

Monte Carlo study of the influence of the structural heterogeneity of the surface in the CO–NO reaction on Pd and its relation with experimental data

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A B S T R A C T

The reduction reaction of NO by CO over Pd is studied by means of a Monte Carlo simulation. A reaction mechanism similar to that established previously in the literature for Rh and a set of recently published kinetics parameters for Pd determined from experimental work are assumed. The heterogeneous effects of the catalytic substrate are analyzed by simulating various surfaces: a uniform square and hexagonal lattice, the incipient percolation cluster (IPC) fractal, and a lattice formed by a cluster distribution supported on a deterministic fractal. The results interpret reasonably the experimental data published recently in the case of crystals and supported catalysts.

1. Introduction

Surface reactions have attracted the attention of researchers over the last decades because of their importance in heterogeneous catalysis and because they are good examples for the study of irreversible dynamics systems that exhibit complicated behaviours such as oscillations, kinetic phase transitions, and other interesting phenomena [1], aspects that have also been very well reviewed by Evans [2], Zhdanov and Kasemo [3], and Albano [4]. Among them, the catalytic reduction of NO by CO (CO–NO reaction) over noble metals has been studied extensively over the last 20 years [5] because of its importance, together with the oxidation of CO, in catalytic converters used to control the pollutant emissions from mobile sources such as automobile exhaust gases.

Rhodium and platinum have traditionally been the most widely used metals because of their excellent catalytic behaviour in the CO–NO reaction. During the last few years, however, there has been increasing interest in the use of palladium in commercial catalysts because although it has lower activity, it is more abundant in nature and is therefore less expensive. Furthermore, it has shown excellent characteristics for the oxidation of hydrocarbons and is more durable at high temperatures because of its resistance to sintering [6–8]. On the other hand, continuous improvement in the quality of gasoline has decreased the negative impact of the lower resistance of Pd to poisoning by S compared to other metals.

Because of the above reasons, knowledge of the microscopic behaviour of the CO–NO reaction on Pd is less than that on Rh and Pt [6,8]. Only recently experimental information has been published on the magnitude of the activation energy and frequency factor of the elementary steps of the kinetics mechanism of this system,

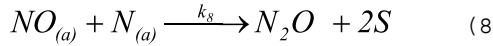
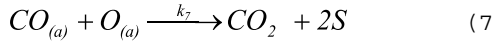
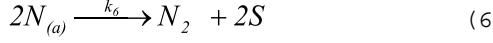
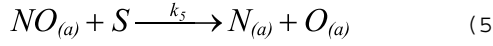
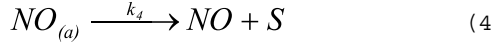
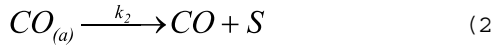
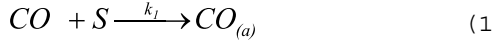
assuming a mechanism similar to that of Rh and in the case of experiments carried out at low pressure and ultra high vacuum (UHV) [6,7]. The interest in the use of Pd in commercial catalysts, the scarce information on kinetics results under moderate pressure, the difficulty to establish the true reaction mechanism, and the well-known general effect of the structural sensitivity shown by that reaction make the study of the CO–NO reaction on Pd a challenge of great current interest. In this Letter, an attempt is made to interpret and discuss, through the use of Monte Carlo simulations, the experimental kinetics information published in the literature for this system at moderate pressures (1–5 torr), and to analyze some general characteristics of the systems studied. For that purpose, a reaction mechanism similar to that of Rh, recently published experimental kinetic parameters, and some models that simulate the characteristics of uniform and supported catalysts that have been proposed or used by the authors in previous papers [9] will be considered.

2. The reaction mechanism

As commented in recent papers [6,8], to date there is no agreement on the kinetic mechanism for the CO–NO reaction on Pd. However, as a first approach to the problem, and given the closeness of Pd and Rh in the periodic table, in a series of recent papers [6–8] it has been assumed that it is identical to that proposed a few years ago by Peden [10] and Permana [11] for Rh. This mechanism is shown in Scheme 1, where S represents a vacant site and $\text{CO}_{(a)}$, $\text{NO}_{(a)}$, $\text{N}_{(a)}$, and $\text{O}_{(a)}$ are the species adsorbed on the surface.

