Methane oxidation over a honeycomb Pd-only three-way catalyst under static and periodic operation

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This document is the accepted manuscript version of the following article:
Ferri, D., Elsener, M., & Kröcher, O. (2018). Methane oxidation over a honeycomb Pd-only three-way catalyst under static and periodic operation. *Applied Catalysis B: Environmental*, 220, 67-77.
<https://doi.org/10.1016/j.apcatb.2017.07.070>

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Abstract

Natural gas is receiving increasing awareness as fuel for passenger vehicles due to its very low specific CO₂ emissions. However, control of CH₄ emissions from natural gas combustion in stoichiometric engines requires a specific three-way catalyst (TWC). The understanding of the TWC chemistry of CH₄ under the periodic rich/lean reaction conditions is a key issue for targeted catalyst development. A commercial Pd-only TWC was tested under various reaction conditions to characterize the chemical processes and the mode of operation leading to efficient operation. It was demonstrated that periodic rich/lean operation obtained by variation of the mean O₂ concentration fed to the catalyst with various amplitudes is highly beneficial for CH₄ oxidation. Especially asymmetric oscillations into rich of stoichiometry produced higher CH₄ conversion. Compared to operation with gasoline fuel using propene as the model hydrocarbon, substantial differences were observed in static experiments that reflect the different chemistry at work with the two hydrocarbons. In particular, the stoichiometric point ($\lambda = 1$) did not coincide with maximum CH₄ oxidation, which was obtained rather under rich conditions. The shift of the optimum stoichiometric point was associated with the necessity to consume CO and O₂ before CH₄ can react. Spectroscopic characterization during reaction aimed at rationalizing the role of NO in isothermic experiments when varying stepwise the oxygen concentration from net oxidizing to net reducing reaction conditions. The overall results should provide recommendations for the design of TWC for natural gas operation and for control strategies to improve CH₄ emission levels.

Introduction

Natural gas plays a central role for the reduction of CO₂ road emissions, especially because of the growing importance of addition of bio-gas and synthetic natural gas to the existing distribution network. Vehicles fueled with natural gas and bio-gas are powered by either stoichiometric or lean burn engines depending on the size and purpose of the vehicle. Emissions of methane (CH₄), the major component of these fuels, remain a concern because of its global warming potential and are thus controlled efficiently by exploiting catalytic converters [1]. Three-way catalysts (TWC) represent the current technology in the case of the exhaust of natural gas passenger vehicles operating with stoichiometric engines [2, 3]. The catalyst composition is adapted from the gasoline TWC counterpart by additional platinum group metals (PGM), mostly palladium (Pd), in order to improve the efficiency of CH₄ oxidation, which is more difficult to activate than longer chain hydrocarbons representative of gasoline exhaust (propane, propene) [4]. A stoichiometric air-to-fuel ratio ($\lambda = 1$) is required for the TWC operation in order to remove simultaneously the three pollutants, CO, NO and hydrocarbons [5]. This type of operation is characterized by the point at which CO oxidation activity increases to full conversion and the NO reduction activity decreases simultaneously while moving towards lean conditions [6], the CO-NO crossover point [7]. Around this point, the conversion of the three pollutants is most efficient. It is known [7-10] that in the case of TWC for natural gas fuel this point does not correspond to stoichiometry ($\lambda = 1$) but is shifted into slightly rich of stoichiometry, essentially because of the low reactivity of CH₄. This practical observation reflects also the different chemistry of abatement of the exhaust pollutants between gasoline and natural gas. Despite the extensive knowledge on the chemistry of CH₄ oxidation on PGM based catalysts under lean conditions [11-17] that in the automotive sector pertains to lean burn engines of large vehicles, e.g. buses and trucks, a systematic investigation of the complex chemistry involved in CH₄ oxidation on TWC is

rare. On the one side, this knowledge is crucial for the design of catalysts specialized on the abatement of emissions from natural gas fueled engines in contrast to catalysts for gasoline operation. On the other side, the knowledge should also be used to develop catalyst control strategies tailored for operation with this fuel. While little information is available on the behaviour of simplified catalyst formulations, which are desirable in order to rationalize the involved chemistry, the majority of the studies in the open literature focused on the characterization of complex or even commercial TWC compositions. A rigorous derivation of the mutual effects of chemical and material components is difficult based on these premises. Subramanian et al. [10] were the first to subject a Pd/Al₂O₃ catalyst to various reaction environments with the aim to derive the essential chemistry of CH₄ oxidation on a TWC. Besides reporting higher CH₄ conversion under reducing conditions than under oxidizing conditions, critical observations revealed a substantial inhibition of CH₄ oxidation in the presence of CO under net oxidizing conditions. Moreover, CH₄ oxidation by NO was emphasized as a route for CH₄ removal under net reducing conditions, while steam reforming was considered negligible, in marked contrast to observations by others on commercial catalysts of complex composition [18, 19] and on Pt-Rh/CeO₂-Al₂O₃ [20]. The presence of the oxygen storage component (Ce) and of rhodium may contribute to explain the beneficial role of steam on CH₄ conversion. Additionally, NO reduction by hydrogen (NO+H₂) and by CH₄ (CH₄+NO) were identified at different temperature regimes [18, 20]. Hence, it is important to underline that the typical reaction responsible for NO reduction on gasoline TWC, i.e. CO+NO, does not contribute appreciably when CH₄ is the hydrocarbon. These data were obtained predominantly under static reaction conditions exploiting temperature programmed ramps in either rich or lean feeds and lambda sweeps, where the air-to-fuel equivalence ratio is varied stepwise at various temperatures. Bounechada et al. [19] analyzed this chemistry on a commercial Pd-Rh-Al-Ce catalyst under periodic rich/lean reaction

conditions that better mimic the operating conditions of the TWC. It was demonstrated that short rich pulses can sustain CH₄ oxidation at higher conversion levels than static experiments and that small amplitude oscillations of O₂ concentration around stoichiometry were more beneficial than large amplitude oscillations. Hence, these experimental conditions are favorable to CH₄ oxidation compared to either rich or lean conditions.

