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Mathematical modelling of oscillatory behaviour during methane oxidation over palladium catalysts

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HIGHLIGHTS

- ► Oscillations during methane oxidation over Pd catalysts are modelled.
- ▶ The model simulates anti-phase oscillations of two reaction products, CO₂ and H₂O.
- ► Oscillations occur due to periodic oxidation and reduction of the Pd catalyst.
- ► The origin of the anti-phase oscillations is the carbon diffusion into Pd bulk.
- ► Carbon diffusion rate and a large depth of its penetration into Pd are important.

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1. Introduction

The catalytic oxidation of methane has been extensively studied during last years and this subject was reviewed in papers (Trimm, 1983; Prasad et al., 1984; Enger et al., 2008). In methane-rich mixtures oscillatory behaviour has been observed over Ni, Co and Pd catalysts (Zhang et al., 2005; Bychkov et al., 2009a). Although this phenomenon has been intensively studied experimentally there are only a few reports in the literature on the mathematical modelling of the oscillatory behaviour during methane oxidation over metallic catalysts. The reason is that the detailed mechanism of this reaction, including the elementary reaction steps is still debated (Enger et al., 2008). The other important difficulty for the simulation of an oscillatory behaviour is that reliable and universal values of the kinetic constants are missing. Recently, much

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ABSTRACT

The paper presents the first mathematical model that can simulate the oscillatory behaviour during methane oxidation over Pd catalysts. The main experimental results are reproduced, including the antiphase oscillations of the concentrations of the reaction products, CO_2 and H_2O . In line with the experimental results, it is demonstrated that the oscillations are related to periodic oxidation and reduction of the Pd catalyst. The complicated waveform of the oscillations and the anti-phase oscillations of two reactant products originate due to the periodic accumulation and removal of bulk carbon. The simulation results show that the anti-phase oscillations of CO_2 and H_2O concentrations can occur only in the case of a high rate of carbon diffusion and a large depth of penetration of carbon into the Pd catalyst.

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progress in this area has been obtained due to the application of first-principles techniques, and specifically Density-Functional Theory (DFT) (van Santen and Neurock, 1995; Norskov, 1999). These estimation methods and their successful applications have been reviewed by Salciccioli et al. (2011). Microkinetic models of methane oxidation were developed mainly for the simulations of the steady state partial oxidation of methane to syngas over Pt and Rh catalysts at millisecond contact times (Deutschmann and Schmidt, 1998; Veser and Fraunhammer, 2000; Tavazzi et al., 2006). The analysis of the dynamic behaviour of systems, containing more than 30 elementary steps and finding there a limit cycle behaviour is a very difficult task. Moreover, in many cases the literature values of parameters can produce only a steady state behaviour. Therefore, the main task of mathematical modelling of the oscillatory behaviour in complex systems is to reveal the essential features of the reaction mechanism, which generates an oscillatory behaviour with realistic values of parameters.

The first mean-field model, including only 6 reaction stages, which simulated oscillatory behaviour during methane oxidation,

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was developed in our group for Ni catalysts (Slinko et al., 2006). The simulation results qualitatively reproduced the main properties of reaction rate oscillations for low O_2/CH_4 ratios. It was demonstrated that the oscillatory behaviour during methane oxidation over Ni catalysts originated due to periodic oxidation and reduction of the catalyst surface, variation of the selectivity of the process and the competition of reactants for the free active sites. Later Ren et al. (2008, 2009) carried out Monte Carlo simulations of oscillatory behaviour during methane oxidation. However their isothermal and nonisothermal models of kinetic oscillations were based on the reaction mechanism, which did not consider the occurrence of total methane oxidation over NiO surface and the authors did not make a comparison of known experimental data, published by Zhang et al. (2002,2003a) and by Bychkov et al. (2006) with the results of their simulations.

The oscillatory behaviour during methane oxidation has been discovered by König et al. (1994) over a thick Pd-film catalyst. Later the oscillations in this reaction had been studied over supported (Deng and Nevell, 1996) and massive Pd catalysts (Zhang et al., 2003b). It was demonstrated that in contrast to Ni and Co, oscillations during methane oxidation over Pd were observed at much lower temperatures and the main reaction products detected were CO₂ and H₂O. Recently, we investigated the oscillatory behaviour during methane oxidation over a Pd powder catalyst with the help of thermogravimetric analysis (TGA) combined with on-line massspectrometry of the effluent gas mixture and temperature programmed oxidation (TPO) experiments (Bychkov et al., 2009b). For the first time it was found that hundreds of carbon monolayers could be periodically accumulated in the Pd powder catalyst and then removed during one oscillatory cycle. Furthermore, a very interesting phenomenon, namely an anti-phase relationship of the oscillations of the concentrations of the reaction products CO₂ and H₂O was observed over the Pd powder catalyst. Although König et al. (1994), Deng and Nevell (1996), Zhang et al. (2003b) suggested an oxidation/ reduction mechanism for the oscillations no simulations of the oscillatory behaviour during methane oxidation have been done yet. The goal of the present study is to develop a simple mathematical model with realistic values of the parameters, describing the main features of the observed oscillatory behaviour, including the phase shift between the oscillations of the concentrations of CO₂ and H₂O.

The organisation of this paper is as follows. The next section summarises the basic experimental findings and the development of the reaction model. We then find the conditions of the appearance of an oscillatory behaviour in the model and discuss the mechanism of the oscillations. The simulated oscillations will be compared with the experimental data and the ability to produce the anti-phase oscillations of the concentration of the reaction products CO_2 and H_2O will be chosen as the main criterion of the adequacy of the model. The next section will describe modifications of the developed model, necessary for the description of the experimentally observed properties of oscillations. Finally, the origin of the phase shift between CO_2 and H_2O partial pressure oscillations will be revealed and the role of carbon in the mechanism of oscillations will be discussed.