One of the most interesting aspects of the interpretation of the experimental kinetics information is to have adequate kinetic parameters for the steps of the mechanism. Since they are often available for UHV conditions, an important matter that has been discussed in the literature is whether it is possible to use those

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Scheme 1. Mechanism of the CO–NO reaction used in the Letter.

data to describe the reaction kinetics at the higher pressures used in practice, e.g. from a few torr to atmospheric. This matter, which is called the ‘pressure-gap problem’ [12], has been discussed in detail by Zhdanov [13] in the case of the CO–NO reaction over Rh with rather discouraging results.

In the recent literature there have been two papers with a number of activation energy and frequency factor data for modeling the behaviour of the CO–NO reaction over Pd [6,7]. Both studies used a molecular-beam reaction system under low pressure and UHV conditions, respectively, assuming the mechanism given in Scheme 1 with the exclusion of the N₂O production of step (8), because under the conditions of the experiments only CO₂ and N₂ were produced in appreciable amounts. The experimental kinetics constants published by these authors have been determined on a single crystal. In the recent literature interesting values of the activation energy for this system obtained by quantum methods through the density-functional theory (DFT) have been published [14], but unfortunately no adequate values for the corresponding frequency factors are yet available.

As far as the present authors have found, there does not seem to be available in the literature more information on kinetic parameters for the system in which we are interested than that in the papers mentioned above. We have chosen the set of parameters published in 2005 by Nakao et al. [7] for the CO–NO reaction on the Pd(110) surface that are shown in Table 1, to discuss some aspects of the results obtained by simulations for this reaction over some interesting surfaces modeled on the computer and compare them with recently published experimental data. The set of parameters chosen corresponds to the range of pressures (0.1–0.01 torr) close to atmospheric, minimizing the error due to the ‘pressure-gap problem’ and the crystal surfaces of Pd do not have the additional complexities of supported catalysts.

The simulations of this work were made at moderate pressures of the order of those used for some recently published kinetics experiments, with the purpose of enriching the discussion, establishing an interaction between experiments and Monte Carlo simulations of the mechanism’s kinetic equations. In the analyses we have considered additionally the kinetic parameters published for Rh [15] in the case of step (8).

3. Simulation procedure

The MC algorithm used in this Letter is similar to one used previously by our group [16] for the CO oxidation reaction, based on

one proposed earlier for this system [17] and recently for the CO–NO reaction [18]. For the CO–NO reaction the simulation process starts by selecting an event from the mechanism (adsorption, desorption, dissociation or reaction) according to the probability, p_i , of the event defined by

$$p_i = k_i / \sum_i k_i \quad (1)$$

where k_i corresponds to the rate constant of step i of the mechanism. It is assumed that the rate constants k_i can be expressed as functions of temperature T according to Arrhenius’ equation:

$$k_i = \nu_i \exp(-E_i/RT) \quad (2)$$

where E_i is the activation energy and ν_i is the frequency factor. In the case of adsorption, k_i is calculated according to the expression of the kinetic theory of gases

$$k_i(\text{ads}) = S_i \sigma (2\pi M_i RT)^{-1/2} \quad (3)$$

where M_i is the molecular mass of i , S_i is the corresponding sticking coefficient, and the coefficient σ is the area occupied by 1 mol of superficial metal atoms.

The substrates used in the simulations were a uniform surface made of sites located in an $L \times L$ square lattice, a hexagonal lattice, a statistical fractal, the incipient percolation cluster (IPC), and a surface formed by a set of clusters supported on a deterministic fractal according to a procedure proposed by our laboratory in a recent paper [19]. The active sites of the IPC were generated by blocking a fraction equal to 0.407254 of the $L \times L$ sites (impurities) of the square lattice, with a fractal dimension equal to 91/48 [20]. The substrates are obtained in this case by considering only the spanning cluster of the remaining sites computed by Kopelman’s algorithm [21]. Since the IPC is probabilistic or nondeterministic, it was necessary to generate a number of them, so that the properties obtained from MC for the CO–NO reaction are the average of the results of the simulations carried out on those substrates.