Here, we demonstrate the beneficial effects of the periodic operation of a Pd-only TWC for the abatement of CH₄ compared to steady state operation. We also attempt to show the influence of CO, NO and oxidation state of Pd on the CH₄ oxidation activity on a catalyst of reduced complexity and functionality (only one PGM).

Experimental

The catalyst used in this study was a full-size honeycomb Pd-only three-way catalyst (56.6 g/ft² Pd; 600 cpsi) kindly provided by Umicore containing Al, Ce, Zr and promoters in unknown ratios. Prior to use, the full-size monolith was degreened in static air at 600°C for 10 h.

Catalytic measurements

Monolith pieces of $2.3 \times 1.8 \times 1.2$ cm³ were cut from the full-size monolith and used for the catalytic measurements. The reactor was adapted from the one described previously for selective catalytic reduction of NO [21]. Gases were dosed by electronic mass flow controllers (Brooks), while water was provided through a water evaporator. The monolithic sample was wrapped with ceramic tape, inserted in a homemade steel support and placed in a quartz tube in which the inlet zone upstream the sample was filled with ceramic beads to preheat and mix the gas feed. The reactor was heated using three independent heating tapes while the temperature was read upstream and downstream the sample by two thermocouples

inserted in the middle of the quartz tube. All gas lines were of stainless steel and were heated to 170°C to avoid water condensation. The outlet of the reactor was interfaced to a FTIR spectrometer (Thermo Nicolet, gas cell 2 m heated to 180°C) to measure online the concentrations of CH₄, CO, NO, CO₂, H₂O, N₂O, NH₃ and a mass spectrometer (Pfeiffer Omnistar) equipped with a stainless steel capillary (d_i= 0.12 mm) heated to 180°C to monitor the concentrations of O₂ and H₂.

If not otherwise specified, the feed to the catalyst consisted of 1500 ppm CH₄, 1600 ppm NO, 7000 ppm CO and 5 vol% water (bal. N₂) representative of the exhaust of a natural gas vehicle and the catalyst load was GHSV= 75000 h⁻¹. According to the definition of λ [22], 5700 ppm O₂ were added to the continuous feed for stoichiometric dosage of oxygen, corresponding to nominal λ = 1. For the periodic oscillations, the mass flowmeters controlling the flowrates of oxygen and nitrogen were programmed to oscillate between given values as indicated. This together with the characteristic time of analysis of the residual gas products and the residence time of the reactor limits the pulse frequency that we can achieve to 5 s.

Conversion values of CH₄, CO and NO are provided as $X_i(\%) = 100 \times (C_{i0} - C_i) / C_{i0}$, where C_{i0} and C_i are the initial concentration of the i^{th} component in the feed (upstream of the catalyst) and its concentration downstream of the catalyst, respectively.

Spectroscopic measurements

Diffuse reflectance UV-vis (DRUV) and infrared Fourier transform (DRIFT) spectroscopy measurements were performed using the same gas feeding system described above for the catalytic measurements. For these measurements, the catalytic reactor was by-passed and the feed gas was directed either to the UV-vis spectrometer (Cary 4000, Agilent) or the FTIR spectrometer (Vertex 70, Bruker). The sample was cut from the full-size monolith and

crashed to fine powder before mounting in the diffuse reflectance reactor cell attached to a Praying Mantis mirror unit (Harrick) fitting both spectrometers.

DRUV and DRIFT spectra were collected at steady state at 350°C while decreasing stepwise the O₂ partial pressure in the CH₄-CO-H₂O and CH₄-NO-CO-H₂O feeds from 7000 ppm to 0 ppm. DRUV spectra were obtained between 400 and 800 nm. DRIFT spectra were acquired at 4 cm⁻¹ resolution between 4000 and 1000 cm⁻¹ by co-adding 50 interferograms. The background spectrum was obtained at 350°C prior to admittance of the reaction feed.

Results and Discussion

Temperature programmed reaction

Periodic rich/lean reaction conditions are beneficial for the efficiency of a three-way catalyst (TWC) [23] also for aftertreatment of natural gas vehicles [19] and represent realistic operation conditions. The effect of oscillating reaction conditions was verified on the Pd-only honeycomb catalyst and compared to steady state reaction conditions. Methane (CH₄) conversion in continuous stoichiometric feed representative of the exhaust gas of natural gas fueled engines proceeded as shown in **Figure 1**. Light-off occurred at ca. 350°C but CH₄ conversion was not complete even at 600°C and the maximum value was ca. 30%. Despite the impossibility to control the catalyst composition, meaning that possibly other catalysts could provide better performance, the data reveals the difficulty to remove CH₄ from exhaust gases under steady state stoichiometric conditions ($\lambda = 1$) questioning the suitability of this type of measurements for the evaluation of the TWC on a honeycomb catalyst. Full CH₄ conversion was observed at ca. 500°C under comparable feed composition on a model Pd-Al₂O₃-CeO₂-ZrO₂ TWC in powder form [24]. The limited CH₄ oxidation activity achieved with the present catalyst needs to be attributed to the vastly different conditions inherent to experimentation with honeycomb monolith and powder catalysts, e.g. the space velocity or

catalyst load. A significant negative hysteresis was observed in the cooling segment, CH₄ conversion being only ca. 5% at 450°C. This picture changed significantly when the concentration of oxygen in the feed was varied symmetrically around stoichiometry by ± 1000 ppm (i.e. between 4700 and 6700 ppm, 5700 ppm O₂ being the nominal stoichiometric point) with a pulse duration of 15 s during heating and 5 s during cooling between 200 to 650°C. This measurement simulated the periodic conditions that may be encountered during operation of the TWC under realistic conditions. The average conversion remained below 15% below 500°C while it increased steeply above 500°C reaching ca. 90% at 550°C, standing in marked contrast to the result obtained with the continuous stoichiometric feed. The temperature of 50% conversion of CH₄ (T₅₀) was ca. 510°C in the heating segment and ca. 410°C in the cooling segment indicative of a positive hysteresis, contrary to the temperature programmed reaction in continuous feed. The periodic variation of the O₂ concentration was responsible for the pronounced periodic variation of the CH₄ conversion when the temperature was raised.

