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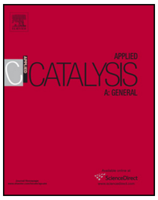

Self-oscillations during methane oxidation over Pd/Al_2O_3: Variations of Pd oxidation state and their effect on Pd catalytic activity

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ABSTRACT

Oscillations of the rate of methane oxidation under methane-rich conditions over Pd/Al_2O_3 were studied by in situ thermogravimetry and mass-spectrometry. Structural transformations of Pd in the oscillation cycle went through fast reduction of Pd oxide, metal carbonization, removal of deposited carbon as CO_2 and gradual oxidation of metallic Pd. Simultaneous measurement of the weight changes and CO_2 production during oscillations helped to elucidate a relationship between catalytic activity of Pd and its oxidation state. Metallic Pd showed the highest activity which dropped sharply as metal surface became oxidized and then increased gradually as Pd oxidized further into $PdO_{0.3}$.

1. Introduction

Oxidation of methane over Pd foil or powder was often in focus of catalytic research in view of Pd application for catalytic combustion. The rate of methane oxidation in methane-rich mixtures was shown to oscillate at certain reaction conditions [1–6]. It was demonstrated in Refs. [1–3] that the oxidation state of Pd in foil changes from metallic Pd to PdO in a given oscillatory cycle. Catalytic activity of oxidized and reduced Pd in small alkane oxidation was approached in numerous publications over the past two decades [7–24]. The authors of Refs. [7–10] concluded that oxidized Pd is more active, while others reported higher activity of reduced Pd [11] or partially reduced PdO_x species [12]. The advent of advanced experimental techniques and computational modelling methods at the turn of the century did not result in a conclusive answer to the above question [13–24].

In our previous contributions [4–6], we reported on oscillatory oxidation of methane and other low alkanes over Pd foil and powder studied by in situ thermogravimetry (TG) combined with mass-spectrometry (MS). It was established that in a single oscillatory cycle, Pd not only changes its oxidation state, but also accumulates carbon and releases it in form of CO_2 [4]. Coupling TG and MS analyses revealed that the states of Pd when it accumulates carbon and when it becomes oxidized are clearly separated on time scale. With these two processes resolved, TG analysis can be used for experimental measurement of both Pd carbonization and oxidation rates during methane oxidation reaction. For instance, with the combined TG-MS analyses we demonstrated that in the oscillatory regime of methane oxidation, carbon dissolution/removal proceeds ~30 times faster than Pd oxidation [6]. A simultaneous rise of Pd weigh and CO_2 concentration in the products observed in our other work on methane oxidation indicated higher catalytic activity of Pd at higher oxidation state [4]. However, because of rather large size of the studied Pd particles (~1 μm [4] or ~75 μm [6]), the gravimetric data did not allow quantitative determination of Pd oxidation state at each point. At this size range, oxygen diffusion into Pd bulk is not fast enough to achieve a uniform oxidation of entire particle.

The size of Pd particles on supported catalysts is on nanoscale, hence such particles are more likely to change their oxidation state uniformly. Oscillatory oxidation of methane over supported Pd catalysts was studied earlier in Refs. [25–29]. The authors relate periodic changes of weight to oxidation-reduction cycles of Pd. In situ XAS [28] and QEXAFS [29] methane oxidation experiments over 5% Pd/Al_2O_3 were performed in a flow-through reactor with a sufficiently long catalytic bed to detect different states of Pd along it. The methods allowed detection of altering oxidized and metallic Pd phases, carbon deposits on metallic Pd and variations in the

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state of Pd. During oscillations, the bed contained up to 3 sequential zones with Pd in different states. Yet, catalytic activity of Pd in a particular state could not be determined since the out stream contained products from all zones.

In the current work, we aimed to gain a mechanistic insight into periodic changes in the state of supported Pd particles during oscillatory methane oxidation and to find a quantitative correlation between Pd oxidation state and its catalytic activity. To this end, Pd/Al_2O_3 catalysts with different Pd particle size prepared in earlier study [30] were tested in methane oxidation under methane-rich conditions in a thermogravimetric instrument coupled with a mass-spectrometer.

