



Oscillatory behavior during CO oxidation over Pd supported on glass fibers: experimental study and mathematical modeling

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Abstract

The oscillatory behavior during CO oxidation over Pd supported on glass fibers was studied in a recycle reactor. The properties of oscillations as a function of temperature and inlet CO concentration were investigated in detail. The peculiarity of the observed oscillations is their long period up to 6 h. Mathematical model considering oxidation–reduction processes of the Pd has been developed to describe the experimental results. The model accounts for the observed reaction rate dependence on the CO inlet concentration, the region of oscillations and the dependence of the oscillatory behavior upon temperature and CO inlet concentration. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Besides pellets or honeycomb monolith catalysts noble metals supported on glass fibers (GF) are applied in processes related to catalytic converter technology (Nicholas, Shah & Zlochower, 1976; Neyestanaki & Lindfors, 1995; Kiwi-Minsker, Yuranov, Siebenhaar, & Renken, 1999). Recently, the preparation of Pd supported on silica glass fibers (SGF) and their activity in CO oxidation has been reported (Yuranov, Kiwi-Minsker, Barelko & Renken, 1999). The influence of catalyst microstructure, specific surface area, surface concentration and dispersion of palladium on the catalyst performance was shown.

Three reactivity regions were found for the catalyst as a function of temperature and CO concentration: (1) a high reactivity region with conversion close to 100%, (2) a low reactivity region and (3) an intermediate region, where oscillatory behavior was observed. Self-sustained oscillations of high regularity with a period of up to 6 hours were observed for 0.2% Pd/SGF.

The decreased Pd loading on SGF support results in decaying oscillations as observed over 0.02% Pd/SGF catalyst.

This study reports the detailed experimental data on self-sustained oscillations during the CO oxidation over 0.2% Pd/SGF catalyst and the mathematical modelling of the observed phenomena.

2. Experimental

Commercial silica glass fibers (SGF) in the form of woven fabrics produced by “Steklovolokno” (Polotsk, Belarus) was used as a support. The chemical composition of the SGF support consists of ~97% SiO₂. The fabrics were made up from long threads of elementary bundled filaments. The diameter of each filament was 7 μm. The BET specific surface area (SSA) of the SGF fabric was ~2 m²/g, which is in the range of the geometrical surface area of the filaments.

Palladium (II) chloride PdCl₂ (purum, Fluka Chemie AG, Buchs, Switzerland) was used as the precursor of the active component during the catalyst preparation. The Pd with loading of 0.2 wt% supported on SGF (abbreviation of this catalyst from now on is 0.2Pd/SGF-2) was prepared by Pd deposition from aqueous NH₃ solutions

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via wet-impregnation followed by calcination at 550°C in air during 3 h.

The BET surface area of the support and the catalyst was measured using the N₂ adsorption–desorption isotherms at 77 K via a Sorptomatic 1990 (Carlo Erba) unit.

The CO oxidation was studied in a continuous fixed bed reactor (volume $0.4 \times 10^{-3} \text{ m}^3$) provided with an external recycle loop and a membrane compressor. The recycling ratio in the system was always > 100 . The reactor used presented the behavior of an ideal continuous-stirred tank reactor (CSTR) (Kiwi-Minsker et al., 1999).

Rolled up woven 0.2Pd/SGF-2 catalyst (about 0.8 g) was placed into the middle of the reactor. The temperature in the catalytic bed was measured by a sheathed thermocouple. The gases CO, CO₂, O₂, and Ar (99.99%, Carba-Gas, Lausanne, Switzerland) were used without further purification. The gas feed rate was $F = 12 \text{ l/h}$ (STP) and was controlled by a mass flow controller. CO and CO₂ concentrations were continuously monitored by an infrared analyzer Ultramat 22P (Siemens).

The CO oxidation over 0.2Pd/SGF-2 catalyst was studied in the temperature range of 160–250°C with CO variation in the feed from 0.1 to 2.5 vol%. The O₂ inlet concentration was kept always at 10 vol% and argon was used as a diluent.

