

Monte Carlo simulation studies of the catalytic combustion of methane

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A Monte Carlo (MC) simulation is carried out of the catalytic oxidation of methane based on the pseudo-Langmuir-Hinshelwood (LH) mechanism proposed by Iglesia *et al.*, that attempts to interpret the behavior of this reaction, which from experiments is assumed to be of the Mars-van Krevelen type. The results interpret reasonably some experimental findings (reaction order with respect to H₂O, CH₄, activity and structural sensitivity) if certain criteria based on the experiment and some laboratory data for the kinetic and thermodynamic parameters from the literature are considered.

KEY WORDS: Monte Carlo simulation; catalytic combustion of methane.

1. Introduction

The field of surface reactions has had a great development in recent decades due to their applications in catalysis and in the solution of ecological problems related to environmental pollution as well as for their theoretical interest in fields such as physics and biology, among others [1,2]. One of the first catalytic reactions studied considerably was the oxidation of CO followed by the reduction of NO by CO, due to its importance in automotive exhaust emission control [3]. For many years we have been interested in these reactions from the experimental viewpoint [4] as well as from more fundamental aspects [5]. More recently a new kind of reaction corresponding to the catalytic oxidation of hydrocarbons, in particular methane, have become very important both for pollution abatement as well as for power generation, and they are being studied mainly from the experimental standpoint, as shown by a recent review [6].

We have been carrying out research along these lines, as shown by our recent papers [7], with the additional purpose of extending their understanding to more fundamental aspects. In this paper, based on the interesting mechanism proposed recently by Iglesia *et al.* [8] for the catalytic oxidation of methane, we have developed a Monte Carlo (MC) type simulation program for this system with the purpose of analyzing some phenomena seen in the experiments, as well as to integrate this kind of complex reactions with the studies of nonequilibrium systems that appear frequently in journals with a theoretical orientation.

2. The catalytic combustion of methane

During the last decade there has been a proliferation of papers in various journals on this interesting reaction, because methane is a well-known greenhouse gas and the most stable and abundant alkane. Combustion of hydrocarbons, of great importance in power generation, occurs at such high temperatures that it favors thermodynamically the formation of nitrogen oxides (NO_x), thereby contributing to the problem of environmental pollution. This accounts for the interest in carrying out these reactions catalytically, drastically decreasing the temperature of the process. In the case of methane, the effluent streams from natural gas combustion processes also contain small amounts of methane that must be removed through catalytic postcombustion.

Most of the research has considered the use of noble metals, particularly Pd and Pt, as catalysts for these processes because of their high catalytic activity per site and their greater resistance to sulfur poisoning (below 773 K). From the economic standpoint, however, of great interest are those catalysts consisting of metals on various supports such as Al₂O₃ and SiO₂ [9] and more recently ZrO₂ [10], as discussed in some recent papers, including some of our own [7].

In spite of the large amount of experimental information over the last few years, not much work has been directed at the elucidation of the characteristics of the mechanism of the catalytic combustion of methane reaction, although there seems to be agreement that it occurs by direct interaction of the reactants with lattice oxygen via a Mars-van Krevelen type mechanism [11]. Recently, E. Iglesia *et al.* [8] proposed the following mechanism for the oxidation of methane on PdO_x/ZrO₂ at low temperature, which includes the steps shown on the left of table 1.

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In these reactions the asterisks represent an oxygen vacancy on the PdO_x surface, corresponding to Pd sites either existing or introduced originally in the lattice, which are oxidized and regenerated during the process. The vacancies are necessary for the linear adsorption of methane and oxygen from the gas phase as well as for the dissociation of the adsorbed oxygen, O₂*. The mechanism assumes the existence of some irreversible steps and others under quasi-equilibrium conditions. The subsequent irreversible hydrogen-abstraction, kinetically insignificant steps after step (4), which are shown on the right column of table 1, were proposed by us to be used in the MC simulations of this paper, as will be seen below.

It is interesting to comment that even though the above scheme should correspond to a Mars–van Krevelen type mechanism, it is not distinguishable in the form represented in table 1 from that of Langmuir–Hinshelwood (LH), which is how we will develop it in the MC simulation. In their original paper, Iglesia *et al.* [8] propose the mechanism shown in table 1 commenting that “this elementary step sequence resembles the Mars–van Krevelen reduction-oxidation pathways.” This is an important aspect that will be taken up and discussed below.