2. Experimental

The catalysts were prepared by an incipient wetness impregnation method. γ-Al_2O_3 supplied by Sasol (TKA-432, $S_{BET} = 215\,m^2/g$) and α-Al_2O_3 obtained by prolonged calcination of γ-Al_2O_3 at 1150 °C ($S_{BET} = 6\,m^2/g$) were dried at 120 °C for 2 h and then impregnated with $Pd(NO_3)_2$ solution. Pd loading was set to 1 wt.% for γ-Al_2O_3 and to 5 wt.% for α-Al_2O_3. The catalysts were denoted as 1Pd/Al and 5Pd/Al respectively. All impregnated samples were dried at 120 °C for 3 h and then calcined at 400 °C for 4 h. The preparation method is described in detail elsewhere [31].

Pd particle morphology and size distribution were determined earlier [30] by transmission electron microscopy (TEM, JEM-2010, JEOL Co., Japan), the samples were prepared by dispensing catalysts powder on holey carbon supported on copper grid. Particle size distribution was calculated in "AnalySIS iTEM" v.5 software (Soft Imaging System GmbH), size distribution histograms were drawn from 200 to 700 measurements.

Catalytic experiments were carried out in a tubular quartz flow-through reactor (i.d. 5 mm), operated at atmospheric pressure under shallow bed conditions. Catalyst weight was 20 mg. A mixture containing 41.5 vol.% CH_4, 7.5 vol.% O_2, 2 vol.% Ar and 49 vol.% He was fed at 20–30 mL/min.

Thermogravimetric analysis (TGA) was performed on Setaram SETSYS EVOLUTION 16/18 instrument coupled with Pfeiffer OmniStar GSD 301 quadrupole mass-spectrometer. The operation unit of the thermogravimetric setup consisted of a vertical flow tubular furnace with an inner alumina tube. The inner diameter of the alumina tube was 20 mm and the length of the controlled temperature zone was ~30 mm. The instrument is described in detail elsewhere [32]. The catalyst samples were loaded in a quartz cup suspended in the center of a heated zone. The gas mixture of 41.5 vol.% CH_4, 7.5 vol.% O_2, 2 vol.% Ar and 49 vol.% He was fed through the top of the tube, the products were sampled below the catalyst via a stainless capillary connected to the mass-spectrometer. The flow rate of the gas mixture was maintained at 20 mL/min by the flow controller built into the SETSYS instrument. During the experiments, 40 mg of a catalyst were heated at 10/min to a selected temperature and held at this temperature for the rest of the experiment. The weight change was normalized to the initial sample weight and further on will be expressed as mg/g_{cat}. Atomic mass units (AMU) of 2 (H_2), 15 (CH_4), 18 (H_2O), 28 (CO, CO_2), 32 (O_2), 40 (Ar), and 44 (CO_2) were detected. Ar MS signal was applied as internal standard for MS measurement of the gaseous products concentrations. CO concentration in the outflow was very low under all experimental conditions.