2. Reaction mechanism and model formulation

Oscillatory behaviour during methane oxidation has been observed over Pd catalysts in the form of a foil and a powder. Fig. 1 shows the effect of temperature on the oscillatory behaviour during methane oxidation over the Pd foil in a flow reactor. The calculations of the axial Peclet number and the characteristics of residence time spectra indicate that for the given experimental conditions the behaviour of the flow reactor is similar to a continuous stirred tank reactor (CSTR). The main reaction products detected are CO_2 and H_2O . Only traces of CO and H_2 are observed. At low temperature the concentrations of both products oscillate synchronously. However already at 375 °C the H₂O signal does not follow the CO₂ signal during some part of the oscillatory cycle. At point a both CH₄ and CO₂ concentrations decrease, while H₂O and H₂ concentrations rise. Visual observations of the Pd foil surface revealed that at point **a** the colour of the catalyst changed from dark grey to light grey indicating the reduction of PdO to metallic Pd. The decomposition of methane over the reduced Pd leads to the formation of carbon and hydrogen species. Hydrogen interacts with adsorbed oxygen and a significant increase in the H_2O production rate can be detected at point *a* together with the CH₄ consumption from the gas phase. In contrast, at point **b** the peak of CO_2 concentration takes place, while there are no CH₄ and H₂O concentration peaks coinciding with the CO₂ production rate increase. Evidently, carbon species resulting from CH₄ decomposition were accumulating after point **a**, and they oxidised at point **b** producing a peak of CO₂ evolution.

The accumulation of carbon in the Pd catalyst was proved by using thermogravimetric analysis in combination with on-line mass-spectrometry of the effluent gas mixture. In the TGA measurements Pd was used in the form of a powder. As shown by Fig. 2 large weight variations were observed during the oscillatory behaviour of methane oxidation over the Pd powder. The main characteristic features of the oscillations observed over Pd foil and powder were nearly the same, namely the oscillation phases could be detected, with the in phase ($b \rightarrow a$) and the anti-phase ($a \rightarrow b$) evolution of CO₂ and H₂O products (compare Figs. 1 and 2). The Pd weight increase at point a in Fig. 2 corresponds to the simultaneous drops of CH₄ and CO₂ concentrations and the rise of H₂O concentration. As with the Pd foil before point b, the peak of CO₂ concentration is observed, while there are no CH₄ and H₂O concentration peaks coinciding with the CO₂ production rate increase.

The temperature programmed oxidation experiments demonstrated that the large increase of the catalyst weight from point *a* to point C corresponded to the accumulation of carbon in the catalyst. Between points C and E the CO₂ peak could be detected, while the methane and water concentrations were decreasing. This fact indicated that during this time interval the accumulated carbon was oxidised and the peak of CO₂ concentration appeared. Between points E and F the content of carbon was constant and it was demonstrated that the weight increase corresponded to the increase of the oxygen content in the catalyst. At point *a* reduction occurred, methane dissociated on the reduced surface, carbon accumulated in the catalyst and the cycle began again. It was found that hundreds of carbon monolayers could be periodically accumulated in the Pd powder catalyst and then removed during one oscillatory cycle. Details of the experimental results can be found elsewhere (Bychkov et al., 2009b).

The following information about the properties of the oscillations and the reaction mechanism was obtained due to the experimental study of the oscillatory behaviour:

- 1. Oscillations were detected in various reactors and a TGA cell with different conditions of heat and mass exchange. The mass-transfer rate in CSTR was estimated to be about 2 orders of magnitude higher than the reaction rate. Therefore, the oscillatory behaviour during methane oxidation over Pd was observed in the kinetic regime. The kinetic oscillations were caused by the periodic oxidation and reduction of the Pd catalyst.
- 2. The degree of methane conversion and therefore the activity of the oxidised catalyst (point F in Fig. 2) is higher than the activity of the reduced Pd blocked by oxygen (point E in Fig. 2), but lower than the activity of the reduced catalyst (point C in Fig. 2). These results are in line with DFT calculations, which demonstrated that the lowest energy barriers for the reaction of C–H bond cleavage were obtained over Pd stepped surface (Liu and Hu, 2003) and the

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Fig. 1. The effect of temperature on the oscillatory behaviour at the feed rate of 20 ml/min: (a) T_r =350 °C, H_2 (×100, -1.8×10^{-6}), O_2 , CO_2 (+1.8 × 10⁻⁶), H_2O (+2.0 × 10⁻⁶), CH_4 (-2.3 × 10⁻⁶), (b) T_r =375 °C, H_2 (×100, -1.8×10^{-6}), O_2 , CO_2 (+1.6 × 10⁻⁶), H_2O (+1.8 × 10⁻⁶), CH_4 (-2.3 × 10⁻⁶) (Bychkov et al., 2009b).



Fig. 2. Self-sustained weight oscillations and the corresponding oscillations of gas ion currents related to all gas phase components (CH₄:O₂:Ar=82:14:4, 300 °C, O₂ (-1.0×10^{-6}), CO₂ ($+1.5 \times 10^{-6}$), H₂O ($+0.6 \times 10^{-6}$), CH₄ ($\times 10, -5.97 \times 10^{-5}$)) (Bychkov et al., 2009b).

barriers increase with increasing oxygen coverage (Lv et al., 2009; Xing et al., 2011). The activation energy of methane dissociation over PdO(100) was calculated to be larger than over the Pd(100) surface (Valden et al., 1997).

- 3. Mainly metallic reduced sites are active for CH_4 dissociation under conditions of the oscillatory behaviour.
- 4. Both carbon and oxygen can diffuse into Pd, increasing the catalyst weight.
- 5. Carbon can be removed from the bulk of the Pd catalyst, producing CO₂.
- 6. As only traces of CO and H_2 were detected, the water–gas-shift reactions and the partial methane oxidation steps can be excluded for the mechanism of oscillations.

Based on these experimental findings and the available literature data the following minimum set of the reaction steps is proposed:

- 1.1 (R_{ach4}) $CH_4 + 2Pd_s \rightarrow Pd_s CH_3 + Pd_s H$
- 1.2 (R_{dch3}) $Pd_s-CH_3+Pd_s \rightarrow Pd_s-CH_2+Pd_s-H$
- 1.3 (R_{dch2}) $Pd_s-CH_2+Pd_s \rightarrow Pd_s-CH+Pd_s-H$
- 1.4 (R_{dch}) $Pd_s-CH+Pd_s \rightarrow Pd_s-C+Pd_s-H$
- 2. (R_{ao2}) $O_2 + 2Pd_s \rightarrow 2Pd_s O$
- 3. (R_{sco2}) $Pd_s C + 2Pd_s O \rightarrow CO_2 + 3Pd_s$ (1)
- 4. (R_{sh2o}) 2Pd_s-H+Pd_s-O \rightarrow H₂O+3Pd_s
- 5. (R_{do}) $Pd_s-O+Pd_v \rightarrow Pd_v-O+Pd_s$
- 6. (R_{dc1}) $Pd_s-C+Pd_v \rightarrow Pd_v-C+Pd_s$
- 7. (R_{bco2}) $Pd_v-C+2Pd_s-O \rightarrow CO_2+2Pd_s+Pd_v$
- 8. (R_{bh2o}) $Pd_v O + 2Pd_s H \rightarrow H_2O + 2Pd_s + Pd_v$

