# **Experimental Studies and Redox-Type Monte Carlo Simulations for the Reduction Reaction of NO by CO over Supported Copper**

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Kinetics experiments for the CO–NO reaction over copper oxide supported on zirconia are interpreted adequately by theoretical activity decay models. A redox-type reaction mechanism is proposed for the process. A kinetic Monte Carlo simulation algorithm is developed for the case of a redox mechanism. Its results give a reasonable interpretation of the order of the experimental reaction.

Nitrogen oxides NO<sub>x</sub>, i.e., NO and N<sub>2</sub>O, are well known to be responsible for detrimental effects to the environment such as the greenhouse effect, acid rain, and ozone formation. Catalytic NO<sub>x</sub> abatement reactions are considered very important for the effluent gases from diesel and lean-burn engines. Such is the case of those that occur in the catalytic converters used to control NO<sub>x</sub> emission from mobile sources, such as automotive exhaust gases, like the reduction of NO by CO (CO-NO reaction) on supported noble metals, that has been studied extensively over the last 30 years, as has been reported in the reviews by Taylor<sup>1</sup> and Shelef and Graham.<sup>2</sup> This reaction has also been one of the classical prototype surface reactions which under flow conditions are good examples of nonequilibrium systems that show interesting behaviors such as dissipative structures, oscillations, kinetics phase transitions, and so forth, as has been very well reviewed by Evans,<sup>3</sup> Zhdanov,<sup>4</sup> and Albano.<sup>5</sup> The relation between both aspects have been of great interest to our research group for several years in our experimental work<sup>6</sup> as well as in the lines in which we use Monte Carlo (MC) simulations<sup>7</sup> and theoretical developments.8

Especially for economic reasons, over the last few years there has been increasing interest in the literature to study supported copper catalysts that have shown activity in the CO–NO reaction<sup>9</sup> and in another important reaction in converters, namely the oxidation of CO (CO–O<sub>2</sub> reaction).<sup>10</sup> These new systems show an important difference in the microscopic behavior of the reaction with respect to noble metal catalysts. While most of the latter seem to take place through a Langmuir–Hinshelwood (LH) type mechanism, copper catalysts act by a redox or Mars–van Krevelen<sup>11</sup> type mechanism.

This paper reports kinetics experiments with the CO–NO reaction over copper catalysts supported on ZrO<sub>2</sub>, and a Monte Carlo simulation algorithm is developed for a redox mechanism, which in this case will be used to interpret the system.

#### **Reaction Mechanism**

The study of the CO–NO reaction mechanism has a long history that does not lack interesting controversies. Among the most representative work in this relation, the old papers on the BZ mechanism by Brosilow and Ziff or Yaldran and Khan,<sup>12</sup> Hecker and Bell,<sup>13</sup> Oh et al.<sup>14</sup> and later those of Cho<sup>15</sup> should be mentioned. Later, as a result of experimental work with rhodium, Permana et al.<sup>16</sup> and Peden et al.<sup>16</sup> proposed a mechanism that has been largely accepted in current literature, while Chuang and Tan<sup>17</sup> take into account the existence of the positively or negatively charged NO species Rh–NO<sup>+</sup> and Rh–NO<sup>-</sup> on the surface to explain the behavior of the CO–NO reaction on supported Rh catalysts. Later, our group proposed a new mechanism<sup>18</sup> for the same system that took into account the last experiments made by Zaera et al.<sup>19</sup>

Most of the mechanisms proposed for the CO–NO reaction on noble metals assume that the process occurs by an LH-type mechanism. However, according to published studies, in the case of supported copper oxide catalysts the reaction occurs through a redox or Mars–van Krevelen<sup>11</sup> mechanism. This kind of mechanism, which we will discuss below, will be used in the simulations and analysis of this paper based on schemes proposed previously in the literature.

