Influence of CO on Dry CH₄ Oxidation on Pd/Al₂O₃ by Operando Spectroscopy: A Multitechnique Modulated Excitation Study

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Abstract

Carbon monoxide (CO) is a major pollutant present in automotive exhaust gases, including stoichiometric engines fuelled on natural gas. In this work, the inhibiting role of CO on the chemistry responsible for the abatement of methane (CH₄) is studied on a Pd/Al₂O₃ catalyst using a multitechnique approach combined with modulated excitation and mass spectrometry to obtain operando conditions. Identical modulation experiments were carried out with X-ray diffraction, X-ray absorption, diffuse reflectance infrared spectroscopy by pulsing alternately CH₄ and O₂ or CH₄+CO and O₂ at 320°C in the absence of steam. During the O₂ pulse, re-oxidation of metallic Pd was observed to occur in two steps that are associated with the initial formation of a surface layer followed by crystalline PdO. The time-resolved study allowed to show that reduction is faster than oxidation and that it is promoted by the presence of CO. Beside determining the redox properties of the catalyst under these conditions, the presence of hydrides and Pd carbide-like species could be followed by exploiting phase sensitive detection and its power to enhance subtle changes in the spectroscopy and diffraction data. While at the beginning of the reduction pulse CO₂ was produced from reaction of CH₄ with PdO, CH₄ decomposition occurred on reduced Pd within the reduction pulse. In the presence of CO, CH₄ oxidation at the beginning of the reduction pulse was significantly limited by reaction of CO with PdO and by blockage of the accessible Pd surface by CO adsorption.

Keywords: Pd/Al₂O₃; CH₄ oxidation; XRD; EXAFS; DRIFTS; modulated excitation

1. Introduction

Transportation fuels containing predominantly methane (CH_4) such as natural gas, biogas and their blends are increasingly promoted as a clean alternative to gasoline and diesel in both light and heavy duty vehicles in order to reduce urban air pollution, and ultimately our dependence on imported oil.¹⁻² Beside the numerous advantages of natural gas, on-road nitrogen oxides emissions from passenger vehicles have been shown to be abundantly below the 168 mg/km target of autumn 2019.³ However, CH_4 is a potent greenhouse gas,⁴⁻⁵ thus requiring the control of the emissions of unburned CH_4 by suitable catalytic after-treatment technologies. Currently, palladium (Pd) based three-way catalysts (TWC) are used in stoichiometric engines of passenger vehicles. This metal is considered the most efficient for CH_4 oxidation under lean conditions^{4, 6} and while a large degree of understanding has been achieved for CH_4 oxidation by oxygen, CH_4 abatement on TWC in a gas mixture representative of exhaust gases from natural gas vehicles is comparatively less studied.⁷⁻¹² In particular, only few studies have addressed the influence of other major pollutants, e.g. CO and NO, despite their presence in exhaust gas streams and their probable influence on the reactivity of the catalyst. To the best of our knowledge, the only study that explicitly considered the effect of CO¹³ on methane abatement on a TWC showed an inhibition of CH_4 oxidation under net oxidizing conditions, because of changes in the Pd-oxygen interaction or competitive chemisorption in the presence of CO. Another aspect of the presence of CO is that it does not contribute appreciably to reduction of NO contrary to the typical behavior of TWC for gasoline applications.¹⁴ At low temperature, only CO oxidation by O_2 and NO reduction by H_2 were observed on a commercial TWC.¹⁴ CH_4 was shown to react with NO at high temperatures, while also the steam reforming reaction was found to be relevant for CH_4 abatement. The simultaneous oxidation of CO and CH_4 in oxygen excess was investigated on Pt/CeO₂.¹⁵ In the