3. Results

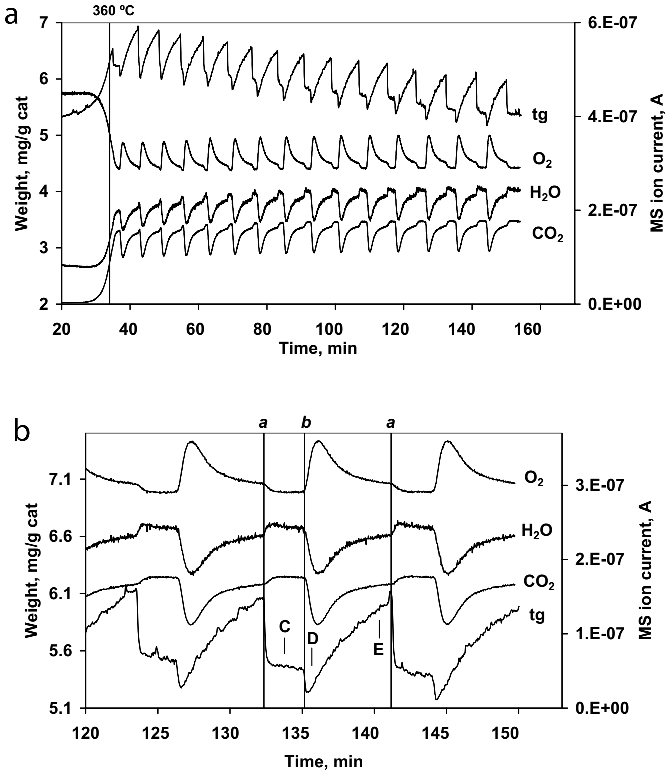

Fig. 1. (a) Oscillations of catalyst weight and gas components during methane oxidation over 5Pd/Al at 360 °C in CH_4—O_2—Ar—He flow in TGA-MS instrument. (b) Last 3 cycles of the oscillations shown in a. Intervals ***a-b*** and ***b-a*** are the high- and low-activity phases respectively. Separate experiments with identical catalyst loadings were stopped at points C, D, and E and the samples weight loss was measured during reduction in CO/He mixture.

Size and morphology of Pd particles were characterized by TEM in our previous work [30]. The micrographs of the catalysts and the Pd particles size distribution on 1Pd/Al can be found in the Supporting Information in Figs. S2a,b and S3 respectively. An average Pd particles size in 1Pd/Al was 16 ± 7 nm, while Pd/α-Al_2O_3 contained large particles agglomerates of various sizes. They can be seen as dark structures in Fig. S2b among which smaller ones marked by white arrows measured ~30 nm across whereas larger aggregates were well over 100 nm, hence meaningful particle size evaluation was not possible.

Self-oscillations of the rate of methane oxidation over 1Pd/Al and 5Pd/Al in the in situ TGA experiments were observed at 400 and 360 C respectively. Fig. 1a shows oscillations of the 5Pd/Al weight and of O_2, CO_2 and H_2O MS signals during methane oxidation at 360 °C. The waveform of all oscillations changed with time on stream starting from a simple "mono-phase" (first 3–4 oscillation cycles in Fig. 1a) and gradually progressing to a more complex "double-phase" form (last 3–4 oscillation cycles in Fig. 1a). The mono-phase oscillations demonstrated periodic increase and decrease of the catalyst weight. The double-phase oscillations have characteristic points ***a*** and ***b*** where abrupt changes of the catalyst weight and the reaction rate took place (Fig. 1b). The oscillation periods then can be divided into the high-activity phase ***a-b*** and the low-activity phase ***b-a***. The weight of 5Pd/Al remained nearly constant during ***a-b*** and increases noticeably during ***b-a***.

Fig. 2a and b shows oscillations observed on 1Pd/Al during in situ TG experiment at 400 °C. As in case of 5Pd/Al, the oscillation cycles can be divided into the ***a-b*** and phases where the catalyst has high and low activity respectively. Unlike the oscillations on 5Pd/Al, waveforms of the oscillations on 1Pd/Al did not evolve with time on stream.

In order to verify whether the weight changes during the ***b-a*** phase were related to the oxygen content in the catalyst, the experiments with reproducible oscillations over 5Pd/Al were stopped