The surface formed by a cluster distribution, such as the example shown in Fig. 3, has been proposed by the authors in a previous paper [19]. The corresponding substrate has been constructed over a deterministic fractal based on a symmetry-theoretical concept of fractal geometry [22], that simulates the catalyst’s support, as follows: A first point of the fractal is chosen as the center of a first element of radius R (that may represent a supported metal atom like Pd, for example), and then all the points on the fractal located within a sphere of radius $2R$ are discarded from the list of possible centers. Then the point of the fractal closest to the first element is chosen as the center of the second element, and once again all the points located within a sphere of radius $2R$ centered at that point are discarded, and this is done repetitively until there are no points on the support with sufficient space to locate a new element. The radius R of the element is defined as a function of the average distance d between a site and its nearest neighbour in the fractal according to $R = \text{FD} \times d$, where factor FD is varied with the purpose of changing the cluster distribution obtained. The values used are properly indicated in the Letter. At the end of this process, a set of catalytically active sites of radius R is obtained whose centers are located in a fractal. If a maximum distance allowed between the sites for them to be considered neighbours is defined adequately, the sites of the catalyst’s set are grouped in clusters, with each cluster containing those sites that have a neighbourhood relation between them. In this Letter, we have assumed that two sites are nearest neighbours (nn) if their centers are at a distance between $R_1 = 2R$ and $R_2 = 2Rf_v$. The value of the neighbourhood factor f_v used in this Letter was equal to 1.1.

In general, to reach an adequate stability in the results, use was made of a number of iterations of the order of 3×10^7 MCS (Monte Carlo steps), defined as a number of attempts equal to the number of active sites in the substrate.