3. Monte Carlo simulations

The MC algorithm developed in this paper is similar to others used previously by our group for various reactions, both abstract and real, such as the oxidation of CO or the reduction of NO by CO [12]. The simulation process began by selecting an event from the mechanism (adsorption, desorption, dissociation or reaction) according to the probability p_i of the event defined by

$$p_i = k_i / \sum k_i \quad (8)$$

where k_i corresponds to the rate constant of step i of the mechanism. In the case of adsorption, k_i was calculated from the expression of the kinetic theory of gases:

$$k_i(\text{ads}) = s_i \sigma (2\pi M_i RT)^{-1/2} \quad (9)$$

Table 1
Kinetic mechanism for the combustion of CH₄

| | |
|---|--|
| (1) $\text{O}_2(\text{g}) + * \xrightleftharpoons{K_1} \text{O}_2^*$ | 4 (a) $\text{CH}_3^* + \text{O}^* \rightarrow \text{CH}_2^* + \text{OH}^*$ |
| (2) $\text{O}_2^* + * \xrightleftharpoons{K_2} 2\text{O}^*$ | 4 (b) $\text{CH}_2^* + \text{O}^* \rightarrow \text{CH}^* + \text{OH}^*$ |
| (3) $\text{CH}_4(\text{g}) + * \xrightleftharpoons{K_3} \text{CH}_4^*$ | 4 (c) $\text{CH}^* + \text{O}^* \rightarrow \text{CHO}^* + *$ |
| (4) $\text{CH}_4^* + \text{O}^* \xrightleftharpoons{K_4} \text{CH}_3^* + \text{OH}^*$ | 4 (d) $\text{CHO}^* + \text{O}^* \rightarrow \text{CO}^* + \text{OH}^*$ |
| 4 (a) $\longrightarrow \dots\dots$ | 4 (e) $\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2^*$ |
| 4 (f) \longrightarrow | 4 (f) $\text{CO}_2^* + \text{O}^* \rightarrow \text{CO}_3^*$ |
| (5) $2\text{OH}^* \xrightleftharpoons{K_5} \text{H}_2\text{O}(\text{g}) + \text{O}^* + *$ | |
| (6) $\text{CO}_2^* \xrightleftharpoons{k_6} \text{CO}_2(\text{g}) + *$ | |
| (7) $\text{CO}_3^* \xrightleftharpoons{k_7} \text{CO}_2(\text{g}) + \text{O}^*$ | |

where M_i is the molecular mass of i , S_i is the corresponding sticking coefficient ($S_i = 1$ in this case) and the coefficient σ is the area occupied by 1 mol of superficial metal atoms ($4.74 \cdot 10^8 \text{ cm}^2/\text{mol}$ for Pd). The remaining k_i constants will be discussed in the next section. The MC algorithm begins with the selection of the event. If it corresponds to the adsorption of O₂, a site is chosen randomly on the surface, and if it is vacant a molecular oxygen particle, O₂*, will remain adsorbed. If the site is occupied, the attempt is ended. If the adsorption of CH₄ is chosen, the procedure is completely analogous, and a CH₄* particle remains adsorbed. If the adsorption of H₂O is chosen and the site is empty, the sites neighboring the original site are revised. If no O* particle is found, the attempt is ended. If one of the neighbors is occupied by O*, both sites are occupied by OH* particles. If there is more than one neighbor occupied by O*, one of them is chosen randomly.

If O₂ desorption is chosen, a surface site is selected randomly. If it is occupied by a particle different from O₂* or it is vacant, the attempt is ended. However, if it is occupied by an O₂* particle, desorption occurs and the particle is replaced by a vacant site. The procedure is analogous in the case of choosing the desorption of CH₄ and CO₂. In the case of the desorption of CO₃, the particle is replaced by an adsorbed atomic oxygen, O*, and a molecule of CO₂ leaves the surface.

In the case of chemical reaction events that involve two reactant particles, a site of the surface is first chosen randomly. If it is occupied by a particle corresponding to one of the reactants, a neighboring 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 the corresponding reaction is carried out. For example, if the first particle is CH₄* and the second is O*, a particle of CH₃* remains in the first site and one of OH* in the second, and if both particles are OH*, one molecule of H₂O leaves the surface and a particle of O* remains in the first site.