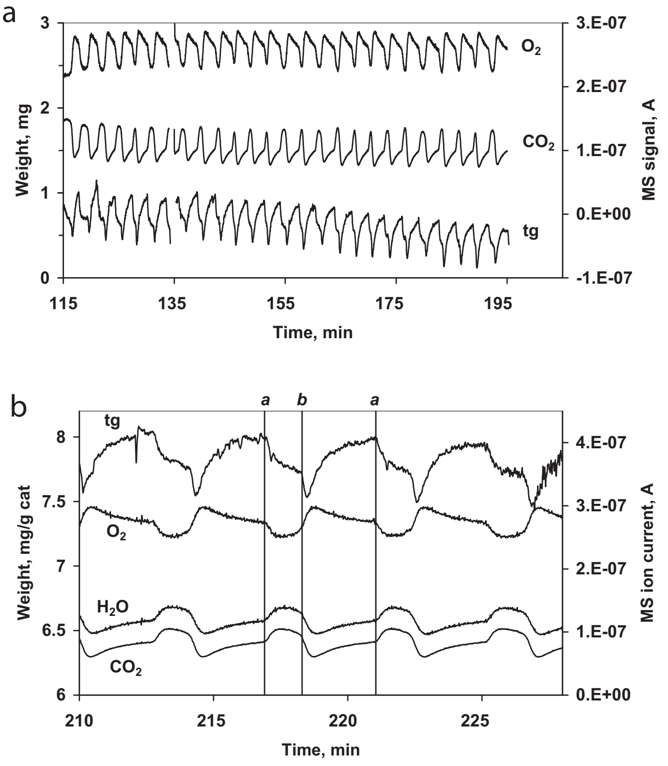

Fig. 2. (a) Oscillations of catalyst weight and gas components during methane oxidation over 1Pd/Al at 400 °C in CH_4—O_2—Ar—He flow in TGA-MS instrument. (b) Selected 4 cycles of the oscillations shown in a. Intervals ***a-b*** and ***b-a*** are the high- and low-activity phases respectively.

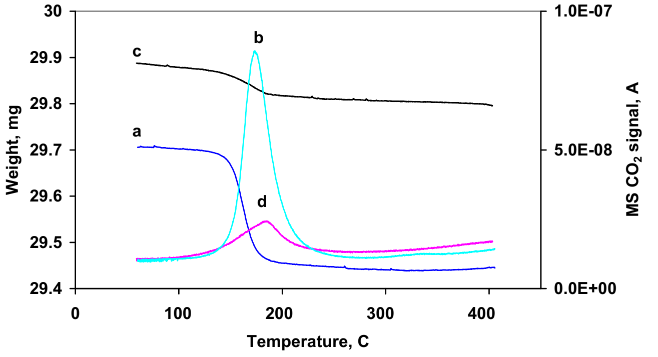

Fig. 3. Weight variations (a, c) and CO_2 evolution (b, d) during heating of 5Pd/Al sample in 10% CO/He flow: (a, b) the sample pre-oxidized in 5% O_2/He mixture at 500 °C; (c, d) the sample after the oscillation stopped at point E.

at points C, D and E as shown in Fig. 1b. Then the sample was cooled in vacuum to 30 °C and heated in 10 vol.% CO/He mixture to observe the weight loss occurring due to PdO_x reduction. The maximum CO_2 evolution and weight loss were observed between 140 and 190 °C (Fig. 3). The values obtained in this experiment are found in Table 1 along with the weight loss measured on 5Pd/Al pretreated in H_2 or in 5 vol.% O_2/He flow at 500 °C. As expected, the pre-reduced catalyst showed very little weight loss, while pre-oxidized one lost 6.4 mg/g thus showing the highest lost among all differently pretreated 5Pd/Al samples. However, the weight loss of 7.5 mg/g corresponding to a complete $Pd^{2+} \rightarrow Pd^0$ reduction on 40 mg of 5Pd/Al is not reached here. The samples taken off stream at points C and D lost almost equal and relatively small amount of oxygen suggesting that Pd in particles and aggregates at these points of the cycle was substantially reduced, whereas at point E its oxidation state was somewhat higher. Correspondingly, these observations indicate that the abrupt weight loss at point ***b*** (Fig. 1b) is not due to Pd reduction, but rather to oxidative removal of carbon accumulated during the ***a-b*** phase, while the weight gain in the ***b-a*** phase is a result of Pd oxidation.

Table 1
Weight loss due to PdO_x reduction measured on 5Pd/Al in different states. The in-situ TGA experiment shown in Fig. 1b was stopped at points C, D and E, the sample was cooled to room temperature and then heated in 10 vol.% CO/He flow. Pre-reduced and pre-oxidized 5Pd/Al were tested in separate experiments.

Sample pretreatment	Weight loss (mg/g cat)
pre-reduced in H_2 at 500 °C	0.07
C	0.71
D	0.76
E	1.46
pre-oxidized in O_2 at 500 °C	6.42

4. Discussion

In the following section we will compare Pd powder and supported Pd catalysts in oscillatory oxidation of methane in terms of TG and MS waveforms, search for a Pd oxidation state – catalytic activity correlation and compare our results to the current knowledge. As demonstrated in our earlier report on methane and ethane oxidation over 75 μm Pd powder, oscillations parameters continuously evolve with time on stream [6]. The evolution was caused by a significant development of Pd surface and gradual dissolution of carbon in Pd bulk. 5Pd/Al sample also demonstrated some evolution of oscillations waveform, but much weaker than that observed on the Pd powder. A decrease in the maximal catalyst weight with rising number of oscillations that can be seen in Fig. 1a may be related to a gradual oxygen removal from progressively deeper layers of large Pd particles at each following cycle. Here it should be recalled that Pd in 5Pd/Al prior to the TG experiments was in form of PdO as the precursor was calcined at 400 °C in air. PdO in deeper layers of large particles could not be completely reduced in the first cycle, but the degree of reduction increased with each following cycle until metallic Pd was formed through entire particles volume. 1Pd/Al sample did not show any significant evolutionary effects (Fig. 2a), most likely because 16 nm Pd particles in 1Pd/Al are too small to undergo morphological transformation. Also, such particles have no “deep” layers to dissolve irreversibly oxygen or carbon in Pd bulk during the oscillations.

In our studies on methane and ethane oxidation over Pd foil or powder [4–6], we assigned periodic patterns in the TG and MS waves to changes in the state of Pd (Fig. S1). The following sequence of transformations was set forth: fast PdO_x reduction to metallic state at point ***a***; carbonization of metallic Pd; removal of carbon as CO_2 up to point ***b***; gradual oxidation of the upper Pd layer followed again by fast reduction. In the ***a-b*** phase, Pd remains in a reduced state and contains dissolved carbon. The latter reacts with adsorbed oxygen thus stabilizing Pd in the reduced state. It is possible only when the O_2 concentration in the gas phase is low, i.e. when the catalyst is active and the O_2 conversion is high. The ***b-a*** phase is characterized by low activity resulting in low O_2 conversion, its high concentration in the reaction mixture and subsequently Pd oxidation.

The same stages are observed on the supported Pd catalysts in Figs. 1b and 2b suggesting that the oscillations on bulk and supported Pd are of the same nature. However, a noticeable weight gain due to carbon dissolution in metal starting after point ***a*** on Pd powder is not observed on 5Pd/Al and 1Pd/Al as evident from Figs. 1b and 2b. Here it should be recalled that the surface/volume ratio of bulk Pd is lower than that of supported Pd because the former has larger particles. For both bulk and supported Pd catalysts, PdO_x

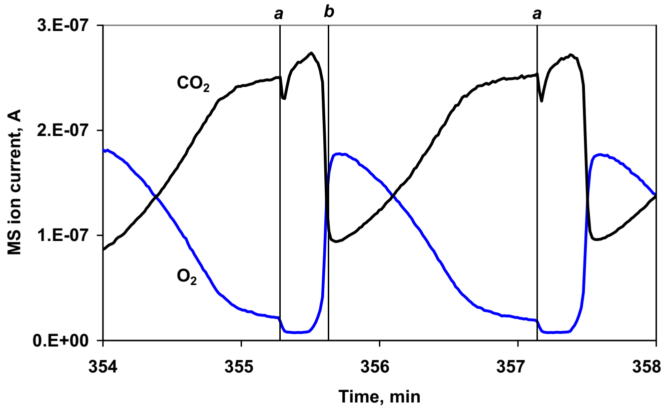

Fig. 4. Oscillations of CO_2 and O_2 during methane oxidation over 5Pd/Al at 360 °C in CH_4—O_2—Ar—He flow in a flow-through quartz tubular reactor.

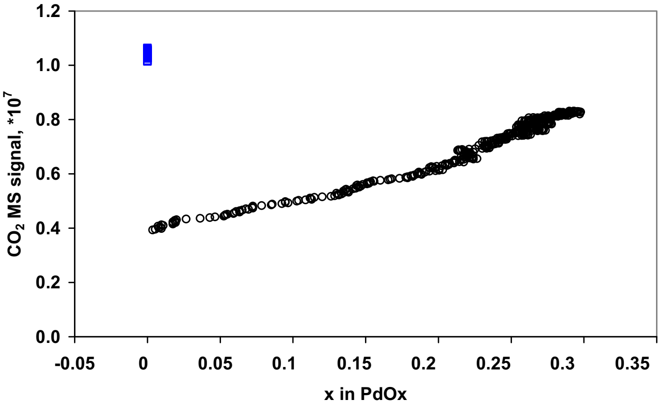

Fig. 5. Effect of the Pd oxidation state in 1Pd/Al on the CO_2 evolution rate. The oxidation state was calculated from the weight changes from the minimum to the maximum in the ***b-a*** phase. Squares show CO_2 evolution rate at point ***b*** on partially carbonized reduced Pd.

reduction and carbon dissolution occur concurrently at the beginning of the ***a-b*** phase. Because of the low surface/volume ratio in case of 75 μm Pd powder, more carbon is dissolved in particles bulk than oxygen removed from particles surface which results in a well-resolved weight maximum in the ***a-b*** phase seen in Fig. S1. In case of the supported catalysts, higher fraction of Pd participates in redox cycles thanks to higher availability of the metal surface. Therefore, per mol of Pd, more oxygen is removed from 5Pd/Al and 1Pd/Al than from bulk Pd. The limit of carbon dissolution in Pd is $PdC_{0.13}$ [33,34], whereas Pd/O of 1 can be reached if all Pd is oxidized to PdO. Hence, it is logical to assume that the weight gain from carbon dissolution in Pd on the supported catalysts is absorbed by the weight loss from oxygen removal during PdO_x reduction.

An incidence of C accumulation on 5Pd/Al was confirmed in the methane oxidation experiment performed in a flow-through quartz tubular reactor. MS signal of CO_2 shown in Fig. 4 exhibits a negative peak immediately after point ***a***. At this point Pd becomes reduced and highly active affording higher conversion of O_2 and CH_4. A portion of carbon from converted CH_4 is not oxidized to CO_2, but dissolved in Pd until saturation ($PdC_{0.13}$) is reached. Hence, a drop in CO_2 concentration that appears at higher methane oxidation rate. The weight of 5Pd/Al saturated by carbon remains nearly constant during the high activity ***a-b*** phase followed by the weight loss at point ***b*** due to the oxidative carbon removal (Fig. 1b). It is possible to observe this loss since Pd oxidation that comes after carbon removal is relatively slow. Thus, the weight minimum immediately after point *b* corresponds to metallic Pd and the weight increase that follows is due to Pd oxidation.

Methane oxidation in the oscillatory mode allows monitoring parallel changes of Pd catalytic activity and its oxidation state over a number of reproducible oscillation cycles. We have selected 1Pd/Al for this study because Pd particles on this catalyst are relatively small and all atoms in such particles are likely to respond to changes in gas phase composition. Hence, changes in their oxidation state calculated from the weight changes should be accurate. Fig. S4 shows evolution of the stoichiometric coefficient x in PdO_x and CO_2 MS signal over the ***b-a*** phase during which Pd loses carbon and becomes oxidized. The value of x was assumed to be 0 at point ***b*** and at the weight minimum right after it because carbon removal does not change Pd oxidation state. At the weight maximum occurring at point ***a***, the value of x reached 0.3. The rate of CO_2 evolution shown as a function of x in Fig. 5 almost doubled in the $0 \le x \le 0.3$ interval indicating that the activity increases with Pd oxidation state. Increase of Pd catalytic activity with its oxidation state was also reported by R. Burch et al. who studied methane oxidation over Pd/Al_2O_3 [9]. Yet, the oxidation state of Pd in this work was measured ex situ in oxygen monolayers consumed by pre-reduced Pd, which may differ from the oxidation state reached in CH_4/O_2 mixture. The trend in the CO_2 formation rate in Fig. 5 is ascending, so higher activity is expected at higher oxidation state, most probably with a maximum encountered at certain x. The latter is supported by findings made in the study of methane oxidation on the (111) face of Pd monocrystal [17]. The measurements were performed on the crystal surface oxidized to a different degree and the oxide with the empirical formula $PdO_{0.8}$ was found to be the most active. The maximum in catalytic activity of oxidized Pd was not encountered in our case because in the oscillatory regime, PdO_x is reduced before the most active oxidation state is reached. The maximum rate of CO_2 formation was detected before point ***b*** (shown as squares) where x = 0, i.e. on partially carbonized reduced Pd. These values by far exceed the rates achieved at x = 0.3. Thus, metallic Pd can exhibit the lowest and the highest catalytic activity depending on the gas phase composition. In particular, maximum and minimum in the activity are registered in oxygen-depleted and oxygen-rich atmosphere respectively. The reason behind this difference is the rate of O_2 chemisorption on metallic Pd surface which is significantly higher compared to that of CH_4. As a result, the surface of metallic Pd in oxygen-rich CH_4/O_2 mixture is covered by adsorbed oxygen that blocks it for methane molecules.