where Pd_s and Pd_v denote free sites on the catalyst surface and in the subsurface layer, and Pd_v -O and Pd_v -C indicate the subsurface O and C θ_{CH3} ,

atoms. The reaction mechanism (1) includes the stages of the dissociative adsorption of methane (R_{ach4} - R_{dch}) and oxygen (R_{ao2}), the stages of the surface interaction of the adsorbed oxygen with adsorbed carbon (R_{sco2}) and adsorbed hydrogen (R_{sh2o}), the dissolution of oxygen (R_{do}) and carbon (R_{dc1}) into the subsurface layer, the stages of the interaction of the dissolved carbon with adsorbed oxygen (R_{bco2}) and the interaction of the dissolved oxygen with the adsorbed hydrogen (R_{bh2o}).

The rate constants k_i are expressed in the Arrhenius form: $k_i = k_{0i} \exp(-E_i/RT)$. The values of prefactors k_{0i} and activation energies E_i are chosen from the available literature data and shown in Table 1. Prefactors k_{01} and k_{04} have been calculated from the expression of the kinetic theory of gases

$$k_{0i} = s_i / [(2\pi m_i k T_g)^{1/2} N],$$

where s_i is the sticking coefficient m_i is the molecular weight, k is Boltzmann's constant, T_g is the gas-phase temperature, N is an average Pd surface atom density for a polycrystalline foil of $1,27 \times 10^{15}$ atoms/cm² (Anderson, 1975). The sticking coefficients of methane and oxygen over Pd shown in Table 1 were estimated experimentally by Valden et al. (1997) and Wolf et al. (2003).

The reaction enthalpies of all surface reactions were calculated using the standard enthalpy of formation ΔH^0 (298 K) of the surface and dissolved species and the heats of adsorption of all gaseous species, presented in Table 2.

The constants of steps 7 and 8 were not found in the literature. As first move it was suggested, that the rates of the interaction of the dissolved oxygen with adsorbed hydrogen (the rate of Pd_v -O reduction) and dissolved carbon with adsorbed oxygen (the rate of carbon removal by O_2 clean off) were 100 times lower than the rates of the same reactions including adsorbed oxygen and carbon.

The rates of reaction steps can be expressed in the following form:

 $\begin{aligned} R_{ach4} &= k_{ach4} P_{CH4} \theta_{*}^{2}, \\ R_{dch3} &= k_{dch3} \theta_{CH3} \theta_{*}, \\ R_{dch2} &= k_{dch2} \theta_{CH2} \theta_{*}, \\ R_{dch} &= k_{dch} \theta_{CH} \theta_{*}, \\ R_{ao2} &= k_{ao2} P_{O2} \theta_{*}^{2}, \\ R_{do} &= k_{do} \theta_{O} \theta_{r}, \\ R_{dc1} &= k_{dc1} \theta_{C} \theta_{r}, \\ R_{sco2} &= k_{sco2} \theta_{C} \theta_{O}^{2}, \\ R_{sh2o} &= k_{sh2o} \theta_{O} \theta_{H}^{2}, \\ R_{bb2o} &= k_{bb2o} \theta_{OV} \theta_{H}^{2}; \end{aligned}$

According to the proposed reaction mechanism, the dynamic behaviour of the system can be simulated by the following equations:

$$\begin{aligned} \theta_{\text{CH3}} &= R_{ach4} - R_{dch3}, \\ \dot{\theta}_{\text{CH2}} &= R_{dch3} - R_{dch2}, \\ \dot{\theta}_{\text{CH}} &= R_{dch2} - R_{dch}, \\ \dot{\theta}_{\text{C}} &= R_{dch} - R_{sco2} - R_{dc1}, \\ \dot{\theta}_{\text{H}} &= R_{ach4} + R_{dch3} + R_{dch2} + R_{dch} - 2R_{sh2o} - 2R_{bh2o}, \\ \dot{\theta}_{\text{O}} &= 2R_{ao2} - 2R_{sco2} - R_{sh2o} - 2R_{bco2} - R_{do}, \\ \dot{\theta}_{\text{Ov}} &= R_{do} - R_{bh2o}, \\ \dot{\theta}_{\text{Ov}} &= R_{dc1} - R_{bco2}, \\ \dot{\theta}_{\text{CH4}} &= (P_{\text{CH4}}^0 - P_{\text{CH4}})/\tau - \gamma R_{ach4}, \\ \dot{P}_{\text{O2}} &= (P_{\text{O2}}^0 - P_{\text{O2}})/\tau - \gamma R_{aco2}, \\ \dot{T} &= \alpha (T^0 - T) + \beta \sum Q_i R_i. \end{aligned}$$
(3)

Here $\alpha = hS/WC_p$; $\beta = SN/WC_p$; $\gamma = SNRT_0/V$; $\tau = V/F$, where: h is the heat transfer coefficient, S – the catalyst surface area, W – the catalyst weight, C_p – the catalyst heat capacity; N – the adsorption capacity of Pd; R – the universal gas constant, V – the reactor volume; F – the flow rate of the reactant mixture, Q_i – the heat effects of the corresponding studies of the reaction mechanism. The numerical values of these parameters correspond to the conditions of the experimental study of the oscillatory behaviour during methane oxidation in a CSTR over the Pd foil presented by Bychkov et al. (2009b): h=0.003 cal/(s × K), S=0.27 cm², W=0.065 g, C_p =0.057 cal/(g × K), N=1.6 × 10⁻⁹ mol/cm², V= 0.126 cm³, F=0.33 cm³/s. The external values of parameters were also taken from the study of Bychkov et al. (2009b) and were equal to P_{CH4}^0 = 621 T, P_{O2}^0 = 109 T, Torr=618 K. Following the experimental

(2) Table 2 Heats o

Heats of adsorption of gaseous species.