presence of CH₄, CO conversion shifted to higher temperatures suggesting the blockage of the Pt active sites by CH₄ dissociation products that cannot be oxidized at low temperature. From the perspective of CH₄ oxidation, the reverse hysteresis, i.e. extinction at higher temperature than ignition, originated likely from the oxidation of Pt, since reduced Pt is more active for CH₄ oxidation. In a previous study, we have addressed the influence of CO and NO on CH₄ oxidation on Pd/Al₂O₃ under simulated TWC exhaust gas conditions by combining temperature programmed reaction with operando X-ray absorption spectroscopy (XAS) and diffuse reflectance infrared Fourier transform infrared (DRIFT) spectroscopy.¹⁶ We observed inhibition by CO, which was manifested in the shift of the CH₄ conversion to higher temperature and which we ascribed to the competition of both CO and CH₄ oxidation reactions for similar if not identical reaction sites. Recently, we have also shown that CO causes the shift of the optimal air-to-fuel ratio (λ) value for CH₄ oxidation towards rich of stoichiometry compared to gasoline operation, where λ corresponds typically to 1.¹⁷ This suggests a strong inhibition of CH₄ oxidation by CO.¹⁸

The operation of a TWC around stoichiometry is a crucial aspect, which is often simulated in fundamental level studies by exploiting repeated redox pulses.¹⁹⁻²⁰ In general, experimentation under periodic operation attempts at mimicking real working conditions of the catalyst and can provide insight into kinetics and mechanisms beyond that achievable with steady state measurements.²¹ This type of periodic operation also stabilizes the catalytic performance and improves the conversion of unburned CH₄.^{10-11, 18} The presence of a mixed PdO/Pd⁰ oxidation state in the Pd catalyst was used to explain the enhancement of the catalytic performance.¹⁰ Pulsing between O₂ and H₂ was found to be beneficial for CH₄ conversion over Pt catalysts, whereas lean conditions were advantageous for Pd/Al₂O₃.²²⁻²³ Oxidation of Pd was shown to occur in two steps²⁴⁻²⁵ and maximum CH₄ oxidation activity was obtained only after reaching full Pd

oxidation.²⁶ The reversible reduction/oxidation of Pd was probed by rich/lean cycling of oxygen in a constant CH₄ flow on Pd catalysts.²⁷⁻²⁸ The addition of Ce greatly enhanced CH₄ conversion due to the redox properties of ceria.²⁷⁻²⁸ A transient CH₄ conversion enhancement was also observed in correspondence of every change of feed composition on LaFe_{0.95}Pd_{0.05}O₃ that was attributed to the fraction of Pd emerging on the LaFeO₃ surface under reducing conditions at 500°C and re-entering the LaFeO₃ structure under oxidizing conditions.²⁹ Hence, substantial efforts have been undertaken to study CH₄ oxidation on TWC under transient conditions using spectroscopic methods, but the influence of CO, present in real gas fueled cars exhaust streams, has not been considered so far.

In this work, we study the influence of CO on the chemistry of CH₄ abatement on Pd/Al₂O₃ under cycling conditions consisting of alternate pulses of CH₄ or CH₄+CO and O₂, in order to address the elementary steps involved in CH₄ oxidation. Operando time-resolved X-ray diffraction and XAS were combined to correlate the changes in the oxidation state and structure of Pd with its activity measured online by mass spectrometry, while DRIFT spectroscopy was employed to follow the evolution of the adsorbates. Where required, phase sensitive detection was exploited to enhance sensitivity to subtle structural changes not accessible directly from time-resolved data.

2. Material and methods

2.1 Sample and characterization

The catalyst investigated in this work, 1.4 wt% Pd/ γ -Al₂O₃ (Pd content measured by inductively coupled plasma optical emission spectrometry, ICP-OES) was kindly provided by Umicore and was calcined in air at 500°C for 4 h. Nitrogen adsorption-desorption was performed at -196°C on a Quantachrome Autosorb 1C instrument. The specific surface area (SSA) was

determined using the Brunauer–Emmett–Teller (BET) model. Prior to the measurement, the sample was outgassed in vacuum at 200°C for 90 min. The microstructure of the calcined and pretreated (section 2.3) Pd/Al₂O₃ was imaged using a Jeol 2200FS transmission electron microscope equipped with a 200 kV field emission gun. The samples were prepared by evaporation of an alcohol suspension on a copper grid (coated with a carbon film). Phase contrast images were obtained in scanning mode with a high-angle annular dark field detector (HAADF-STEM). The particle size distribution was obtained by measuring 108 and 214 particles of the calcined and pretreated sample, respectively.