As is well known, three oxidation states are found on the copper oxide surface, CuO (Cu<sup>2+</sup>), Cu<sub>2</sub>O (Cu<sup>+</sup>), and Cu (Cu<sup>0</sup>), which change thermodynamically between each other as a function of temperature and the partial pressure of oxygen. Temperature-programmed reduction (TPR) studies of copper supported on zirconia (Cu/ZrO<sub>2</sub>)<sup>9</sup> showed that Cu<sup>2+</sup> species are reduced stepwise to Cu<sup>0</sup> via Cu<sup>+</sup> species in a stream of CO  $(Cu^{2+} to Cu^{+} at 100 \circ C and Cu^{+} to Cu^{0} at 170-180 \circ C)$ . On the other hand, the reduced Cu/ZrO2 surface is restored by NO treatment (1% in He), a process that takes place completely at a temperature above 250 °C. The above explains the redox mechanism of the CO-NO reaction on Cu/ZrO<sub>2</sub> suggested by Okamoto,9 who used XAFS techniques showing the reducing action of CO and the oxidizing action of NO, recovering the surface during the process of the reaction. The products of the CO-NO reaction are CO<sub>2</sub> over the whole temperature range, with N<sub>2</sub> produced especially at high temperatures and N<sub>2</sub>O at low temperatures, as will be seen later.

The redox mechanism mentioned above, which we will use to interpret the experimental information, is shown in Scheme 1, valid at low temperatures at which  $N_2$  production is

1) 
$$CO(g) + Cu^{2+} - O - Cu^{2+} \rightarrow CO_2(g) + Cu^+ - S + Cu^+$$
  
2)  $NO(g) + Cu^+ - S \rightarrow Cu^+ - NO_{adsorbed}$   
3)  $NO(g) + Cu^+ - NO_{adsorbed} - Cu^+ \rightarrow N_2O(g) + Cu^{2+} - O - Cu^{2+}$   
4)  $Cu^+ - NO_{adsorbed} + Cu^+ - NO_{adsorbed}$   
 $\rightarrow N_2O(g) + Cu^{2+} - O - Cu^{2+} + S$ 

S: oxygen vacancy

#### Scheme 1.

considered negligible. The first step shows the reducing action of CO(g) present in the gas phase, where the  $CO_2(g)$  product is obtained in an Elev Rideal (ER) form, which is desorbed reducing the surface of the catalyst and producing an oxygen vacancy, S. The recovery of the original surface occurs by the oxidizing action of NO(g) in the gas phase, which is first adsorbed on the Cu<sup>+</sup> active sites as shown in step (2). This is in agreement with the literature9 and with confirmations in our laboratory using FTIR techniques. It is assumed that the oxidation of the surface occurs through an ER type form according to the scheme of stage (3) between a molecule of gaseous NO and an adsorbed one, or through an LH type mechanism between two molecules of adsorbed NO according to step (4). Both steps produce  $N_2O(g)$  which is desorbed as a product, recovering the original surface. The necessary neighborhoods between the reacting species in the corresponding cases are taken into account in the Monte Carlo simulations as will be explained later.

The mechanism of Scheme 1 should become complicated at higher temperatures at which N<sub>2</sub> production is significant in relation to that of N<sub>2</sub>O. In this case superficial NO dissociation steps could be included, for example, with the corresponding production of  $\beta$  N<sub>2</sub> (2N<sub>adsorbed</sub>  $\rightarrow$  N<sub>2</sub>(g)) as we have considered in previous studies.<sup>7,8</sup>

#### Experimental

A 2% Cu/ZrO<sub>2</sub> catalyst was prepared by impregnating zirconia (ZrO<sub>2</sub>) with an appropriate amount of aqueous solution of copper nitrate trihydrate (Merck, p.a.). ZrO<sub>2</sub> was obtained by direct calcination of a commercial hydrated zirconium oxide (Zr(OH)<sub>4</sub>, MEI Chemical Corporation, FZ0922) at 500 °C for three hours. The impregnated support was then dried in an oven at 105 °C for 12 h.

