here) quite similar to that of Fig. 1 is found. Therefore this effect seems not to be relevant, at least for the steady-state behavior of the system.

#### 4. Conclusions

A model for NO reduction by CO on Rh(1 1 1) has been proposed that incorporates realistic characteristics dictated by recent experimental results, namely, the production of  $N_2$  through the formation and subsequent decay of a N–NO in-

termediate species and the facilitation of this process by the presence of neighboring co-adsorbed NO and CO molecules (in addition to the classical N + N recombination step), the formation of N-islands, the increasing of NO dissociation probability with the number of neighboring vacant sites and the depression of this dissociation probability by the presence of neighboring co-adsorbed NO and CO species. In addition, other elementary processes such as the desorption and surface diffusion of NO and CO have also been considered.

The overall behavior of the reaction in steady-state, obtained by Monte Carlo simulations when all these characteristics are taken into account, is found to be in good qualitative agreement with experimental observations. Furthermore, the effects of neglecting each one of the above elementary processes were estimated, thus exposing their relative importance in the kinetics of the overall reaction. The most important effects were shown to be due to the right balance between the N–NO and the N + N pathways to produce  $N_2$ , the formation of N-islands, and the blocking effect of co-adsorbed NO and CO on the NO dissociation probability.

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