NO conversion was negligible above 350°C in continuous feed while it followed essentially the behavior of CH₄ conversion during the periodic operation around stoichiometry in agreement with previous observations [20]. In particular, when CH₄ conversion started increasing at 500°C, NO conversion increased simultaneously reaching an average value higher than 70% above 550°C. In the cooling segment of the oscillating temperature programmed ramp, the same hysteresis observed for CH₄ recurred for NO, and NO conversion sharply dropped to below 30% at 350°C. Since short excursion into net reducing conditions was beneficial to CH₄ oxidation, the λ cycling experiment was repeated with a maximum λ value corresponding to stoichiometry (i.e. between 2700 and 5700 ppm O₂) and the average O₂ concentration in the feed gas under net reducing conditions. Hence, when the O₂ concentration was varied by ± 1500 ppm symmetrically around $\lambda = 0.992$ (corresponding to

a mean value of 4200 ppm O₂; every 5 s), T₅₀ further decreased significantly (370°C and 350°C in the heating and cooling segments, respectively), which was mirrored by the improved low temperature abatement of NO. The average NO conversion was ca. 40% until 350°C and increased to full conversion at 400°C. N₂O was produced below 350°C (max. 200 ppm) while NH₃ was detected above 400°C with a maximum of 430 ppm at ca. 500°C suggesting a possible change of NO reduction pathway (not shown) [18]. A positive hysteresis in CH₄ oxidation was observed also in the cooling segment but was accompanied by lower mean conversion between 600 and 350°C than in the heating segment. CO conversion was always complete in the temperature range 200-600°C except for a slight decrease in this latter experiment likely as a result of the large excursion into reducing conditions.

The data of **Figure 1** demonstrates clearly that CH₄ oxidation can be significantly improved upon variation of the feed concentration of oxygen repeatedly. This produces lower light-off temperatures and allows the attainment of higher CH₄ conversion at lower temperature. NO_x abatement proceeds parallel to CH₄ conversion confirming earlier observations indicating that the kinetics of NO reduction is controlled by that of the CH₄-O₂ reaction [8]. Moreover, oxygen pulsing under net rich conditions provided lower light-off temperatures of both pollutants.

Isothermic CH₄ oxidation

Based on the previous results, we studied CH₄ oxidation by varying stepwise the concentration of oxygen in the feed, because this parameter affected significantly the activity in a wide temperature regime. These measurements are essentially coinciding with measurements where the air-to-fuel ratio (or λ) is varied and the conversion of CH₄ and of the other pollutants is followed at selected temperatures. Therefore, besides CH₄, NO_x and CO

were also added to the feed to the catalyst in order to follow possible effects of the additional pollutants on CH₄ oxidation performance of the catalyst. Additionally, we carried out similar experiments where the mean O₂ concentration was decreased stepwise rather than the absolute O₂ concentration and the amplitude of the O₂ concentration was varied around selected values. The amplitude was kept constant while increasing the mean O₂ concentration value, and the measurements were repeated at various O₂ concentration amplitudes.

First, we compare the results obtained with CH₄ with those obtained using propene (C₃H₆) as the representative hydrocarbon residue of engine fueled by gasoline. The concentration of propene is typically lower than that of CH₄, while the other pollutants (CO and NO_x) can be considered within the same order of magnitude. The concentration of propene was selected on the base of C₁ equivalents.

Figure 2 demonstrates the results obtained at 425°C while decreasing the O₂ concentration in the feed in order to achieve the stepwise variation of λ . **Figure 2a** shows the data for propene. The concentration of propene was negligible along the whole range of O₂ concentrations that we explored in line with the ease of activation of this hydrocarbon [7]. The variation of NO_x and CO concentrations in **Figure 2a** is consistent with the typical description of the operation of a TWC [25]. The CO-NO crossover point lies clearly at stoichiometry (4950 ppm O₂ in the case of propene). As expected, NO conversion sharply decreased with increasing O₂ concentration above the value corresponding to stoichiometry, while CO concentration increased under increasingly rich conditions. **Figure 2a** also shows that NO concentration started decreasing when the O₂ concentration downstream the catalyst was nil. Non negligible amounts of ammonia (NH₃, maximum 1400 ppm) were detected under rich conditions simultaneous to the emission of hydrogen (1800 ppm). Hence, steam reforming of propene took place in net rich conditions and NO reduction (likely to NH₃) occurred through the

produced hydrogen. Nitrous oxide was also detected for higher O₂ concentrations than 4700 ppm indicating the non-selective reduction of NO slightly above the stoichiometric value.

Figure 2b clearly demonstrates that removal of CH₄ from the exhaust under the same experimental conditions was substantially different. CH₄ conversion at 425°C occurred between 500 and 3600 ppm O₂ with a maximum conversion level of ca. 60% at 3500 ppm O₂, which was very towards higher O₂ concentration. Then, it increased slowly up to less than 10% at 6000 ppm O₂. Contrary to propene, the window of CH₄ conversion was very narrow and conversion was low, in agreement with the difficulty to activate CH₄ compared to propene and propane [7].

