The study of the oscillatory behavior during methane oxidation over Pd catalysts

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ARTICLE INFO

ABSTRACT

The application of the thermogravimetric analysis (TGA) combined with on-line mass-spectrometry of the effluent gas mixture and temperature-programed oxidation (TPO) experiments allowed to demonstrate that significant variation of the carbon content in Pd catalysts occurred during the oscillatory methane oxidation. Together with the visual observation of the color changes due to the periodic variation of the Pd valence, these data indicate a very complicated mechanism associated with the oscillatory behavior, where both Pd oxidation–reduction processes and carbon deposition-removal play a crucial role. Depending on the phase of the oscillatory cycle, three states of metallic Pd with different reactivities were revealed: highly active, freshly reduced, metallic Pd; moderately active metallic Pd modified by carbon; and poorly active metallic Pd with adsorbed oxygen. It was found that hundreds of carbon monolayers could be periodically accumulated in the Pd powder catalyst during the oscillatory cycle. The accumulation of carbon on the Pd catalyst was the reason for the antiphase oscillations of the reaction products CO_2 and H_2O.

1. Introduction

Methane oxidation over palladium catalysts has been intensively studied by many investigators in recent years and a review of the obtained results can be found in [1]. Nevertheless the behavior of this important catalytic system is still not well understood. The actual nature of the active sites on palladium-based catalysts has been debated to a great extent in the literature. Some researchers [2,3] reported that the metal phase was more active, while other studies demonstrated that PdO was the main active phase [4,5]. Recently attempts had been made to solve this problem using the surface science technique. In situ X-ray photoelectron spectroscopy (XPS) measurements had been carried out during heating and cooling of the Pd(1 1 1) surface in the reactant mixture $CH_4:O_2 = 1:5$ [6]. It was demonstrated that the observed hysteresis phenomenon was connected with the variation of the surface oxidation state. The most active surface state in oxygen excess was found to be "PdO seeds + Pd_5O_4 oxide".

A relatively small amount of studies has been devoted to the mechanism of the reaction under methane-rich reactant mixtures [7,8]. However, these conditions are very interesting, because an oscillatory behavior can be observed only in the fuel-rich mixtures. König et al. were the first group who observed the oscillatory behavior during methane oxidation over a thick Pd-film catalyst [9]. Later the oscillatory behavior was observed by other groups over supported [10] and massive Pd catalysts [11]. Although it is generally accepted that transformations of the active Pd phase are the reasons for the oscillations during methane oxidation, there is still some disagreement in the literature concerning the reaction mechanism and particularly the Pd state that is most active. König et al. [9] and Zhang et al. [11] assumed that the Pd surface oscillates between a highly active oxide state and a less active metal-rich state, while Deng and Nevell identified PdO to be the less active catalytic phase [10].

In previous research, we investigated the oscillatory behavior during methane and ethane oxidation over Ni and Co catalysts [12–14]. The application of thermogravimetric analysis (TGA) in combination with on-line mass-spectrometry showed that a significant variation of surface oxygen content (several tens of monolayers) occurred during the oscillations of methane oxidation over Ni catalysts, verifying the periodic oxidation and reduction of the metal surface [12]. The visual observation of periodic color changes during the oscillatory cycle due to the variation of Ni and Co valence provided additional evidence that oxidation–reduction processes played a crucial role in the nature of the oscillatory behavior during methane and ethane oxidation over these catalysts [12–14]. The goal of this study was the application of TGA analysis in combination with on-line mass-spectrometry to investigate the mechanism of the oscillatory behavior during methane oxidation over Pd catalysts.

2. Experimental

The most stable and reproducible oscillations were obtained during methane oxidation over Pd catalysts in the form of a foil

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(3 × 3 × 0.35 mm) or a powder (Aldrich, 99.9+%, 1.05 μm average particle size). The study of the oscillatory behavior during methane oxidation over the Pd foil was carried out in a quartz flow reactor (i.d. 5 mm), operated at atmospheric pressure. The reactor was inserted into a furnace which allowed the observation and recording of the state of the sample surface by a video camera (JVC, model GR-D230). Bare chromel–alumel thermocouples can be effective catalysts for methane oxidation, which can generate oscillatory behavior in the temperature range from 650 to 730 °C [15]. To avoid any contact with the reactant mixture during the measurement of the catalyst temperature (T_{cat}), a piece of the palladium capillary (diameter of 2 mm) was used to prepare the Pd foil sample. Ends of chromel and alumel wires were inserted inside the capillary and compressed with the capillary to form the Pd foil sample with the internal thermocouple. Free ends of the wires were inserted into the holes of a ceramic tube and had practically no contact with the reaction gas. The temperature of the reactor (T_r) was controlled by a thermocouple on the outer side of the reactor.

Thermogravimetric analysis (TGA) was performed using a Setaram SETSYS EVOLUTION 16/18 instrument, combined with a mass-spectrometer. Details of the set-up are described in [12]. In the TGA measurements 40 mg of the Pd powder was used.

The initial gas mixture ($CH_4:O_2:Ar = 82:14:4$) was supplied at flow rates of 10–30 ml/min, using mass flow controllers. A quadrupole mass-spectrometer (Pfeiffer, model OmniStar GSD 301) was employed to analyze the composition of the gas flow directly after exposure to the catalyst. Ions at 2, 15, 16, 17, 28, 30, 32, 40, and 44 m/z values were detected during on-line measurements. The magnitude of the signal at 40 m/z related to Ar could be used to calculate the percentage composition of the reaction mixture. However, it was very difficult to calibrate the H_2O concentration and all experimental data will be presented as ion currents. The value of CO product concentration was very low under all conditions of this experimental study. Our attempts to calculate the CO signal using the peak with $m/z = 28$ after the subtraction of the intensity of the CO_2 cracking fragment ($\sim$10% of the intensity of $m/z = 44$ signal) were unsuccessful.

An X-ray study was carried out with a Dron 3.0 X-ray diffractometer with Cu Kα radiation. The spectra of a mixture of the standard crystalline Si with the investigated sample were analyzed for the precise evaluation of lattice parameters.

3. Results

3.1. Oscillatory behavior during methane oxidation over the Pd foil

Oxidation of methane over the Pd foil has been studied at flow rates from 10 to 40 ml/min at T_r temperatures of 300–485 °C (reaction mixture $CH_4:O_2:Ar = 82:14:4$). Table 1 demonstrates the effect of temperature on concentrations of reaction products at a flow rate of 20 ml/min. As the reactor temperature was increased stepwise from 30 °C to 350 °C the rate of methane oxidation was very low and only traces of CO_2 product were detected at 350 °C. In T_r temperature range between 350 and 400 °C, only a steady state with a very low catalytic activity was observed. Under these conditions T_{cat} was lower or nearly the same as T_r. At 450 °C the extent of CH_4 conversion and the concentration of CO_2 increased significantly. The steady state was slowly approached and during 10 min the CO_2 concentration increased from 1% to 2%. The temperature rise up to 475 °C led to an increase in CO_2 concentration up to 5.5% and the slow development of oscillations was detected. At 485 °C the oscillations became irregular and a further temperature increase caused the disappearance of the oscillatory behavior. Table 1 shows that quite different dynamic behavior was observed

Table 1
The effect of temperature (°C) on the dynamic behavior as well as on the products concentrations (vol.%) during heating and cooling of the Pd foil in the reactant mixture ($C_2H_6:O_2:Ar = 82:14:4$; 20 ml/min).

T_r (°C)	T_{cat}	CO_2 (vol.%)[a]	CO (vol.%)[b]	The dynamic behavior
300	290	Traces		Stationary reaction
350	340	Traces		Stationary reaction
400	394	$\sim$0.015		Stationary reaction
450	475	$\sim$2		Stationary reaction
475	550–560	6–7	0.025	Self-sustained oscillations
485	555–565	6–7	0.137	Damped oscillations
450	505–515			Irregular oscillations
425	480–500	6–8	0.032	Self-sustained oscillations
400	440–470	5–6	0.012	Self-sustained oscillations
375	390–440			Self-sustained oscillations
350	350–400			Irregular oscillations

[a] CO_2 concentration, on-line monitored by mass-spectrometer.
[b] Average CO concentration, measured by chromatographic method.

during the temperature decrease. The oscillations became more regular after stepwise cooling of the catalyst to 425 °C. They again became irregular after cooling to 350 °C, and finally disappeared below 350 °C.

Fig. 1a–c shows the effect of temperature (T_r and T_{cat}) on the oscillatory behavior at a flow rate of 20 ml/min. It can be seen that the main reaction products detected are CO_2 and H_2O. Only traces of CO and H_2 are observed. The increase in temperature leads to the decrease in the period of the oscillations and to the variation of the waveform of the oscillations. It can be seen that in the T_r temperature range from 375 to 400 °C, the H_2O signal does not follow the CO_2 signal during some part of the oscillatory cycle. This fact is a very interesting one, because both species are products of methane oxidation. Moreover, at point **a** both CH_4 and CO_2 concentrations decrease, while H_2O and H_2 concentrations rise. Visual observations of the Pd foil surface revealed that at point **a**, a color wave quickly spread from the downstream part of the foil to the top. The color of the catalyst changed from dark gray to light gray. The spreading of the color wave was accompanied by a temperature increase. All these experimental data indicate that at point **a** the reduction of PdO to metallic Pd occurred. 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 CH_4 consumption from the gas phase. In contrast, at point **b** the peak of CO_2 concentration takes place, while there are no CH_4 and H_2O concentration peaks coinciding with the increase in the production rate of CO_2. Evidently, carbon species resulting from CH_4 decomposition accumulated after point **a** and they oxidized at point **b**, producing a peak of CO_2 evolution.

The period of time between points **a** and **b** of the oscillatory cycle and the period of oscillations depend greatly upon the temperature and the gas phase composition. The period of oscillations increases with the decrease in temperature and the increase in $CH_4:O_2$ ratio. These dependencies are similar to those observed in the study of Zhang et al. [11]. Fig. 2 demonstrates that at a T_r of 400 °C and at a feed rate of 30 ml/min, the O_2 concentration in the reactor is very low. The system spends much time on the high activity branch of the oscillatory cycle, where accumulation of carbon in the catalyst occurred.

3.2. Application of TGA to the study of the oscillatory behavior of methane oxidation over the Pd powder

To establish the variations of the state of the Pd catalyst during the oscillations, TGA measurements were carried out using the Pd
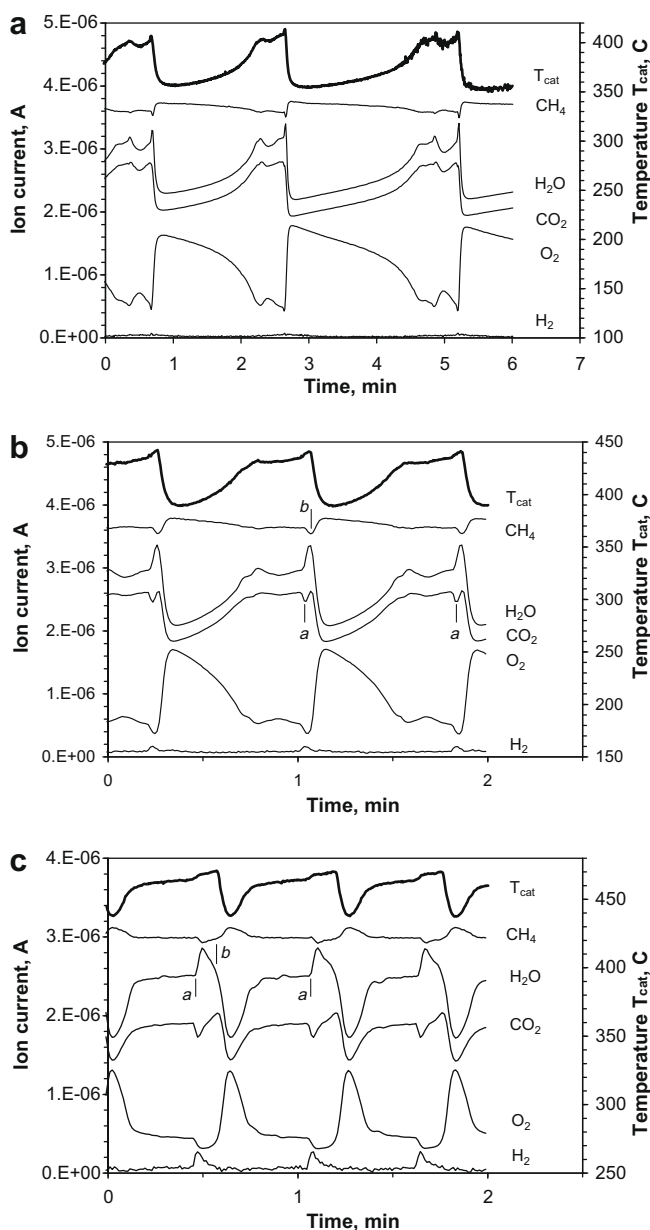
Fig. 1. The effect of temperature (T_r and T_{cat}) on the oscillatory behavior at the feed rate of 20 ml/min: (a) T_r = 350 °C, H_2 ($\times100$, -1.8×10^{-6}), O_2, CO_2 ($+1.8 \times 10^{-6}$), H_2O ($+2.0 \times 10^{-6}$), CH_4 (-2.3×10^{-6}), (b) T_r = 375 °C, H_2 ($\times100$, -1.8×10^{-6}), O_2, CO_2 ($+1.6 \times 10^{-6}$), H_2O ($+1.8 \times 10^{-6}$), CH_4 (-2.3×10^{-6}), (c) T_r = 400 °C, H_2 ($\times200$, -3.9×10^{-6}), O_2, CO_2 ($+0.8 \times 10^{-6}$), H_2O ($+1.2 \times 10^{-6}$), CH_4 (-3.0×10^{-6}).

Fig. 2. The increase in the duration of the phase $a \rightarrow b$ with the increase in the feed rate up to 30 ml/min: T_r = 400 °C, H_2 ($\times100$, -1.8×10^{-6}), O_2, CO_2 ($+0.9 \times 10^{-6}$), H_2O ($+1.3 \times 10^{-6}$), CH_4 (-3.0×10^{-6}).

Fig. 3. (a) The TGA heat-up profile and the development of the oscillatory behavior of the catalyst weight at 300 °C. CH_4:O_2:Ar = 82:14:4, a feed rate of 20 ml/min, a heating rate of 10 °C/min. (b) The development of the oscillatory behavior of the catalyst weight together with the corresponding oscillations of ion currents related to all gas phase components under the same conditions (O_2 ($+1.0 \times 10^{-7}$), CO_2 ($+1.7 \times 10^{-6}$), H_2O ($+0.9 \times 10^{-6}$), CH_4 ($\times10$, -5.85×10^{-5})).

powder. Fig. 3a and b shows the results of a typical TGA experiment. The fresh portion of the Pd powder was heated from 30 °C to 300 °C with a heating rate of 10 °C/min in a flow of reactant mixture CH_4:O_2:Ar = 82:14:4 of 20 ml/min and then held at 300 °C. As can be seen from Fig. 3, the catalyst was not active in methane oxidation until 200 °C. A slow growth of the Pd weight was the result of the decrease in the gas phase density with the temperature increase. At ~200 °C, CO_2 and H_2O products appeared in the gas phase and their concentrations increased with the temperature rise up to ~275 °C accompanied by a slight increase in the weight that cannot be seen due to the large scale in Fig. 3. At 275 °C the weight of the catalyst sharply increased, CH_4 and O_2 concentrations dropped, and H_2O concentration rose. CO_2 signal started to rise after some delay. At a constant furnace temperature of 300 °C, the Pd weight reached a maximum value and stabilized
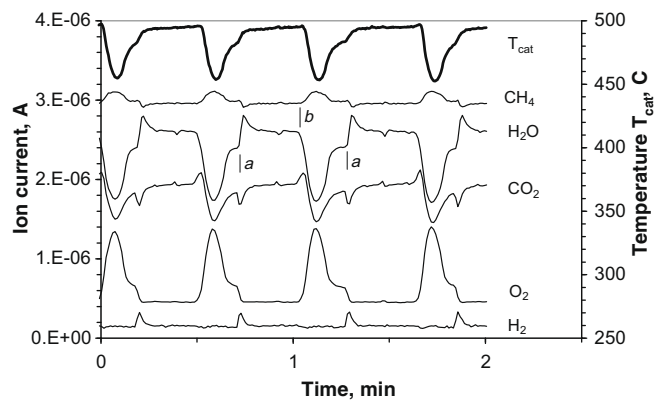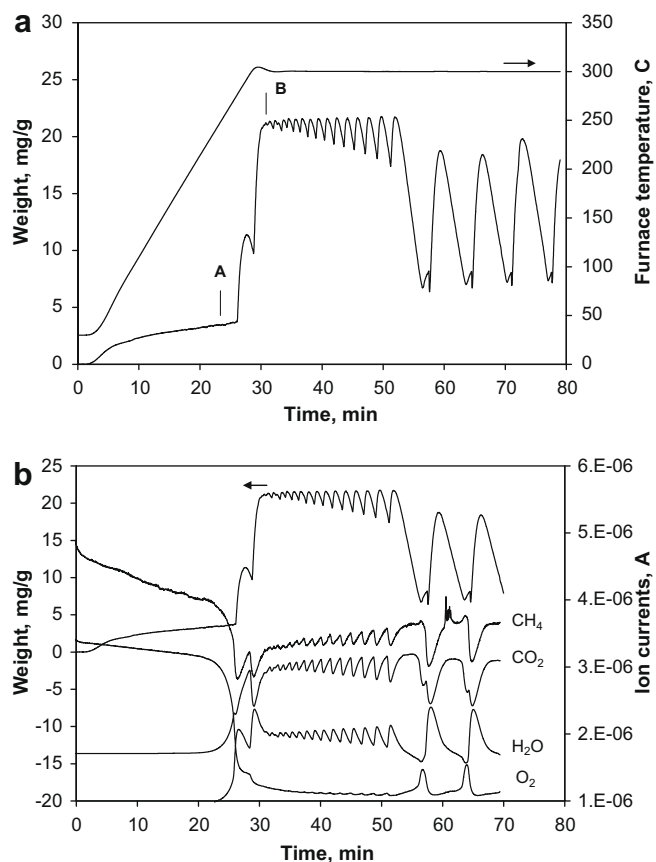
for a few minutes. Then small amplitude oscillations of the catalyst weight developed together with the oscillations of the gas phase composition. During the oscillations the Pd weight periodically decreased and then returned to the maximum value. The decrease in weight corresponded to an increase in CH_4, O_2, and CO_2 concentrations and a decrease in the H_2O concentration. The amplitude of the oscillations was growing with time and at a certain moment these oscillations were transformed into large-amplitude oscilla-

tions with a more complicated waveform. With time on stream the period of the oscillations was slowly increasing and finally the oscillatory behavior shown in Fig. 4 was established. The large volume of the TGA cell together with the relatively high surface area of the Pd powder may be the reason for the shift of the temperature interval and the increase in the period of the oscillations over the Pd powder in comparison with the oscillations over the Pd foil. However, the main characteristic features of the oscillations observed over both catalysts were nearly the same, namely the oscillation phases could be detected with the in-phase ($\boldsymbol{b} \to \boldsymbol{a}$) and the antiphase ($\boldsymbol{a} \to \boldsymbol{b}$) evolution of CO_2 and H_2O products (compare Fig. 2 and 4). The increase in the weight of Pd at point $\boldsymbol{a}$ in Fig. 4 corresponds to the simultaneous drops of CH_4 and CO_2 concentrations and the rise of H_2O concentration. As with the Pd foil at point $\boldsymbol{b}$, the peak of CO_2 concentration takes place, while there are no CH_4 and H_2O concentration peaks coinciding with the increase in the production rate of CO_2.

In additional experiments, it was demonstrated that the increase in temperature up to 320 °C led to the steady state with the large weight. This state corresponded to the Pd catalyst with a large amount of the accumulated carbon. At temperatures lower than 260 °C, the steady state with the small weight was attained. Here the state of the Pd catalyst was a metallic one.

It is worth noting that waveform and properties of the oscillations over the Pd powder were very sensitive to the history of the catalyst. The most reproducible results could be obtained over a fresh catalyst. The heating of the Pd powder up to 700 °C followed by cooling to room temperature caused a decrease in the catalytic activity. The region of the oscillations over the deactivated catalyst was shifted to higher temperatures. Fig. 5 shows the oscillatory behavior over a partially deactivated catalyst at 310 °C. It can be seen that the period of the oscillations shown in Fig. 5 is larger than the period of the oscillations demonstrated in Fig. 4 despite the higher temperature. The rise of the period is mainly caused by the increase in the time between points $\boldsymbol{a}$ and $\boldsymbol{b}$ of the oscillatory cycle.

3.3. The study of the Pd state in various phases of the oscillatory cycle

The catalyst weight variation in TGA experiments may correspond to changes in carbon and/or oxygen amounts in the bulk and at the surface of the Pd catalyst. To reveal the state of the Pd catalyst during the oscillatory behavior, we carried out experiments with interruptions of the reaction at various stages of an oscillatory cycle followed by temperature programed reaction
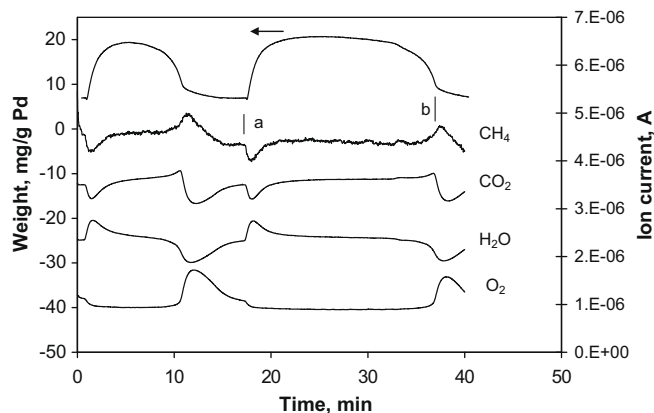
Fig. 5. The oscillatory behavior over the deactivated catalyst at 310 °C ($CH_4:O_2:Ar = 82:14:4$, O_2 (-1.0×10^{-6}), CO_2 ($+1.5 \times 10^{-6}$), H_2O ($+0.6 \times 10^{-6}$), CH_4 ($\times 10$, -6.0×10^{-5})).

(TPR). In our previous studies, we applied this method to the study of the oscillatory behavior during methane oxidation over a Ni foam catalyst [12]. After switching off the furnace power and the reactants feed at various moments of an oscillatory cycle, and cooling the sample down to room temperature in vacuum, H_2-TPR experiments were carried out. The values of weight losses due to reactions of oxygen and carbon hydrogenation allowed the evaluation of carbon and oxygen contents in the Ni foam. Unfortunately, it was not possible to apply similar H_2-TPR experiments for Pd catalysts. The absorption of hydrogen occurred already at room temperature. Moreover, significant amounts of hydrogen desorbed in the temperature range 140–150 °C masked other reaction peaks. An attempt to determine the amount of carbon using its reaction with CO_2 in CO_2-TPR experiments was also not successful, because of the low carbon activity under the conditions of our experiment. Finally, to evaluate the carbon content in the catalyst we carried out O_2-TPR experiments. During these experiments the accumulated carbon was oxidized to CO_2 with the corresponding weight loss. However, in the temperature range 250–700 °C the Pd sample was also oxidized forming PdO leading to an increase in weight. As it was difficult to distinguish these two processes in the TGA curve, we applied only mass-spectrometric data for the quantitative determination of the accumulated carbon content.

Fig. 6 demonstrates CO_2 responses during the heating of the Pd powder in a flow of 5% O_2–He mixture after the reaction of methane oxidation was interrupted before and after the sharp increase in weight (points A and B in Fig. 3a) and at various moments of the
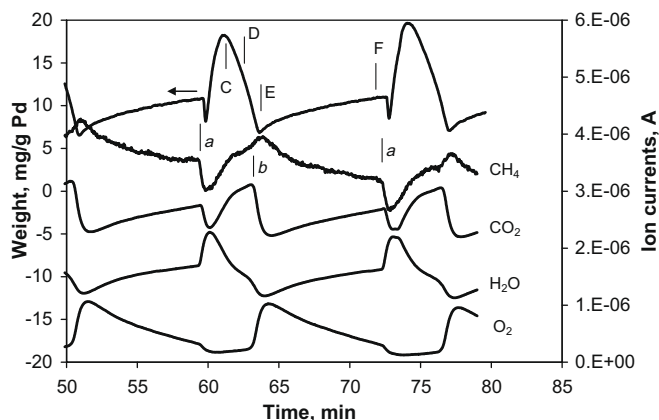
Fig. 4. Self-sustained weight oscillations and the corresponding oscillations of gas ion currents related to all gas phase components ($CH_4:O_2:Ar = 82:14:4$, 300 °C, O_2 (-1.0×10^{-6}), CO_2 ($+1.5 \times 10^{-6}$), H_2O ($+0.6 \times 10^{-6}$), CH_4 ($\times 10$, -5.97×10^{-5})).
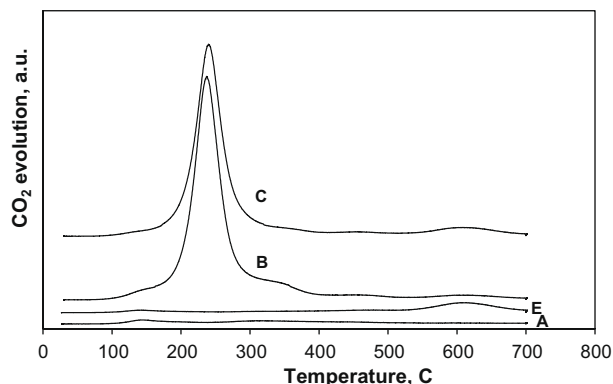
Fig. 6. CO_2 responses for the heating of the Pd powder in 20 ml/min 5% O_2–He flow after interruptions of the oscillations at various stages (points A and B in Fig. 3a and points C and E in Fig. 4).

oscillatory cycle (points C and E in Fig. 4). In O_2-TPR experiments the accumulated carbon was oxidized and removed into the gas phase producing some peaks of CO_2 in the temperature range 100–700 °C. Three peaks of CO_2 concentration can be observed at temperatures of 150, 240, and 615 °C (I, II, and III peaks, respectively). The small peak I at 150 °C exists in all TPR spectra. TPR spectra corresponding to points B and C contain a large peak II centered at 240 °C with a shoulder at 340 °C. This peak does not appear in the TPR spectra corresponding to points A and E. Finally, the high temperature peak III at 615 °C can be detected in the TPR spectra taken at points C, B, and E. Based on the amounts of CO_2 associated with all three peaks the contents of carbon in the Pd powder at various moments were calculated and the data are presented in Table 2.

Table 2 and Fig. 6 show that the increase in weight between points A and B proceeds due to the accumulation of carbon corresponding to peak II. However, the value calculated from the CO_2 response is less than the value 17 mg/g Pd corresponding to the increase in weight during the transition from point A to point B, shown in Fig. 3. Special experiments with a variation of a pumping rate after the interruption of the reaction have been carried out. It was demonstrated that as the pumping rate was reduced, the amount of CO_2 in TPR peaks decreased. Therefore, the difference between the observed weight increase in Fig 3 between points A and B and the measured CO_2 amount can be explained by the partial carbon oxidation during the pumping. The comparison of the weight oscillations shown in Fig. 4 and data presented in Fig. 6 and Table 2 reveals that the increase in weight during the time interval from point a to C is the result of the carbon accumulation in the Pd catalyst. The decrease in weight at stage C → E of the oscillatory cycle is connected with the carbon oxidation. While the amount of carbon species corresponding to peak II oscillated with the large amplitude, the amount of carbon species corresponding to peaks I and III did not vary significantly during the oscillatory cycle. It is worth noting that the value of the carbon species corresponding to peak III at points C, D, E, and F was nearly the same, while this form was not detected at point A over the fresh catalyst. The amount of this form at point B was larger than that at point A, but smaller in comparison with the amounts at points C, D, E, and F. This fact indicates that the active carbon (peak II) transforms with time on stream to the less active carbon (peak III) which does not participate in the oscillatory cycle.

Another very significant observation is a nearly constant value of the carbon content during the increase in weight between points E and F. As the increase in weight could be associated also with an increase in the oxygen content in the Pd catalyst, a series of TPD experiments had been carried out. First of all it was shown that the Pd powder was oxidized almost completely into PdO as the temperature increased from 25 to 700 °C in 5% O_2–He mixture with a flow rate of 20 ml/min. After the sample was cooled down to 30 °C, the O_2–He stream was replaced by pure He and the sample

was heated to 700 °C at a heating rate of 10 °C/min. Decomposition of PdO and oxygen release were detected at 600–700 °C, proving the possibilities of the application of this method for the detection of the PdO state. Second, after the oscillatory behavior was established the furnace power and the reactants feed were switched off at moments E and F of the oscillatory cycle (see Fig. 4) and the catalyst was heated in He at a heating rate of 10 °C/min from 30 to 700 °C. Fig. 7 demonstrates the effect of temperature on the weight variation together with the obtained TPD spectra. It can be seen that similar weight changes in temperature ranges 200–270 °C and 400–530 °C corresponded with the CO_2 desorption peaks. The important difference between the curves E and F can be detected in the temperature range 550–610 °C. The essential weight loss of about 3.6 mg/g Pd observed for the curve F corresponded to a large O_2 desorption peak. This value was nearly equal to the increase in weight during the time interval between points E and F of the oscillatory cycle shown in Fig. 4. Therefore, the obtained data clearly indicate that during the stage E → F of the oscillatory cycle the oxidation of Pd into PdO occurred.

The specific surface area of the Pd powder is ∼500 cm^2/g and the calculated capacity of one monolayer can be evaluated as 10^{-6} mole/g Pd. It may contain 0.012 mg C atoms/g Pd or 0.016 mg O/g Pd. These rough calculations demonstrate that during the oscillations the variation of the carbon content attains hundreds of monolayers (see Table 2). Also at least several tens of layers of the bulk palladium can take part in the oxidation and reduction processes during the oscillations.

3.4. X-ray diffraction study of the Pd state

X-ray diffraction has been applied to characterize the bulk state of the Pd powder during the oscillatory methane oxidation. Fig. 8 shows XRD spectra for the fresh and used catalysts. X-ray diffraction pattern of the fresh catalyst agrees well with a face-centered cubic (f.c.c.) structure of palladium metal with the lattice constant $a = 3.890$ Å [16,17]. The used catalyst was treated by the reaction mixture $CH_4:O_2:Ar = 82:14:4$ for 20 min at 320 °C. The TGA results indicated a rapid increase in the weight of Pd similar to the transition from point A to point B shown in Fig. 3. However, the high activity steady state was attained instead of an oscillatory behavior over the used catalyst. After 20 min the steady state reaction was interrupted as described earlier. XRD spectrum of the used catalyst after its cooling is shown in Fig. 8. A new f.c.c. structure appears in the X-ray diffraction pattern with a lattice constant $a = 3.996$ Å exceeding that of palladium metal. This phase is known in the literature [17,18] as palladium carbide PdC$_x$, which is the result of carbon dissolution in palladium. The subscript x in PdC$_x$ was esti-

Table 2
The content of carbon in the Pd powder at different moments shown in Figs. 3 and 4, calculated from CO_2-TPR spectra.

Moments at which the reaction was interrupted	The sum of CO_2 species in different peaks (mgC/g Pd)			
	∼150 °C	∼250 °C	∼600 °C	Total amount[a]
A	0.25	0.57	0	0.82
B	–	11.5	0.22	12.3
C	–	9.4	0.81	10.5
D	–	6.7	1.11	7.9
E	0.16	0	0.96	1.4
F	0.24	0	1.03	1.5

[a] The value was calculated considering not only three CO_2 desorption peaks, but also the total profile of CO_2-TPR spectra.
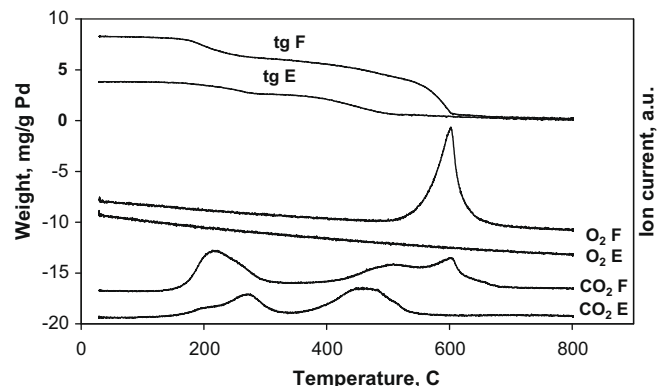

Fig. 7. Weight variations together with O_2 and CO_2 evolution during the heating of the Pd powder in He flow after interruptions of the oscillations at various stages (points E and F in Fig. 4).

mated to be 0.13–0.15 [17,18]. Asymmetric diffraction peaks of the used catalyst may indicate the existence of intermediate forms of PdC_x with x being less than this value.

In another experiment the oscillations were established (30 min) over the fresh catalyst at 300 °C and the reaction was interrupted at point F (see Fig. 4). Then the reactant mixture was pumped out following the cooling of the catalyst. The obtained XRD spectrum was identical to the X-ray diffraction pattern of palladium metal and did not contain any peaks attributed to PdO. As the TGA and TPR data demonstrated the large amount of accumulated oxygen at point F one can suggest that palladium oxide, which was forming during the oscillatory cycle, had an amorphous nature.

4. Discussion

The application of the thermogravimetric analysis combined with on-line mass-spectrometry of the effluent gas mixture together with the visual observation of the color changes due to the periodic variation of the Pd valence indicated a very complicated mechanism of the oscillatory behavior, where both the oxidation–reduction processes and carbon deposition-removal play essential roles. The mechanism of the oscillations can be presented as follows: at point F (see Fig. 4) the catalyst is in the oxidized state. The TGA data showed that about 200 Pd layers participated in the oxidation–reduction processes. The activity of the oxidized catalyst during the stage E → F increased causing an increase in the temperature and a decrease in the oxygen concentration. As a result of these processes at the moment marked as *a*, the sharp weight loss that occurred indicated the quick PdO reduction to metallic Pd. Visual observations of the Pd foil surface revealed that at point *a* of the oscillatory cycle (see Fig. 1), the color wave quickly spread from the downstream part of the foil to the top. The color of the catalyst changed from dark gray to light gray. The reduced metallic catalysts were very active in the dissociative adsorption of methane. The decomposition of methane on reduced Pd led to the formation of adsorbed carbon and hydrogen species. The data presented in Fig. 2 and 4 show that the accumulation of carbon in the catalyst occurred, while hydrogen atoms interacted with oxygen producing water. This is the reason for the antiphase oscillations of CO_2 and H_2O signals. Carbon penetrated the cubic cell of Pd forming an interstitial Pd–C phase until the atomic ratio C/Pd of ~0.13 was attained at point C (see Fig. 4). At this moment the increase in weight stopped showing the end of the carbon penetration into the catalyst. At stage C → E the accumulated carbon was oxidized producing the additional CO_2 peak. The carbon modifies the activity of the catalyst leading to a decrease in the rate of

methane oxidation. At point E carbon was completely removed from the catalyst, but its activity was not regenerated. The weight measurements and XRD spectra at point E indicated that the bulk state of the catalyst at this moment corresponded to metallic Pd. Nevertheless, the state of this metallic Pd catalyst was essentially different from the state of the reduced Pd at point *a*. We suppose that this state corresponds to the metallic Pd with adsorbed oxygen. This suggestion agrees well with the experimental data, obtained by Burch and Urbano [5], who demonstrated that reduced Pd with chemisorbed oxygen revealed a very small activity in methane oxidation. They also showed that the activity of the supported Pd catalyst was increasing due to the oxidation of the Pd bulk. It can be seen in Fig. 4 that the increase in the activity at stage E → F also corresponds to the oxidation of the catalyst. The activity of the oxidized catalyst (PdO) is higher than the activity of the reduced Pd blocked by oxygen, but is lower than the activity of the freshly reduced catalyst. As the activity was increasing, a rise in the temperature was also observed followed by a decrease in the O_2 concentration. At point *a* the system was ready for the reduction and the beginning of the next oscillatory cycle. The scheme in Fig. 9 shows the mechanistic interpretation of one oscillatory cycle.

One of the most remarkable features of the observed oscillations is that the accumulated carbon did not poison the reaction of methane oxidation for some time during the oscillatory cycle. The reason for such a behavior was the migration of the surface carbon into the bulk, thus leaving the catalyst surface essentially clean. We identified for the first time that hundreds of carbon monolayers could be periodically accumulated in the Pd powder catalyst during the oscillatory behavior. Moreover, it was clearly demonstrated that the accumulation of carbon in a Pd catalyst was the reason for the antiphase oscillations of some reaction products, namely CO_2 and H_2O. Zhang et al. [11] also observed the phase shift between oscillations of CO_2 and H_2O signals. However, the authors supposed that the reason for such dynamic behavior was the accumulation of hydrogen in the bulk of Pd and the delay in its reactivity toward oxygen. This is in contrast to our observations of the large hydrogen solubility in palladium only at temperatures lower than 100 °C. The dissolved hydrogen was completely removed from the catalyst at temperatures higher than 140 °C and could not cause such large difference in the waveforms of the oscillations in CO_2 and H_2O concentrations.

The essential result also revealed in this study concerned the variation of the state of Pd during one oscillatory cycle and reactivity of each state. Depending on the phase of the oscillatory cycle, three states of the reduced Pd with various reactivities were revealed. At point *a* (see Fig. 4), the newly reduced Pd demonstrated the highest degree of CH_4 conversion. However, this very active
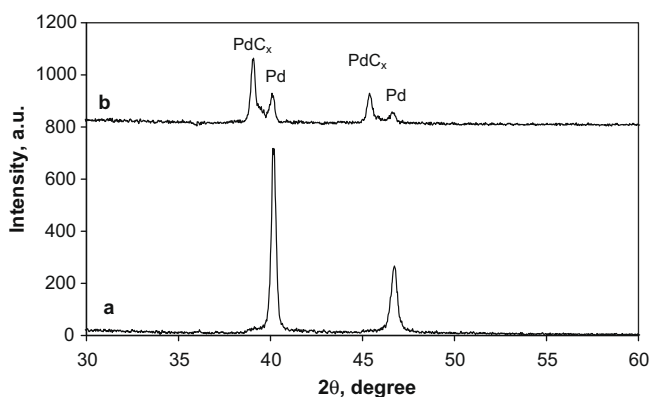