To determine the catalytic activity, 0.1 g of catalyst was loaded into a 50 cm long and 1 cm diameter tubular reactor. The catalyst was calcined in situ for 1 h at 500 °C in a 10 cm<sup>3</sup> min<sup>-1</sup> stream of pure O<sub>2</sub>, cooled to 300 °C, and reduced in a flow of  $30 \text{ cm}^3 \text{ min}^{-1}$  of a 5% H<sub>2</sub>/Ar stream for 1 h. After that, the feed was switched to pure He and maintained at 300 °C for 1 h. The reactor temperature was then decreased to room temperature and the reactants were allowed to flow (90 cm<sup>3</sup> min<sup>-1</sup>) at a CO and NO concentration of 14 torr, the balance He. The temperature was then increased using an RKC model REX-P100 programmer at a rate of 2 °C min<sup>-1</sup> until the desired value was reached. The space velocity (GHSV) was 35000 h<sup>-1</sup>. The reactor inlet and outlet streams were analyzed by gas chromatography using two Perkin-Elmer Autosystem chroma-

tographs equipped with HWD detectors. The chromatographs had a HAYASEP D  $(2 \text{ m} \times 1/8 \text{ inch})$  column to analyze CO<sub>2</sub> and N<sub>2</sub>O. The conversion of NO and CO was calculated from the C and N mass balance, considering that the only nitrogen-containing products are N<sub>2</sub> and N<sub>2</sub>O, and the only carbon-containing product is CO<sub>2</sub>, according to the following reaction pathways:

$$CO + 2NO = CO_2 + N_2O \tag{1}$$

$$\mathrm{CO} + \mathrm{NO} = \mathrm{CO}_2 + \frac{1}{2}\mathrm{N}_2 \tag{2}$$

Therefore, the  $N_{\rm 2}$  concentration was estimated from the equation

$$[N_2] = \frac{1}{2}([CO_2] - [N_2O])$$
(3)

where  $[CO_2]$  and  $[N_2O]$  are the  $CO_2$  and  $N_2O$  concentrations, respectively, in the reactor effluent.

### **Kinetic Monte Carlo Simulations**

The kinetic Monte Carlo (kMC) algorithm developed in this paper is similar to others used previously by our group for various reactions, such as the oxidation of CO or the reduction of NO by  $CO^{20}$  and to that reported recently by our group<sup>21</sup> for the  $CH_4$ – $O_2$  reaction. For those reactions, however, as is often the case, a Langmuir–Hinshelwood (LH) type mechanism was assumed. In this case we used the redox mechanism of Scheme 1 for the CO–NO reaction over Cu/ZrO<sub>2</sub>. As far as we are aware, in the literature there seem to be no Monte Carlo algorithms assuming a redox mechanism for the reaction.

The simulation algorithm begins by choosing an event of the mechanism (adsorption or one of the reactions) according to the probability  $p_i$  of the event defined by

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$$p_i = k_i / \sum k_i \tag{4}$$

where  $k_i$  corresponds to the rate constant of step *i* of the mechanism. In the case of the adsorption steps,  $k_i$  was calculated from the collision of gas A molecules with a solid surface (effusion) expression:

$$k_i(\text{ads}) = S_A \sigma (2\pi M_A RT)^{-1/2} P_A$$
(5)

where  $M_A$  is the molar mass of gas A,  $S_A$  is the corresponding sticking coefficient ( $S_A = 1$  in this case),  $P_A$  is the partial pressure, and coefficient  $\sigma$  is the area occupied by 1 mol of superficial metal atoms and A can be CO or NO.

The Monte Carlo simulations allowed a set of kinetic parameters to be selected according to criteria based on observations of the behavior of the mechanism and on the magnitude of the experimental data found for the system.