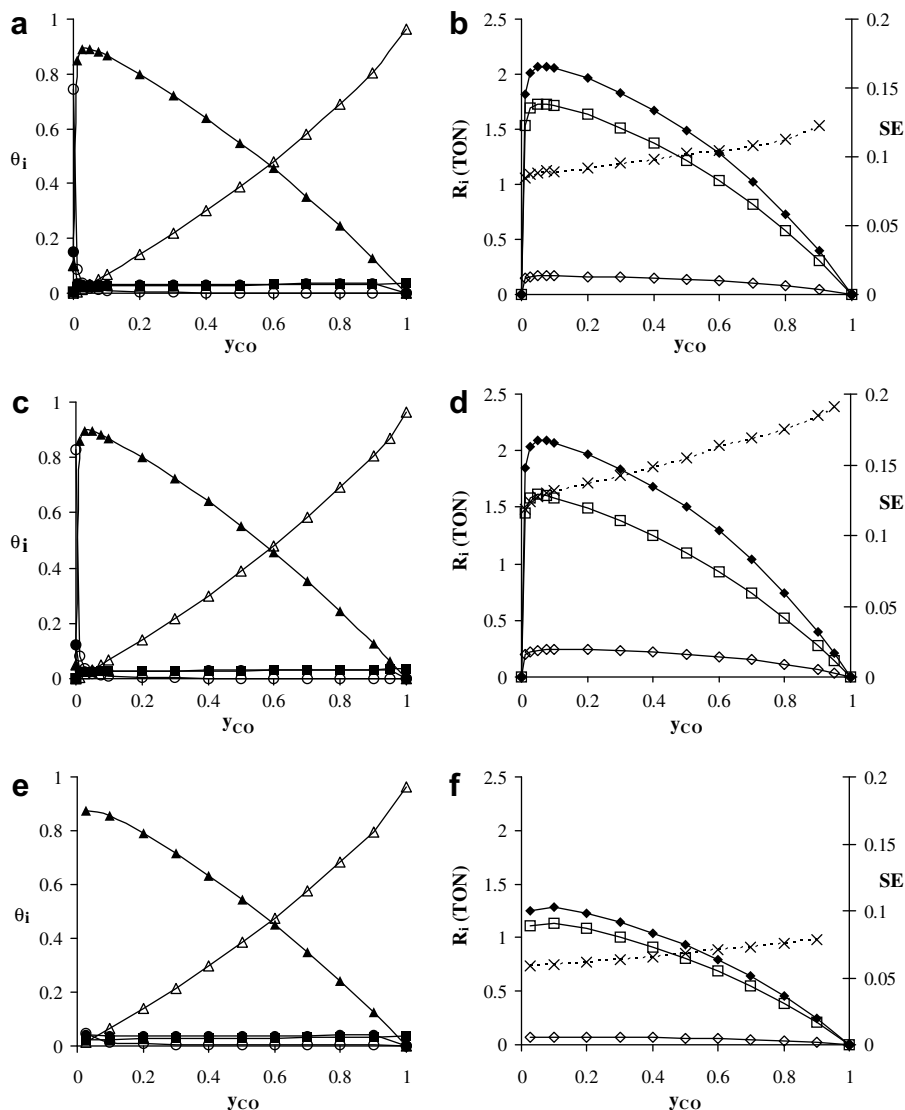


Fig. 1. Phase diagrams (θ_i, y_{CO}), production (R_i, y_{CO}) diagram and selectivity (SE, y_{CO}) diagram in the steady state for the mechanism of Scheme 1, the parameters of Table 1, a uniform surface, and $T = 600$ K. (a,b) Square lattice, (c,d) hexagonal lattice, (e,f) IPC. (\blacklozenge) R_{CO_2} ; (\diamond) R_{N_2} ; (\square) R_{N_2O} ; (\times) SE; (\triangle) θ_{CO} ; (\blacktriangle) θ_{NO} ; (\bullet) θ_N ; (\circ) θ_O ; (\blacksquare) $\theta_V = \text{vacuum}$. The lines have been drawn to guide the eyes.

The MC algorithm begins with selection of the event. If it corresponds to the adsorption of CO, an active site is chosen randomly on the surface, and if it is vacant, a $CO_{(a)}$ particle will be adsorbed. If the site is occupied, the attempt is ended. If the adsorption of NO is chosen, the procedure is completely analogous and an $NO_{(a)}$ particle is adsorbed.

If CO desorption is chosen, a surface active site is selected randomly. If it is occupied by a particle different from $CO_{(a)}$ or it is vacant, the attempt is ended. However, if it is occupied by a $CO_{(a)}$ particle, desorption occurs and the particle is replaced by a vacant site. The procedure is analogous in the case of choosing the desorption of NO.

When the chosen event is the dissociation of NO, a surface active site is chosen randomly. If it is occupied by an $NO_{(a)}$ particle, a nearest neighbour (nn) site is chosen randomly next to the first site. If this is empty, dissociation occurs and an $N_{(a)}$ particle remains in the first site and an $O_{(a)}$ particle in the second site. The nearest neighbour site is chosen among six neighbour sites of the surface in the case of the hexagonal lattice and among the four neighbour sites in the case of the uniform square lattice and the

IPC, but in the latter case not all the neighbours are active sites. In the case of the clusters constructed over the deterministic fractal, the number of nn active sites is variable, the same as in the IPC, and we have made the assumption, with the purpose of approximately homologizing the real situation, that each site has at least four near neighbours, whether they are active or inactive.

In the case of chemical reaction events that involve two reactant particles, an active site on the surface is first chosen randomly. If it is occupied by a particle corresponding to one of the reactants, an nn site is then chosen randomly next to the first site. If the latter is occupied by the other particle of the same reaction, the event is successful and a product molecule is removed from the surface leaving two vacant sites. For example, if the first particle is $CO_{(a)}$ and the second is $O_{(a)}$, a molecule of CO_2 leaves the surface.

4. Results and discussion

A mean field model assumes uniformity of the system that it interprets. Since this does not usually occur in experiments, in the case of heterogeneous catalysis, the kinetic parameters