The major difference between **Figure 2a** and **Figure 2b** is that the CO-NO crossover point in the case of CH₄ did not correspond to stoichiometry (in this case, 5700 ppm O₂) contrary to the case of propene but occurred at 3500 ppm O₂. We define the stoichiometry value necessary to remove CH₄ most efficiently as:

$$R_{O_2/nM} = C_{O_2} \times 2 / C_{CO} \quad \text{eq. 1}$$

where C_{O₂} and C_{CO} are the oxygen and carbon monoxide concentrations, respectively. R_{O₂/nM} corresponds to the stoichiometric factor often reported in the literature [26], with the exception that the concentrations of NO and of the hydrocarbon do not appear in eq. 1. Hence, R_{O₂/nM} considers CH₄ as an inert gas, while NO is not considered because it follows tightly the behavior of CH₄ (**Figure 2b**). Above this point (lean conditions) CH₄ concentration increased instantaneously while below this point (rich conditions) the increase of CH₄ concentration was smoother. It is clear from **Figure 2b** that CH₄ was removed efficiently from the gas feed in correspondence of the point where CO is completely oxidized in agreement with eq. 1. CO concentration was ca. 40 ppm at 3000 ppm O₂ and decreased below 5 ppm at 3600 ppm O₂. The remaining oxygen provided to the catalyst can then be used to oxidize CH₄. This behavior can be ascribed to the easier adsorption and reaction of

CO that cause inhibition of CH₄ oxidation [10] and confirms the impression that the two reactions occur on similar if not identical active sites [27].

Hydrogen was detected also in the case of CH₄. However, its concentration attained the highest value in correspondence of the maximum CH₄ conversion suggesting that steam reforming indeed contributed significantly to CH₄ oxidation under net rich conditions [18-20] also on the Pd-only TWC. Evolution of NH₃ mirrored the formation of H₂ confirming that reduction by H₂ is a crucial NO abatement pathway [18]. It is significant to note that in contrast to propene, no N₂O formation was detected around the point of maximum hydrocarbon conversion. From a practical perspective, **Figure 2** clearly demonstrates that the chemistry of abatement of the major pollutants (CO, NO and hydrocarbon) from stoichiometric engines fueled with gasoline and natural gas is very different. This implies that the TWC for natural gas operation needs to be developed independently.

Given the complex behavior of the catalyst in presence of all pollutants, we investigated the reciprocal effects of water and NO on the chemistry of CH₄ oxidation in more detail by performing experiments where the O₂ concentration was scanned stepwise between 3000 ppm and 0 ppm at constant feed concentration of 1500 ppm CH₄. This approach may appear redundant with other studies mentioned here, but it is justified by the fairly different catalyst composition and highlights again the need for systematic investigations on model catalysts of increasing complexity. We did not address specifically the influence of CO because of the clear inhibiting effect observed in **Figure 2b** and because of the parallel reactions CO can experience (e.g. water gas shift, WGS). Initially, the feed consisted only of CH₄ and O₂, hence demonstrating the effect of O₂ concentration on CH₄ oxidation. The experiment was repeated with 5 vol% H₂O added to the feed and finally once more with 1600 ppm NO added to the CH₄-O₂-H₂O feed (**Figure 3**). CH₄ conversion was 43% at 425°C when 3000 ppm O₂ were dosed (**Figure 3a**), in agreement with the fact that this point represents stoichiometric

conditions. When O_2 was dosed in sub-stoichiometric amounts, the production of H_2 confirmed that CH_4 oxidation by both oxygen and steam reforming are responsible for CH_4 removal under such conditions. Since water was not dosed in this experiment, CH_4 oxidation by oxygen is needed in order to produce the amount of water required for steam reforming. The increasingly reducing conditions inhibit CH_4 oxidation by oxygen and, as a consequence, also steam reforming vanished below 750 ppm O_2 because less and less water was available as probed by the decreasing H_2 concentration. The addition of water to the feed does not move the theoretical stoichiometric point (3000 ppm O_2) but according to these considerations it should improve CH_4 oxidation under rich conditions. **Figure 3b** demonstrates that CH_4 conversion was lower than in the absence of water until 1500 ppm O_2 likely because of the well-known inhibiting effect of water associated with the formation of Pd-OH species [28]. Steam reforming became important only below 1500 ppm O_2 and did not extinguish with decreasing O_2 concentration in contrast to **Figure 3a** because of the constant presence of water in the feed. In the presence of NO (**Figure 3c**) the stoichiometric point moves to 2200 ppm O_2 . CH_4 conversion changed from 13% under net lean conditions (3000 ppm O_2) to 5% in the absence of O_2 . NO conversion was negligible, but increased to 19% when the O_2 concentration was lowered to almost zero in agreement with the observations of **Figure 2b**. In this case, the NO conversion was accompanied by N_2O formation while no NH_3 was observed. The absence of NH_3 and of significant NO conversion may question whether CO contributes to NO abatement indirectly through WGS and production of H_2 when CO is present in the feed. NO could react with this H_2 rather than through the H_2 produced by CH_4 steam reforming. However, CH_4 conversion was so low in presence of NO that the inhibiting effect of NO could be responsible for poisoning the reaction pool. NO was found to compensate the inhibiting effect of water on Pd and PdPt catalysts under lean CH_4 oxidation conditions [29], while in the absence of water we found an

inhibiting effect of NO on a Pd/Al₂O₃ under simulated stoichiometric conditions [27]. The model experiments of **Figure 3** show that CH₄ oxidation activity decreased in the order of increasing feed complexity, CH₄+O₂ > CH₄+O₂+H₂O > CH₄+O₂+H₂O+NO. Hence, CH₄ oxidation by O₂ is inhibited by water, as it is already known, but at low O₂ concentrations steam reforming occurs while CH₄ oxidation by both O₂ and water is inhibited by NO.

