In situ Activation of Bimetallic Pd–Pt Methane Oxidation Catalysts

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This study investigates possible pathways to reduce water inhibition over Pd–Pt methane oxidation catalysts supported on alumina and a ceria-zirconia mixed oxide under conditions typical for lean burn gas engines. Spatially resolved concentration and temperature profiles reveal that addition of hydrogen to the lean reaction mixture leads to significant heat production and an increase in methane conversion. Moreover, reductive pulses during operation are not only able to regenerate the catalyst deactivated by water by removal of OH- groups from the catalyst surface, but even promote its activity after repeated application of pulsing for several hours. X-ray absorption spectroscopy reveals the formation of a partially reduced PdO–Pd mixture during the pulsing, which explains the increase in activity. This state of high activity is stable for several hours under the tested lean conditions. The results presented in this study suggest an efficient in situ activation strategy to overcome water inhibition of methane total oxidation over Pd–Pt catalysts by careful process control.

Introduction

Natural gas engines may increasingly replace diesel and gasoline engines due to the ubiquity of natural gas as fuel and the lower CO₂ and particulate matter emissions resulting from natural gas combustion. Unfortunately, a small amount of methane always remains after combustion. As CH₄ is a much more potent greenhouse gas than CO₂, this CH₄ slip – as much as several hundred ppm depending on the vehicle operation – may become a significant obstacle to the widespread use of natural gas as a transportation fuel.[1] Therefore, an efficient after-treatment system must be able to abate this remaining methane. This is a challenge for both, lean combustion and stoichiometric combustion; in the case of the latter the Three-Way Catalyst (TWC) is largely ineffective.[2]

The typical lean-burn engine exhaust has several challenging obstacles for effective catalytic methane oxidation. The engine exhaust stream is highly lean (up to approximately 10% O₂), contains significant amounts of water (up to 12–15 vol.%), contains SOₓ (fuel source dependent) and has only moderate temperatures (typically below 500°C).[3] Supported platinum group metals (PGM) are the favored active catalytic components for the treatment of methane under these conditions, with Pd-based catalysts showing the highest activity.[4,5] Under lean conditions, the active state of Pd is believed to be PdO, although there is an ongoing debate as to whether other phases of Pd or a combination of phases could be more active.[6–17] In addition to PGM loading, the catalytic activity is affected by the catalyst support, metal dispersion, gas environment and even operating history.[18–23] Bimetallic catalysts, wherein a small amount of Pd is replaced with Pt, have been found to be more active, more hydrothermally stable and sintering resistant, and possess somewhat higher sulfur resistance compared to monometallic Pd catalysts.[24–31] Furthermore, research by Epling and Hoflund has shown that mixtures of Pd⁰ and PdO are more cataclysmically active than pure PdO, presumably due to facilitated CH₄ dissociation on metallic Pd.[32] Recent work by Chin et al. shows that the site pair Pd-PdO is effective for CH₄ dissociation to CH₃ and OH.[33]

Despite the improved performance from the addition of Pt, inhibition from water vapor and sulfur compounds still pose significant challenges. Water vapor inhibits catalytic activity through competitive adsorption with methane as well as deactivation through formation and accumulation of surface hydroxyl species.[34–37]

Previous research has shown that brief reductive periods during lean operation of Pd-based catalysts can not only regenerate catalysts deactivated by water or sulfur compounds, but can also stabilize their catalytic performance above what it would otherwise be.[18,22,38,39] Similarly, Petrov et al. applied periodic rich phases to continuously regenerate a Pd/zeolite catalyst for lean methane oxidation.[40] In the context of methane abatement in the exhaust of a natural gas engine by a TWC, Bounechada et al. similarly found that periodic rich pulses could recover catalytic activity lost due to water inhibition and that periodic oscillations resulted in higher and more stable catalytic methane conversion over a Pd/Rh-based TWC.[41]
Despite some references to the beneficial effects of reductive regenerative periods on Pd-based methane oxidation catalysts that have been deactivated by water in a lean environment,\textsuperscript{[36,40,42]} to our knowledge there has been no substantial systematic investigation on the potential effects and underlying mechanisms by which reductive pulses can benefit lean methane oxidation.