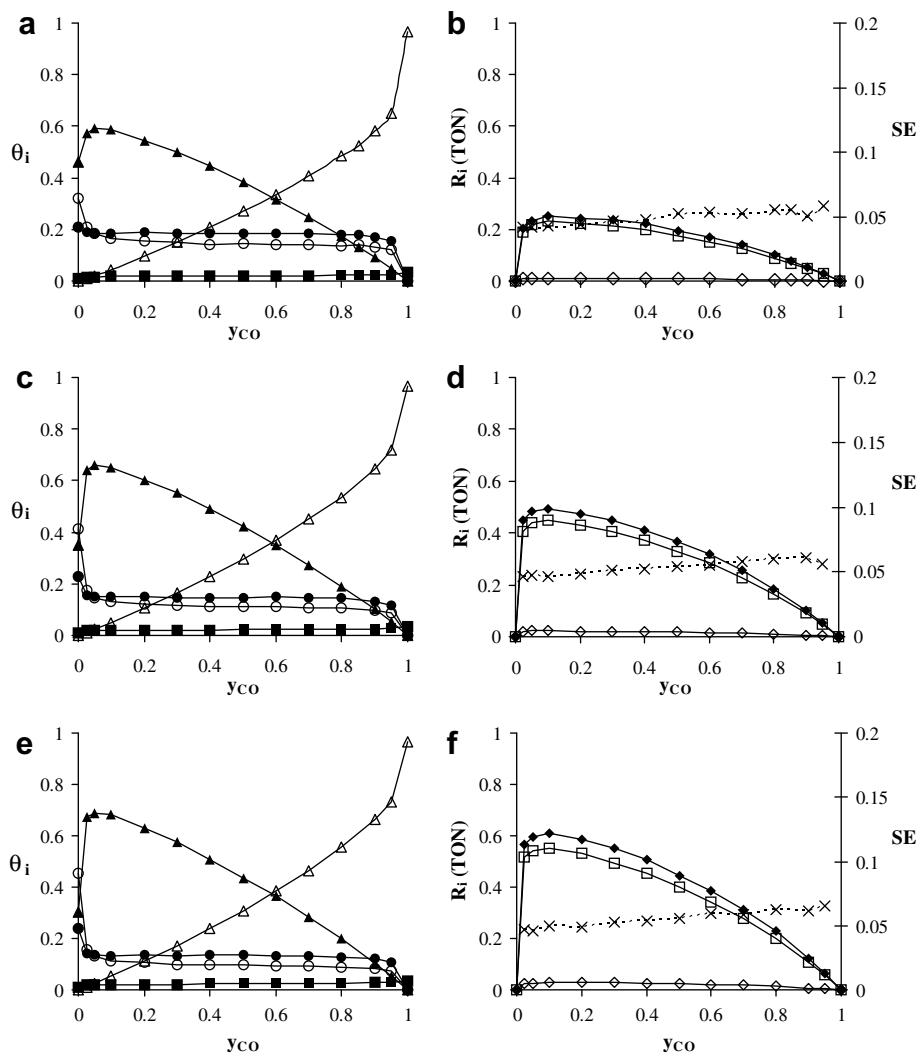


Fig. 2. The same as Fig. 1 for surfaces formed by the cluster distributions of Fig. 4. (a,b) FD = 1.2, (c,d) FD = 1.6, (e,f) FD = 2.0. The lines have been drawn to guide the eyes.

obtained by fitting a model to the experiment, especially over wide temperature intervals, are only approximate mean values, with a reliability that depends on the sensitivity of the parameter. The importance of simulation techniques like Monte Carlo is that with them it is possible to consider heterogeneous effects of the surface.

Fig. 1 shows the production curves and phase diagrams obtained from MC simulations according to the mechanism of Scheme 1 and the parameters indicated in Table 1 for the CO–NO reaction on the following surfaces: a uniform square lattice, a uniform hexagonal lattice, and the incipient percolation cluster (IPC) fractal. On the other hand, Fig. 2 shows the same diagrams over three distribution clusters built on the computer over a determin-

istic fractal, in an attempt to emulate the outer surface of supported Pd clusters, according to a method proposed in a previous paper from our laboratory [19].

The MC technique allows the simulation of various surface lattices homologizing situations that appear in the experiment. In this work, we have built on the computer the uniform square and hexagonal lattices that can be associated in the experiment with the case of different faces of catalysts formed by single crystals. Lattices formed by the incipient percolation cluster (IPC) fractal and a surface of clusters built over a deterministic fractal have also been included according to the procedure that we proposed in a recent paper [19] for homologizing the behaviour of supported metal catalysts used in the experiment.

These simulated lattices make it possible to observe the heterogeneity of these catalytic systems, corresponding to the structure of the surface. The first aspect of the heterogeneity of the surface is then the well-known structural sensitivity shown by the CO–NO reaction, which can be attributed in general to the decrease in the number of neighbours of the site in disordered systems, which affects the efficiency of steps such as those of dissociation and production. This is seen in Figs. 1 and 2, where the production shown is lower in the IPC fractal than in the uniform lattices, and is lower, in this case, in the system of clusters.