3. Results

Fig. 1 shows the dependency of the reaction rate, characterized by the CO₂ outlet concentration, on the inlet pressure of CO for various temperatures. Two branches of the reaction rate were identified: a high reaction rate branch (ignited state), in which the reaction rate increases with CO concentration in the feed and a second low reaction rate branch (extinguished state), where the observed rate decreases with CO inlet concentration. The degree of conversion in the ignited state was always observed to be close to 100%. In spite of this high degree of conversion the mass-transfer rate was estimated to be about 3 orders of magnitude higher than the reaction rate (Kiwi-Minsker et al., 1999). This allows to state that all measurements were performed in the kinetic regime.

In the transition region self-sustained oscillations of the reaction rate were observed. As an example the oscillatory behavior detected for CO concentration of 1.7 vol% at 240°C is shown in Fig. 2. It is important to note that large variations of the CO₂ concentration in the reactor are accompanied by small temperature variations (1–3°C) in the catalytic bed. The waveform of the oscillatory behavior is typical for relaxation type oscillations. Every oscillation period can be divided into steps, during which the system presents high or low activity and the steps, during which the system goes from one state to

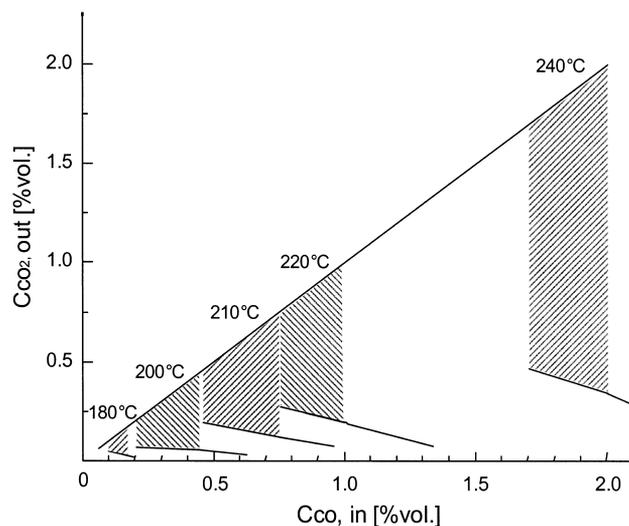


Fig. 1. The reaction rate as a function of inlet CO concentration for different temperatures.

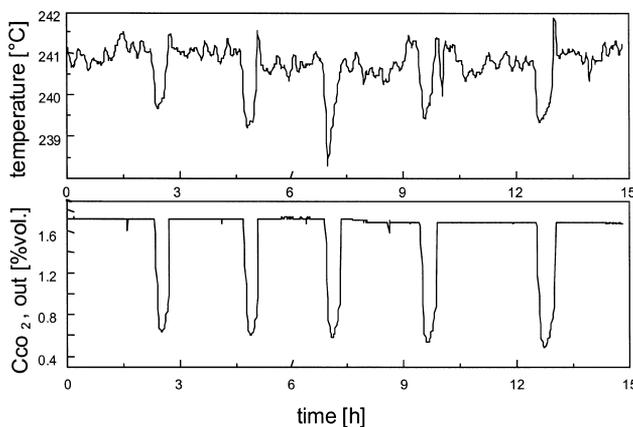


Fig. 2. Reaction rate oscillations and the corresponding oscillations of the temperature in the catalytic bed; $C_{\text{CO},\text{in}} = 1.7 \text{ vol}\%$, $T = 240^\circ\text{C}$.

another. The degree of conversion at the maximum in each oscillation reaches 100%.

Fig. 1 demonstrates that the oscillatory region moves to higher CO inlet concentrations when the temperature is increased. The region of regular periodic oscillations in the T – $C_{\text{CO},\text{in}}$ parameter space is shown in Fig. 3.

The properties of oscillations depend on the temperature and CO feed concentration. The magnitudes of the oscillation amplitude expressed as the CO conversion, X , and period in dependence on these parameters are listed in Table 1. Fig. 4 shows that the period of oscillations decreases as the temperature increases. It is interesting to note that the time, which the system spends in the low activity state decreases with temperature, being 15 min at 210°C and 90 min at 200°C. The time in the high activity state is not affected by the temperature.

The dependence of the properties of oscillations upon the inlet CO concentration at 210°C is depicted in Fig. 5.