Starting from a broad data set of systematic fundamental experiments, this study presents a method for \textit{in situ} activation of Pd--Pt/Al\textsubscript{2}O\textsubscript{3} and Pd--Pt/CeO\textsubscript{2}--ZrO\textsubscript{2}--Y\textsubscript{2}O\textsubscript{3}--La\textsubscript{2}O\textsubscript{3} (in the following referred to as Pd--Pt/CZ) methane oxidation catalysts under different temperatures and gas compositions. Specifically, periodic reductive pulses of hydrogen are demonstrated to result in two distinct effects dependent upon the operating conditions. Further knowledge of the processes on the catalysts were gained by spatial profiling of the gas species concentrations to an unusual convex curve when 5 % H\textsubscript{2} is added to the feed (B) has a well-known significant inhibitory effect on the catalytic activity,\textsuperscript{[9,37,43]} increasing \( T_{50} \) by \( \sim 100 \) °C and the complete conversion temperature to \( \sim 550 \) °C. This is a result of surface hydroxylation formation on top and at the periphery of the noble metal particles, possibly in the form of Pd(OH)\textsubscript{2}.\textsuperscript{[44]} These hydroxylated sites are considered catalytically inactive.\textsuperscript{[36,37]}

Addition of 1 % H\textsubscript{2} to the feed promotes CH\textsubscript{4} oxidation. The conversion obtained with the feed containing H\textsubscript{2} (curve C) has a \( T_{50} \) of 325 °C and a complete conversion temperature of 380 °C. Note that at lower temperatures (<300 °C) the feed with H\textsubscript{2} has a slightly lower CH\textsubscript{4} conversion. This may be a result of inhibition by the water generated from H\textsubscript{2} oxidation, resulting in blockage of active sites. When H\textsubscript{2}O and H\textsubscript{2} are present (D), \( T_{50} \) decreased by 60 °C from that of the wet feed without H\textsubscript{2} (B). This is attributed to a temperature increase from the exothermic H\textsubscript{2} oxidation. The same general trends were also observed for the Pd--Pt/Al\textsubscript{2}O\textsubscript{3} catalyst (Figure 1b). For this catalyst, the addition of H\textsubscript{2} results in a \( T_{50} \) 35 °C lower compared to dry conditions and 45 °C lower under wet conditions.

To examine the impact of H\textsubscript{2} in more detail, light-off experiments for different concentrations of H\textsubscript{2} in the presence of water were conducted. The dry feed with 1 % H\textsubscript{2} is provided for comparison (Figure 2). The general trend is a shift of the light-off curves to the left with the addition of H\textsubscript{2}. It is interesting to note the rather insensitive dependence of the CH\textsubscript{4} conversion on H\textsubscript{2} concentration between 0.2 % and 2 % for the wet feed. However, by 5 % the light-off curve shifts sharply to lower temperature. This nonlinear dependence of the CH\textsubscript{4} conversion on the H\textsubscript{2} concentration is caused by competition between the beneficial impact of heat generation and the detrimental impact of hydroxyl formation. Moreover, there is a shift from the typical sigmoidal shape at low H\textsubscript{2} feed concentrations to an unusual convex curve when 5 % H\textsubscript{2} are

**Results and Discussion**

**Light-off trends at varying feed composition.** Figure 1 compares the light-off curves for Pd--Pt/CZ (Figure 1a) and Pd--Pt/Al\textsubscript{2}O\textsubscript{3} (Figure 1b) in feeds with different combinations of H\textsubscript{2}O and H\textsubscript{2}.

![Figure 1](image1.png)

Figure 1. Light-off curves of a) Pd--Pt/CZ and b) Pd--Pt/Al\textsubscript{2}O\textsubscript{3} in 10 % O\textsubscript{2}, 2000 ppm CH\textsubscript{4}, and bal Ar (A), A plus 12 % H\textsubscript{2}O (B), A plus 1 % H\textsubscript{2} (C), and A plus 12 % H\textsubscript{2}O and 1 % H\textsubscript{2} (D).

