Operando XAS study of the influence of CO and NO on methane oxidation by Pd/Al$_2$O$_3$

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Abstract. Methane oxidation on Pd/Al$_2$O$_3$ has been investigated using operando X-ray absorption spectroscopy (XAS) at the Pd K-edge. The influence of CO and NO on methane abatement has been addressed performing temperature programmed reaction runs while recording simultaneously XANES spectra. During CO oxidation Pd is reduced while methane conversion is shifted to higher temperature. NO strongly inhibits both CO and CH$_4$ oxidation, despite the higher fraction of oxidized palladium.

1. Introduction
Natural gas vehicles are a clean alternative to gasoline and diesel engines. Despite the numerous advantages of natural gas, unburned methane (CH$_4$) is a potent greenhouse gas; therefore, catalytic after-treatment of the exhaust gases is necessary to reduce its emissions. Typically, Pd-based three-way catalysts (TWC) are employed [1]. The oxidation state of Pd is a key parameter in the abatement of CH$_4$ under lean and stoichiometric conditions [2]. X-ray absorption spectroscopy (XAS) is a powerful tool to probe the oxidation state of Pd under relevant reaction conditions. Despite the reported positive effect of pre-reduction that produced the most active catalyst [3], highly dispersed oxidized Pd has been identified as the most active phase at low temperatures [4, 5]. In the case of CH$_4$ oxidation over three-way catalysts (TWC), the presence of CO and NO can modify the oxidation state of Pd, thus strongly influencing its reactivity. Only few spectroscopic studies considered the influence of other pollutants on CH$_4$ abatement on Pd-based catalysts. For example under simulated operation conditions of a TWC, Pd remained reduced at high temperature irrespective of gas feed composition and thus oxygen concentration, unless heavy lean (O$_2$ excess) conditions were applied [6]. Pd$^0$ was reduced at ca. 400°C under stoichiometric conditions of a CH$_4$-CO-NO feed but the effect of each single pollutant on CH$_4$ abatement was not unveiled [7]. Here, we study CH$_4$ oxidation on Pd/Al$_2$O$_3$ by operando XAS and DRIFT spectroscopy with the aim to follow changes of Pd oxidation state during reaction as function of the presence of CO and NO in the feed.

2. Experimental
The sample (1.6% Pd/γ-Al$_2$O$_3$, 40 mg, 50-100 µm sieve fraction, kindly provided by Umicore) was placed in a homemade plug-flow reactor cell [8] equipped with two graphite windows and was subjected to temperature programmed reaction runs (TPRR) under various reaction conditions while collecting XAS spectra in transmission at the Pd K-edge (24.35 keV). The outlet of the cell was connected to a mass spectrometer and to an FT-IR spectrometer for gas analysis. Prior to all experiments the sample was subjected to in situ pretreatment under stoichiometric conditions...
conditions (0.25 vol% CH\textsubscript{4}/1 vol% CO/1 vol% O\textsubscript{2} at 350°C for 1 h, GHSV = 120'000 h\textsuperscript{-1}) in order to equilibrate the catalyst. X-ray absorption near edge spectra (XANES) were collected every 10°C in the middle of the catalyst bed during consecutive TPRR under stoichiometric (0.25 vol% CH\textsubscript{4}/1 vol% CO/1 vol% O\textsubscript{2} and 0.25 vol% CH\textsubscript{4}/0.5 vol% O\textsubscript{2}) and lean (0.25 vol% CH\textsubscript{4}/1 vol% O\textsubscript{2}) conditions at 2.5°C/min at the SuperXAS beamline of the SLS to investigate the influence of CO on CH\textsubscript{4} oxidation. XANES spectra (ca. 5 s/spectrum) were continuously collected during TPRR under stoichiometric conditions (0.25 vol% CH\textsubscript{4}/1 vol% CO/1 vol% O\textsubscript{2} and 0.25 vol% CH\textsubscript{4}/0.5 vol% NO/0.22 vol% CO/0.89 vol% O\textsubscript{2}) at 10°C/min at beamline ID24 of the ESRF to analyse the effect of the addition of NO. Linear combination fitting was performed to quantify the amount of Pd\textsuperscript{2+}; the spectrum of the fresh sample, and the spectrum at the end of the CH\textsubscript{4}/CO/O\textsubscript{2} TPRR, were used as references for Pd\textsuperscript{2+} and Pd\textsuperscript{0}, respectively. All spectra were analysed with the IFEFFIT software package [9]. An identical stoichiometric CH\textsubscript{4}/CO/O\textsubscript{2} TPRR (50-210°C, 10°C/min) was performed while collecting diffuse reflectance infrared spectra (DRIFTS) at 2 cm\textsuperscript{-1} resolution using the same reactor cell equipped with a CaF\textsubscript{2} window. The background spectrum was taken in Ar at 50°C before the pretreatment.