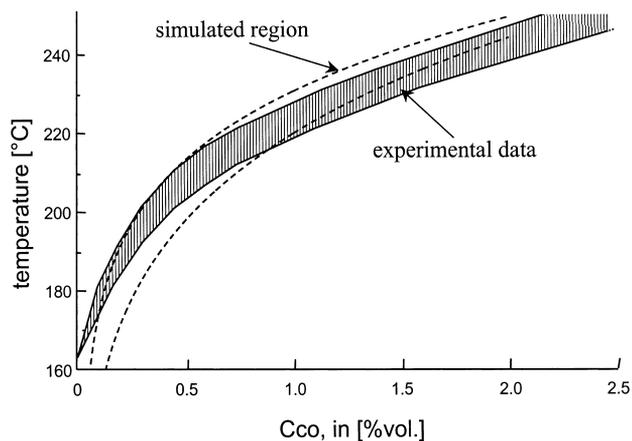


Fig. 3. The region of regular oscillations in the temperature — CO inlet concentration (T – $C_{CO,in}$) parameter space. Experimental and simulated results.

Table 1
Parameters of regular oscillations over catalyst 0.2 Pd/SGF-2

T (°C)	$C_{CO,in}$ (vol%)	Amplitude of X (%)	Period (h)
180	0.1	65	0.5
	0.12	66	0.59
	0.15	82	1.0
	0.17	87	1.2
200	0.3	72	1.3
	0.4	82	1.8
	0.45	84	2.35
210	0.45	59	1.2
	0.5	64	1.37
	0.6	72	2.0
	0.75	83	3.84
220	0.85	72	1.8
	1.0	81	2.7
240	1.7	72	2.8
	2.0	83	3.45

The amplitude and the period of oscillations increase with a higher inlet CO concentration.

Next it was investigated if the observed self-sustained oscillations were connected with periodic oxidation and reduction cycles of the supported Pd. If the catalyst was reduced, under the oscillation regime conditions the system immediately moved to the high activity branch of the oscillatory cycle. The oxidized catalyst displayed low activity. About 1 h was necessary for the system to reach again the high activity branch of the oscillation cycle. Therefore, the high and the low reactivity states of the catalyst can be associated with Pd in the reduced and oxidized states.

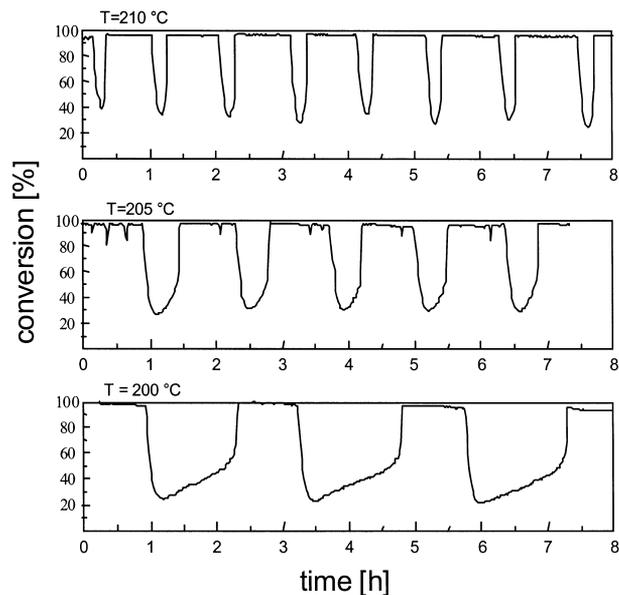


Fig. 4. Influence of temperature on the reaction oscillatory behavior; $C_{CO,in} = 0.45$ vol%.