When the chosen event is the dissociation of O₂, a surface site is chosen randomly. If it is occupied by an O₂* particle, a neighboring site is chosen randomly next to the first site. If this is empty, dissociation occurs and a particle of O* is placed in each of the two previous sites. If the site is occupied, the attempt is ended. Since the mechanism considers that the abstraction reactions (4a–f) of a series of radicals with adsorbed atomic oxygen are instantaneous, it is necessary to review all the neighbors of both O* that have resulted in the dissociation. If some radical is found, the corresponding reaction takes place in a manner similar to the case of the chemical reaction event mentioned in the previous paragraph. If more than one radical is found, one of them is chosen randomly and the process goes on as above.

If a fraction $r < 0.407254$ of the sites of a square lattice of size $L \times L$ is blocked randomly for the process, the remaining active sites will form what is called a

percolation cluster. When $r = 0.407254$, a set of clusters is obtained in which the largest of them percolates in both directions, reaching the two ends of the lattice. This cluster determines a well-known statistical fractal called the incipient percolation cluster (IPC) of size 91/48, that is computed adequately by means of an algorithm developed by Kopelman [13] some years ago. The substrates used in the simulations for this work were a uniform ($r = 0$) square lattice ($L = 50$) and the IPC that we have considered in previous papers [14]. In both cases periodic boundary conditions were considered for the lattice.

The results in the case of the fractal IPC, are the average of experiments on three different fractals, to which was imposed the condition that they should percolate in both directions. As will be commented in the next section, in the processes described above a lattice coordination number of eight was considered that includes the nearest neighbors (nn) and the next nearest neighbors (nnn) located along the diagonals around each site. It is also assumed that the neighbors are equivalent. Computing time was measured in Monte Carlo Steps (MCS), defined as a number of attempts equal to the number of sites in the substrate.

4. Results and discussion

With the purpose of analyzing and discussing the characteristics of the results of the Monte Carlo simulations of the combustion of methane assuming the reaction mechanism represented by equations (1–7) proposed by Iglesia *et al.* [8], it is necessary to know the values of the reaction constants of the proposed steps. In general, this is not feasible with the current experimental knowledge of this reaction. One possibility is to assume arbitrary constants to study the qualitative behavior of the mechanism, as is often done in essentially theoretical work. In this paper an intermediate possibility is considered, as we have done in some previous work [15], using the available experimental information and establishing reasonable criteria for the unknown rate constants, provided that, insofar as possible, results having orders of magnitude close to the experimental data are obtained and the system is not poisoned. In this way, our qualitative analyses will have certain limitations, but they may be partially associated with what happens in the laboratory.

Table 2 shows the kinetic and thermodynamic parameters that have been used in this paper and are commented below. We have assumed that steps (4a–f) are instantaneous in the simulations, because in the experiments it has been established that they are not kinetically significant, and we have used the kinetic theory of gases (equation (9)) for the adsorption constants of steps (1), (3) and (5). For the pseudoequilibrium constant of equation (5) we have considered two

Table 2

Kinetic and thermodynamic parameters used in the MC simulations defined in table 1. $K = k_i/k_{-i}$ k_i = kinetic constant for the adsorption of (equation (9)); k_{-i} = kinetic constant for the desorption of i ($i = 1,3$)

| | |
|-------------------------------|-------------------------------|
| $K_1 = 0.1 \text{ torr}^{-1}$ | K_5 (case I) = 0.084 torr |
| $k_2 = 200 k_1$ | K_5 (case II) = 0.0084 torr |
| $K_3 = 5 \text{ torr}^{-1}$ | $k_6 = k_7 = 50k_1$ |
| $k_4 = 0.01 k_3$ | |

different cases of known experimental situations, indicated by I and II in the table. Case I corresponds to a value of K_5 of the order of those obtained in experiments carried out with palladium supported on silica [7], and in case II a high value, ten times the previous one, found on other surfaces such as palladium on zirconia [7]. We then defined some criteria that we found experimentally reasonable and allow some parameters to be related with one another. For example, a high dissociation was assumed for O_2^* making k_2 be equal to 200 times the adsorption constant of O_2 . Similarly, a value equal to 50 times the adsorption of O_2 for the kinetic constants of reactions (6) and (7) was considered, also assuming that the pressure of CO_2 in the gas phase was equal to zero in these steps. As to step (4), it was assumed that constant k_4 is equal to one hundredth of the desorption constant of CH_4 , which may be determined from the adsorption constant of CH_4 if the pseudoequilibrium constant K_3 is known.