Since step (2) corresponds to the adsorption of NO, we calculated its kinetic constant from the collisions expression assuming that it has no activation energy. Step (1), on the other hand, can be thought of as the combination of the adsorption of CO and a kinetic process that produces  $CO_2$  which is desorbed to the gas phase. The kinetic constant for this stage can be conceived as given by the Arrhenius expression  $k_i = A_i \exp(-E_{ai}/RT)$ , with a frequency factor  $A_i = A_1$  equal to that of the collisions of CO with an additional activation energy  $E_{a1}$ . A similar assumption was made for step (3). In step (4) we

have assumed an arbitrary value for the frequency factors,  $1 \times 10^7$ , similar to the order of magnitude of the collisions of the first two steps. This means that the activation energy obtained is relative to a conventional choice of the frequency factor.

In a first analysis simulations were made eliminating one of the two last steps of the kinetic mechanism. It was seen that when step (3) did not exist and only step (4) was operational, orders close to zero were obtained for NO and CO over a wide range of parameters. In the opposite situation, when step (3) was operational and step (4) was eliminated from the simulation, an order close to one was obtained for NO, and it was not possible to get magnitudes close to those obtained in the experiment, which were in the order of 0.6. This led us to conclude that the mechanism required both steps to interpret experimental behavior. This analysis also made it possible to restrict to a very small range the allowed activation energies of steps (3) and (4) to remain in the range of the experimental activities.

A complementary analysis showed that the activities and orders obtained with the proposed mechanism depend very little on the activation energy of the  $CO_2$  production reaction (step 1), provided the activation energy of step 1 is less than that of step (3). Otherwise an order close to one is obtained for CO and close to zero for NO, contradicting the experiment. It is therefore concluded that experimental production is controlled by the magnitudes of the activation energies of the last two steps, in particular step (3).

Based on the above considerations and assumptions, a set of kinetic parameters was sought that would interpret in the best possible way the orders and experimental data at 403 K, getting the following relative activation energies:  $E_{a1} = 5 \text{ kcal mol}^{-1}$ ,  $E_{a2} = 0$ ,  $E_{a3} = 16 \text{ kcal mol}^{-1}$ , and  $E_{a4} = 17 \text{ kcal mol}^{-1}$ . The reaction orders obtained in the MC simulation are shown in the graphs of Figure 5, at 403 K, a temperature at which N<sub>2</sub> production is small compared to that of N<sub>2</sub>O, a condition that is in agreement with the model used in the MC.

The substrate used in the simulations is a surface made of copper sites located in an  $L \times L$  square lattice (L = 30) with periodic boundary conditions, and sites S located in the center of the squares formed by four neighboring copper sites. It is assumed that copper can only change its charge (in this case  $Cu^{2+}$  and  $Cu^+$ ) and that the S sites can contain oxygen in the  $O^{2-}$  oxidation state or an NO molecule, or they can be vacant.

The MC algorithm begins with the selection of the event. If it corresponds to the adsorption of NO, an S site is chosen randomly and if it is empty, a  $Cu^+$  is sought in the four surrounding sites. A neighboring  $Cu^+$  site is required for the adsorption to take place, so if one of them is found a molecular NO particle is adsorbed on the S site. If no  $Cu^+$  is found, the event ends without change.

If the chosen event is reaction (1), a superficial site S is first chosen randomly. If this site does not contain O, the event ends, but if there is O the search for two  $Cu^{2+}$  continues among the four copper species that surround the oxygen. If there are less than two  $Cu^{2+}$  the event ends, and if there are three or more  $Cu^{2+}$ , two are chosen among the existing ones, which become  $Cu^{+}$ , and one molecule of  $CO_2$  gas leaves the surface, leaving an empty site where the oxygen was.

Now, if the chosen event is reaction (3), an S site is first chosen randomly. If that site does not contain adsorbed NO the event ends, otherwise the search for two Cu<sup>+</sup> continues among the four copper species surrounding the NO. If there are more that two Cu<sup>+</sup>, two are chosen among the existing ones, and if there are less than two the event ends without change. If the event was successful, one molecule of N<sub>2</sub>O gas leaves the surface, the site that contained an NO is occupied by an O atom, and the two Cu<sup>+</sup> become Cu<sup>2+</sup>.