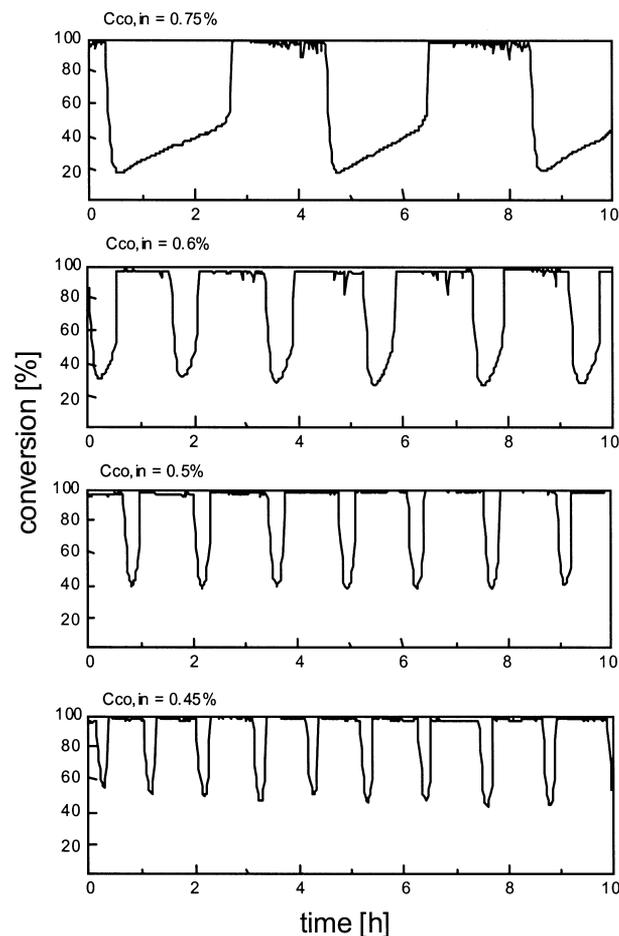
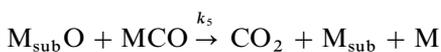
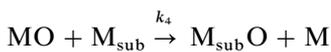
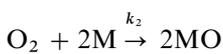
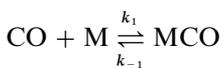


Fig. 5. Influence of inlet CO concentration on the reaction oscillatory behavior; $T = 210$ °C.

4. Discussion

Self-sustained oscillations during oxidation of CO over Pd supported on glass fiber were observed in the absence of mass-transfer limitations to the external catalyst surface. This oscillatory behavior was accompanied by temperature oscillations in the catalytic bed not exceeding 3–5°C. Therefore, the observed oscillations can be considered as kinetic oscillations (Slin'ko & Jaeger, 1994). The large period of these oscillations indicate that slow chemical reactions are at the origin of the observed oscillations. Transient experiments with the variation of reaction mixture composition indicate that the high activity state is associated with the reduced catalyst, while the oxidized catalyst demonstrates low activity. The oxidation–reduction mechanism has been suggested earlier for kinetic oscillations, observed during CO oxidation over Pd (110) single crystal surface (Basset & Imbihl, 1990), Pd wire (Turner, Sales & Maple, 1981) and Pd zeolite catalysts (Jaeger, Möller & Plath, 1986; Slin'ko, Jaeger & Svensson, 1989; Liauw, Plath & Jaeger, 1996). The dependencies of the oscillatory amplitude and period on the reaction temperature and CO concentration observed in this study reveal the similar trends to the ones reported earlier for kinetic oscillations. This provides a further proof that the origin of the observed oscillations may be connected with the ability of Pd to be oxidized and reduced under reaction conditions employed in this study.

The reaction mechanism of CO oxidation over Pd supported on glass fiber is suggested as follows (Sales, Turner & Maple, 1982):



where M denotes vacant sites on the Pd surface, MCO and MO adsorbed CO and oxygen atoms, respectively. M_{sub} indicates free sites in the subsurface layer of Pd and $\text{M}_{\text{sub}}\text{O}$ the sites in the subsurface layer, occupied by the oxygen atoms.

The model applied in this study (Kurkina, Peskov & Slin'ko, 1998) was developed on the basis of two models proposed previously by Sales, Turner, Maple (Sales et al., 1982) and by Basset and Imbihl (1990). However, it differs from previously developed models.

The difference with the mathematical model presented by Sales et al. (1982) is that the dependencies of both the CO adsorption rate upon the oxygen coverage, and the oxygen adsorption rate upon the concentration of the subsurface oxygen have been introduced, which made the model more realistic. The main difference with model developed by Basset and Imbihl (1990) is that the reaction of adsorbed CO with subsurface oxygen as shown in step 5 is considered.

The dynamic behavior of the adsorbed species and the oxygen in the subsurface layer is described as

$$\frac{dx}{dt} = k_1 p_{\text{CO}}(1 - x - \delta y) - k_{-1}x - k_3xy - k_5xz,$$

$$\frac{dy}{dt} = k_2 p_{\text{O}_2} e^{-\alpha z}(1 - x - y)^2 - k_3xy - k_4y(1 - z), \quad (2)$$

$$\frac{dz}{dt} = k_4y(1 - z) - k_5xz,$$

where x , y are CO and O surface coverage, respectively, z is the concentration of oxygen in the subsurface layer, and k_i are constants of the elementary steps of the reaction mechanism. Parameter δ describes the influence of adsorbed oxygen on the CO adsorption rate, while parameter α accounts for the strong effect of the subsurface oxygen on the oxygen adsorption rate.