Species	Heat of adsorption (kJ/mol)	Reference
$\begin{array}{c} H_2\\ O_2\\ CO\end{array}$	103 221 150	Banse and Koel (1990), Stuve et al. (1984) Behm et al. (1980) Tracy and Palmberg (1969)

Table 1	
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Temperature dependent reaction parameters and heat effects of various stages.

k_i^{a}	Reaction step	Prefactor k _{oi}	Activation energy (kJ/mol)	References	Heats of reaction (kJ/mol)
k _{ach4} k _{dch3} k _{dch2} k _{dch} k _{ao2} k _{sco2} k _{sh2o}	$\begin{array}{l} CH_4 + 2Pd_s \rightarrow Pd_s\text{-}CH_3 + Pd_s\text{-}H\\ Pd_s\text{-}CH_3 + Pd_s \rightarrow Pd_s\text{-}CH_2 + Pd_s\text{-}H\\ Pd_s\text{-}CH_2 + Pd_s \rightarrow Pd_s\text{-}CH + Pd_s\text{-}H\\ Pd_s\text{-}CH + Pd_s \rightarrow Pd_s\text{-}C + Pd_s\text{-}H\\ O_2 + 2Pd_s \rightarrow 2Pd_s\text{-}O\\ Pd_s\text{-}C + 2Pd_s\text{-}O \rightarrow CO_2 + 3Pd_s\\ 2Pd_s\text{-}H + Pd_s\text{-}O \rightarrow H_2O + 3Pd_s \end{array}$	$s = 2 \times 10^{-3}$ 10^{13} 10^{13} 10^{13} $s = 1$ 10^{8} 5.1×10^{7}	31 31 31 31 0 60 29	Valden et al., (1997), Dropsch and Baerns (1997) Valden et al., (1997), Dropsch and Baerns (1997) Valden et al., (1997), Dropsch and Baerns (1997) Valden et al., (1997), Dropsch and Baerns (1997) Wolf et al. (2003) Libuda et al. (2001) Engle and Kuipers (1979)	- 103 - 103 - 103 - 103 221 722 30.2
k _{do} k _{dc}	$\begin{array}{l} Pd_{s}\text{-}O \ + \ Pd_{v} \ \rightarrow \ Pd_{v}\text{-}O \ + \ Pd_{s} \\ Pd_{s}\text{-}C \ + \ Pd_{v} \ \rightarrow \ Pd_{v}\text{-}C \ + \ Pd_{s} \end{array}$	1.0×10^{5} 3.9×10^{10}	90 107	Wolf et al. (2003) Gabasch et al. (2006)	0 0

^a The dimensions of k_{ach4} , k_{ao2} are $(s \times \text{Torr})^{-1}$ and the dimension of the other k_{0i} is s^{-1} .

results, the number of carbon layers participating in the oscillatory behaviour n_z was set equal to 100.

3. Results and discussion

3.1. Model simulation results

The system (3) has two degenerate stationary states (each state has four zero eigenvalues of the Jacobi matrix, while the other eigenvalues are negative). The first state is the "oxygenated" state, which exists at $\theta_{\rm O}{=}\,\theta_{\rm Ov}{=}\,1$ and all other surface coverages equal to zero. The second one is the "carbidic" state, appearing at $\theta_{\rm C} = 1$, $\theta_{\rm Cv} = n_z$ and zero coverages of all other species. These states are not active, because they are characterised by the following relations: $P_{CH4} = P_{CH4}^0$, $P_{O2} = P_{O2}^0$, $T = T_0$. There are also other stationary states in system (3) and they are not as trivial as "oxygenated" and "carbidic" states. Altogether bring many difficulties even for numerical qualitative analysis. Therefore we did not try to carry out a bifurcation analysis of the system, but instead we analysed the dynamic behaviour of the system starting with the following initial conditions, $S_{ini} = \{\theta_{CH3} = \theta_{CH2} =$ $\theta_{CH} = \theta_C = \theta_O = \theta_H = \theta_{Cv} = \theta_{Ov} = 0, P_{CH4} = P_{O2} = 0, T = T_0$ }. These conditions were chosen because each experiment was started with the "clean" surface without dissolved carbon and oxygen.

With the values of parameters shown in Table 1, the numerical solution of model (3) with initial state S_{ini} is quickly attracted by the "oxygenated" state and activity nor oscillations were obtained. Apparently this model did not contain any efficient feedback mechanism. However experiments under UHV conditions demonstrated that Pd catalysts incorporated sufficient amount of oxygen and that subsurface oxygen could be formed (Ladas et al., 1989). It is also well-known that coverage dependent activation energies can generate oscillatory behaviour (Belayev et al., 1977). As was shown by Basset and Imbihl (1990) modification of the catalytic activity of Pd by subsurface oxygen occurred through the influence of the rate of oxygen adsorption upon the concentration of the subsurface oxygen. According to this experimental finding the rate of oxygen adsorption could be written as follows:

$$R_{ao2} = k_{ao2} \exp(-\delta\theta_{\rm Ov}) P_{\rm O2} \theta_*^2.$$
⁽⁴⁾

where the parameter δ accounts for a strong effect of the subsurface oxygen upon the rate of oxygen adsorption. This feedback mechanism was successfully applied during the simulations of oscillations during CO oxidation over Pd(110) single crystal surface (Hartman et al., 1994) and Pd zeolite catalysts (Slinko et al., (1999)).

To find out the region of oscillations we solved numerically the model (3) at fixed δ , starting from the initial conditions S_{ini} and followed the solution during sufficiently long time. ("Sufficiently" means that there were several hundreds of oscillatory cycles during the chosen time of simulation, when oscillations existed.) We found out that for all other parameters from Table 1 fixed, an oscillatory solution existed only for δ_1 larger than $\delta_1 \approx 3.44$. For the values of δ set in the range $0 \le \delta < \delta_1$ the numerical solution with initial state S_{ini} was approaching the "oxygenated" state. The time of steady state attainment increased with increasing values

Table 3Parameters of model (3) used in the simulation.

of δ . It should be noted that the "oxygenated" state always coexisted with an oscillatory solution, however for $\delta = \delta_1$ regular oscillations were attained instead of a monotonic approach to the steady-state. The numerical continuation of a limit cycle inside the oscillatory region via decreasing values of δ also provided the boundary value close to δ_1 . Unfortunately, the simulated oscillations appeared with the large amplitude and we could not determine the exact type of bifurcation which gave birth to the oscillations

The most intricate feature of the experimentally observed oscillations is the anti-phase oscillations of the concentrations of the reaction products, H_2O and CO_2 . Therefore an ability to produce such type of oscillations was chosen as the main criterion of the adequacy of a model. To describe the variation of H_2O and CO_2 partial pressures in a CSTR, the following equations were added to system (3):

$$\dot{P}_{H20} = -P_{H20}/\tau + \gamma R_{sh2o} + \gamma R_{bh2o},$$

$$\dot{P}_{C02} = -P_{C02}/\tau + \gamma R_{sco2} + \gamma R_{bco2}.$$
(5)

Table 3 summarises the parameters used in the following simulations. It should be noted that the unknown constants k_{bco2} and k_{bh2o} play the role of fitting parameters to generate a limit cycle behaviour. The oscillations obtained with these parameters for δ =8 is shown in Figs. 3a–c. The simulated oscillations of CO₂, H₂O concentrations and temperature variation can be seen in Fig. 3a. The oscillatory behaviour of surface coverages and the dissolved oxygen are demonstrated in Fig. 3b. Oscillations of carbon surface coverage and carbon content in the bulk are shown in Fig. 3c. It can be seen that the content of the bulk carbon can reach 40 monolayers and there is a phase shift between oscillations of bulk carbon and oxygen concentrations.

The main driving force for the oscillations is the dependence of the oxygen adsorption rate on the concentration of the subsurface oxygen. The mechanism of oscillations can be presented as follows: as the concentration of the subsurface oxygen was increasing (stage 1-2) the surface is covered by oxygen and the dissociative adsorption of methane is inhibited. When the concentration of the subsurface oxygen reaches its maximum (point 2), the rate of oxygen adsorption sharply decreases. The oxygen surface coverage falls down giving rise to the increase of the rate of methane dissociation. C and H coverages reach their maxima, while O coverage is minimal. At the stage 2-1 the subsurface oxygen slowly reacts with adsorbed H species and its concentration slowly decreases. At point 1 the rate of oxygen adsorption sharply increases, the whole surface becomes covered mostly by oxygen and the whole process begins to repeat itself, beginning a new cycle.

The dynamic behaviour shown in Fig. 3 has the form of relaxation oscillations. This means that the reaction mechanism contains fast and slow steps. As can be seen from Table 3 the stages of oxygen adsorption and the surface reaction of oxygen with hydrogen have the largest (except dissociation of CH fragments) constants. The smallest values of constants are attributed to the steps of oxygen diffusion into the subsurface layer and its reaction with the surface hydrogen. Increase of the constant of oxygen diffusion (k_{do}) and decrease of the constant of surface reaction (k_{sh2o}) leads to the observation of oscillations with more harmonic form.

k _i	k _{ach4}	k _{dch3}	k _{dch2}	k _{dch}	k _{ao2}	k _{sco2}	k _{sh2o}	k _{do}	k _{dc}	k _{bco2}	k _{bh2o}
E (kJ/mol)	703.9 0	$\begin{array}{c} 1.0\times10^{13}\\ 20\end{array}$	$\begin{array}{c} 1.0\times10^{13}\\ 20\end{array}$	$\begin{array}{c} 1.0\times10^{13}\\ 20\end{array}$	$\begin{array}{c} 2.5\times10^5\\ 0\end{array}$	$\begin{array}{c} 1.0\times10^8\\ 60\end{array}$	$\begin{array}{c} 5.1\times 10^6\\ 29\end{array}$	$\begin{array}{c} 1.0\times10^5\\ 90 \end{array}$	$\begin{array}{c} 3.9\times10^{10}\\ 107\end{array}$	$\begin{array}{c} 1.0\times10^6\\ 50\end{array}$	$\begin{array}{c} 1.0\times10^6\\ 80\end{array}$



Fig. 3. Simulated oscillations obtained with the help of model (3) with parameters taken from Table 3: (a) CO_2 , H_2O partial pressures and temperature variations; (b) oscillations of surface coverages and (c) oscillations of bulk carbon and oxygen.

The numerical integration of model (3) permits to investigate the sensitivity of the oscillatory region and the properties of the oscillations to the variation of the constants of mechanism (1). The example of some kind of sensitivity analysis is given in the Appendix A. Here the Table A1 demonstrates the variation of the amplitude and the period of H₂O production rate oscillations together with the oscillatory region as a response to the variation of the pre-exponential factors k_{0i} and sticking coefficients. It should be note that if the simulated oscillations displayed a complicated waveform it was not possible to determine their amplitude and period. The calculations show that the most sensitive model parameters are k_{05} and k_{08} . A possible explanation of this fact is that the rates of oxygen diffusion and its reaction with hydrogen in the bulk determine the concentration of the subsurface oxygen θ_{Ov} (see model (3)) and this specie is involved in the feedback mechanism (4). Decreasing k_{05} leads to the increase of the period of the oscillations and the time interval during which an oscillatory state is attained. The amplitude of the oscillations is sensitive to all parameters except k_{05} and k_{06} , the values, which are related to the rates of diffusion of C and O atoms into the subsurface layer. The boundaries of the oscillatory region are mainly sensitive to the parameters, which define the concentration of adsorbed and subsurface oxygen. Thus as the rates of oxygen diffusion (k_{05}), surface interaction of oxygen with atoms of carbon (k_{03}) and hydrogen (k_{04}) decrease, the corresponding increase of oxygen coverage leads to the attainment of the "oxygenated" steady state. The high rates of oxygen diffusion (k_{05}) , of the interaction of the subsurface oxygen with hydrogen (k_{08}) and large S_{CH4} favour to the replacement of the oxygen in the subsurface later by carbon, causing the steady state behaviour.

However, at all values of parameters in the regions shown in Table A1 the reaction products CO_2 and H_2O oscillate in phase. We analysed also various models with different types of lateral interactions and kinetic parameters, but in all cases in-phase oscillations of CO_2 and H_2O concentrations have been observed. Therefore modifications of the model had been studied to reach a better description of the experimental data.

3.2. Modifications of the model

3.2.1. Impact of methane dissociation order upon the dynamic behaviour of the system.

In spite of the large amount of UHV experimental studies and theoretical work done on the adsorption of CH_4 over metallic surfaces the details and the kinetics of this process under high pressure conditions are still not clear. The low-field magnetic method and infrared spectroscopy were applied to measure the adsorption of methane on supported nickel catalysts (Chen et al., 2000). The chemisorbed methane was found to dissociate with the formation of a Ni₃C complex according to the reaction

$CH_4 + 7Ni \rightarrow Ni_3 - C + 4Ni - H$

Details of how methane interacts with the surface of palladium catalysts were much less known. Sensitive FTIR measurements did not reveal the existence of stable CH_x species on the Pd surface following CH₄ decomposition (Solymosi et al., 1994). This fact coincides with the results of our simulations since the steps R_{ach4}- R_{dch} are very fast and θ_{ch3} , θ_{ch2} , θ_{ch} coverages are very small. It is then reasonable to consider the adsorption of methane as one lumped reaction step according to the following brutto-step (Veser and Fraunhammer, 2000)

$$(R_{ach4}) \quad CH_4 + 5Pds \rightarrow Pds - C + 4Pds - H \tag{6}$$

Assuming that three first adsorption steps, R_{ach4} , R_{ach3} , and R_{ach2} are under equilibrium conditions, and the fourth step, R_{dch} , is irreversible the rate of step R_{ach4} can be simulated with the following equation:

$$R_{ach4} = k_{ach4} P_{CH4} \theta_*^5. \tag{7}$$

The heat effect of step (7) now is $Q_{ach4} = -413 \text{ kJ/mol}$.

The replacement of steps R_{ach4} - R_{dch} by one stage (6) changed the dynamic behaviour of the system. In order to obtain oscillations with parameters of steps 2–8 (see mechanism 1) from Table 3, we must increase the parameter δ up to 20. For values

of δ smaller than 17.7, the "oxygenated" state was attained and no reaction products could be detected in the gas phase.

Fig. 4 demonstrates the oscillatory behaviour of the concentrations of both products and catalyst temperature simulated with parameters from Table 3 using the stage (6) of the complete dissociation of methane. It can be seen that oscillations become more stiff and the period of oscillations increases by nearly a factor of 10. However, both reaction products again produced inphase oscillations. Moreover in contrast with the experimental results not more than 50 layers could be filled with carbon during oscillations and so further improvement of the model was sought.

3.2.2. Impact of the rate of carbon diffusion in Pd upon the oscillatory behaviour

Bychkov et al. (2009b) applied X-ray diffraction to analyse the state of the catalyst at the moment of the fast increase of the catalyst weight due to carbon dissolution in palladium. It was demonstrated that carbide PdC_x, was formed during this process. Therefore one can suggest that the surface carbon could penetrate at first into the subsurface layer and then into the bulk of the catalyst forming Pd carbide. It may also happen that the rate of carbon diffusion into the first layer can be different from the rate of carbon diffusion into the deeper layers. Fig. 5 shows a schematic representation of the reaction mechanism. Here carbon in the bulk layers Pdb-C is distinguished from the carbon in the subsurface layer Pdv-C. Therefore in following simulations the variable θ_{Cv} denotes the carbon concentration only in the first subsurface layer $0 \le \theta_{Cv} \le 1$, while a new variable θ_{Cb} , $0 \le \theta_{Cb} \le n_z$, indicates the carbon concentration in the bulk of Pd. n_z now denotes the number of bulk Pd layers which can be filled by Pd carbide. New steps considering carbon diffusion into and out of the bulk layers are also added to the reaction mechanism (1)

$$\begin{array}{ll} (R_{dc2}) & Pd_v - C + Pd_b \rightarrow Pd_b - C + Pd_v, \\ (R_{uc2}) & Pd_b - C + Pd_v \rightarrow Pd_v - C + Pd_b. \end{array}$$

Again we assume that the bulk carbon Pd_b-C is uniformly distributed over n_z bulk atomic layers of Pd, and its average concentration in each layer is θ_{Cb}/n_z . The concentration of free sites in the subsurface layer is now equal to $\theta_r = 1 - (\theta_{OV} + \theta_{CV})$.

The rates of stages (8) can be simulated by the following equations:

$$R_{dc2} = k_{dc2}\theta_{Cv}(1-\theta_{Cb}/n_z),$$

$$R_{uc2} = k_{uc2}(\theta_{Cb}/n_z)\theta_r.$$
(9)



Fig. 4. Simulated oscillations using the brutto-step (6) of the complete dissociation of methane with parameters of steps 2–8 (see mechanism 1) from Table 3 and δ =20.



Fig. 5. Schematic representation of the mechanism of methane oxidation over the Pd catalyst considering the diffusion of carbon into the bulk layers.

where k_{dc2} and k_{uc2} are the constants of carbon diffusion into and out the bulk layers of the catalyst. The rates of other reaction steps are expressed using the equations similar to Eq. (2) except the following stage

$$R_{bco2} = k_{bco2} \theta_{\rm Cv} \theta_{\rm O}^2 \tag{10}$$

As provided by the proposed reaction mechanism, the dynamic behaviour of the system can be described by the following mathematical model

$$\begin{aligned} \theta_{\rm C} &= R_{ach4} - R_{sco2} - R_{dc1}, \\ \dot{\theta}_{\rm H} &= 4R_{ach4} - 2R_{sh2o} - 2R_{bh2o}, \\ \dot{\theta}_{\rm O} &= 2R_{ao2} - 2R_{sco2} - R_{sh2o} - 2R_{bco2} - R_{do}, \\ \dot{\theta}_{\rm OV} &= R_{do} - R_{bh2o}, \\ \dot{\theta}_{\rm CV} &= R_{dc1} - R_{bco2} - R_{dc2} + R_{uc2}, \\ \dot{\theta}_{\rm Cb} &= R_{dc2} - R_{uc2}, \\ \dot{\theta}_{\rm CH4} &= (P_{ch4}^0 - P_{ch4})/\tau - \gamma R_{ach4}, \\ \dot{P}_{\rm O2} &= (P_{o2}^0 - P_{o2})/\tau - \gamma R_{o2}, \\ \dot{T} &= \alpha (T^0 - T) + \beta \sum Q_i R_i. \end{aligned}$$
(11)

The value of parameters k_{dc2} and k_{uc2} are unknown, therefore the variations of k_{dc1} , k_{dc2} , k_{uc2} values have been done and it was shown that mainly the value of k_{dc1} had an influence upon the dynamic behaviour of the system. Therefore the further calculations have been done with equal values of carbon diffusion through the whole volume of the catalyst: $k_{dc1} = k_{dc2} = k_{uc2} = k_d$. It was shown that oscillations could originate in model (11) with diffusion constant k_d and all other constants equal to the values presented in Table 3. The oscillatory behaviour of CO₂, H₂O partial pressures and the temperature variation together with the oscillations of carbon concentration on the surface, in the subsurface layer and in the bulk of the catalyst simulated with model (11) are shown in Fig. 6. It can be seen that the waveform and the period of the oscillations of CO₂ and H₂O concentrations are similar to those shown in Fig. 4. However, in this case more than 90 layers of carbon can participate in the oscillatory behaviour. Therefore the modification of the model yields a better agreement with experimental data.

The main shortcoming of model (11) is that an oscillatory behaviour could be obtained with the parameters from Table 3 only with the low methane activation energy of 20 kJ/mole, whereas the lowest methane activation energy of the C–H bond reported for a stepped Pd(111) single crystal surface was 29 kJ/mol (Kinnunen et al., 2011). The methane activation energy increase in the model (11) led to the attainment of the "oxygenated" state. Oscillations with the methane activation energy equal to 40 kJ/mol could be obtained only if the rate of the



Fig. 6. Simulated oscillatory behaviour, calculated using mathematical model (11) with parameters from Table 3 with δ =20, n_z =100. (a) Oscillations of the partial pressures of H₂O and CO₂ together with temperature variation and (b) oscillations of carbon on the catalyst surface, in the subsurface region and in the bulk of the catalyst.

Table 4Parameters of model (11) used in the simulation.

k ⁱ	k _{ach4}	k _{ao2}	k _{sco2}	k _{sh2o}	k _{do}	k _{dc}	k _{bco2}	k _{bh2o}
k <mark>i</mark> E (kJ/mol)	703.9 40	$\begin{array}{c} 2.5\times 10^5 \\ 0 \end{array}$	$\begin{array}{c} 1.0\times10^8\\ 60\end{array}$	$\begin{array}{c} 5.1\times10^6\\ 40\end{array}$	$\begin{array}{c} 1.0\times10^5\\ 80\end{array}$	$3.9 imes 10^{10}$ 107	$\begin{array}{c} 5.0\times10^6\\ 60\end{array}$	$\begin{array}{c} 0.5\times 10^6\\ 80\end{array}$



Fig. 7. Simulated oscillatory behaviour, calculated using mathematical model (11) with parameters from Table 4 for various activation energies of carbon diffusion E_d . Left panel: oscillations of the partial pressures of H₂O and CO₂ (a) E_d =107 kJ/mol. (b) E_d =90 kJ/mol, (c) E_d =70 kJ/mol. Right panel: oscillations of the surface carbon coverage, carbon concentration in the subsurface layer and in the bulk of Pd (d) E_d =107 kJ/mol. (e) E_d =90 kJ/mol and (f) E_d =70 kJ/mol.

activation energy of oxygen diffusion into the subsurface layer was decreased from 90 to 80 kJ/mol. The set of parameters shown in Table 4 significantly extended the region of oscillations and it became possible to find out that the value of k_d and, therefore, the rate of carbon diffusion have a pronounced effect upon the waveform of oscillations. Fig. 7 (a–f) demonstrates the results of

these simulations. One can see that the essential phase shift between the partial pressures of H_2O and CO_2 (see Fig. 7c) appears when the activation energy of carbon diffusion is decreased from 107 kJ/mol to 70 kJ/mol. Fig. 7(d–f) shows the variation of the surface carbon coverage, carbon concentration in the subsurface layer and in the bulk of Pd for various rates of carbon diffusion.



Fig. 8. Simulated oscillatory behaviour, calculated using mathematical model (11) with parameters from Table 4 for the value of activation energy of carbon diffusion in Pd equal to 50 kJ/mol and various numbers of palladium layers for carbon diffusion. Left panel: oscillations of the partial pressures of H₂O and CO₂: (a) n_z =1, (b) n_z =30, (c) n_z =70. Right panel: oscillations of the sufface carbon coverage, carbon concentration in the subsurface layer and in the bulk of Pd (d) n_z =1, (e) n_z =30, (f) n_z =70.

The simulations make obvious that the phase shift between the concentrations of both products happens when the concentration of carbon atoms on the catalyst surface is extremely small, while large amplitude oscillations of carbon in the subsurface layer and in the bulk of the catalyst occur.

3.2.3. Impact of the number of palladium layers for carbon diffusion upon the oscillatory behaviour

The next step we took in trying to understand the origin of the phase shift between the oscillations of the partial pressures of two products was to study the effect of the number of palladium bulk layers for carbon diffusion n_z upon the dynamic behaviour of the system. Fig. 8 shows the results of simulations for the lowest value of activation energy of carbon diffusion in Pd equal to 50 kJ/ mol. It can be seen that if only one bulk layer of Pd is filled $(n_z=1)$ the carbon concentration on the surface is large and the CO₂ and H₂O partial pressures oscillate in-phase (see Fig. 8a and d). With increasing n_z the waveform of H₂O partial pressure oscillations became more complex and different from the waveform of CO₂ partial pressure oscillations (see Fig. 8b). With a further increase of n_z till 100 the anti-phase oscillations of two reaction products were detected (see Fig. 8c). The variation of the surface carbon coverage and carbon concentration in the subsurface layer for various numbers of palladium layers for carbon diffusion is depicted in Fig. 8d-f. Again the results of simulations shown in Fig. 8f indicate that the phase shift between concentrations of both products happens when the concentration of carbon atoms on the catalyst surface is extremely small.

3.3. The origin of the anti-phase oscillations of CO_2 and H_2O partial pressures oscillations

The origin of the phase shift between the oscillations of CO_2 and H_2O partial pressures is schematically shown in Fig. 9. While H_2O is formed due to the fast surface reaction between adsorbed oxygen and hydrogen atoms, surface carbon atoms must not react with the surface oxygen and have to move into the subsurface layer and later into the bulk of the catalyst. Only after passing



Fig. 9. Schematic representation of the origin of the phase shift between the oscillations of CO_2 and H_2O concentrations.

through this long route do carbon atoms return back and react with the surface oxygen. In the case of the slow rate of carbon migration into Pd, surface carbon atoms similar to adsorbed hydrogen atoms immediately react with the adsorbed oxygen and in-phase oscillations occur. These results are in line with the experimental results obtained over the Pd powder catalyst shown in Fig. 2. Here methane dissociates over the reduced surface and no CO₂ concentration peak occurs. The sharp increase of the catalyst weight corresponds to the incorporation of large amounts of carbon atoms into the catalyst bulk. Later the peak of CO₂ concentration is observed, while there are no CH₄ and H₂O concentration peaks coinciding with the CO₂ production rate increase, indicating that only bulk carbon reacts with the surface oxygen. Therefore the simulations results agree with the experimental results, demonstrating that C atoms have to pass a long way (see Fig. 9) before they can react with surface oxygen atoms to produce CO₂, while there is a short route for hydrogen atoms,

which can quickly react with adsorbed oxygen atoms, producing H_2O immediately after the dissociative adsorption of methane.

4. Conclusions

Our results demonstrate that the same feedback mechanism which causes oscillatory behaviour during CO oxidation could also produce kinetic rate oscillations during methane oxidation over Pd catalysts. However, the latter oscillating system is more complicated. First of all, not one but two different reaction products CO_2 and H_2O are formed under the conditions of the oscillatory behaviour. Moreover, the formation rate of CO_2 can oscillate out-of-phase with the rate of H_2O production. Secondly and in agreement with experimental results, hundreds of carbon monolayers in the bulk of the catalyst can participate in the oscillatory behaviour.

The model (11) which has been developed qualitatively reproduces many of the important features of the oscillatory behaviour of methane oxidation over Pd catalysts. The experimental results shown in Fig. 1 illustrate that at lower temperatures CO_2 and H_2O partial pressures oscillate in-phase and the difference in the waveform of these oscillations increases with increasing temperature. The simulations showed that in-phase oscillations were also obtained if the value of the rate of carbon diffusion into the subsurface layer was not large enough, as in the case of experimental oscillations shown in Fig. 1 at 350 °C. With increasing the rate of carbon diffusion into Pd the difference in the waveform of simulated oscillations of different reaction products also became more significant.

In the case of the Pd powder the weight and the specific surface of the catalyst was larger than the same parameters for the Pd foil. Oscillations with bigger period (\sim 15 min) in comparison with the period of rate oscillations over the Pd foil (\sim 1-2 min.) were obtained. This could be the reason of a larger amount of bulk Pd layers participating in the oscillatory behaviour and the appearance of the anti-phase oscillations over the Pd powder catalyst. In agreement with experimental observations the anti-phase oscillations of CO₂ and H₂O partial pressures were obtained in model (11) only for the large amount of bulk layers.

The key results of our simulations are shown in Figs. 7 and 8. They clearly indicate that elements for reproducing the antiphase oscillations of CO_2 and H_2O partial pressures can be formulated as follows:

- 1. The rate of carbon incorporation into Pd (R_{dc}) has to be greater than the rate of surface CO₂ formation (R_{sco2}) and carbon surface coverage has to be extremely low.
- 2. The subsurface carbon atoms has to move rapidly into the deeper layers and the amount of bulk layers must be larger than 50.

The simulations demonstrated that no any model could reproduce the experimentally observed properties of oscillations with the literature value of carbon incorporation into Pd determined by Gabasch et al. (2006) and equal to 107 kJ/mol. This value was obtained as a result of the simulations of the variation of dissolved C atoms, as a function of temperature on the basis of the steadystate reaction kinetics of C_2H_4 dissociative adsorption. As a result of DFT calculations considerably lower values of 50–80 kJ/mol were obtained (Gracia et al., 2005; Kozlov et al., 2009). The results of our study demonstrate that, in order R_{dc} should be greater than R_{sco2} , the activation energy of the carbon diffusion process had to be decreased in the simulations till 70 kJ/mol-the quantity, which was closer to the value determined from DFT calculations.

We understand that the replacement of the stages of the dissociative adsorption of methane (Rach4- Rdch) by one irreversible brutto-step is a deviation from the microkinetic modelling. However, considerably worse agreement with the experimental data was obtained, when the parameters for which the anti-phase oscillations of two reaction products were detected in model (11). were introduced in model (3). Moreover, the introduction of the stages of the dissociative adsorption of methane $(R_{ach4}-R_{dch})$ into model (11) instead of the brutto-step (6) also yielded considerably worse agreement with the experimental data. Always in-phase oscillations of the concentrations of two reaction products were obtained in the simulations during the variation of constants and/ or introduction of various types of lateral interactions. Therefore according to the results of our analysis a strong competition between CH₄ and O₂ molecules for the free adsorption sites may also be necessary for the appearance of the anti-phase oscillations.

In conclusion one of the main results of this work is the demonstration of how powerful can be the simulation of the properties of experimentally observed oscillations. We have analysed more than 65 various oscillating mathematical models and the simulations showed that only one model (11) could generate the anti-phase oscillations. This fact may indicate that the basic features of the mechanism of oscillations were

Table A1

The variation of the amplitude and the period of H_2O production rate oscillations together with the oscillatory region as a response to the variation of the pre-exponential factors k_{0l} and sticking coefficients.

Pre- exponential factor k _{0i}	The oscillatory region	The variation of the period τ , s	The variation of the amplitude, A ML/s	Comments
k ₀₃	$0.45 \times 10^8 < k_{03} < 2 \times 10^8$	$21 < \tau < 31$	3 < A < 36	The period and the amplitude of the oscillations increase with the k_{03} increase
k04	$0.7 \times 10^6 < k_{04} < 8.6 \times 10^6$	$10.3 < \tau < 35$	4.7 < A < 28.3	The period and the amplitude increase with the k_{04} increase
k ₀₅	$3.0 < k_{05} < 2 \times 10^5$	$52542 > \tau > 14$	15.1–15.3	The period of the oscillations decreases with the k_{05} increase, while the amplitude is nearly constant
k ₀₆	$3.9 \times 10^{-4} < k_{06} < 3.9 \times 10^{20}$	Min $\tau = 25$, Max $\tau = 236$	15.1–17.6	Complex oscillations, the amplitude nearly constant
k ₀₇	$10 < k_{07} < 1 \times 10^{20}$	$2500 > \tau > 8.3$	Min $A = 5.8$; max $A = 17.6$	The period of the oscillations decreases with the k_{07} increase, while the amplitude goes through the maximum
k ₀₈	$0.49 \times 10^6 < k_{08} < 18 \times 10^6$	$50 > \tau > 10$	38 > A > 7.1	The period and the amplitude of the oscillations decrease with the k_{08} increase
s _{CH4}	$2.5 \times 10^{-5} \! < \! S_{CH4} \! < \! 6.5 \times 10^{-3}$	$500 > \tau > 25$	8.1 < A < 26.4	The period of the oscillations decreases, while the amplitude increases with the S_{CH4} increase
s ₀₂	$0.2 < S_{O2} < 1$	$27.5 > \tau > 25$	32.6 > A > 17.6	The period and the amplitude of the oscillations decrease with the $\ensuremath{S_{\text{O2}}}$ increase

simulated successfully although quantitative agreement of the reaction rate values is not yet satisfactory.

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Appendix A

See Table A1.

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