Returning to the stepwise scan of O₂ concentration in the full exhaust mixture, the behavior of CH₄ at 350°C was qualitatively similar to that observed at 425°C except for the obvious lower levels of conversion (**Figure 4**). However, the CO-NO crossover point was shifted notably further to lower O₂ concentration (2700 ppm, **Figure 4a**) to a new point that we define as the stoichiometric factor R_{ox/nM},

$$R_{ox/nM} = (C_{O_2} \times 2 + C_{NO}) / C_{CO} \quad \text{eq. 2}$$

now taking into account all oxidants, including C_{NO}, the NO concentration [26]. At this temperature N₂O was produced (maximum 300 ppm) between 2700 and 3500 ppm O₂. The further shift of the CO-NO crossover point towards richer reaction conditions prompted us to repeat the same measurement in absence of NO and by decreasing stepwise the O₂ concentration from 6000 ppm to 0 ppm to investigate the role of NO under these conditions. **Figure 4b** shows that the concentration of CH₄ followed a similar behavior to that observed at 425°C and exhibited a minimum value at 3500 ppm O₂ (ca. 33% conversion) with an abrupt increase for O₂ concentration above 3500 ppm and a smooth change below this value. The minimum in CH₄ concentration coincided again with the full conversion of O₂ and CO. The value of O₂ concentration at which CH₄ was efficiently converted and corresponding to the CO-NO crossover point defined in eq. 1 (R_{O2/nM}) was identical to the value observed in presence of NO at 425°C. Hence, at lower temperature, NO appears responsible for the shift of the window of efficient removal of CH₄ to lower O₂ concentrations that forced us to include it in the R_{ox/nM} stoichiometric factor. At low temperature the total concentration of the

oxidizing agents becomes the limiting factor for CH₄ abatement. It should be noted that despite the shift of the stoichiometric factor, indicating that CH₄ removal is substantially more difficult, CH₄ conversion improved (ca. 47%) and broadened significantly into net rich conditions in presence of NO compared to the situation in absence of NO (ca. 33%) revealing a possible promoting effect of NO at low temperature. Upon careful inspection of the H₂ and NH₃ concentration values of Figure 4a and Figure 4b we speculate that CH₄ oxidation activity under reducing conditions in presence of NO is promoted by the removal of adsorbed hydrogen by NO from the catalyst. Nevertheless, the overall catalytic behaviour described in **Figures 2-4** suggests that CO, NO and the majority of oxygen need to be removed from the exhaust before CH₄ can react, thus reinforcing the opinion that CH₄ acts as an inert gas over a wide range of reaction conditions and that active sites for CH₄ oxidation need to be freed from competing reactions involving CO and NO.

Isothermic oscillating CH₄ oxidation

Based on the behavior observed in **Figure 1**, similar measurements to those shown above (**Figure 2b**) were repeated under periodic operation conditions. Hence, at fixed CO, NO and CH₄ concentrations, the mean O₂ concentration was decreased stepwise. The average O₂ concentration was the mean value obtained from pulses of increasing amplitudes. Experiments were repeated with O₂ dosages varying symmetrically between ± 1000 , ± 2000 and ± 3000 ppm O₂ every 5 s. This pulse frequency is the one that we can presently attain with the described setup. **Figure 5(b-d)** compare these experiments with that already shown in **Figure 2b** for no periodic operation that is reported in simplified form in **Figure 5a** (only CO, NO and CH₄ concentrations). Introduction of oscillations of ± 1000 ppm O₂ confirmed the beneficial effect of rich/lean periodic operation on CH₄ removal already observed in **Figure 1**. CH₄ concentration increased abruptly at 4200 ppm O₂ when moving towards larger

mean O₂ concentrations (**Figure 5b**). It remained constant at 600 ppm (60% conversion) between 4200 and 3500 ppm O₂ before increasing smoothly below 3500 ppm O₂. The abrupt change of CH₄ concentration at 4200 ppm O₂ coincided again with the CO-NO crossover point. Under these conditions, the hydrogen concentration (not shown) exhibited a peak maximum at R_{O₂/nM} (3500 ppm O₂) and the NH₃ concentration decreased steadily with increasing the mean O₂ concentration from 1000 to 4500 ppm O₂. Increasing the amplitude of the O₂ pulses to ± 2000 ppm (**Figure 5c**) further increased CH₄ conversion with a maximum of ca. 77% at 5000 ppm O₂ and stretched the window of CH₄ conversion into the rich regime. Finally, CH₄ conversion was improved to a value of ca. 87% over a broad window (5700 to 4500 ppm O₂) of operation when the amplitude was increased to ± 3000 ppm (**Figure 5d**). The highest value of O₂ concentration of this window reached the point corresponding to the conventional stoichiometry value ($\lambda = 1$, 5700 ppm O₂). These results are summarized in **Figure 6a** for the sake of clarity for CH₄ and NO conversions as functions of pulse amplitude at constant pulse frequency (5 s). CH₄ conversion increased from ca. 58% in steady state operation to around 90% with pulses of ± 3000 ppm amplitude. The most notable change was that the window of operation of the Pd-only TWC broadened significantly as a function of pulse amplitude indicating that compared to the very narrow window observed under steady state conditions (**Figure 2b**) [7] periodic operation could relax the optimal control conditions required to achieve efficient CH₄ abatement. N₂O was detected with a maximum concentration of 117 ppm at ± 3000 ppm O₂ that moved following the shift of the CO-NO crossover point towards the stoichiometry value, while NH₃ production vanished from between 2000 ppm and 5250 ppm O₂ without following significantly the shift of the CO-NO crossover point (not shown in **Figure 5**). Our results showing a relationship between oscillation amplitude and CH₄ conversion does not match totally with the results reported in the only work that to our knowledge dealt with rich/lean periodic operation of a TWC for

natural gas operation [19]. The discrepancy can be solved tentatively by considering the vastly different experimental conditions between that work, oscillations around stoichiometry, and this work, oscillations around moving O₂ concentration, but deserves certainly further consideration.