2.2 Experimental set-up

Approximately 50 mg of the powder catalyst (50-100 µm sieved fraction) were placed into a home-made reactor cell³⁰⁻³¹ between two plugs of quartz wool. A K-type thermocouple (d= 0.5 mm) was inserted at the inlet of the catalyst bed to monitor the sample temperature continuously. The reactor cell was equipped with either a CaF₂ or a graphite window for the experiments with infrared or X-ray radiation, respectively. The cell enables the repetition of identical experiments under exactly the same conditions using different spectroscopy/diffraction techniques as detailed below. The gas manifold consisted of mass flow controllers (Bronkhorst) while two solenoid valves (Parker) permitted the rapid switch of the gas feed to the reactor cell. Stainless steel 1/16" tubing was used after the switching valves in order to minimize the dead volume. The outlet of the cell was connected to a mass spectrometer (Pfeiffer Vacuum OmniStar GSD 320) for online residual gas analysis.

2.3 Experimental procedure

Prior to the experiments the catalyst was subjected to in situ pretreatment under stoichiometric feed conditions consisting of 0.25 vol% CH₄/1 vol% CO/1 vol% O₂ (balance Ar). After heating the catalyst from room temperature to 350°C at 10°C/min, the temperature was held at 350°C for 1 h and then diminished to 320°C without changing feed.

The CH₄/O₂ modulation experiment at 320°C consisted of the periodic admittance of 0.25 vol% CH₄ and 1 vol% O₂ to the reactor cell for an equal time of 60 s. Time-resolved spectra or diffraction patterns were collected continuously during these repeated pulses. A full modulation period (T=120 s) is defined as the time required to conclude a full CH₄ vs O₂ sequence. The experiment started with a series of dummy periods to allow the system to reach equilibrium under the applied pulses, which were then followed by actual data acquisition. The data collected over several modulation periods were averaged in order to improve the signal to noise ratio. CO (1 vol%) was added to the reduction pulse (hereafter labelled CH₄+CO/O₂ modulation experiment) in order to study the influence of CO on CH₄ oxidation. Ar and He were the carrier gases for the DRIFT/XAS and XRD experiments, respectively. The total flow rate was set to 100 mL/min, corresponding to a gas hour space velocity (GHSV) of 120'000 h⁻¹. All measurements were carried out in dry conditions.

2.3.1 X-ray diffraction (XRD)

XRD measurements were carried out at beamline ID11 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Diffraction data were collected at 69.525 keV with a Frelon camera (ca. 100 mm x 100 mm, 2048 x 2048 pixels) installed at ca. 273 mm from the sample position. During a full modulation period, 106 XRD patterns were collected at a frequency of 1 Hz, with an exposure time of 1 s (detector readout time ca. 0.13 s, time resolution ca. 1.13

s/pattern). A H₂/O₂ modulation experiment was also performed for the sake of comparison using 1 vol% H₂/He in the reduction pulse. Time-resolved data were processed by phase sensitive detection (PSD)³² exploiting the demodulation frequency $k\omega$, with $k=1$ and $k=2$, the latter being more suitable for treating diffraction data.³³

2.3.2 X-ray absorption spectroscopy (XAS)

Time-resolved XAS data were collected at the SuperXAS beamline of the Swiss Light Source (SLS, Villigen, Switzerland). Quick-scanning extended X-ray absorption fine structure (QEXAFS) spectra were collected in transmission mode at the Pd K-edge using a Si(311) channel-cut monochromator (beam size of 500 μm $\times$ 100 μm at the sample position) and by using ionization chambers filled with Ar. The Si(311) crystal was rotated at a frequency of 1 Hz, and the signals of the ionization chambers and the angular encoder were sampled with 2 kHz. During a full modulation period 120 spectra were collected (1 s/spectrum time resolution, only the spectra in the increasing energy direction were used). Reference XAFS spectra were collected in step scan mode of the calcined catalyst at room temperature and after pretreatment in 0.25 vol% CH₄/1 vol% CO/1 vol% O₂/Ar at 50°C. Energy calibration was accomplished using a Pd foil mounted between the second and third ionization chambers and measured simultaneously with the operando data. All spectra were background corrected, normalized and analyzed using the Demeter software package.³⁴ Linear combination fitting (LCF) of the normalized averaged time-resolved spectra was performed in the 24310-24420 eV range to quantify the amount of Pd²⁺ and Pd⁰. The variable weights were constrained to be between 0 and 1. The spectra of the calcined sample and of the Pd foil were used as references for Pd²⁺ and Pd⁰ oxidation states, respectively. **Figure S1b-d** compares selected experimental and fit data obtained from the LCF. In order to improve the signal-to-noise