There is also low selectivity for nitrogen, less than 20% in all the cases studied in the Letter. The largest value of selectivity is found

Table 1

Kinetics parameters of Nakao et al. [7] and the fitting parameters used in the Letter

Event	Activation energy E_i (kcal/mol)	Frequency factor ν_i (s^{-1})
CO desorption (k_2)	35.5	1.0×10^{17}
NO desorption (k_4)	36	1.0×10^{17}
NO dissociation (k_5)	34.2	2.7×10^{14}
N ₂ production (k_6)	29	6.5×10^{13}
N ₂ O production (k_8)	32.7 ^a	5.3×10^{13a}
CO ₂ production (k_7)	33.6	7.1×10^{15}

^a Parameters of Ref. [15].

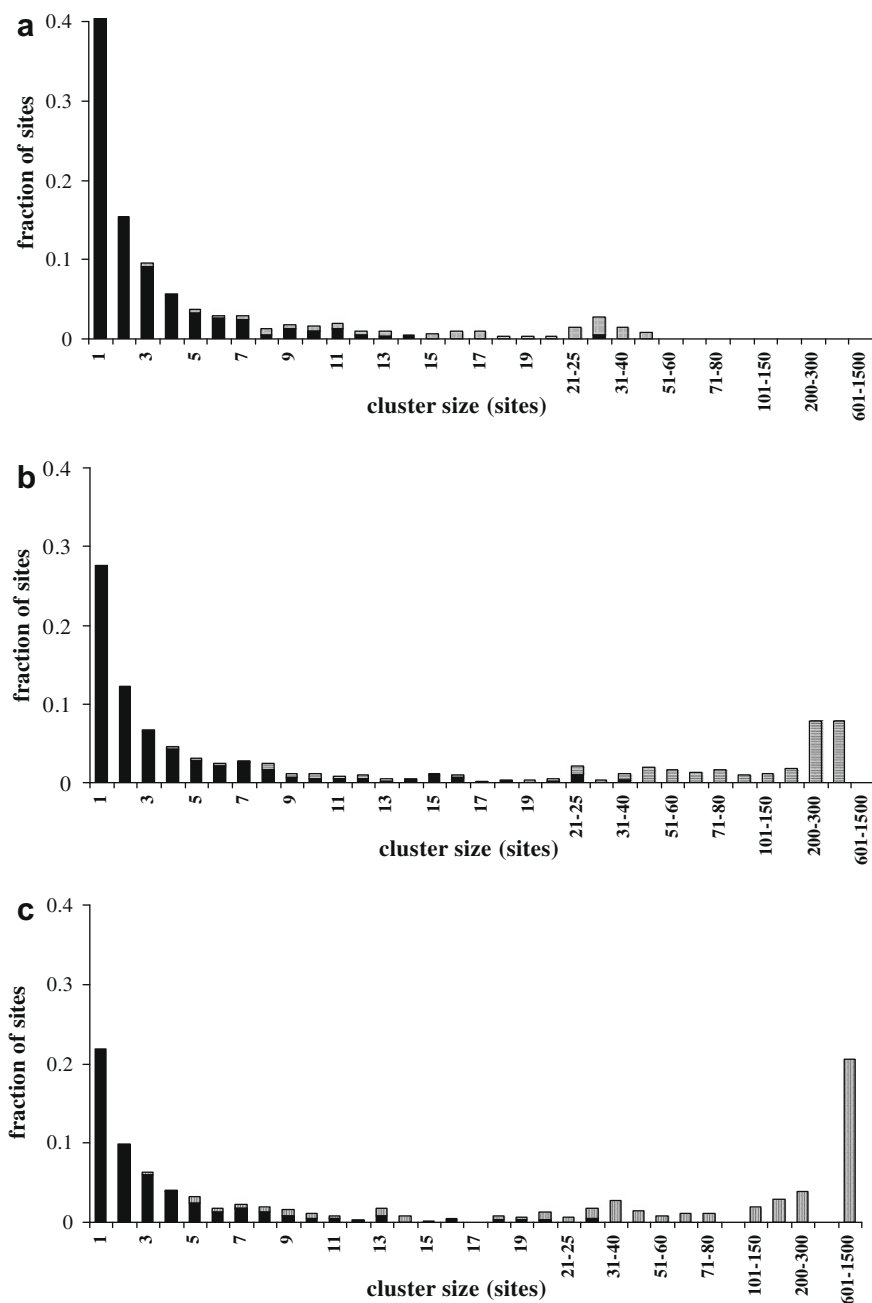


Fig. 3. Cluster distributions used in the Letter corresponding to the parameters defined in Ref. [14] for $f_v = 1.1$ and different FD. (a) FD = 1.2, (b) FD = 1.6, (c) FD = 2.0. ■: three graph, ▨: cyclic graph.

in the case of the hexagonal surface, as shown in Fig. 1. This is because all the pairs of neighbour nitrogen of this lattice are reactive, in contrast with the case of a square lattice, which has the unreactive diagonal pairs, both in the uniform lattice and in the IPC. On the other hand, the lower value of the selectivity is obtained in the case of the surfaces formed by cluster distributions, as seen in Fig. 2. This is accounted for by the smaller number of pairs of neighbour nitrogen that can be found in this kind of disordered lattices.

In the literature on the subject, experimental information on the CO–NO reaction over Pd is scarce. The results published by Holles et al. [23,24] and Reiner et al. [25,26] using a conventional atmospheric flow reactor are of great interest because they are carried out at medium pressures, they show in some detail for this system the effect of structural sensitivity. Some of the results of

Reiner can also be comparable quantitatively with those of this work. For example, the experimental TOF value of CO₂ production over Pd(100) at 600 K is somewhat greater than 2.0, of the order of that seen in Fig. 1b and d over a uniform surface at 600 K, obtained by MC for the square and hexagonal lattices. In the case of the IPC fractal, on the other hand, Fig. 1f shows a value at 600 K similar to the TOF of CO₂ equal to 1.0, obtained by Reiner et al. [25] for small particles of Pd/Al₂O₃/Ta(110).