Fig. 8. XRD characterization of (a) the fresh Pd powder and (b) Pd powder which was treated by the reaction mixture $CH_4:O_2:Ar = 82:14:4$ for 20 min at 320 °C.
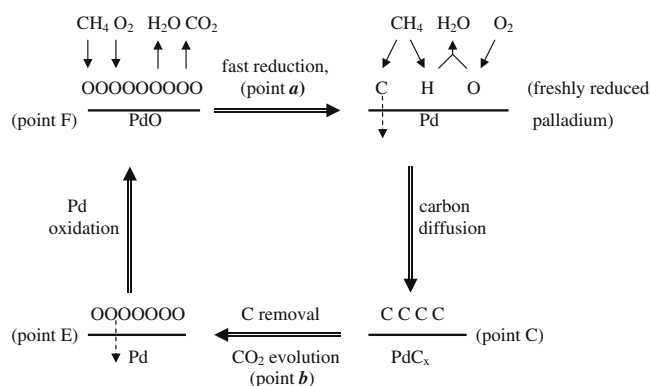

Fig. 9. The mechanistic interpretation of one oscillatory cycle. Various phases of the oscillatory cycle are marked with the corresponding letters (see Figs. 1, 2 and 4).

state of the reduced Pd was very quickly modified by carbon (point C in Fig. 4). The reduced Pd modified by carbon displayed the intermediate degree of CH_4 conversion and was active in the reactions of H_2O and CO_2 production. Finally, the last state of the reduced Pd was reached at point E (see Fig. 4). Here the least active state of the reduced Pd was obtained due to the blocking of the active sites by adsorbed oxygen. It can be seen that the oxidized state of Pd (PdO) (point F on Fig. 4) is more active than the reduced state blocked by oxygen (point E) and is less active than the newly formed reduced state without carbon (point *a*). Therefore the reason for the disagreement in the literature on the state of Pd which is more active can be recognized, because various authors obtained a variety of states of the reduced Pd during methane oxidation at different temperatures and compositions of a reactant mixture.

The reason for the disagreement between various authors on the state of Pd which is more active during the oscillatory cycle could also be connected with numerous types of catalysts and experimental conditions in different studies. König et al. [9,19] applied ellipsometry to monitor the surface of a thick palladium film during the oscillatory behavior of methane oxidation at 500 °C. The authors observed that the PdO layer formed under lean or stoichiometric conditions was dense and smooth, similar to the oxide produced without CH_4. It had a lustrous green color and was not active in methane oxidation. Under rich conditions the authors detected a very porous, rough more active catalytic surface of a dull brown color. They attributed this surface to a highly porous oxide and explained its high activity by the large surface area. The possibility of the carbon formation was not analyzed by the authors. The oscillatory behavior had been observed under rich conditions over the porous surface. The authors [9,19] reported that the oxidation state of palladium was changing from PdO to metallic Pd and the last state was less active. However, the observed oscillations were obtained in the mass-transfer limited regime, where significant amounts of CO were detected. Moreover, in contrast to our study the temperature oscillations were out of phase with the oscillations in CO_2 production rate indicating another type of oscillations proceeding during methane oxidation. Deng and Nevell [10,20] observed the oscillatory behavior during methane oxidation over alumina-supported palladium catalysts. They believed that the origin of the oscillations was connected with the periodic oxidation and reduction of the Pd surface and drew a conclusion that PdO was the less active catalyst phase during the oscillatory behavior. The waveform of temperature oscillations observed in [10,20] was very similar to that obtained in this study. However, the authors did not publish the oscillatory behavior of concentrations of various species and a detailed comparison of oscillations is not possible. The variations of all concentrations and catalyst temperature were presented by Zhang et al. [11]. As was discussed earlier, the authors detected various waveforms of oscillations of H_2O and CO_2 concentrations, but did not correlate this phenomenon with the carbon formation. The authors [11] did not detect carbon by XRD analysis in the Pd foil after the reaction of methane oxidation. However, our data showed that the amount of carbon drastically decreased with the increase in pumping time, during which the sample was in contact with a reactant mixture containing oxygen. The authors [11] detected a very reactive form of carbon which was accumulated on the surface of the catalyst when the oxygen supply was cut off, and this carbon produced a CO_2 peak as soon

as the O_2 supply was restored. Moreover, the data presented in this study showed that the Pd foil accumulated much less carbon than the Pd powder per gram of Pd. Therefore, we suppose that the reason for the phase shift between the oscillations of H_2O and CO_2 concentrations, observed in [11], could be also connected with the carbon accumulation in the catalyst.

5. Conclusions

The experimental results presented in this paper demonstrate how the study of oscillatory behavior allows the extraction of the new information about the reaction mechanism. The application of TGA analysis in combination with on-line mass-spectrometry allowed to identify the variation of the Pd state during one cycle of the oscillations and to correlate the various states of Pd with a catalytic activity. It was demonstrated that the nature of the oscillations was connected with periodic oxidation and reduction of a Pd catalyst. The complicated waveform of oscillations and the anti-phase oscillations of two reactant products resulted due to accumulation of carbon on the catalyst surface under methane-rich conditions. While a tentative mechanism of the oscillatory behavior during methane oxidation over Pd catalysts could be proposed, mathematical modeling of the observed dynamic behavior is necessary. This will be the topic of future studies.

Acknowledgment

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