Despite the fact we have devoted less attention to this issue, **Figure 6b** demonstrates that the pulse frequency had far less influence on CH₄ abatement than the pulse amplitude in the case of ± 1000 ppm O₂ pulses in agreement with previous observations [30]. In fact, CH₄ conversion decreased significantly with increasing pulse frequency. Moreover, despite its broadening from steady state operation to periodic operation, the window of O₂ concentration corresponding to optimal CH₄ abatement remained constant irrespective of pulse frequency. N₂O (not shown) was detected between 4000 and 5000 ppm O₂ (maximum ca. 80 ppm at 5 s pulses) while NH₃ decreased steadily between 3000 and 5000 ppm O₂ from a maximum of 760 ppm in the pulse experiment with 60 s pulses.

Figure 6 clearly demonstrates that the optimum CH₄ oxidation activity moved from the value of R_{o2/nM} to that corresponding to stoichiometry with increasing pulse amplitude. It also shows once more the intimate correlation between CH₄ oxidation and NO reduction activities. Finally, it also suggests that high CH₄ abatement efficiency can be achieved by careful control of the rich/lean sequence.

Spectroscopy study

It is recognized that the oxidation state of Pd plays a key role in the chemistry of CH₄ oxidation on PGM based catalysts [11]. The linear scan of the O₂ concentration in static experiments and especially, the continuous rich/lean variation of the feed to the TWC in pulsed experiments can provoke a change of oxidation state that is responsible for the observed reactions under net reducing and net oxidizing conditions. Therefore, operando

diffuse reflectance UV-Vis (DRUV) and infrared (DRIFTS) spectroscopies were used to monitor the Pd oxidation state and the adsorbate speciation of the Pd-based catalyst, respectively while measuring the gaseous products by FTIR spectroscopy as described in the case of the catalytic reactor tests. Measurements were performed in a single cell directly attached to the gas setup used to feed the monolithic sample in order to ensure identical feed conditions to the reactor study. The O₂ concentration was decreased continuously from 7000 to 0 ppm at 350°C in order to work at a suitable temperature for infrared observation thus avoiding the influence of emission of infrared radiation from the sample at higher temperatures. Additionally, in order to evaluate the effect of NO on CH₄ conversion from a chemical perspective, the O₂ concentration sweeps were carried out in presence and in absence of NO in the feed. Hence, the experiments are equivalent to those shown in **Figure 4**. **Figure 7** shows the DRUV spectra obtained under these experimental conditions. Despite the absence of any defined feature, a clear change occurred in the wide range of 450-800 nm while decreasing the O₂ concentration in the feed irrespective of NO. This change was likely caused by variations of the plasmonic resonance of palladium particles [31, 32] and we assign it to the oxidation state variation imposed by the PdO/Pd equilibrium under the specific environmental conditions applied during the experiment. We cannot exclude a significant contribution of Ce⁴⁺/Ce³⁺ to the spectral changes, but the optical absorption edge of ceria and Ce-Zr solid solutions occurs typically below 450 nm [33]. The color change of the sample from brown to grey witnessed the spectroscopic observation of the change of oxidation state when moving from the high to the low O₂ concentration regime (insets of **Figure 7**), respectively. It is evident from the two series of spectra that the variation of this spectral region followed different kinetics depending on the presence of NO. In the absence of NO, an abrupt change occurred between 3250 and 3000 ppm O₂ (**Figure 7a**) while the change was

smoother and occurred over a wider concentration regime (6000 and 1000 ppm O₂) when NO was present in the feed (**Figure 7b**).

If we turn our attention to CH₄ conversion in these experiments, the result of this exercise was comparable to the catalytic data obtained at 350°C (**Figure 4**). The largest value of CH₄ conversion in the absence of NO occurred at 3500 ppm O₂ and extended towards lower O₂ concentrations (ca. 2000 ppm O₂; **Figure 8a**). This value corresponds again to $R_{O_2/nM} = 1$ as in the case of the catalytic activity of the monolithic catalyst shown above and reflects the need of consuming O₂ prior to the onset of conversion of CH₄. The course of CH₄ conversion in **Figure 8a** is further compared with the O₂ concentration dependence of the point at 650 nm in the DRUV spectra taken as the descriptor of the change of Pd oxidation state in **Figure 8b**. While decreasing the O₂ concentration in the absence of NO, CH₄ conversion changed from below 10% to ca. 35% at 3500 ppm O₂, when the intensity of the 650 nm point was low and thus the catalyst still largely oxidized as obvious from **Figure 8b**. The abrupt change of oxidation state (**Figure 8b**) occurred immediately after the maximum of CH₄ conversion. In the presence of NO, the highest value of CH₄ conversion shifted from 3500 ppm O₂ to 2750 ppm O₂ (**Figure 8a**) and coincided with the stoichiometric factor $R_{ox/nM}$ and with complete conversion of NO and O₂. The window of O₂ concentration corresponding to optimum CH₄ conversion remained broad and extended to ca. 500 ppm O₂ but the increase of activity from below 5% to more than 40% coincided with a gradual change of the oxidation state monitored by DRUV spectroscopy (**Figure 7b**) in marked contrast to the case without NO in the feed. Hence, the shift of the maximum CH₄ conversion towards richer reaction conditions in the presence of NO coincided approximately with the point where the signal at 650 nm had almost reached the maximum of its ascent. It is clear that a close link exists between the catalytic parameters, e.g. CH₄ conversion and the CO-NO crossover point (**Figure 8a**), and the change of oxidation state delivered by DRUV (**Figure 8b**).