Then, and with the purpose of obtaining reasonable values for the thermodynamic equilibrium constants K_7 and K_3 , we considered the simulation of the system for a methane pressure of 12 (torr), an oxygen pressure of 47(torr), approximately four times the former, as has been the case in recently published experiments [7–10], a small water pressure of 1 (torr), and at temperature of 600 K. In the initial state an oxidized surface was set in the computer consisting of 95% of the lattice sites covered randomly by adsorbed atomic oxygen O^* and the remaining 5% consisting of empty sites that simulate the Pd vacancies on an oxidized PdO surface. Considering for K_5 the value of case I of table 2 commented above, we set constants K_7 and K_3 in such a way that the results in the final state of the simulation would retain a high concentration of superficial oxygen, e.g. greater than 90%, CO_2 activity values close to the experimental ones, and the additional condition that the surface does not become poisoned, thereby remaining in a steady state situation. We have assumed that the latter condition is achieved when the system is not poisoned and production remains stable at computing times as high as 800 million MCS, for example.

In this way we have generated a set of values for the mechanism's parameters used in our simulations that are summarized in table 2. This will allow us to keep our analyses with results that have realistic order of magnitude.

In the experiment relatively small CO_2 productions are seen, of an order less than one for the TON [6,7] in most of the cases, up to values of 5.6 found by Hicks *et al.* [16] on supported Pd. In general, the experimental activity values found in the literature have some degree of uncertainty in these cases due to the little known phenomenon observed in this system of an increase of the initial rate over a long period of time, to decrease later to real steady state conditions [7]. Also, as commented by Ribeiro *et al.* [17], great differences in the TON in the literature have been attributed to the use of incompletely activated samples.

The catalytic surface has been simulated assuming a square lattice of nodes on which the oxygen or the palladium atoms corresponding to the vacancies would be located. Simulations were carried out first considering only the four nn sites. With the constants of table 2

the system is poisoned rapidly for high O_2 concentrations and much more slowly for low concentrations, with no reactive window found for this set of parameters over the whole range of concentration values y_{O_2} . Since a coordination number of 4 is generally too small, particularly on disordered surfaces such as the case of supported catalysts, for this study we chose to keep the square lattice and assume that the nn and nnn are equivalent, which facilitates the calculations in the simulation and is a situation that is closer, within the approximations of the study, to a hypothetical real system.

Figure 1 shows some snapshots obtained in our simulations that allow the observation of some interesting aspects. Figure 1a, for example, shows the steady state situation on a uniform surface for P_{CH_4} equal to 12 torr, P_{O_2} equal to 47 torr, and a small partial pressure of