ratio, the time-resolved spectra were averaged over 4 s, thus decreasing the time resolution from 1 to 4 s/spectrum. Fourier transformation was performed over the k -range of 3-10 $\text{\AA}^{-1}$. A curve fitting analysis of the FT EXAFS spectra was carried out in the 1.6-3 $\text{\AA}$ range, where only the first Pd-Pd shell was considered and metallic Pd was used as reference.³⁵ The amplitude reduction factor was set to 0.85 and was obtained from the EXAFS fit of the spectrum of the Pd foil.

2.3.3 Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy

During a full modulation period, 112 time-resolved DRIFT spectra were acquired using a Vertex 80V spectrometer (Bruker) equipped with a liquid nitrogen cooled HgCdTe detector and a Praying Mantis mirror accessory by co-adding 4 interferograms at 2 cm^{-1} resolution and 80 kHz scanner velocity delivering a time resolution of 1.07 s/spectrum. The background spectrum was measured in Ar at 320°C after the pretreatment by co-adding 200 interferograms. A filter was employed to cancel the emitted infrared radiation. Synchronization between the switching valves and spectral acquisition was achieved via the rapid scan mode of the OPUS software. In addition to the experiments described in the experimental procedure, a CO/O₂ modulation experiment was also performed using 1 vol% CO/Ar in the reduction pulse for the sake of comparison. Time-resolved DRIFTS data were treated by PSD using the fundamental demodulation frequency ($k=1$).

3. Results and discussion

3.1 Sample characterization

Prior to all experiments, the Pd/Al₂O₃ sample (171 m²/g) was subjected to in situ pretreatment under stoichiometric feed conditions (0.25 vol% CH₄/1 vol% CO/1 vol% O₂) at 350°C in order to

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3 equilibrate the catalyst and prevent further extensive and irreversible structural alteration during
4 the modulation experiments. The X-ray diffraction (XRD) patterns of the calcined and the
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6 pretreated samples (**Figure S3**) are dominated by the reflections of γ - Al_2O_3 and no relevant
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8 difference can be observed after the pretreatment. No evidence of reflections of PdO or metal Pd
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10 phases could be found, suggesting that Pd is well dispersed on Al_2O_3 also after pretreatment. Pd
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12 nanoparticles, mainly in the size range of 2-5 nm (average size, 4 ± 1 nm), were observed by high
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14 angle annular dark field scanning transmission electron microscopy (HAADF-STEM; **Figure S4a-**
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16 **c**). The particle size distribution slightly broadened after the pretreatment (**Figure S4d-f**), the
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18 median of the particle size distribution increased from 3-3.5 nm for the calcined sample to 3.5-4
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20 nm after the pretreatment thus reducing the Pd dispersion from 25% to 21%. The pretreatment in
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22 the stoichiometric mixture also affected the average oxidation state of Pd determined using X-ray
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24 absorption spectroscopy (XAS, **Figures S5 and S6**), which changed from fully oxidized Pd in the
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26 calcined sample to ca. 28% of Pd^{2+} after pretreatment.¹⁶
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35 3.2 High energy X-ray diffraction (HEXRD)