3. Results and discussion

3.1. CH\textsubscript{4} abatement

Fig. 1 shows the transmission XANES spectra collected during the CH\textsubscript{4}/O\textsubscript{2} TPRR in lean conditions. Initially, Pd is fully reduced. During the lean TPRR, the spectra exhibit a progressive increase in the edge energy and in the white line intensity with increasing reaction temperature that reflect the gradual oxidation of Pd. Fig. 2 displays the corresponding temperature evolution of the fraction of Pd\textsuperscript{2+} and the activity expressed in terms of CH\textsubscript{4} conversion. CH\textsubscript{4} conversion begins at about 230°C in presence of a mixed Pd/PdO phase (ca. 30% Pd\textsuperscript{2+}); the fraction of Pd\textsuperscript{2+} increases with the reaction progress but full oxidation is not attained when full CH\textsubscript{4} conversion is reached at ca. 430°C. In an identical experiment under stoichiometric conditions, the fraction of Pd\textsuperscript{2+} increases as well until about 380°C before Pd fully reduces as a consequence of the consumption of all available oxygen. PdO decomposition is a spontaneous thermodynamic process, which is strongly affected by the O\textsubscript{2} partial pressure [10]. The average oxidation state of Pd in stoichiometric conditions is lower than under lean conditions and CH\textsubscript{4} conversion occurs at higher temperature. The reaction mechanism for methane oxidation was found to be different for highly oxidized Pd nanoparticles [2, 11], possibly explaining the improvement in the catalytic activity in excess of O\textsubscript{2}. The levels of Pd\textsuperscript{2+} in both TPRR are different when CH\textsubscript{4} oxidation sets in and probably as a consequence the light-off is shifted to higher temperature in stoichiometric conditions.

3.2. Influence of CO

In presence of CO in the feed, the initial Pd\textsuperscript{2+} fraction is higher (ca. 30%) because the experiment was directly subsequent to the pre-treatment. The gradual oxidation of Pd observed in lean conditions is perturbed by an initial slow reduction to ca. 15% Pd\textsuperscript{2+} until 175°C. The quick partial re-oxidation to ca. 30% Pd\textsuperscript{2+} coincides with the sudden increase in CO conversion, which proceeds to completeness at ca. 220°C. The O\textsubscript{2} concentration decreases simultaneously.
to 50% when full CO conversion is reached in agreement with the stoichiometry of the CO oxidation reaction. An identical DRIFTS experiment (Fig. 3 a) demonstrates that the initial slow reduction is caused by CO adsorption on reduced Pd as monitored by the signal of CO bridged bonded to twofold metal sites (ca. 1986 cm$^{-1}$) [12]. Above 175°C the signal quickly vanishes concomitantly to the sudden but partial Pd re-oxidation. CO adsorption inhibits O$_2$ dissociation until the temperature is attained where the oxygen surface coverage is sufficient to boost CO oxidation. CO also inhibits methane oxidation because CH$_4$ conversion is retarded by ca. 20°C. Under these conditions, there is a higher fraction of Pd$^{2+}$ during CH$_4$ oxidation compared to the TPRR without CO, probably due to the lower CH$_4$ conversion and the consequent higher concentration of available oxygen. On the contrary, during the stoichiometric TPRR in presence of CO the same extent of Pd$^{2+}$ to the lean TPRR is attained. However, CH$_4$ oxidation is even more inhibited. Probably, both oxidation reactions can occur on similar sites, but the ease of coordination of CO to Pd favours CO oxidation even when CH$_4$ can be activated. CO does not affect the second reduction temperature (380°C) but induces full Pd reduction compared to the stoichiometric TPRR without CO.

**Figure 2.** Temperature profiles of (a) the fraction of Pd$^{2+}$ and (b) CH$_4$ (open symbols) and CO (full symbols) conversions under various reaction conditions at 2.5°C/min. CO$_2$ and H$_2$O were the only detected products.

**Figure 3.** (a) Fraction of Pd$^{2+}$ and DRIFT signal of adsorbed CO (ca. 1986 cm$^{-1}$). (b) Conversion of CH$_4$, CO, and NO and FTIR signals of gaseous N$_2$O and NO$_2$ under various reaction conditions at 10°C/min.

The evolution of Pd$^{2+}$ obtained during the CH$_4$/CO/O$_2$ TPRR at 10°C/min (Fig. 3) is very similar to that obtained at 2.5°C/min (Fig. 2). The extent of Pd re-oxidation during CH$_4$
conversion is lower when using a faster heating ramp but the temperature of Pd reduction is identical (175 and 380°C). Hence, we assume that the data obtained during CH$_4$/CO/O$_2$ TPRR are comparable despite the different temperature ramp.

3.3. Influence of NO
The influence of NO on CH$_4$ abatement is shown in Fig. 3. In the presence of NO, the initial Pd reduction is accompanied by the undesired NO reduction to N$_2$O. The onset of Pd re-oxidation after the low temperature reduction is shifted by ca. 10°C to higher temperature, which reflects the correspondingly later onset of CO oxidation. After attaining full CO conversion at ca. 220°C, the fraction of Pd$^{2+}$ increases gradually to a higher extent than in the absence of NO. This is concomitant to the development of NO$_2$ from the NO+O$_2$ reaction. CH$_4$ conversion is also shifted to higher temperature by ca. 40°C and sets in at ca. 280°C when the NO$_2$ concentration starts decreasing. Therefore, NO inhibits both CO and CH$_4$ oxidation reactions. The presence of NO$_2$ and the increased fraction of Pd$^{2+}$ are tentatively associated with the poorer performance in CH$_4$ oxidation. Finally, from ca. 350°C NO reduction produces N$_2$O and N$_2$ while Pd reduces to metal because of the lack of oxygen in the feed.

4. Conclusions
Methane oxidation on Pd/Al$_2$O$_3$ has been examined using operando XAS and DRIFT spectroscopy to correlate the oxidation state of palladium with its catalytic activity in the presence of CO and NO in the feed. The data indicate that a mixed Pd/PdO phase is present at the onset of methane oxidation irrespective of reaction conditions and that both CO and NO inhibit methane oxidation. In presence of CO, Pd is reduced until CO is fully oxidized, then Pd suddenly re-oxidizes before CH$_4$ oxidation can start. We ascribe the CO inhibition to the competition of CO and CH$_4$ oxidation reactions for similar if not identical reaction sites. In the case of NO, the inhibition of CH$_4$ oxidation is tentatively associated with the constantly higher oxidation state of Pd due to NO interaction with Pd.

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