![Figure 2](image2.png)

Figure 2. Light-off curves of Pd--Pt/CZ in 10 % O\textsubscript{2}, 2000 ppm CH\textsubscript{4}, bal. Ar, and (if wet) 12 % H\textsubscript{2}O under increasing concentrations of H\textsubscript{2}.

after oxidative pretreatment (1 h in 10 % O\textsubscript{2} bal. Ar at 550 °C). For the Pd--Pt/CZ catalyst under baseline operating conditions (A) \( \sim \) no H\textsubscript{2}O or H\textsubscript{2} in the feed -- the light-off temperature is \( \sim 360 \) °C and complete CH\textsubscript{4} conversion is achieved at 450 °C. The addition of water to the feed (B) has a well-known significant inhibitory effect on the catalytic activity,\textsuperscript{[9,37,43]} increasing \( T_{50} \) by \( \sim 100 \) °C and the complete conversion temperature to \( \sim 550 \) °C. This is a result of surface hydroxylation formation on top and at the periphery of the noble metal particles, possibly in the form of Pd(OH)\textsubscript{2}.\textsuperscript{[44]} These hydroxylated sites are considered catalytically inactive.\textsuperscript{[36,37]}

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added. This conveys the much lower activation energy for H₂ oxidation compared to CH₄ oxidation.

Spatially resolved species concentration and temperature profiles (so-called spatial profiling, hereinafter mentioned as SpaciPro) provide further insight. Figure 3 shows the concentration measurements along the catalyst. When O₂ is present, CH₄ is completely oxidized to CO₂ and no CO was detected during these experiments. SpaciPro measurements under steady state conditions consistently suggest that only minor amounts of H₂ reach the front heat shield (FHS, used to minimize temperature gradients) zone or the catalyst itself. Similar behavior was observed for the Pd–Pt/CZ catalyst. In one light-off experiment, the capillary connected to the mass spectrometer (MS) was placed in-between the FHS and the catalyst. According to the MS data, 94% of the H₂ reacted with oxygen before it reached the catalyst; as the temperature increased this value approached 99%. The remaining H₂ was quickly converted to water upon contact with the catalysts.

This behavior is attributed to a combination of effects. With its small size, H₂ is able to back-diffuse against the convective current, which can potentially lead to apparent pre-catalyst consumption due to mixing. In addition, the MS settings could cause a reaction of H₂ with O₂ inside the ionization chamber, which may result in misleading high H₂ conversion. Thus, it is likely that H₂ reaches the catalyst but cannot be detected due to experimental hurdles. As H₂ oxidation is a highly exothermic reaction, the temperature profiles discussed later clarify this open question and confirm that H₂ in fact is converted at the catalyst inlet.

The presence of H₂ affects the catalyst during both pretreatment and operation. Discussed in more detail in the following section, spatial temperature measurements during transient operation show a significant temperature rise as a result of the exothermic oxidation of H₂. This in turn leads to an increase in CH₄ oxidation rate. That the relationship between H₂ feed concentration and CH₄ oxidation light-off is nonlinear underscores contributions from the reaction exothermicity and the aforementioned sensitivity to H₂O.

The enhancement in light-off behavior due to the reductive pretreatments may be ascribed to separate interactions between H₂ and the support and Pd complexes. Bazo et al. showed that CZ plays an active role in CH₄ oxidation, augmenting the supply of oxygen. Reductive pretreatments of H₂ were shown to create surface oxygen vacancies in the CZ, allowing electron transfer to the Pd and resulting in higher catalytic activity. Xiong et al. and Mahara et al. reported that reductive treatments of PdO complexes resulted in the formation of metastable PdO–Pd⁰ domains which are more active for CH₄ oxidation.

**Effect of pulses: continuous O₂ stream while pulsing H₂**

The catalysts were exposed to pulses of H₂, with all other gases kept constant, for the duration of the SpaciPro measurements. Figure 4 shows the CH₄ conversion and effluent temperature for Pd–Pt/CZ under steady-state operation and during H₂ pulses for dry and wet conditions.

For a dry feed, introduction of 1% H₂ results in an initial decrease in conversion due to the H₂O generation and its subsequent adsorption. For a wet feed, the additional water generated by the H₂ oxidation has little effect. As discussed above in the context of Figure 3, most of the H₂ appeared to be converted before reaching the catalyst during steady-state operation. The MS data suggest a similar behavior during H₂ pulsing experiments. SpaciPro temperature probes show the temperature at the front of the catalyst by 85 °C higher during the 1% H₂ pulse, regardless of initial catalyst temperature or the absence/presence of water. The measured temperature rise, evident in Figure 5, points to the fact that most of the H₂ reaches the monolith, in contrast to the concentration profile obtained from evaluation of the SpaciPro data. The temperature increase during H₂ pulsing leads to a cycle average increase in the CH₄ conversion under 2% and 3% H₂ pulses, and no net change for the 1% pulses. In all cases, the H₂ pulsing is unable to prevent the long-term decline in the CH₄ conversion over several hours.

The temporal profiles of CH₄ conversion and effluent temperature during 30 s/180 s H₂ pulsing over Pd–Pt/CZ at three different H₂ feed concentrations reveal an initial conversion decrease of ~15–20% during the 30 s H₂ pulse followed by a sharp 30–40% increase just after the pulse (Figure S7). The CH₄ conversion decrease encountered during the H₂ pulse is attributed to the nearly instantaneous inhibition of CH₄ oxidation by H₂O produced from H₂ oxidation. Afterwards, the effluent temperature increases during the 180 s H₂-off period, attributed to the heat generated by the exothermic H₂ oxidation.
oxidation propagating down the catalyst. Effluent temperatures (Figure 5) reach a maximum 40 s after the end of the H₂ pulse, consistent with the effluent temperature profiles in Figure S7b.

As previously stated, spatial temperature profiles for the 1 % and 2 % H₂ feed concentrations explain the effects of H₂ pulsing. The initial temperature profile (time = 0 s, before H₂ pulse initiation) shows that the temperature increases along the monolith length due to the incomplete conversion of CH₄. Over the next 30 s the pulsed H₂ oxidizes and results in a dramatic temperature increase at the front of the monolith. A maximum temperature rise of ~85 °C is observed for the 1 % H₂ pulse while a ~155 °C increase is encountered when pulsing 2 % H₂. After the H₂ pulse ends, the heat diffuses down the catalyst. The heat from H₂ oxidation remains well after the produced H₂O, resulting in the temporary boost to CH₄ oxidation. With respect to the experimental data shown in Figure 3b, the temporal temperature increase around the catalyst inlet (Figure 5) that originates form the high exothermicity of the H₂ oxidation clearly indicates that H₂ actually reaches the catalyst and is not consumed before.

**Effect of pulses: switching between O₂ and H₂ streams.** Alternating between O₂ and H₂ pulses has a dramatic effect on catalytic performance. Figure 6 shows the CH₄ conversion for Pd–Pt/CZ over a period of about 4 h during lean-rich (O₂/H₂) pulsing. Figures 6a and 6b correspond to a dry feed carried out at 295 °C and 315 °C, respectively. The experiments demonstrate the sustained CH₄ conversion achieved with the H₂/O₂ pulsing, in contrast to the gradual conversion decline over the same period for the H₂ pulsing in a constant 10 % O₂ (Figure 4). At 290 °C (Figure 6a) the conversion is sustained at ~5–22 % from its ~30 % initial level while at 315 °C (Figure 6b) the conversion is sustained at ~5–70 % from its ~60 % initial level.

Under wet conditions, H₂/O₂ pulses result in sustained, boosted catalyst activity. At 400 °C (Figure 6c) the conversion is sustained at ~30–70 % from its ~40 % initial level while at 430 °C (Figure 6b) the conversion is sustained at ~70–95 % from
its ~60% initial level. Similar results were obtained for Pd–Pt/Al₂O₃ (Figure S8).

Spatially resolved temperature profiles shown in Figure 7 for the 315°C dry feed experiment reveal temperature changes along the catalyst bed consistent with the slowing and accelerating of the CH₄ oxidation reaction. Between 0 s and 30 s, H₂ is admitted while between 31 s and 210 s O₂ is admitted. During the H₂ feed the temperature drops due to the lack of O₂. Upon the admission of O₂ heating of the entire catalyst is observed. Unlike in the case of H₂ pulses in a constant O₂ flow for which a significant hot spot was observed in the front region, the temperature profile during H₂/O₂ pulses are much more gradual and have the same shape as the initial temperature profile.

A more detailed look at the CH₄ conversion and effluent monolith temperature for the 315°C dry-feed and 400°C wet-feed experiments (Figure S9) reveals additional information. For the dry feed experiment the initial decrease in conversion is likely due to the rapid consumption of H₂ by stored O₂. This results in the generation of water and the rapid inhibition of CH₄ oxidation by surface hydroxyls. An even larger drop in performance quickly follows this initial decrease as gaseous O₂ is fully removed from the system and CH₄ conversion ceases. At the end of the H₂ pulse and the start of the O₂ pulse, the CH₄ conversion returns to a value slightly higher than that at the start of the cycle. Over many cycles, this slight increase in activity can result in substantial reactivation of the catalyst. More complex behavior is seen in the experiments conducted in the presence of water (Figure S9b). A brief spike in CH₄ conversion is observed when the feed is switched from lean to rich. This is followed by a steep drop in conversion as the available oxygen is consumed. Finally, as oxygen reenters the system, the conversion overshoots its value at the start of the cycle before rapidly deactivating in the lean phase.

Experiments carried out over a range of conditions indicated that the first pulse typically resulted in the largest change in the CH₄ conversion. The ultimate change depends on the initial state of the catalyst. For example, in Figure 8a, for a dry feed at 290°C the H₂ pulse led to a sharp decrease from an initial conversion of 30% to just ~3%. Subsequent H₂/O₂ pulsing did not restore the conversion, with conversion ranging from 3–25% and a cycle-average value of 21%. Under wet conditions, the first pulse significantly raised CH₄ conversion. At 400°C, the conversion rose from an initial value of 30% to 75% and an ultimate cycle-average value of 57% (Figure 6c). At 430°C, the conversion jumped from 55% to 98% and a cycle-average value of 96% (Figure 6d). Again, these conversions were sustained for several hours as the catalyst remained under lean/rich switching.
Carbon monoxide was observed during wet experiments (Figure S10), particularly over the Pd–Pt/Al₂O₃ catalyst. The formation of CO occurred only when the H₂ stream was engaged. CO concentration increased with increasing temperature; at 430 °C nearly 130 ppm of CO was produced during the switching pulse by the Pd–Pt/Al₂O₃ catalyst. The Pd–Pt/C catalyst produced only 30 ppm of CO under identical experimental conditions. Under dry conditions, CO formation was below 10 ppm if its formation was observed at all. While under highly lean conditions (10% O₂) the dominating process is the total oxidation of methane to carbon dioxide [Eq. (4)], CO formation is likely the result of steam reformation between the water and methane [Eq. (5)]:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2
\]

(5)

The improvement in CH₄ oxidation performance by applying rich pulses is long-lasting and persists between experiments and after numerous pretreatments. For illustration of this observation, the catalyst was exposed to the dry conditions of the experiment in Figure 6b. After an initial decrease in the conversion to 50%, a gradual increase in conversion was observed over a several hour period of pulsing (2000 ppm CH₄, bal. Ar with 30 s/180 s of 1% H₂/10% O₂ at 315 °C). Steady state operation on the following day resulted in 15% higher initial CH₄ conversion compared to the previous day’s experiment. Furthermore, it took several hours before the deactivation seen during the prior day was reached. Initial steady-state SpaciPro measurements and light-off curves showed CH₄ conversion of 20% over the Pd–Pt/CZ catalyst at 315 °C. After several experiments with O₂/H₂ switching pulses, a CH₄ conversion as high as 80% was observed.

Figure 8a shows the light off-curve of a fresh Pd–Pt/CZ catalyst and subsequent light-off curves after varying durations of H₂/O₂ switching pulses, while Figure 8b shows the behavior of the Pd–Pt/Al₂O₃ catalyst after four hours of pulsing. After 10 hours of H₂/O₂ pulsing, the Pd–Pt/CZ catalyst has experienced a 30 °C shift of the T₉₀ to 330 °C. The Pd–Pt/Al₂O₃ catalyst shows an even more pronounced shift in the T₉₀ from 350 °C to 270 °C, as well as the development of a non-monotonic light-off curve. This effect has been demonstrated with H₂/O₂ pulses as short as 10 s and separated by lean-phases as long as 600 s, suggesting that the pulse duration, quantity of H₂ involved and pulse separation time can be optimized for a maximal CH₄ oxidation activity.

Our results suggest that PdO particle size/dispersion and temperature effects play a minor role and cannot explain the enhanced CH₄ oxidation in the experiments described before. Transmission electron microscopy (TEM) measurements of Pd–Pt/CZ and Pd–Pt/Al₂O₃ reveal no significant change in PGM dispersion between freshly prepared samples and samples that experienced H₂/O₂ pulsing (30 s/180 s) for 4 h at 315 °C for either catalyst (Figures S3–S5). These findings are similar to results of Mahara et al. Reduction of PdO/Al₂O₃ below 415 °C does not affect the particle size of PdO. The previously discussed spatial-temperature measurements of H₂/O₂ pulses (Figure 7) do not show the large exothermicity responsible for

For the dry feed, the only source of H₂O is the oxidation of CH₄, so the surface coverage with hydroxyls is low. The admission of H₂ leads to a large increase in the hydroxyl coverage as a result of reactions [Eq. (2)] and [Eq. (3)], which increase the H₂O concentration by H₂ oxidation, leading to the formation of hydroxyls via [Eq. (1)]. For a wet feed the already high H₂O feed concentration results in a large fraction of the surface occupied by hydroxyls. The admission of H₂ shifts the equilibrium of [Eq. (1)] to the left through the consumption of PdO in [Eq. (2)], which is more effective at higher temperature.

The difference in behavior between wet and dry conditions can be explained by two competing factors. The first is the catalysts sensitivity to water. For a dry feed, the H₂O resulting from the reductive H₂ pulse inhibits CH₄ oxidation over PdO. At higher temperature the H₂ pulse is more effective in removing surface hydroxyls. The processes on the catalyst can be summarized considering the following four reactions [Eqs. (1–4)]:

\[
PdO + H_2O \rightarrow Pd(OH)_2
\]

(1)

\[
PdO + H_2 \rightarrow Pd + H_2O
\]

(2)

\[
H_2 + \frac{1}{2} O_2 \rightarrow H_2O
\]

(3)

\[
CH_4 + 2 O_2 \rightarrow 2 H_2O + CO_2
\]

(4)
the \( \text{H}_2 \) pulsing and steady-state effects (Figure 8). Hence, we attribute the enhanced \( \text{CH}_4 \) oxidation seen during \( \text{H}_2/\text{O}_2 \) switching results to the contributions of several, simultaneous, independent effects occurring during the reductive treatment; namely: (i) removal of accumulated hydroxyl species; (ii) formation of metastable PdO–Pd complexes; (iii) creation of oxygen vacancies in the catalyst supported on CZ. These are described next.

The inhibitory effects of hydroxyl surface species accumulation have already been discussed; removal of these species can be clearly concluded from the SpaciPro results during the \( \text{H}_2/\text{O}_2 \) pulse experiments. \( \text{H}_2 \) is observed to decrease in concentration along the length of both catalysts concurrent with the release of \( \text{H}_2\text{O} \) from the catalyst. Removal of these hydroxyl species also explains the observed brief boost in \( \text{CH}_4 \) conversion under wet conditions at 400 °C (Figure 59). By keeping water from the catalyst surface, the catalyst can briefly take advantage of the higher temperatures before \( \text{O}_2 \) completely leaves the system. That the catalysts do not lose activity over several hours under \( \text{H}_2/\text{O}_2 \) pulsing conditions implies that the rate at which \( \text{H}_2 \) removes the OH species is far faster than they can accumulate.

The second effect concerns the active metal Pd. Both Mahara et al. and Xiong et al. found that reductive conditions partially reduce PdO complexes into metastable PdO–Pd structures that were reported to show higher catalytic activity than pure PdO.\(^5\,\text{[46]}\) Xiong et al. went further and showed distinct regions of PdO and Pd on the same particle in high resolution TEM images.\(^5\) Although we cannot see this in our TEM images, XAS spectra of Pd–Pt/CZ and Pd–Pt/AlO\(_x\) samples which were pretreated by \( \text{H}_2/\text{O}_2 \) pulsing reveal reduced Pd coexisting with PdO (Figure 9). These samples were pulsed for four hours at 315 °C and were exposed to oxidizing conditions for over a minute before being cooled in Ar to room temperature. To determine the amount of metallic Pd and PdO before and after the pulse treatment, a linear combination fitting (LCF) of the Pd and PdO reference spectra was performed in the range of -20 to 30 eV around the Pd K-edge. The results obtained show that the fresh samples are fully oxidized after preparation. After pulsing, however, the fraction of metallic Pd is ~55% on Pd–Pt/AlO\(_x\), while the fraction of Pd is only ~14% on Pd–Pt/CZ. Additionally, TEM revealed more pronounced alloying between the Pd and Pt on the AlO\(_x\) support than on the CZ support (Figure S3). This is true not only in the fresh state, but also after \( \text{H}_2/\text{O}_2 \) pulsing (Figure S4) and is consistent with the findings of Xiong et al. who found that the Pt helped maintain the reduced state of Pd under oxidizing conditions.\(^5\) We attribute the decrease in the light-off temperature of these catalysts predominantly to this effect. Furthermore, we attribute the larger improvements over the Pd–Pt/AlO\(_x\) catalyst, as seen in Figure 8, to the increased amount of metallic Pd in combination with pronounced alloying between Pd and Pt. Apparently the activity can be maximized by the right Pd/PdO ratio, especially if promoted or at least stabilized by Pt. According to the found PdO/Pd ratios we can speculate, that \( \text{CH}_4 \) oxidation still takes place according to a Mars-van-Krevelen mechanism on PdO as frequently claimed.\(^5\,\text{[46]}\) The presence of metallic Pd may destabilize the Pd–O bond, which could ultimately result in a significant increase of the catalytic activity.

The final of the three effects concerns the Pd–Pt/CZ catalyst but not the Pd–Pt/AlO\(_x\) catalyst. The reductive pulses of \( \text{H}_2 \) result in oxygen vacancies on reducible the ceria-zirconia support. Bozo et al. found that the CZ support played an active role in \( \text{CH}_4 \) oxidation for a Pd/CZ catalyst.\(^20\) In the absence of gas phase oxygen, lattice oxygen was easily removed and the subsequent vacancies promoted electron transfer from the support to the Pd as well as increased lability and mobility of further lattice oxygen atoms. Hence, we can assume a similar behavior for our catalyst sample for two reasons. First, the \( \text{H}_2 \) pulses utilized in this experiment are much more reductive than the \( \text{CH}_4 \) pulses utilized by Bozo et al.\(^20\) in their studies; second, SpaciPro results during pulsing revealed the release of \( \text{H}_2\text{O} \) during the reductive pulse. However, in the current study we are unable to distinguish what percentage of those released species are surface hydroxyl species and which are the result of reactions with the lattice oxygen. For this, further investigations

![Figure 9. XANES spectra of a) Pd–Pt/AlO\(_x\) and b) Pd–Pt/CZ, both in fresh state and after 4 h of \( \text{H}_2/\text{O}_2 \) pulsing at 315 °C and the references Pd and PdO.](image-url)
are needed, including more advanced methods such as isotopically labelled experiments. Finally, we believe that these CZ support effects explain why Pd–Pt/Al₂O₃ exhibits a higher degree of metallic Pd and subsequent increased CH₄ oxidation activity. The increased mobility of lattice oxygen of the CZ support allows either the easy reoxidation of metallic Pd to PdO or hinders the reduction of PdO to metallic Pd in the first place when compared to a support such as Al₂O₃.

Effect of pulses: O₂ pulses. A single experiment was carried out at 315 °C wherein H₂ was shut-down completely and O₂ was pulsed over the catalyst. Under these dry conditions, CH₄ became a reducing agent for 30 s. Figure 10 shows the long-term pulse behavior of the Pd–Pt/CZ catalyst during these pulses. Under O₂ pulses, CH₄ oxidation was stabilized between 85% and 30%. While these bounds remained constant through the pulses, sharper activity changes were observed as O₂ turned on and off – catalytic activity decreased faster during the reductive CH₄ pulse and rose higher when gaseous O₂ returned as the experiment progressed. This activity was balanced out by a sharp increase in activity – similar to the spike seen under wet H₂/O₂ pulsing at 400 °C (Figure 5b) – that decreased as time went on. This experiment suggests that the strength of H₂ as a reductive agent plays a role at least in the low temperature range in the improvements seen during H₂/O₂ pulsing experiments, but that some benefits can be obtained from weaker reducing agents or simply shutting off O₂ periodically.

Conclusions

While in the lively debate concerning the active phase of Pd during methane oxidation a consensus has formed around PdO as the active phase under typical lean conditions, recent research has suggested that some amounts of metallic Pd might possibly boost catalytic activity. Our research joins the latter corpus of work and suggests a process controlled increase in methane oxidation activity. In situ pulses of H₂ reversed catalytic deactivation of bimetallic Pd–Pt methane oxidation catalysts and maintained high activity over several hours that persisted into future experiments. The presence of H₂O resulted in a much higher methane oxidation activity during the rich pulse while methane activity dropped to zero under dry conditions. XAS revealed exclusively PdO on fresh samples, while a combination of metallic Pd and PdO was found for samples after pulsing. This suggests that a metastable PdO–Pd structure is the predominant cause behind the increased activity of pulsed catalysts, either due to an enhanced activity via the Mars-van-Krevelen mechanism or because the formed Pd–PdO species is less prone to water poisoning. Moreover, pulse-induced removal of surface hydroxyl species and the formation of lattice oxygen vacancies contribute to the increased activity. Pd–Pt/Al₂O₃ had a higher concentration of alloyed Pd–Pt and a higher percentage of metallic Pd after pulsing, resulting in a larger shift in light-off temperature compared to pulsed Pd–Pt/CZ samples.

The effects of H₂ were also dependent upon the gas environment of the catalyst. In the presence of constant O₂ flow, pulses of additional H₂ reacted over the Pd to form H₂O, resulting in a high temperature region at the front of the catalyst. Under dry conditions, the inhibition due to the H₂O negated the improvements from the increased temperature. Under wet conditions modest improvements were observed as the catalyst was already saturated. Under steady-state conditions, however, the raised catalytic temperature promoted the activity, resulting in light-off curves significantly shifted to lower temperatures.

Experiments varying the pulse durations of H₂/O₂ switching revealed that the beneficial effects could still be obtained with shorter reductive pulses and longer oxidative periods. An experiment with O₂ on/off pulsing showed that CH₄ could stabilize catalytic activity to a lesser degree than H₂ pulsing accomplished. Future experiments concerning the strength of different reductive agents as well as the duration and frequency of reductive pulses could result in an optimized method for maintaining high methane oxidation under wet conditions at low operating temperatures, which is a key step in making natural gas processes sustainable and competitive.

Experimental Section

Powder catalyst samples were prepared by incipient wetness impregnation of Al₂O₃ or CeO₂-ZrO₂-Y₂O₃-La₂O₃ using tetraammine-platinum(II)nitrate and tetraamminepalladium(II)nitrate as precursors. After coating cordierite substrates with the received powder, the monolith samples were tested under model exhaust gas conditions in a quartz glass tubular reactor. For spatially resolved experiments the setup could be equipped with a movable thin thermocouple or a thin capillary connected to a mass spectrometer (HPR-20, Hiden Analytical) placed within one of the monolith’s middle channels. For all experiments, also during spatially resolved experiments, the end-of-pipe gas composition was analyzed with an MG2030 FTIR (MKS). TEM data were obtained at the LEM (KIT, Germany) using an FEI OSIRIS ChemiSTEM microscope and Pd K-edge XAS data were obtained in transmission mode at the ROCK beamline (SOLEIL, France). Comprehensive experimental details are provided in the Supporting Information.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords: methane oxidation · palladium · emission control · heterogeneous catalysis · spatial resolution technique

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