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37 After pretreatment in a stoichiometric feed at 320°C, the catalyst was submitted to CH_4/O_2
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39 and $\text{CH}_4+\text{CO}/\text{O}_2$ modulation experiments consisting of alternate CH_4 or CH_4+CO and O_2 pulses.
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41 Similar to the static XRD data, the averaged time-resolved patterns obtained at the end of both the
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43 O_2 and the CH_4 pulses were dominated by the reflections of γ - Al_2O_3 (**Figure 1a**). Small intensity
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45 differences were visible at ca. 2.33, 2.74, 3.15, 5.32 $\text{\AA}^{-1}$ that can be attributed to the periodic
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47 reduction and oxidation of palladium.³⁶⁻³⁷ Enhanced sensitivity towards these structural changes
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49 and the subtle ones that may not be visible by inspection of the time-resolved XRD data was
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51 obtained using phase sensitive detection (PSD),³² which in first instance removes the contribution
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of alumina because it is not responding to the chemical stimulus. The selected phase-resolved patterns of this analysis (**Figure 1b**) exhibited only the reflections that experience changes in response to the CH₄/O₂ modulation thus facilitating their identification and the extraction of their exact position. The reflections at ca. 2.35, 2.78, 3.21 and 5.31 Å⁻¹ correspond to the variations in the small intensity changes observed in the time-resolved patterns. In addition, the intensity change of the reflections at ca. 3.74, 4.08, 4.52, 4.75, and 5.54 Å⁻¹ becomes clearly visible only in the PSD data. The signals at 2.78, 3.21, 4.52, 5.31, and 5.54 Å⁻¹ (corresponding to 2θ = 39.9°, 46.4°, 67.3°, 81.2°, and 85.6° for CuKα radiation, respectively) are associated with the metallic palladium phase, while those at ca. 2.35, 3.74, 4.08, and 4.75 Å⁻¹ (33.5°, 54.6°, 60°, and 71.2°, respectively) are associated with the PdO phase.³⁶ The phase angle dependence of the signals (**Figure 2a,b**) shows that these two sets of reflections exhibited opposite phase indicating the reversible reduction and oxidation of a fraction of Pd. The PdO reflections exhibited maximum intensity in the pattern obtained at φ^{PSD} = 130° and shown in **Figure 1b**. As observed earlier for a similar type of synchrotron XRD experiment but with more complex gas feed,²⁵ these reflections present a complex shape, which derives evidently from the overlap of at least two PdO contributions that can be better isolated in the data obtained at φ^{PSD} = 200° and 60°. At φ^{PSD} = 200° all features that should appear in correspondence to the reflections of crystalline PdO are very broad. For instance, a single broad feature is visible at 3.74 and 4.08 Å⁻¹ instead of two well-defined peaks. It should be emphasized that where no PdO or Pd reflections are expected, the phase-resolved data are nil, confirming that Al₂O₃ remains silent to the repeated pulses. The PdO reflections are more defined and sharper in the pattern corresponding to φ^{PSD} = 60°. The broad and undefined features observed in the pattern at φ^{PSD} = 200° were associated with the formation of a disordered phase that we define as ‘amorphous oxide phase’ (*PdO_a*) for simplicity, whereas the peaks visible in the pattern at φ^{PSD} =

60° reveal the development of an oxide phase of increased crystallinity (PdO_c).²⁵ **Figure 2a** displays the phase-angle dependence of two XRD signals selected so to represent these two PdO elements. The reflection at $2.360 \text{ \AA}^{-1}$ arises predominantly from PdO_c but its intensity is increased by the contribution of the amorphous phase. The behavior of PdO_a can be isolated by selecting a point, e.g. at $2.136 \text{ \AA}^{-1}$, that lies on the tail of the broad feature, but does not contribute much to PdO_c (**Figure 1b**). The signal of PdO_c can be determined by subtracting the contribution of PdO_a from the peak at $2.360 \text{ \AA}^{-1}$. The contribution of PdO_c to this reflection was estimated by the following formula:

$$PdO_c(\varphi^{PSD}) = I(2.360 \text{ \AA}^{-1}, \varphi^{PSD}) - \left(I(2.136 \text{ \AA}^{-1}, \varphi^{PSD}) * \frac{I(2.360 \text{ \AA}^{-1}, 200^\circ)}{I(2.136 \text{ \AA}^{-1}, 200^\circ)} \right)$$