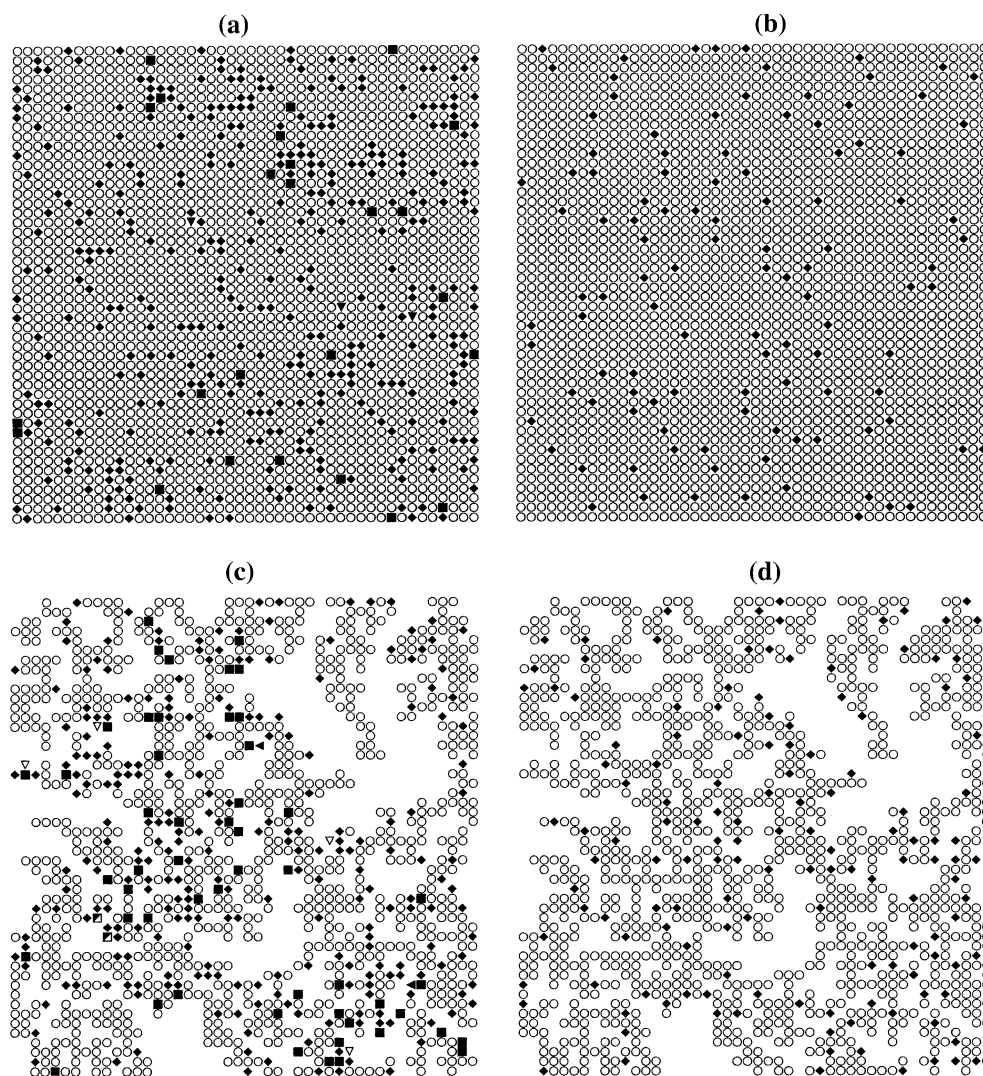


Figure 1. Snapshots of one part of the substrate's surface (under steady state conditions) for the catalytic combustion of methane for $p_{\text{H}_2\text{O}} = 1$ torr, (○) O; (■) CH_4 ; (◆) OH; (◄) CH; (▽) CO; (◩) CH_2 (a) Uniform surface: $p_{\text{O}_2} = 50$ torr, $p_{\text{CH}_4} = 9$ torr, $K_5 = 0.0084$ torr (b) Uniform surface: $p_{\text{O}_2} = 52$ torr, $p_{\text{CH}_4} = 7$ torr, $K_5 = 0.084$ torr (c) On the IPC fractal: $p_{\text{O}_2} = 35$ torr, $p_{\text{CH}_4} = 24$ torr, $K_5 = 0.0084$ (d) The same as (c) for $p_{\text{O}_2} = 47$ torr, $p_{\text{CH}_4} = 12$ torr.

water equal to 1(torr). In this case approximately 18% of the surface is seen to be covered by OH* groups immersed in a sea of oxygen and some particles of methane. This shows that the progress of the reaction occurs through alterations in only small sectors of the catalytic surface when the methane reacts with a neighboring oxygen or is desorbed, leaving vacant sites that allow later adsorptions, or through reaction of neighboring OH* groups. A similar situation occurs in the case of the IPC fractal as seen in a figure 1c.

Setting the values of the equilibrium and rate constants, the phase and production diagrams were then determined, changing the methane to oxygen ratio and keeping constant the total pressure in the gas phase. In all the above cases the initial state of the catalytic surface was 95% oxygen and 5% vacancies. The phase and production diagrams were also determined for a maximum process equal to 50 million MCS for a uniform substrate, and 100 million in the case of the IPC fractal.

One of the most interesting aspects of this kind of diagram is the size of the reactive window defined by the concentration interval y_{O_2} in which the system is productive. Figure 2 shows the production curves versus the oxygen fraction y_{O_2} of the gas phase for different K_5 and total pressure values. In all those cases a maximum is found for production, with the width of the reactive window increasing as the value of K_5 decreases or the total pressure increases. This is reasonable, since production must increase with the value of the equilibrium constant of step (5) because the decrease in superficial OH* produces vacant sites available for the adsorption steps. The figure also shows that concentration y_{O_2} , corresponding to maximum production, is independent of the value of K_5 and decreases as the total pressure drops, even though the maximum is independent of it. Figure 2 also shows the curve that corresponds to the case in which the catalytic surface is the IPC fractal, and the production value and the width of the reactive