The findings made in our work are in agreement with literature reports on the subject. Studies on stationary oxidation of methane in oxygen-rich mixtures over Pd catalysts indicate higher catalytic activity at higher oxidation state of Pd [7–10,13,15,16,18]. However, complete reduction of PdO_x and carbon accumulation do not occur at constant excess of oxygen in gas phase, thus the catalytic activity of reduced Pd is never reached. Also, oxygen depletion was shown to stimulate catalytic activity of Pd. An isotope method used in [14] revealed that a probability of reactive CH_4 collision increases with decreasing coverage of Pd surface with oxygen. The authors of Ref. [19] reported that the activity in methane oxidation was higher under oxygen-lean conditions than in oxygen-rich feed where Pd is more oxidized. In Ref. [20] metallic Pd surface was found to be significantly less active in methane oxidation than PdO surface under near-stoichiometric conditions. However, the metallic surface became very active under oxygen-lean conditions. According to Ref. [21], methane oxidation over Pd/Al_2O_3 under oxygen-lean conditions gave TOF rise from 0.05 to 0.25 with Pd/PdO_x ratio increase from 1 to 2.5, i.e. the activity dropped at higher oxidation state of Pd. The results of DFT calculations presented in Refs. [22–24] were contradictory. Authors of Ref. [22] report that on PdO clusters (predominantly PdO(101) surfaces), both Pd and O ions activate C—H bonds more efficiently than Pd atoms in Pd^0 clusters, either free or with adsorbed O*. Calculations performed by authors of Ref. [23] show that both thick films of PdO (101) and metallic Pd afford high methane conversion.

Knowing the activity of different states of metallic Pd is important for kinetic modelling of methane oxidation over Pd. Composed of elementary reactions, such models may be quite complex as, for instance, the one presented in Ref. [35]. It was developed to model the hysteresis effect occurring during methane oxidation under methane-lean conditions and comprised 43 elementary reactions. Basing on the results of Burch et al. [9] the authors of Ref. [35] assume that the rate of methane reaction on Pd surface is slow, and the activation energy of the $CH_4 + 2Pd(s) \rightarrow CH_3(s) + H(s)$ reaction is high – 160 kJ/mol. However, our results indicate that the rate of such reaction on truly metallic Pd surface is high, whereas the processes occurring on the oxygen-blocked Pd surface under methane-lean conditions cannot be accurately described by the above elementary equation.

5. Conclusions

Methane oxidation in oscillatory regime under methane-rich conditions was studied over supported Pd catalysts by in situ thermogravimetric analysis coupled with mass-spectroscopy. Simultaneous changes in CO_2 and O_2 concentrations in the outflow stream and in the catalyst weight suggest that during oscillations, Pd atoms in supported particles progress through periodic redox transformations very similar to those observed in Pd powder under the methane-rich reaction conditions. The states of Pd are: rapid reduction of PdO_x to metallic Pd; carbonization of metallic Pd; removal of dissolved carbon in form of CO_2; gradual oxidation of Pd to PdO_x. The in situ thermogravimetric experiments on the catalyst containing 16 nm Pd particles allowed monitoring changes in Pd oxidation state during activity oscillations. Catalytic activity increased as Pd^0 became oxidized to $PdO_{0.3}$ which is in agreement with earlier literature reports, but the highest catalytic activity was observed after a rapid reduction step as Pd went over to metallic state. High activity of the metallic state is specific for methane-rich conditions where the metal surface remains substantially free of chemisorbed oxygen and thus available for C—H bond activation in methane molecules.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2016.04.024.

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