The spectral region 2250-1250 cm^{-1} of the DRIFT spectra collected during identical measurements is shown in **Figure 9a** and **Figure 9b** for the NO free and NO containing feeds, respectively. Some observations are common to the two experiments irrespective of NO. The spectra obtained at 7000 ppm O_2 were dominated by signals between 1700 and 1300 cm^{-1} that can be attributed to adsorbed carbonate species (1514, 1415 and 1340 cm^{-1} , Table 1) [34]. Decreasing the O_2 concentration caused a gradual increase of the carbonate coverage. The fraction of carbonates increased significantly and suddenly below 3250 ppm O_2 in absence of NO and more gradually at 2000-1000 ppm O_2 in presence of NO. This increase of surface coverage was accompanied by new signals at 1585 and 1376 cm^{-1} , which together with those at 2907, 2838 cm^{-1} (not shown, Table 1) are indicative of adsorption of formate species [35]. The origin of this species is likely to be found in the reducing conditions under which they formed and in the presence of Ce in the catalyst composition that promotes WGS and steam reforming reactions. Finally, a signal extending between 2050 and 1800 cm^{-1} became increasingly visible, which was readily assigned to adsorbed CO on metallic Pd [36], together with the gas phase signature of unreacted CO (2200-2050 cm^{-1}). While no other specific feature characterized the spectra in absence of NO, the presence of NO in the feed at 7000 ppm O_2 produced additional signals at 1545 and 1482 cm^{-1} that we assign to adsorbed nitrates in various configurations [37-39]. While decreasing O_2 concentration these species disappeared in the spectrum obtained at 2750 ppm O_2 , which corresponds to the transition from the low to the high CH_4 conversion regime in **Figure 8a**. Hence, CH_4 conversion becomes possible when NO has been consumed (**Figure 4**) and the catalyst surface is free from NO-adsorbed species. This observation confirms our previous conclusion that NO inhibits CH_4 oxidation through formation of adsorbed species [27]. Sadokhina et al. [29] assigned the inhibiting effect of NO in dry conditions to competition for active sites, while in

the presence of water (similar to the conditions used in the present work) NO mitigated the water deactivation effect upon formation of HNO_2 species.

All IR spectral changes were accompanied in both situations by strong baseline variations that were comparable to those observed for the signal at 650 nm in the DRUV spectra. Taking the point at 2500 cm^{-1} as a descriptor of the baseline change, a point where no absorption is expected, the evolution of the baseline as a consequence of O_2 variation is shown in **Figure 8b**. The baseline changed abruptly between 3500 and 3250 ppm O_2 in the absence of NO thus mirroring the change of oxidation state fingerprinted by the DRUV signal at 650 nm. Therefore, for analogy with the DRUV data we attribute these baseline changes to the change of oxidation state of Pd also in the case of the DRIFT experiments [40]. Moreover, the smooth change of both signals at 2500 cm^{-1} and at 650 nm can be correlated to the gradual consumption of nitrate species on the catalyst surface. Hence, in a catalytic system that apparently requires a significant portion of the PGM to be reduced because CH_4 abatement is most efficient under net reducing conditions, we may observe that nitrate species, e.g. more in general NO, maintain Pd oxidized [27]. This shifts the optimal point of CH_4 conversion to even richer conditions, where CH_4 oxidation by remaining O_2 and water becomes favored by the presence of reduced Pd.

We conclude by speculating on the situation the catalyst may experience under periodic rich/lean oscillations. The continuous change between rich and lean conditions on the one hand repeatedly changes the oxidation state of Pd between reduced and oxidized [41, 42], the extent of oxidation and reduction depending plausibly on the extent of amplitude of O_2 concentration variation. On the other hand, it also guarantees that the conditions of oxidation state and speciation of the catalyst surface do not incur in one of the two extremes, either rich or lean conditions, over an extended period of time.

Conclusions

A honeycomb Pd-only three-way catalyst was subjected to various experimental conditions under both static and periodic operation in order to study the chemistry at work responsible for CH₄ oxidation. Despite the possibility that the observed behavior may be unique to the selected catalyst sample, the following points appear clear:

- the TWC demonstrated significant CH₄ oxidation activity only under periodic rich/lean reaction conditions and NO conversion essentially followed that of CH₄;
- the point of optimal CH₄ conversion did not correspond to the nominal stoichiometric point ($\lambda = 1$) but was placed under net reducing conditions; this was clearly demonstrated by comparison with operation using propene as representative hydrocarbon of gasoline that satisfied the conventional stoichiometric point;
- CO inhibited CH₄ oxidation: this was demonstrated by the fact that the new stoichiometric point of optimal CH₄ conversion coincided with the complete removal of CO;
- CH₄ oxidation occurred likely via steam reforming under net reducing conditions;
- water inhibited CH₄ oxidation both under net reducing and net oxidizing conditions;
- NO was reduced most likely by the H₂ produced by steam reforming and water gas shift rather than by CO;
- NO shifted the point of optimal CH₄ conversion into net reducing conditions but also increased the overall CH₄ oxidation activity;
- NO inhibition under net oxidizing conditions was most likely induced by formation of nitrate species that were identified by operando infrared spectroscopy;
- under oscillating rich/lean reaction conditions, CH₄ oxidation was significantly enhanced and the amplitude of the oscillations appeared more crucial than their frequency;
- operando spectroscopy also identified the transition from oxidized Pd to metallic Pd when passing from net oxidizing to net reducing conditions, which coincided with the point of

optimal CH₄ conversion; the transition was abrupt in the absence of NO while it was smooth in the presence of NO as a result of the persistence of oxidized Pd in the presence of NO.

