



Short communication

## Self-oscillations of methane oxidation rate over Pd/Al<sub>2</sub>O<sub>3</sub> catalysts: Role of Pd particle size



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### ABSTRACT

Oscillations of the methane oxidation rate were studied under methane-rich conditions on Pd/Al<sub>2</sub>O<sub>3</sub> catalysts differing in Pd particle size. It was demonstrated that the temperature interval where oscillations occur narrows from 300–360 °C for the catalyst with Pd particle aggregates from 50–100 nm to 345–355 °C for the catalyst with isolated Pd particles of ~5 nm in size. At the same time, the period of oscillations showed ~6-fold increase. Structural transformations of Pd in the oscillation cycle were similar to those observed on bulk Pd used as a catalyst in the same reaction.

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### 1. Introduction

Pd-based catalysts are used for methane oxidation in off-gas afterburners and catalytic combustors employed in energy production and transportation. The reaction was studied extensively in the past decades, the findings made until 2002 are summarized in the review [1]. More recent reports deal with mechanistic studies of catalytic methane oxidation including changes in the state of Pd assisted by operando methods such as DRIFTS [2–4], FTIR [7], XPS [4–6] as well as DFT calculations [8–10]. Most of the investigations were carried out under methane-lean conditions where methane oxidation proceeds in a stationary mode. However, it is known that methane oxidation over Pd falls into an oscillatory regime at high concentrations of methane in the feed [11,12], which is undesirable for commercial devices.

Rate oscillations during catalytic oxidation of methane were studied for methane-rich mixtures oxidized over Pd foil or powder [13–18]. It was demonstrated in [13,14] that the oxidation state of Pd in foil changes from metallic Pd to PdO in a given oscillatory cycle with the lowest methane oxidation rate detected on metallic Pd. The authors of [15] presented a detailed report on the influence of the CH<sub>4</sub>/O<sub>2</sub> mixture composition and Pd foil temperature on such oscillation parameters as period, amplitude and waveform. In our previous works [16–18], we

studied oscillatory oxidation of methane and other low alkanes over Pd foil and powder by in situ thermogravimetry combined with mass spectrometry. It was established that in a single oscillatory cycle, Pd not only changes the oxidation state, but also accumulates carbon and releases it in form of CO<sub>2</sub> [16]. Moreover, this in situ technique allowed quantification of carbon and oxygen stored in/on Pd at different stages of the cycle. Catalytic activity of Pd was shown to increase with the oxidation state, although the maximum activity was observed on carbonized metallic Pd. Based on the experimental data obtained in [16–18], a model describing methane oxidation on Pd was developed [19].

Oscillatory methane oxidation over supported Pd catalysts was studied in [20–24]. The temperature of a metallic support coated with a 15%Pd/γ-Al<sub>2</sub>O<sub>3</sub> suspension was monitored under during methane oxidation in [20,21]. It was found that the temperature changed periodically suggesting that the rate of methane oxidation also had a periodic character. In situ XAS [23] and QEXAFS [24] methane oxidation experiments over 5%Pd/Al<sub>2</sub>O<sub>3</sub> were performed in a flow-through reactor with a sufficiently long catalytic bed to detect different states of Pd along the bed. The methods allowed detection of altering oxidized and metallic Pd phases, carbon dissolution in metallic Pd. During oscillations, the bed contained up to 3 sequential zones with Pd in different states. Yet, the influence of metallic Pd particle size or support nature on such oscillation parameters as period, amplitude, waveform and the temperature interval where oscillations occur is yet to be studied. With the aim to carry out such investigation, we prepared Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with different Pd particle size by impregnating low- and high-surface area Al<sub>2</sub>O<sub>3</sub>

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with a Pd precursor. The catalysts were tested in methane oxidation under methane-rich conditions at various temperatures in a flow-through reactor.

## 2. Experimental

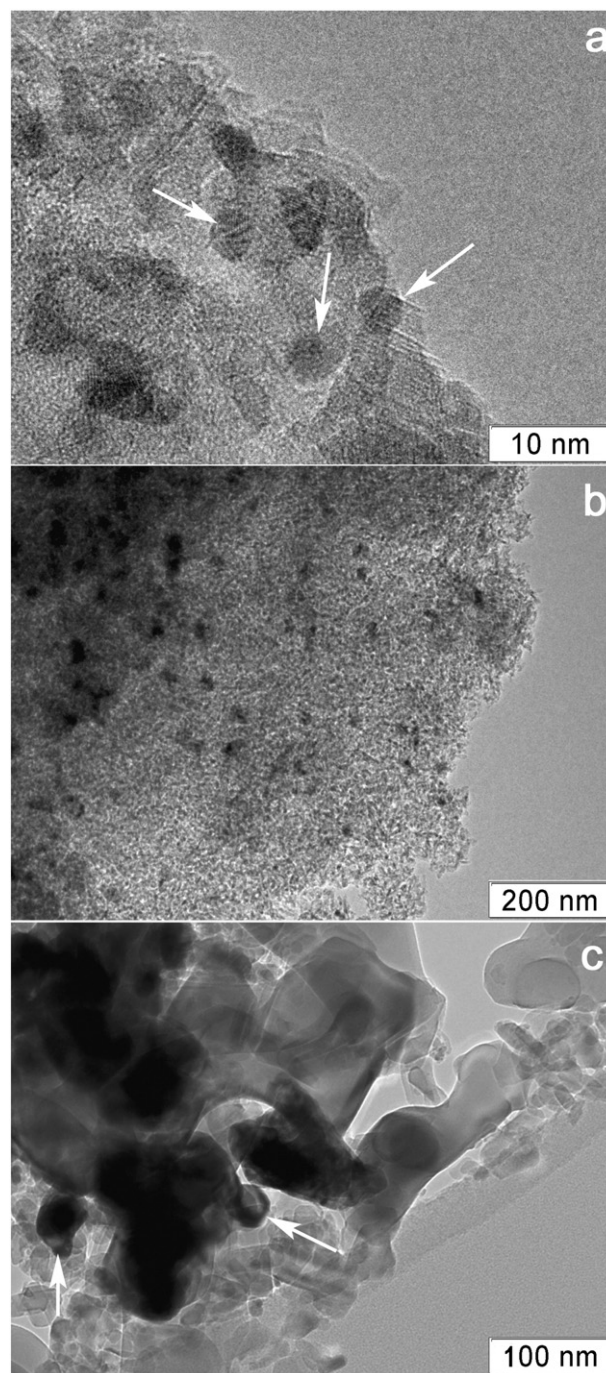
Catalysts were prepared by an incipient wetness impregnation method.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supplied by Sasol (TKA-432,  $S_{\text{BET}} = 215 \text{ m}^2/\text{g}$ ) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> obtained by prolonged calcination of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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(NO<sub>3</sub>)<sub>2</sub> solution. Pd loading was set to 1 wt.% for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 5 wt.% for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The catalysts were denoted as 1Pd/Al and 5Pd/Al respectively. To obtain larger supported Pd particles on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, this support was impregnated with Pd(NO<sub>3</sub>)<sub>2</sub> solution acidified with acetic acid. All impregnated samples were dried at 120 °C for 3 h and calcined at 400 °C for 4 h. The preparation method is described in detail elsewhere [25].

Pd particle morphology and size distribution were determined by a transmission electron microscopy (TEM, JEM-2010, JEOL Co., Japan), the samples were prepared by dispensing catalyst 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 200–700 measurements. Specific Pd surface was measured by pulse CO chemisorption at room temperature using Chemosorb analyzer (Russia). Chemisorption results were also used for the estimation of Pd particle size.

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 in most experiments. Both the furnace temperature ( $T_{\text{fur}}$ ) and the reactor temperature near the catalyst ( $T_{\text{cat}}$ ) were measured. A mixture containing 41.5 vol.% CH<sub>4</sub>, 7.5 vol.% O<sub>2</sub>, 2 vol.% Ar and 49 vol.% He was fed at 20–30 mL/min. Gas phase composition was analyzed by a Pfeiffer OmniStar GSD 301 quadrupole mass-spectrometer. Atomic mass units (AMU) of 2 (H<sub>2</sub>), 15 (CH<sub>4</sub>), 18 (H<sub>2</sub>O), 28 (CO, CO<sub>2</sub>), 32 (O<sub>2</sub>), 40 (Ar), and 44 (CO<sub>2</sub>) were detected. Ar MS signal was used as an internal standard for MS measurement of the gaseous product concentrations. CO concentration in the outflow was very low under all experimental conditions. Our attempts to account for CO as for a difference of AMU 28 signal intensity and the value from the standard fragmentation pattern of CO<sub>2</sub> (~10% of the AMU 44 signal intensity) resulted in values fluctuating around zero. GS analysis revealed that the CO concentration was approximately two orders of magnitude lower than that of CO<sub>2</sub> under the conditions of our experiments.

## 3. Results and discussion

Morphology and size of Pd particles were characterized by TEM and CO chemisorption. The micrographs of the three catalysts are shown in Fig. 1a–c while the size distribution of Pd particles on the 1 wt.% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts is found in Fig. S1. Table 1 presents values of Pd particle size calculated from TEM and chemisorption data. Impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with an aqueous solution of Pd(NO<sub>3</sub>)<sub>2</sub> yields Pd particles with the size distribution of  $4.8 \pm 1.1 \text{ nm}$  in diameter which are seen in Fig. 1a as spherical objects (marked by white arrows). Lowering pH of the impregnation solution with acetic acid resulted in larger Pd particles with broader size distribution of  $16 \pm 7 \text{ nm}$ . They appear on the alumina surface as dark spots (Fig. 1b) that vary in their size and shape. These two catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are further abbreviated as 1Pd/Al-5 and 1Pd/Al-16 respectively. The catalyst supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> contained large Pd particle agglomerates. They can be seen as dark structures in Fig. 1c among which smaller ones measured ca. 30 nm across (marked by white arrows) whereas larger aggregates were well over 100 nm, hence meaningful particle size evaluation was not possible.



**Fig. 1.** TEM images of 1Pd/Al-5 (a), 1Pd/Al-16 (b) and 5Pd/Al (c). Selected Pd particles are shown by white arrows.

Fig. 2 shows the temperature intervals where the studied catalysts exhibited oscillations in methane oxidation. 1Pd/Al-5 with the smallest Pd particles sustains this regime in a narrow temperature interval of

**Table 1**  
Characterization of the catalysts.

Catalyst	Support	S support, m <sup>2</sup> /g	Pd content, wt.%	<sup>a</sup> Pd size, nm	<sup>b</sup> Pd size, nm
1Pd/Al-5	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	215	1	$4.8 \pm 1.1$	2.6
1Pd/Al-16	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	215	1	$16 \pm 7$	9.6
5Pd/Al	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	6	5	50–100	~125

<sup>a</sup> Calculated from microscopy data.

<sup>b</sup> Calculated from chemisorption data.

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