If the chosen event is reaction (4), two NO adsorbed on nearest neighbor S sites are required, and we proceed as follows: a superficial site is first chosen randomly. If this site corresponds to  $NO_{(a)}$ , a neighboring S site is chosen. If this site does not contain an adsorbed NO, the event ends, otherwise the search for Cu<sup>+</sup> continues in the six copper sites neighboring both. If two or more Cu<sup>+</sup> are found the event is successful, and sometimes it is necessary to choose randomly two of those sites, which change their charge to Cu<sup>2+</sup>. Otherwise the event ends without change. If the event was successful, an N<sub>2</sub>O gas molecule is produced and an O particle remains in the first chosen S site. Computing time was measured in Monte Carlo Steps (MCS), defined as a number of attempts equal to the number of sites in the substrate. Times on the order of 250 to 600 million MCS were used in the simulations.

#### **Results and Discussion**

Kinetics experiments were carried out with the CO–NO reaction over copper oxide supported on zirconia, observing first a general vision of its behavior with temperature. Then the time evolution of activity toward the steady state was determined, allowing the system to be analyzed in the light of deactivation models. Finally, determination of the reaction order allowed the experiment to be compared with the mechanism of the reaction using simulation techniques of the Monte Carlo type.

Behavior of Activity with Temperature. Figure 1 shows the behavior of the system's activity with temperature through the conversion of CO into  $CO_2$  and of NO into  $N_2$  and  $N_2O$ , similar to what was reported by Okamoto et al.<sup>9</sup> No other



Figure 1. Catalytic activities of  $2 \text{ wt }\% \text{ Cu/ZrO}_2$  for CO– NO reaction as a function of the reaction temperature. CO conversion ( $\bigcirc$ ), NO conversion to N<sub>2</sub> ( $\blacktriangle$ ), NO conversion to N<sub>2</sub>O ( $\bigcirc$ ), total NO conversion ( $\square$ ).



Figure 2. Arrhenius like expression in the final steady state  $P_{\rm CO} = 7.6$  torr,  $P_{\rm NO} = 3.8$  torr.



**Figure 3.** Experimental decay of normalized production versus time at various temperatures ( $\bigcirc$ ) 403, ( $\bigcirc$ ) 463, and ( $\blacksquare$ ) 523 K at  $P_{\rm CO} = 15.2$  torr and  $P_{\rm NO} = 7.6$  torr. The lines have been drawn to guide the eyes.

products were found as a result of the reaction. An increasing conversion of CO over the whole temperature range was observed. Conversion of NO, on the other hand, shows that  $N_2$  increases constantly after about 100 °C, with lower conversion into  $N_2O$  at an intermediate temperature range. At temperatures higher than about 200 °C  $N_2O$  production decreases strongly until it disappears at approximately 300 °C, and above that the only reaction products are CO<sub>2</sub> and  $N_2$ . This results in the maximum observed for the conversion of NO into  $N_2O$ . Figure 2 presents the thermal behavior of the reaction by means of an Arrhenius graph in the indicated zone, which shows an apparent activation energy for the system equal to 11 kcal mol<sup>-1</sup>.

**Catalyst Deactivation Models.** Figure 3 describes the temporal evolution of the system's activity through the conversion of CO versus reaction time at constant temperature and pressure of the gas phase. These results show a deactivation phenomenon observed at three temperatures. Deactivation is practically not observed at 250 °C.

 
 Table 1. Fitting Parameters of the Corresponding Models and Some Experimental Data of Figure 3

Equation	Т	K	$\phi$
$A = 1 - K_1 t $ (6) Linear (Ref. 22)	${ 403 \\ 463 }$	$\begin{array}{c} 0.00094 \ (K_1) \\ 0.001367 \ (K_1) \end{array}$	0.1247 0.4833
$A = \frac{1}{1 + K_2 t}$ (7) Hyperbolic (Ref. 23)	${403 \\ 463}$	$0.001773 (K_2)$ $0.00434 (K_2)$	0.0392 0.1082
$A = K_4 \exp(-K_3 t) $ (8) Exponential (Ref. 24)	403 463	$0.0009 (K_3)$ $0.87 (K_4)$ $0.00158 (K_3)$ $0.77 (K_4)$	0.0287 0.1020
$A = \frac{1}{1 + K_5 t^{K_6}} $ (9) (Ref. 25)	$\begin{cases} 403 \\ 463 \end{cases}$	$\begin{array}{c} 0.023 \ (K_5) \\ 0.56 \ (K_6) \\ 0.08547 \ (K_5) \\ 0.47 \ (K_6) \end{array}$	0.0022 0.004149

One of the most interesting problems in catalysis, which is also important because of its clear practical applications, is the loss of catalytic activity that occurs in some systems when the reaction takes place. The complexity of the phenomenon, due to its multiple possible causes, makes it difficult to establish models for its interpretation, explaining why it has not been given sufficient importance in recent literature. In spite of this, a number of models have been proposed, some of them with a rather empirical character and others corresponding to an assumed deactivation mechanism.

It is interesting to contrast these results with deactivation models. Table 1 shows some cases of models for the activity decay that we have considered as the most representative in the literature and that we have used to interpret our experimental data, such as eq 6, whose linear shape is the simplest possible;<sup>22</sup> a hyperbolic law represented by eq 7 that has been proposed in case the deactivation is due to aging by sintering of the catalytic substrate;<sup>23</sup> eq 8, which corresponds to an exponential law proposed in some cases of poisoning by molecules that are irreversibly chemisorbed on the surface;<sup>24</sup> and eq 9, proposed in some examples of coking or dirtying of the surface.<sup>25</sup> The experimental activities  $R_{CO_2}(exp)$  of the system for initial time (t = 0) and for any time t are obtained in the experimental case from the conversion values of CO ( $X_{CO}$ ) that are shown in Figure 3, using the expression  $R_{\rm CO_2} = F_{\rm CO} X_{\rm CO} / n_{\rm Cu}$ , where  $n_{\rm Cu}$  is the number of moles of active sites on the surface and  $F_{\rm CO}$  is the flow rate of CO in moles per second. This relation is valid for  $X_{CO} < 10\%$ , which is the case of our experimental results. These values allow the determination of the decay of CO<sub>2</sub> production expressed through the normalized variable at the initial time defined by the relation  $A_{CO_2}(\exp) = R_{CO_2}(t = t) / R_{CO_2}(t = 0)$ .

The  $A_{CO_2}(exp)$  values obtained in the experiment were later adjusted by the theoretical deactivation models that express  $A_{CO_2}(te)$  as a function of time and of the parameters of each model as shown in Table 1. The fit was obtained on the computer according to the least-squares criterion, which



Figure 4. Experimental reaction order of (a) CO, 403 K,  $P_{NO} = 1.9$  torr (b) CO, 523 K  $P_{NO} = 7.6$  torr (c) CO, 403 K,  $P_{NO} = 15.2$  torr (d) NO, 403 K,  $P_{CO} = 15.2$  torr (e) NO, 523 K,  $P_{CO} = 15.2$  torr (f) NO, 403 K,  $P_{CO} = 3.8$  torr.

allows getting the optimum parameters of the model as those that correspond to the minimum value of the function  $\phi = \sum_i (A_{\text{CO}_2}(\text{te})_i - A_{\text{CO}_2}(\exp)_i)^2$  where the sum is made over all the experimental points (*i*), comparing the values of  $A_{\text{CO}_2}(\exp)_i$ with those corresponding to each theoretical model  $A_{\text{CO}_2}(\text{te})_i$ .

Table 1 shows, for two temperatures, the optimum parameters of the corresponding equation and the value of the quadratic function  $\phi$  for each of the minima. It is seen that in the case of our experimental data the best fit with the model is given by eq 9. This equation, on the other hand, has been used to interpret deactivation results due to coking of the catalytic surface. This phenomenon has been reported by Rainer et al.<sup>26</sup> in the case of the CO–NO reaction over small supported Pd particles, commenting that a possible cause of the deactivation was the blocking of active sites with carbon atoms produced by the dissociation of CO on the surface. In our case we do not have good arguments to accept that situation. However, eq 9 can be associated in a wide sense with the alterations of the active sites due to the mechanism of the reaction, such as the variation of the chemical state of superficial Cu as will be commented in the following section.

Okamoto et al.<sup>9</sup> carried out experiments with the CO–NO reaction over Cu/ZrO<sub>2</sub> and got a curve similar to that of Figure 1, which shows the relation of activity with temperature, also showing a decay of the activity at low temperatures like that obtained by us in Figure 3. They also related these results with the catalytic hysteresis ( $X_{NO}$  vs. *T*) that they found in their experiments, which they associated with the gradual deactivation of the active species during the course of the reaction. Although this agrees with the alteration of the superficial active species that we commented in the previous paragraph, they also relate it with a sintering effect that they found in their



Figure 5. Monte Carlo reaction order of (a) CO,  $P_{NO} = 1.9$  torr (b) CO,  $P_{NO} = 15.2$  torr (c) NO,  $P_{CO} = 3.8$  torr (d) NO,  $P_{CO} = 15.2$  torr.

experiments. This phenomenon, on the other hand, has been excluded by Rainer et al.,<sup>26</sup> who comment that "the catalyst has been exposed to much harsher temperature conditions during initial reduction than it experiences in the CO–NO run." Since this has also been the case in our experiments, we have no arguments to consider the effects of sintering. Neither do we believe that the fits of Table 1 are sufficient proof to exclude sintering, such as from the values of  $\phi$  of eq 7 in relation to those of eq 9 if we consider that both equations were fitted with different numbers of parameters.

Another possible explanation of the phenomenon, given by Rainer et al.,<sup>26</sup> is the presence of inactive nitrogen atoms adsorbed on the surface, like those proposed by Oh and Eickel<sup>14</sup> to explain the behavior of the system in the case of rhodium. However, associating this case with a given decay equation is not a simple matter.

Decreasing activity was seen with time in the MC simulations measured in Monte Carlo Steps (MCS) that is not simple to associate with the deactivation observed in the experiment, since in this case the decay includes the natural stochastic evolution characteristic of MC. This, however, is an interesting aspect that we are currently exploring. In this paper we have used the steady state MC values corresponding to long times in which the activity remains constant to compare them with the theoretical mechanism. In our case this corresponded to values on the order of 600 million MCS.

**Reaction Order and Kinetics Mechanism.** A practical way of expressing the relation between the activity of a catalytic system and the pressure of the reactants in the gas phase is to define the order of the reaction for a given temperature, for

example in the case of the CO–NO reaction, by an empirical expression between the activity of  $CO_2$  and the pressure of CO and NO:

$$R_{\rm CO_2}(\rm TON) = k P_{\rm CO}{}^m P_{\rm NO}{}^n \tag{10}$$

The order *m* for CO or *n* for NO can be obtained, both in the experiment and in the Monte Carlo simulations, from the slope of the graph of the logarithm of  $R_{CO_2}$  versus the logarithm corresponding to each of the pressures while keeping the other constant.

Figure 4 shows the experimental results of these graphs for the various situations indicated in each of the cases. In general terms, straight lines with good correlation are found, showing that the system's experimental behavior fits reasonably well the approximation that is assumed by eq 10. Figure 5 shows, on the other hand, the same type of graphs obtained in the Monte Carlo simulations assuming that the reaction behaves according to the redox mechanism suggested in Scheme 1 and the activity remains within the observed range in the experimental information around 403 K, when the production of  $N_2$  is small compared to that of  $N_2O$ .

Table 2 gives a summary of the orders obtained from the experiment and from the Monte Carlo simulations, together with the only values we have found in the literature for the same system.

Figure 6 shows in general that production decreases with the concentration of CO,  $y_{CO}$ , in the gas phase. On the other hand, it is seen that the superficial configuration remains approximately constant over the whole range of CO concentrations, with slight variations such as, for example, an increase of Cu<sup>2+</sup>

**Table 2.** Reaction Order for CO–NO Reaction over Cu/ ZrO<sub>2</sub>  $R_{CO_2}$ (TON) =  $kP_{CO}{}^mP_{NO}{}^n$ : (a) Experimental 2 wt % Cu/ZrO<sub>2</sub> (Figure 4); (b) Experimental 1 wt % Cu/ZrO<sub>2</sub> (fresh) (Ref. 9); (c) The Same as (b) Cu/ZrO<sub>2</sub> (Deactivated); (d) Monte Carlo Simulation (Figure 5)

	T/°C	т	п	
$P_{\rm CO} > P_{\rm NO}$	130	-0.11	0.48	(a)
	250	0.13	0.58	(a)
	130	-0.003	0.63	(d)
$P_{\rm NO} > P_{\rm CO}$	130	0.17	0.25	(a)
	130	-0.06	0.65	(d)
	250	0	0.85	$(b)_{ref(9)}$
	250	-0.1	1.0	$(c)_{ref(9)}$



**Figure 6.** Production of CO<sub>2</sub> and the surface concentration  $\theta_i$  of species *i* versus concentration  $y_{CO}$  (phase diagram) obtained from Monte Carlo simulations for  $P_{CO} + P_{NO} = 30 \text{ torr } (\Box) \theta_O$ , ( $\blacktriangle$ )  $\theta_{NO}$ , ( $\bigcirc$ )  $\theta_{Cu}^{2+}$ , ( $\blacklozenge$ )  $\theta_{Cu^+}$ ,  $R_{CO_2}$  (—).

corresponding to a small decrease of Cu<sup>+</sup>. Over the whole range of  $y_{CO}$ , on the other hand, the concentration of vacant sites is extremely small, indicating that only a small fraction of the surface participates in the CO–NO redox reaction and the surface always remains reduced. It should be recalled, however, that the mechanism assumes that there is only production of N<sub>2</sub>O as well as of CO<sub>2</sub>. The experiments were performed in the zones in which they can be compared with the assumptions of the Monte Carlo simulations, which requires N<sub>2</sub> production to be low with respect to N<sub>2</sub>O.

Table 2 shows an order for CO close to zero in all cases, both in our experimental results as well as in those from the literature. These values are also well interpreted by the results of our Monte Carlo simulations. In the case of the order for NO, on the other hand, in general positive values less than 1.0 are found in the experiments as well as in the simulations.

#### Conclusion

Kinetics experiments were run for the CO–NO reaction over copper oxide supported on zirconia, which were interpreted reasonably well by means of activity decay models and Monte Carlo simulations, in the latter case assuming a redox mechanism for the reaction. The variation of the activity of  $CO_2$  with temperature shows an increasing evolution of  $CO_2$  and  $N_2$  with temperature, while  $N_2O$  production presents a maximum.

The experiments were carried out in zones in which  $N_2$  production was small, in order to contrast their results with a simplified mechanism that assumes that  $CO_2$  and  $N_2O$  are the only products of the reaction.

The experiments showed a time decay of the activity at moderately low temperatures that was interpreted by models which show that the decay is not caused by structural changes of the substrate, but by alterations of the number of active sites due to the mechanism of the reaction, for example by the variation of the chemical state of superficial Cu.

A Monte Carlo type simulation algorithm was developed for a redox type reaction mechanism. Its results interpret reasonably well the order of the reaction.

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