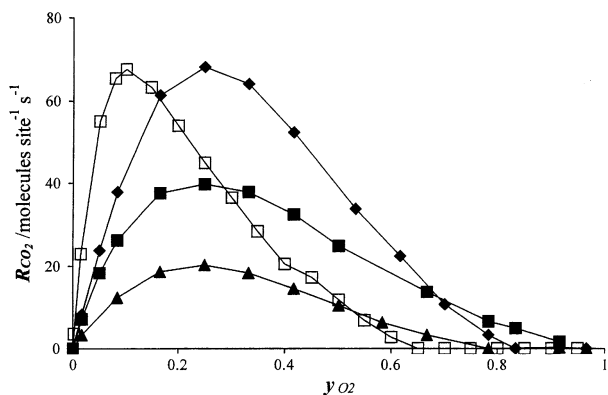


Figure 2. Production of CO_2 , R_{CO_2} , (obtained by MC) for the catalytic combustion of methane under different pressures of the gas phase P and parameter K_5 . The lines have been drawn to guide the eyes. $P_{H_2O} = 0.2$ torr, $P = 10$ torr, $K_5 = 0.084$ torr (\square) $P_{H_2O} = 1$ torr, $P = 60$ torr, $K_5 = 0.084$ torr (\blacklozenge) $P_{H_2O} = 1$ torr, $P = 60$ torr, $K_5 = 0.0084$ (\blacksquare) The same as (c) of figure 1 but on the IPC fractal (\blacktriangle).

window are seen to be smaller than for the uniform surface, even though the phase diagrams are practically identical on both surfaces, which would indicate that the system is structurally sensitive. This can be compared to the relation that is seen in the production experiment between supported metallic catalysts and those consisting of single crystals. In the literature there are interesting studies with crystalline particles of different sizes [6,7,18] in which the TON increases with the size of the crystal, making it possible to state that in the experiment the reaction is structurally sensitive. However, as commented by Ribeiro *et al.* [17], this is an aspect that has been somewhat controversial in the literature on the subject.

Figure 3 shows the phase diagrams corresponding to different total pressures and values of K_5 . Looking at the surface configuration represented in figure 3 for the maximum production graphed in figure 2, an interesting correlation was seen for all the cases analyzed: the maxima of the production curves coincide with the intersect of the coverage curves of superficial oxygen and methane in the phase diagram. This is because for the set of data of table 2, step 4 is the controlling step of the overall reaction, and therefore, given its stoichiometry, the maximum rate is achieved when the oxygen and methane coverages are equal.

The catalytic surface is poisoned for high oxygen concentration values, and the system becomes unreactive. In figure 1b for a uniform surface and in figure 1d for the IPC substrate shows the snapshots of high oxygen concentration in which isolated superficial OH particles and a large amount of oxygen are seen. This configuration does not allow any reaction, so the process ends and the surface remains poisoned over time. When production increases, superficial OH concentration also increases, as can be seen in the phase diagrams, an example of which is shown in figure 3, and the probability of having isolated OH in the lattice decreases, so that it is possible to achieve a steady state situation in the usual working times on our computer. In all cases the window is closed in the oxygen-rich zone for some value of y_{O_2} . However, the system remains reactive until the origin of the phase diagram in the zone of low y_{O_2} values

In the phase diagram it can be seen that only at high y_{O_2} concentrations the surface retains a fraction of superficial oxygen greater than 90%, which is an order similar to the initial one, a situation that coincides with a low production of CO_2 . Both circumstances are those that are seen in the experiment. Naturally, if y_{O_2} is greater, production decreases dangerously, reaching the zone poisoned with oxygen and isolated OH shown before. This situation has been commented in some experimental papers. Yang *et al.* [19], for example, show with FTIR experiments that if the $(O_2)/(CH_4)$ ratio of the gas phase increases, the proportion of PdO_x increases at the expense of the Pd^0 sites on the surface.