The observation that the very same catalyst did not perform well in CH₄ oxidation under static conditions compared to periodic rich/lean conditions and that the amplitude of rich/lean oscillations significantly affected CH₄ oxidation activity hold important implications for the development of suitable catalysts and control strategies for optimal abatement of CH₄ from vehicles fueled with natural gas.

Acknowledgments

A. Marberger is kindly acknowledged for support with the spectroscopic measurements. This work was conducted in the framework of the Swiss Competence Center for Energy Research (SCCER) BIOSWEET program.

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Figure captions

Figure 1. CO (black), NO (blue) and CH₄ (red) conversions obtained from ascending and descending linear temperature ramps (a) in continuous stoichiometric feed, (b) in oscillating feed with symmetric O₂ pulses of 1000 ppm around stoichiometry (corresponding to mean 5700 ppm O₂) and (c) in oscillating feed with symmetric O₂ pulses of 1500 ppm around $\lambda=0.992$ (corresponding to mean 4200 ppm O₂). The dark lines within the conversion profiles of CH₄ represent the mean conversion. Arrows indicate direction of ramp segment.

Figure 2. Concentrations of CO, NO, C₃H₆, CH₄, O₂, H₂, NH₃ and N₂O after catalyst at 425°C in continuous feed of (a) 7000 ppm CO, 1600 ppm NO, 500 ppm C₃H₆ (equivalent to 1500 ppm C₁), 5 vol% H₂O and (b) 7000 ppm CO, 1600 ppm NO, 1500 ppm CH₄, 5 vol% H₂O while decreasing the O₂ concentration from 7000 to 0 ppm. The vertical dash lines mark the position for stoichiometry (see text for details).

Figure 3. Concentrations of CH₄, O₂, H₂, NO and N₂O after catalyst at 425°C in continuous feed of (a) 1500 ppm CH₄, (b) 1500 ppm CH₄, 5 vol% H₂O and (c) 1500 ppm CH₄, 1600 ppm NO, 5 vol% H₂O while decreasing the O₂ concentration from 3000 ppm to nil. The real H₂ concentration in (b) is twice that displayed.

Figure 4. Concentrations of CO, NO, CH₄ and O₂ after catalyst at 350°C in continuous feed of (a) 7000 ppm CO, 1500 ppm CH₄, 1600 ppm NO, 5 vol% H₂O and (b) 7000 ppm CO, 1500 ppm CH₄, 5 vol% H₂O while decreasing the O₂ concentration from 6000 ppm to nil. The vertical dash lines mark the position of $R_{O_2/nM}=1$, $R_{ox/nM}=1$ and $\lambda=1$ (see text for details).

Figure 5. Concentrations of CO, NO, CH₄ and O₂ after catalyst at 425°C in (a) continuous feed of 7000 ppm CO, 1600 ppm NO, 1500 ppm CH₄, 5 vol% H₂O while decreasing the O₂ concentration from 7000 ppm to nil, and in oscillating feed with symmetric O₂ pulses of (b) 1000 ppm, (c) 2000 ppm and (d) 3000 ppm while decreasing the mean O₂ concentration. Pulse duration was 5 s. The vertical dash lines mark the position of $R_{O_2/nM} = 1$ (see text for details).

Figure 6. (a) Amplitude and (b) frequency dependent CH₄ and NO conversions corresponding to the data of Figure 5. (□) Continuous feed of 7000 ppm CO, 1600 ppm NO, 1500 ppm CH₄; oscillating feed with symmetric O₂ pulses of (○) ± 1000 ppm, (△) ± 2000 ppm and (◇) ± 3000 ppm. The vertical dash lines mark the positions of $R_{O_2/nM} = 1$ and $\lambda = 1$ (see text for details).

Figure 7. Operando DRUV spectra obtained in continuous feed of 7000 ppm CO, 1500 ppm CH₄ while decreasing the O₂ concentration from 7000 ppm to nil (bottom to top) at 350°C (a) in the absence and (b) in the presence of 1600 ppm NO. The two images on the bottom and on the top represent the sample in the spectroscopy cell under the feed containing 7000 ppm and 0 ppm O₂, respectively.

Figure 8. (a) CH₄ conversion in continuous feed of 7000 ppm CO, 1500 ppm CH₄ at 350°C while decreasing the O₂ concentration from 7000 ppm to nil (□) in the presence and (○) in the absence of 1600 ppm NO. (b) Evolution of the signal (solid line) at 650 nm in the DRUV data and (dash line) at 2501 cm⁻¹ in the DRIFTS data while decreasing the O₂ concentration

from 7000 ppm to nil. The vertical dash lines mark the position of $R_{\text{ox/nM}} = 1$, $R_{\text{O}_2/\text{nM}} = 1$ and $\lambda = 1$ (see text for details).

Figure 9. Operando DRIFT spectra obtained in continuous feed of 7000 ppm CO, 1500 ppm CH₄ while decreasing the O₂ concentration from 7000 ppm to nil (top to bottom) at 350°C (a) in the absence and (b) in the presence of 1600 ppm NO.

Table 1

Assignment of the vibrational modes of species observed in the DRIFT experiments of Figure 9.

wavenumber (cm ⁻¹)	species	vibrational mode ^a	ref.
1955+1909	Pd-CO	$\nu(\text{CO})$	36
1585+1376	bridged formates ^b	$\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$	35
1514, 1415 and 1340	various carbonate species	$\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$	34
1545 and 1482	various nitrate species	$\nu_{\text{as}}(\text{ONO})$ and $\nu_{\text{s}}(\text{ONO})$	37-39

^a ν , stretching; ν_{as} : asymmetric stretching; ν_{s} , symmetric stretching; δ , deformation mode.

^b Beside $\nu_{\text{as}}(\text{OCO})+\delta(\text{C-H})$ and $\nu(\text{C-H})$ modes at 2907 and 2838 cm⁻¹, respectively, not shown in Figure 9.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9