



Self-oscillations during methane oxidation over Pd/Al₂O₃: 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/Al₂O₃ 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 CO₂ and gradual oxidation of metallic Pd. Simultaneous measurement of the weight changes and CO₂ 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}.

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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 accumu-

lates carbon and releases it in form of CO₂ [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 weight and CO₂ 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/Al₂O₃ 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/Al₂O₃ 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 -Al₂O₃ supplied by Sasol (TKA-432, $S_{\text{BET}} = 215 \text{ m}^2/\text{g}$) and α -Al₂O₃ obtained by prolonged calcination of γ -Al₂O₃ at 1150 °C ($S_{\text{BET}} = 6 \text{ m}^2/\text{g}$) were dried at 120 °C for 2 h and then impregnated with Pd(NO₃)₂ solution. Pd loading was set to 1 wt.% for γ -Al₂O₃ and to 5 wt.% for α -Al₂O₃. 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 dispersing 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.% CH₄, 7.5 vol.% O₂, 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.% CH₄, 7.5 vol.% O₂, 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 (H₂), 15 (CH₄), 18 (H₂O), 28 (CO, CO₂), 32 (O₂), 40 (Ar), and 44 (CO₂) 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

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 Support-

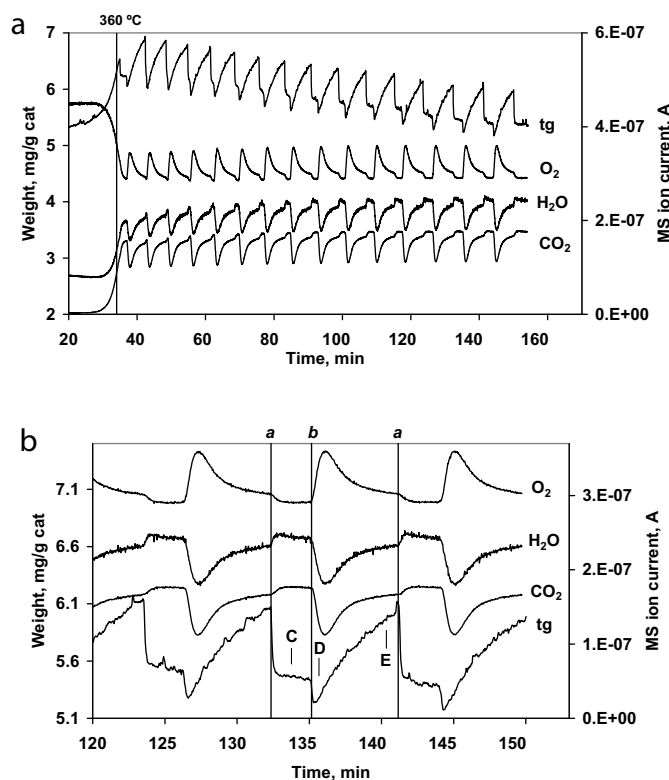


Fig. 1. (a) Oscillations of catalyst weight and gas components during methane oxidation over 5Pd/Al at 360 °C in CH₄–O₂–Ar–He flow in TGA-MS instrument. (b) Last 3 cycles of the oscillations shown in a. Intervals **a–b** and **b–a** are the high- and low-activity phases respectively. Separate experiments 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.

ing Information in Figs. S2a,b and S3 respectively. An average Pd particles size in 1Pd/Al was $16 \pm 7 \text{ nm}$, while Pd/ α -Al₂O₃ 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 O₂, CO₂ and H₂O 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

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