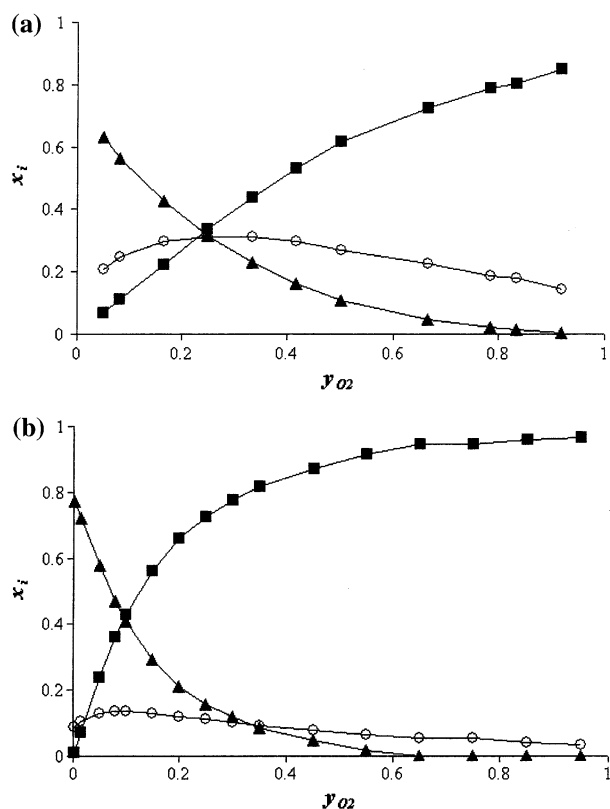


Figure 3. Surface concentrations x_i of species i versus concentration y_{O_2} (phase diagram) obtained by MC for the catalytic combustion of methane on a uniform surface and total pressure P . The lines have been drawn to guide the eyes. (■) x_O ; (○) x_{OH} ; (▲) x_{CH_4} (a) $p_{H_2O} = 1$ torr $P = 10$ torr $K_5 = 0.0084$ torr (b) $p_{H_2O} = 0.2$ torr $P = 60$ torr, $K_5 = 0.084$ torr.

However, if the proportion keeps increasing, oxidation increases too much, decreasing the activity, which is in agreement with what is seen in our production curves. In this way the experiment shows a relation between the system's activity and the Pd^0/PdO_x ratio, in agreement with that found between the production and phase diagrams in our MC simulations. A maximum in the experimental production curve has also been found by Yazawa *et al.* in the case of the oxidation of propane [20].

Simulations carried out in the low production zone with different initial configurations of the catalytic surface, from the extreme situation of 100% vacancies, which can be likened to a reduced real surface, through the case of a completely oxidized initial surface covered with O^* , showed interesting results. In all cases the same final situation was reached with the same O^* fraction and CO_2 production for a given value of y_{O_2} . This was the expected situation in an LH mechanism. Although the oxidation of methane in general takes place through a Mars–van Kreveler mechanism [11], it is seen that the mechanism proposed by Iglesia *et al.* [8] is a good approximation of the phenomenon that may be called pseudo-LH. It should be kept in mind, however, that the mechanism of Iglesia *et al.* does not distinguish between

the kind of oxygen belonging to the surface, like PdO and chemisorbed oxygen. That distinction is not possible with the above mechanism either in the Monte Carlo simulations or in the solution of the kinetics equations.

Now we assume an expression for production of the type

$$R_{CO_2} \sim P_{CH_4}^a P_{O_2}^b P_{H_2O}^c,$$

where a, b and c are the corresponding reaction orders. This allows the determination of the partial order by changing the pressure of one component while keeping constant the pressure of the other two. Figure 4 gives some examples in the low production zone, showing the linearity of the logarithmic curves from whose slope the corresponding order is obtained. An order equal to 1.24 is found for methane, partially in agreement with the first order found in several experiments in the literature [7,17,21]. The inhibition caused by water in this reaction