The experiments of Reiner et al. [25,26] indicate in all the cases of supported catalysts an increase of the TOF of CO₂ with increasing mean size of the substrate's particles. This qualitative result agrees with that seen in Fig. 2 in the case of three surfaces consisting of cluster distributions modeled on the computer, which are shown in Fig. 3. In quantitative terms, on the other hand, the experiments of Reiner et al. show at 600 K, in the case of surfaces

supported on Al_2O_3 and $\text{Al}_2\text{O}_3/\text{Ta}(110)$, TOF values going from 0.1 to 2 depending on the size of the particles. These values are of the same order of magnitude as our productions.

The phase diagrams of Fig. 1 and 2 show a qualitatively similar behaviour in all cases for CO and NO, with an increase of the CO fraction and a decrease of the adsorbed NO depending on the variation of their respective concentrations in the gas phase. The fractions of adsorbed N and O atoms, however, are negligible in the lattices of Fig. 1, while they retain a value between 10% and 20% on the surfaces formed by the cluster distributions. This is interesting because it accounts in part for the decrease in production due to the existence of unproductive N and O atoms that are found in the small clusters that are poisoned with those atoms, something that does not happen in the lattices of Fig. 1.

It is interesting to make some general comments as to the limitations of the paper's results and conclusions related to the system's heterogeneity. This has been considered in the surface geometry of the catalytic substrate in the cases of the IPC and the surface formed by cluster distributions, but not in the case of uniform square and hexagonal lattices in which the existence of the terraces and steps that are usually observed experimentally has not been included. On the other hand, the kinetics parameters used have been obtained on a single crystal. In this relation, as commented in a previous section, some recent theoretical results published recently for the activation energy of some stages [14], calculated for the CO–NO reaction over Pd, seem promising, distinguishing different values obtained on the steps and the terraces.