The reactor used in this study was modeled as a CSTR type of reactor due to the high recycling ratios employed. The reaction of CO oxidation has been studied in excess of oxygen, therefore only variation of CO partial pressure in the reactor is considered below

$$\frac{dP_{\text{CO}}}{dt} = \gamma(P_{\text{CO}}^0 - P_{\text{CO}}) - \beta(k_1 P_{\text{CO}}(1 - x - \delta y) - k_{-1}x), \quad (3)$$

where $\gamma = F/V$, $\beta = (N_s SRT)/V$ and F is the flow rate of the reactant mixture, which is $3.33 \times 10^{-6} \text{ m}^3/\text{s}$, V is the reactor volume, equal to $0.4 \times 10^{-3} \text{ m}^3$. S denotes the Pd surface area, which is equal to $3.2 \times 10^{-3} \text{ m}^2$, and N_s is the adsorption capacity of Pd equal to $1.67 \times 10^{-13} \text{ mol/m}^2$.

The parameters of the model were chosen at a first approximation as close as possible to the literature data (Basset & Imbihl, 1990; Sales et al., 1982) and subsequently adjusted to fit available experimental data. The values of parameters, which simulate the experimental data are summarized in Table 2.

Eqs. (2) and (3) were used to calculate period and amplitude of the oscillations under the conditions of this study and with the values of rate constants and experimental conditions shown in Table 2. Fig. 6a demonstrates the simulated dependency of the reaction rate upon inlet CO concentration for various temperatures.

Table 2
The parameters of the mathematical model used in the calculations^a

k	k_1 ($\text{s}^{-1} \text{Pa}^{-1}$)	k_{-1} (s^{-1})	k_2 ($\text{s}^{-1} \text{Pa}^{-1}$)	k_3 (s^{-1})	k_4 (s^{-1})	k_5 (s^{-1})
k_0	0.602	8.1×10^9	1.9	2.1×10^8	1.5×10^{-3}	11.5
E (kJ/mol)	0	83.740	4.187	58.618	4.187	41.870
K_{483}	0.602	7.014	88.067	95.16	5.284×10^{-4}	3.384×10^{-4}

^a $\delta = 0.8$, $\alpha = 10$.

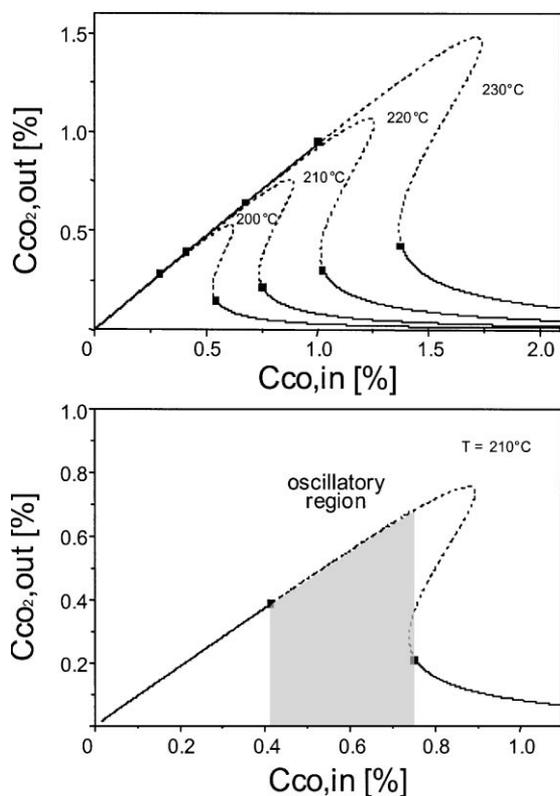


Fig. 6. Simulated reaction rates and oscillatory regions as a function of inlet CO concentration for different temperatures.

Full lines indicate a stable steady state, dashed lines an unstable steady state. Andronov–Hopf bifurcations are marked by filled squares. The region of oscillations for each temperature is located between Andronov–Hopf bifurcations (see Fig. 6b). At both limits the amplitude of oscillations changes abruptly. This behavior resembles a subcritical Andronov–Hopf bifurcation, where the amplitude of oscillations changes discontinuously at the bifurcation point. However, no hysteresis phenomenon was detected during the variation of $C_{\text{CO},\text{in}}$, in the vicinity of the bifurcation points. The system behavior in these points is a characteristic feature of the subcritical Andronov–Hopf bifurcation. The study of the limit cycle stability and its characteristic multipliers allowed excluding saddle-node bifurcation of periodic orbits (SNP bifurcation). Investigating the amplitudes of the limit cycles in the vicinity of Andronov–Hopf bifurcations one can

recognize a very narrow region of small-amplitude oscillations followed by a rapid increase in the amplitude. This behavior is typical for the “canard” type bifurcation in the systems with a small parameter (Peng, Gaspar & Showalter, 1991).

The simulated region of oscillatory behavior in the $T, C_{\text{CO},\text{in}}$ parameter space is shown in Fig. 3 together with the experimental findings. The results of mathematical modelling reproduce the experimental results quite satisfactorily. As in experimental study for higher temperatures the region of self-sustained oscillations is shifted to higher CO concentrations.

Oscillatory behavior in the system under investigation arises due to the periodic oxidation and reduction of Pd particles of the catalyst. The necessary feedback mechanism occurs through the strong dependence of the oxygen adsorption rate upon the concentration of the subsurface oxygen. The mechanism of oscillations can be presented as follows: starting with the oxidized catalyst, the concentration of the subsurface oxygen is high, the adsorption of oxygen is inhibited, the reaction rate is small and the catalyst surface is covered with CO molecules. The subsurface oxygen slowly reacts with adsorbed CO species. The decrease in the subsurface oxygen concentration leads to an increase of the oxygen adsorption rate and the system moves to the high activity state, where the surface is covered mainly by oxygen. With the oxygen coverage being high, the concentration of the subsurface oxygen slowly increases. Consequently, the rate of oxygen adsorption decreases and the system returns to the low activity state, where the oxidized surface is covered with CO molecules.

The model based on this mechanism describes the oscillatory behavior experimentally observed. Fig. 7 demonstrates the influence of the reaction temperature on the properties of oscillations. Similar to the experimental observations (see Fig. 4) the time, which the system spends in the high activity state during the oscillatory cycle, does not depend on the temperature. This period of high activity corresponds to the process of Pd oxidation known to have activation energy as low as 4 kJ/mol (Sales et al., 1982). More drastically, the temperature effects the time, which the system spends in the low activity state. During this period the reduction of Pd takes place with the activation energy of 40 kJ/mol.