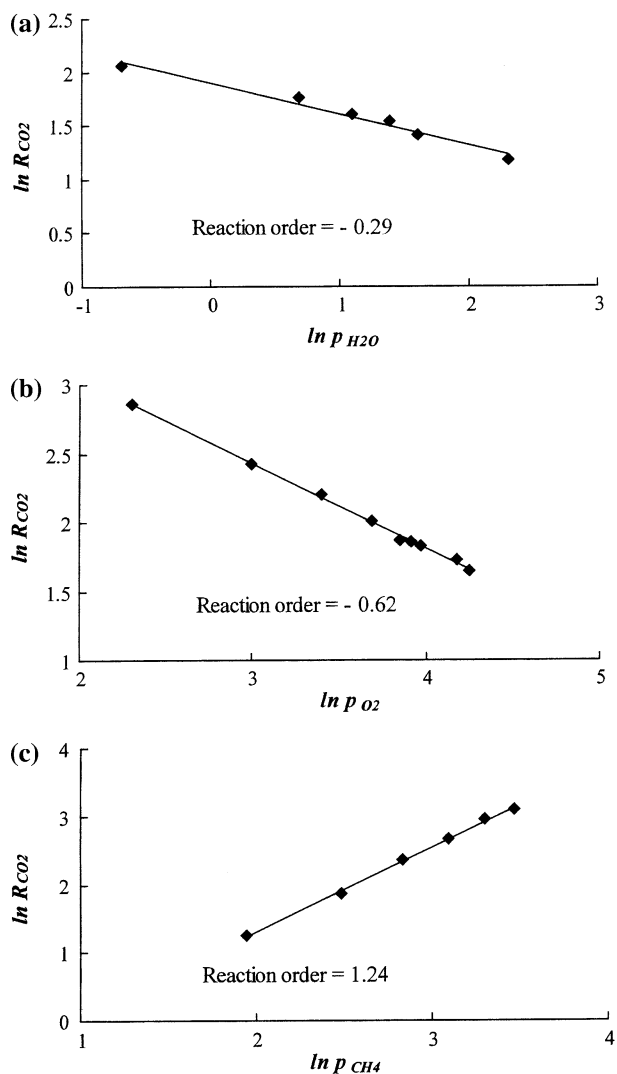


Figure 4. Reaction order of (a) H_2O (b) O_2 (c) CH_4 for the catalytic combustion of methane obtained by MC on a uniform surface. $p_{O_2} = 47$ torr, $p_{CH_4} = 12$ torr $p_{H_2O} = 1$ torr, $K_5 = 0.0084$ torr.

is also seen, with an order equal to -0.3 , in agreement with the value of -0.25 obtained in our laboratory for Pd on silica [7], while we obtained a value of -1 , frequently mentioned in the literature [7,17,21], in the experiments with Pd supported on ZrO_2 [7]. In the cases studied with our simulations we did not obtain zero order for oxygen, which is often mentioned in the literature [6,21] and which we also obtained in our laboratory experiment [7]. This can be explained because, in contrast with the Mars–van Kreveler mechanism in which methane can be adsorbed on the surface of the oxidized Pd, in the mechanism proposed by Iglesia *et al.* the methane is adsorbed on oxygen vacancies on the surface. These vacancies can be occupied by molecular oxygen in a linear way in step (1) and then by atomic oxygen as described in step (2), making the number of vacancies dependent on the pressure P_{O_2} of the gas phase, therefore making the reaction rate dependent on P_{O_2} . As this pressure increases, the number of vacancies decreases and the order with respect to P_{O_2} is negative. In the Mars–van Kreveler mechanism, and as seen in the experiments, the O_2 can never inhibit the reaction.

The overall values of the reaction order for the substances mentioned in the previous paragraph remained similar for various y_{O_2} concentrations on the uniform surface as well as in the case in which the structure of the catalytic surface was the IPC fractal.

5. Conclusions

For the first time a kinetic Monte Carlo study has been developed to simulate the catalytic oxidation of methane, assuming the validity of the pseudo-Langmuir–Hinshelwood mechanism proposed recently by Iglesia *et al.* to interpret the Mars–van Krevelen type of behavior assumed from the experiments on this reaction. Considering rate constants known from the literature and assuming experimentally reasonable criteria for those that have not yet been determined, the following results should be noted:

In the zone in which the concentration ratio in the gas phase of CH_4 and O_2 is of the order of that used in the experiment, the simulations interpret reasonably well the experimental production, and the phase diagrams show a high fraction of superficial oxygen as has been found in FTIR experiments (high PdO/Pd⁰), accounting for the fact that Iglesia's model is a good approximation of that of Mars–van Krevelen.

Maximum production coincides with the intersection point of x_{O_2} and x_{CH_4} in the phase diagram, indicating that, for the values chosen for the rate constants, step 4 is the controlling step of the mechanism.

The snapshots show that the reaction occurs in a small area of the surface where the fraction of the surface covered with OH is sufficiently high to have a low

probability for isolated OH to exist. When this probability increases, the surface becomes poisoned in time and the system becomes unproductive.

If an expression of type $R_{CO_2} \sim P_{CH_4}^a P_{O_2}^b P_{H_2O}^c$ is assumed for production, the simulations show a reaction order equal to 1.24 for CH_4 , approximately in agreement with the first order found in the experiment. A reaction order equal to -0.29 is found, on the other hand, for the inhibition of water, in agreement with the -0.25 found in the experiment for the Pd/SiO₂ catalyst. Finally, the dependence of the activity on the oxygen pressure seen in the simulations is the result of assuming a LH mechanism instead of the experimental one of Mars–van Krevelen.

Simulations on the IPC fractal showed a qualitative behavior similar to that of the uniform surface, but with a lower production in agreement with what was found in the experiment, in which the supported catalysts are less active than on single crystals and the TON increases as the size of the supported particle increases. The structural sensitivity found in the experiment for this reaction is therefore also seen in the simulations.

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