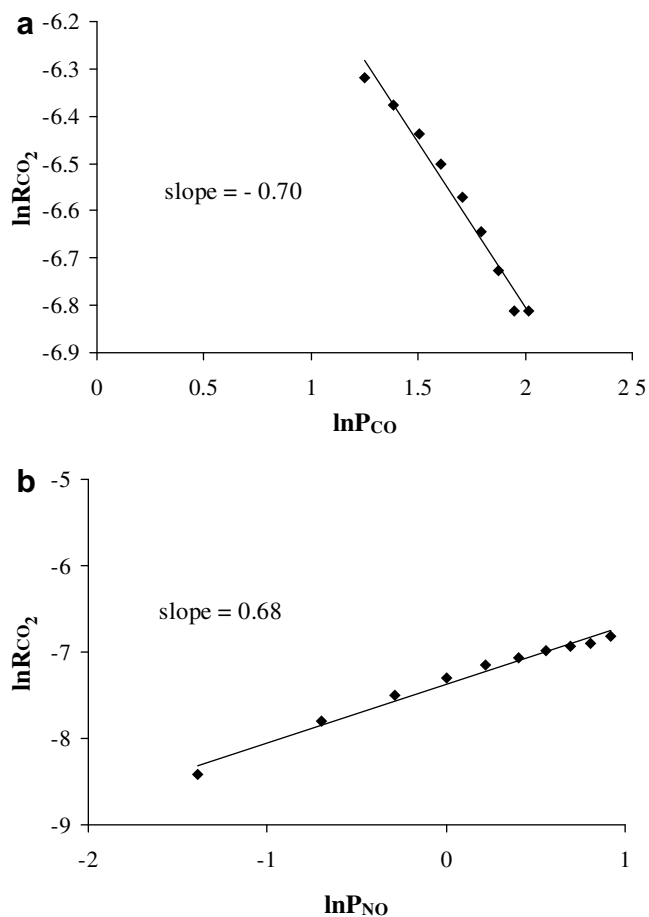


Fig. 4. (a) CO₂ production as a function of CO pressure with a fixed NO pressure of 6.6 torr at 550 K in the steady state for the constants of Table 1 and the MFT model. (b) The same as (a) as a function of NO pressure with a fixed CO pressure of 7.0 torr.

Unfortunately, no adequate values for the corresponding frequency factors are yet available.

Usually, experimenters try to fit their results to empirical equations that define different reaction orders. In the case of the CO–NO reaction, for example, the order m with respect to CO and n with respect to NO is defined by the expression

$$R_{\text{CO}_2} = kP_{\text{CO}}^m P_{\text{NO}}^n \quad (4)$$

Through mean field calculations and MC simulations, we could only fit Eq. (4) to our results in very small pressure ranges at each temperature. This means that the reaction order is strongly dependent on temperature and on the pressure of CO and NO, thereby severely limiting its practical application. Rainer et al. [26] published values for reaction orders in experiments with the CO–NO reaction at 550 K and moderate pressures on a Pd/ Al_2O_3 surface corresponding to an average particle size of 125 Å ($m = -0.85$ and $n = 0.50$), for which they obtain a very low production. Using the solutions of the kinetics equations published previously [15] for the mechanism of scheme 1 to the same conditions, we were unable to reproduce the production values using the parameters of Table 1, but an approximate agreement with the reaction orders was obtained. The corresponding curves are shown in Fig. 4.

4. Conclusions

- (1) Considering for the CO–NO reaction over Pd catalysts, a mechanism similar to that used previously in the case of Rh and recently published low pressure kinetics parameters data for Pd, the MC results over various lattices simulated on the computer interpret qualitatively and quantitatively the experimental information at moderate pressures recently reported in the literature. For example, the R_{CO_2} production values found in the experiments over Pd(100) agree with those of a uniform surface formed by square and hexagonal lattices, and those obtained over Pd/ $\text{Al}_2\text{O}_3/\text{Ta}(110)$ with those of the IPC fractal. The experimental data over supported Pd particles of different sizes, on the other hand, are interpreted quantitatively by a surface modeled on the computer, formed by various cluster distributions.
- (2) The lower production usually obtained over supported catalysts in relation to the crystals is partially accounted for in the superficial clusters model by the existence of unproductive N and O atoms located in small clusters poisoned by those atoms.
- (3) The reaction order determined from the mean field and MC results are highly dependent on temperature and on CO and NO pressure. The mean field results and the parameters of Table 1 reproduce experimental orders obtained from the literature, but in this case the values corresponding to production are not reproduced.

Acknowledgments

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