that is, by multiplying the intensity of the signal of PdO_a ($2.136 \text{ \AA}^{-1}$) for the ratio of the intensities of the signals at 2.360 and $2.136 \text{ \AA}^{-1}$ in the pattern obtained at $\varphi^{PSD} = 200^\circ$, i.e. the one corresponding only to PdO_a . In order to understand the relation between phase angle and temporal appearance of a species, **Figure 2c** presents the phase-angular dependence of the inlet concentration of CH_4 and O_2 . As expected, since CH_4 and O_2 are alternately admitted to the reactor cell, their phase-resolved signals are opposite in phase and exhibit maxima and minima at 0° , 180° , and 360° . The maxima in the phase angular dependence of the signals of PdO_a (150°) and PdO_c (110°) are centered at lower φ^{PSD} compared to the phase-resolved signal of the inlet O_2 concentration. Applying the notion that signals possessing fast kinetics in the time-domain appear at higher φ^{PSD} in the phase-domain compared to signals evolving more slowly (**Figure S7**)²⁵ and because intuitively the formation of PdO can only be subsequent to O_2 admittance to the cell, the larger φ^{PSD} value obtained for PdO_a compared to PdO_c suggests the initial formation of an amorphous oxide phase and the subsequent slower evolution into a crystalline oxide phase.

Despite the shape change, the PdO reflections did not show a noticeable shift in peak position (**Figure 1b**). On the contrary, the position of the well-defined reflections of metallic Pd in the PSD data changed suggesting a periodic variation of the lattice parameters in response to the modulation. **Figure 2b** shows that the maxima/minima in the phase angular dependence of the Pd(111) (ca. $2.78 \text{ \AA}^{-1}$), Pd(200) (ca. $3.21 \text{ \AA}^{-1}$), and Pd(220) (ca. $4.52 \text{ \AA}^{-1}$) reflections coincided suggesting that the process was isotropic. The shift of the Pd reflections is not accessible from the time-resolved patterns of **Figure 1a** because of the overlap with the dominant reflections of Al_2O_3 . The shift becomes visible in the phase domain (**Figure 1b** and **Figure 2b**) where the Pd(111) reflection was positive at $\varphi^{\text{PSD}} = 50^\circ$, intensified with decreasing φ^{PSD} and reached its maximum intensity at ca. 330° (corresponding to -30°). Pd(111) shifted from $2.796 \text{ \AA}^{-1}$ at $\varphi^{\text{PSD}} = 60^\circ$ to $2.738 \text{ \AA}^{-1}$ at $\varphi^{\text{PSD}} = 240^\circ$, which corresponds to ca. 2.1% lattice expansion. The minimum occurred at ca. $\varphi^{\text{PSD}} = 146^\circ$, which is shifted by 34° compared to the phase-resolved signal of the inlet CH_4 concentration (**Figure 2c**). PdO_a and PdO_c phases were shifted by 30° and 70° , respectively, compared to the phase-resolved signal of the inlet O_2 concentration. Therefore, the formation of Pd^0 upon reduction was faster than the formation of PdO_c upon oxidation, but slower than the formation of PdO_a .

Figure 3 compares selected phase-resolved XRD patterns collected during the CH_4/O_2 , $\text{CH}_4+\text{CO}/\text{O}_2$ and H_2/O_2 modulation experiments with demodulation frequency ω ($k=1$; **Figure 3 a,c,e**) and 2ω ($k=2$; **Figure 3 b,d,f**). For simplicity, only the range $2\text{--}3 \text{ \AA}^{-1}$ is reported, which contains the reflections of PdO(002) at $2.35 \text{ \AA}^{-1}$ and of Pd(111) at $2.78 \text{ \AA}^{-1}$. Irrespective of the reducing agent, the evolution of the PdO reflection in the oxidation pulse was similar in the three modulation experiments. Upon addition of CO (**Figure 3c**) or replacement of CH_4 by H_2 (**Figure 3e**) in the reduction pulse, the PdO peak was characterized by the broad shape of PdO_a at $\varphi^{\text{PSD}} =$

210°. The peak increased in intensity with decreasing ϕ^{PSD} , reached its maximum at ca. $\phi^{\text{PSD}} = 140^\circ$ and consisted of the contributions of the two PdO phases. At $\phi^{\text{PSD}} = 70^\circ$ the peak exhibited the characteristic shape of PdO_c . Therefore, the different reducing agents did not influence the re-oxidation process significantly, which always occurred through the initial formation of PdO_a , followed by the development of PdO_c .

In the reduction pulse, the evolution of the Pd(111) reflection was similar when using CH_4 (**Figure 3a**) and H_2 (**Figure 3e**). