



Short communication

Oxygen step-response experiments for methane oxidation over Pd/Al₂O₃: An in situ XAFS study

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ABSTRACT

Methane oxidation over Pd/Al₂O₃ has been investigated by in situ XAFS characterization during oxygen step-response experiments. With a net-reducing feed gas, Pd is in a reduced state and the introduction of oxygen leads to oxidation of palladium as well as increased methane conversion. When the rate of Pd oxidation is slow, a transient surface oxidized state is observed with low activity for methane oxidation. The activity increases when palladium is further oxidized and the highest activity is observed for palladium oxide.

1. Introduction

Hydrocarbon emissions from natural gas vehicles consist mainly of uncombusted methane. Methane is a strong greenhouse gas and it is important to minimize the emissions of uncombusted methane. This can be achieved using a catalytic converter that facilitates the total oxidation of methane to carbon dioxide and water. As methane is the most difficult hydrocarbon to oxidize catalytically, highly effective catalyst designs are required to obtain sufficient conversion over a wide temperature range.

Palladium is the most active metal for the catalytic total oxidation of methane under lean (net-oxidizing) conditions [1, 2]. Under lean conditions, the stable form of palladium at temperatures below ca. 790 °C is palladium oxide. However, palladium can readily be reduced if the temperature is raised or the feed gas is changed to a net-reducing composition [3–5]. Palladium oxide has high activity for methane oxidation and has been assigned as the active phase for methane oxidation at low temperatures under lean conditions [3, 6, 7]. In particular, the PdO(101) facet has been identified as highly active for methane oxidation with low barrier for hydrogen abstraction on under-coordinated surface sites [8, 9].

However, there are still uncertainties regarding the structure-activity relationship for methane oxidation over Pd catalysts at intermediate oxidation states. With a feed gas composition close to stoichiometric, palladium has been reported to be predominately in a

reduced state during methane oxidation [10]. For Pd surfaces completely saturated with oxygen, a significant decrease in methane oxidation activity has been reported [11, 12]. It has been suggested that the equilibrium between bulk Pd and surface PdO is important for the activity at stoichiometric conditions [13].

In this report, we have investigated methane oxidation over a Pd/Al₂O₃ catalyst using in situ X-ray absorption fine structure (XAFS) to follow the oxidation state of Pd during the reaction. Oxygen step-response experiments were performed where the feed gas composition was switched rapidly from a rich composition containing only methane to a net-oxidizing feed containing both methane and oxygen. The effluent stream from the reactor was monitored by mass spectrometry and time-resolved XAFS in combination with linear combination fitting was used to quantify the oxidation state of Pd as a result of the changing feed gas composition. In this way, we were able to investigate how the dynamics of Pd oxidation affect the catalytic activity for methane oxidation.

2. Materials and methods

The 5 wt% Pd/Al₂O₃ catalyst was prepared through incipient wetness impregnation by mixing 10 g of γ -alumina (Puralox SBa 200, Sasol) with 10 g of aqueous Pd(NH₃)₂ solution (Alfa Aesar). The slurry was stirred for 15 min, frozen with liquid nitrogen, and freeze-dried. The freeze-dried powder sample was calcined in air at 500 °C for 1 h,

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starting from room temperature with a heating rate of 5 °C/min. The calcined catalyst was characterized by X-ray diffraction using a Bruker XRD D8 Advance instrument using monochromatic $\text{CuK}\alpha_1$ radiation. The 2θ angle was varied from 20 to 65.9° and the step size and time was 0.029° and 1 s, respectively.

The energy-dispersive XAFS measurements were performed at the ID24 beamline at the European Synchrotron Radiation Facility, France [14]. X-ray absorption spectra were recorded in transmission mode at the Pd K edge at 24.35 keV, with an energy range of approximately 23 500 to 26500 eV, and a time-resolution of 500 ms. A Pd foil (Goodfellow, 99.99% purity) was used for energy calibration of the XAFS spectra. A flow-through type catalytic cell, developed at ESRF was used [14]. The powder sample was placed in a sample holder, with diameter of 5 mm, made of Inconel. The sample holder was loaded with approximately 40 mg of catalyst. The gas flows from top to bottom and the sample is kept fixed at the bottom by a stainless steel gauze. The X-rays penetrate the sample from side to side near the top of the catalyst bed through carbon windows in the wall of the sample holder. Rapid switching between feed gas compositions were facilitated by the small dead volume of the cell ($< 0.5 \text{ cm}^3$) and performed using air-actuated four-way gas valves (Valco, VICI).

Helium was used as carrier gas and the total flow was kept constant at 75 ml/min. Step-response experiments were performed at temperatures of 320, 360, and 400 °C. The catalyst was reduced in a stream of 0.2% methane for 15 min before oxygen was added to the feed. For each temperature, three different experiments were performed with an oxygen concentration of 2.5, 1.2, and 0.6%, respectively, with net-oxidizing conditions held for 15 min. The effluent stream from the reactor was continuously analyzed using mass spectrometry (Prisma, Pfeiffer) following the m/z 4 (He), 15 (CH_4), 32 (O_2) and 44 (CO_2).

XAFS data processing was performed using the Larch software [15]. Linear combination fitting was used to determine the fraction of Pd^{2+} in the catalyst. The spectrum of the fresh catalyst and a spectrum of the catalyst reduced in H_2 were used as references for Pd^{2+} and Pd^0 , respectively. The reference spectra and the measured spectra for fitting were normalized using the standard pre-edge function in Larch, by subtracting the pre-edge and normalizing the spectra by the edge step. The reference spectrum for Pd^0 was assigned a linear coefficient x_1 and the Pd^{2+} reference spectrum a linear coefficient x_2 . Furthermore, x_1 was set to be a free parameter while x_2 was constrained to $(1 - x_1)$. Fitting was performed by minimizing the residual between the measured spectra and the linear combination of the reference spectra using an energy range from 24000 to 24800 eV. The estimated standard error in the fit of the linear coefficients is 0.02–0.03.

3. Results and discussion

The XRD patterns for the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst and the pure γ -alumina support are shown in Fig. 1. For alumina, reflections appear at $2\theta = 37.6, 39.5, 45.9,$ and 60.9° . Compared to the support material, the catalyst shows additional reflections at $2\theta = 34.1, 42.1$ and 55.0° . Comparison with the JCPDS reference cards confirms that this set of signals correspond to palladium oxide. Using the Scherrer equation and the peak width at half maximum for the reflections at $2\theta = 34.1$ and 55.0° , the PdO crystallite size is estimated to be about 6 nm. However, since XRD is not sensitive to very small nanoparticles (below 2–3 nm) it should be noted that the average crystallite size can be overestimated using this method.

Fig. 2 shows the XAFS spectra for the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst recorded in situ before the oxygen step, in a flow of 0.2% methane, and after the oxygen step, in a flow of 0.2% methane and 2.5% oxygen. The major difference between the two spectra is found in the area just above the absorption edge where the position of the first peak is shifted to lower energies in the more oxidized Pd sample. Compared to a spectrum recorded at a conventional monochromator beamline, the increase in intensity just after the absorption edge is lower due to the lower energy

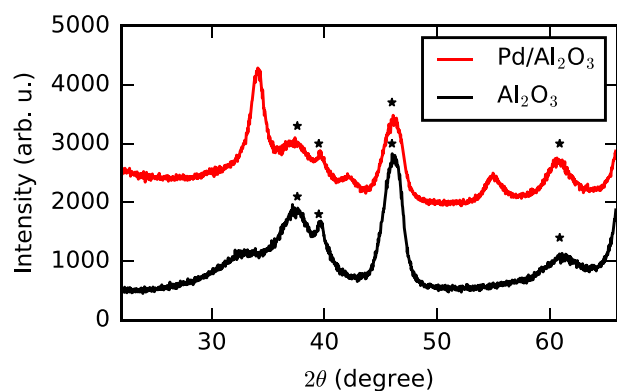


Fig. 1. XRD pattern of the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst and the γ -alumina support. The reflections from γ - Al_2O_3 are indicated by (*).

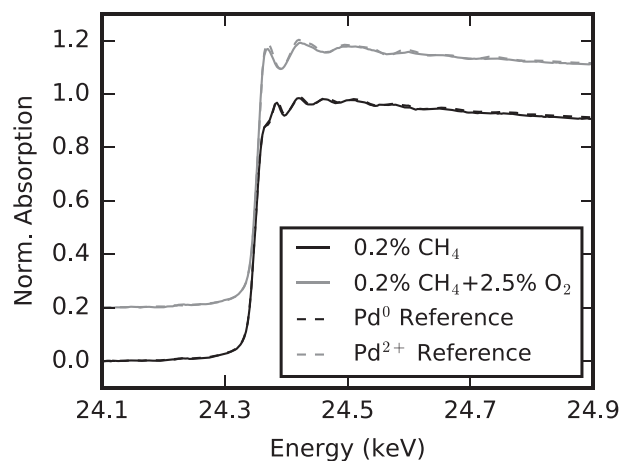


Fig. 2. XAFS spectra of the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst recorded in situ under a flow of 0.2% CH_4 (solid black line) and 0.2% $\text{CH}_4 + 2.5\% \text{O}_2$ (solid grey line, offset by 0.2) at 400 °C. Included are also the reference spectra for Pd^0 (dashed black line) and Pd^{2+} (dashed grey line, offset by 0.2).

resolution in the energy-dispersive geometry. To quantify the oxidation of Pd during the experiment, linear combination fitting was performed by fitting the measured spectrum during the methane oxidation experiment to reference spectra of Pd^{2+} and Pd^0 . From this procedure, the fraction of oxidized Pd in the catalyst is determined.

Fig. 3 shows the outlet concentration of products and reactants as well as the fraction of Pd^{2+} calculated from the linear combination fitting of the XAFS spectra, for experiments performed at 320, 360, and 400 °C. During the net-reducing period, before oxygen is added to the feed at 900 s, carbonaceous species accumulate on the surface of the catalyst. The XAFS linear combination fitting gives a slight increase of the fraction of Pd^{2+} during this period. This increase of the Pd^{2+} fraction is not a result of an oxygen induced oxidation of the catalyst but rather due to the carbonaceous species that accumulate on the catalyst. Changes in the XANES spectra similar to a slight oxidation have been reported between Pd and $\text{PdC}_{0.13}$ [16]. This behaviour is more prominent for the experiments performed at high temperature where the methane conversion is fairly high before the start of net-oxidizing step. When oxygen is added to the feed at 900 s, the combustion of the carbonaceous species results in an increased production of CO_2 at the start of the net-oxidizing period. The methane conversion increases after oxygen has been added to the feed, and the increase of the methane conversion is rapid for the experiments performed at higher temperature and with higher oxygen concentration. A temporary minimum in the methane conversion is observed in the beginning of the net-oxidizing period in all experiments. However, the profile of the

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