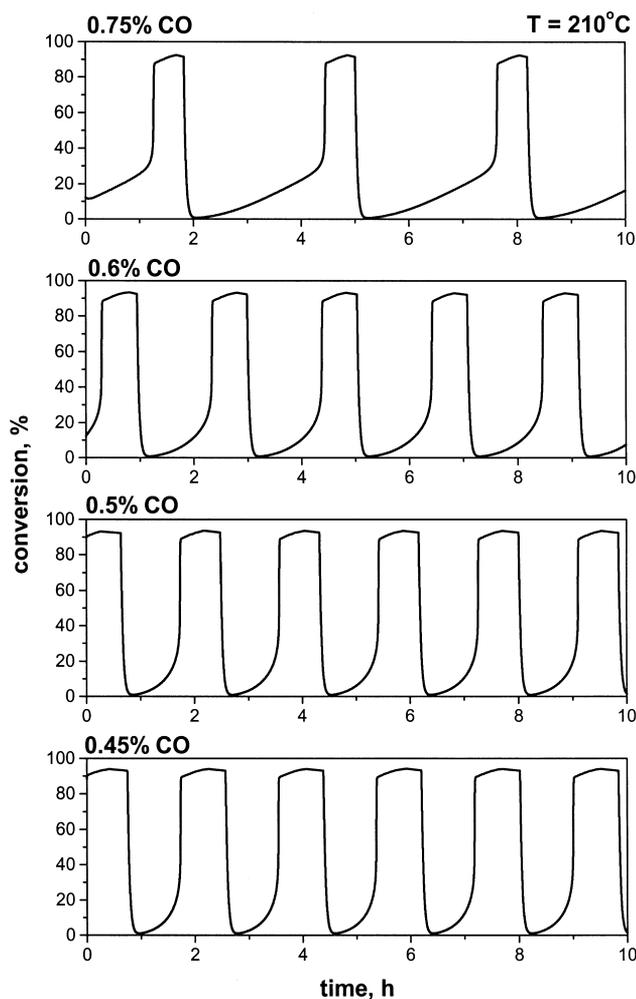


Fig. 7. Simulated influence of temperature on the reaction oscillatory behavior; $C_{\text{CO,in}} = 0.45 \text{ vol\%}$.

Fig. 8 shows kinetic oscillations calculated for various inlet CO concentrations. The developed model reproduces the main experimental trends. First, the increase of the amplitude and the period of oscillations with the increase of CO concentration. Second, the predicted shape of oscillations showing a broad minimum, a fast rise to a maximum, a plateau at the maximum and the fast decrease to the minimum of the reaction rate is in agreement with the experimental data. The increased period of oscillations for higher inlet CO concentration is due to the deeper reduction of the catalyst, which needs more time.

The best description of experimental data has been obtained with the values of oxidation–reduction constants, which were smaller than reported in the literature. While the activation energies were assumed to be the same as during the modeling of oscillatory behavior over metallic foil (Sales et al., 1982), the pre-exponential factor of oxidation constant is 2 orders smaller and the pre-exponential factor of reduction constant is one order smaller.

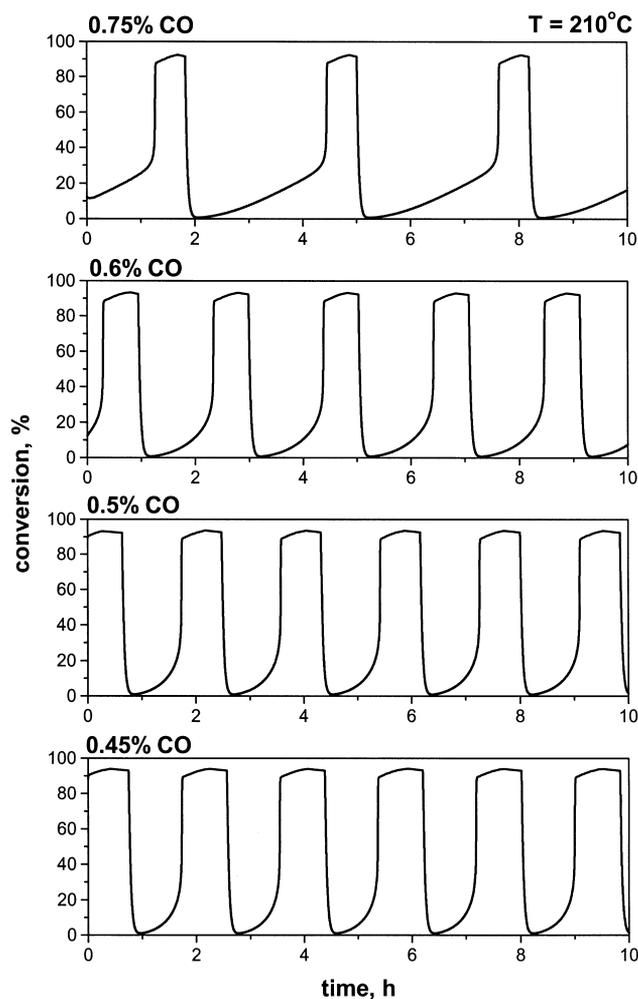


Fig. 8. Simulated influence of inlet CO concentration on the reaction oscillatory behavior; $T = 210^\circ\text{C}$.

5. Conclusions

Kinetic self-sustained oscillations during CO oxidation have been observed over Pd supported on silica glass fibers. The oscillations show unusual long periods of up to 6 h. Mathematical modeling describes the observed oscillatory behavior in T – $C_{\text{CO,in}}$ parameter space, the waveform of oscillations, the period and the amplitude variation with temperature and inlet CO concentration. Assuming relatively small rate constants for the Pd oxidation and reduction, it was possible to simulate the long periods of oscillations. The origin of such low values may be due to the fact that another type of oxide can be formed over Pd supported on glass fibers.

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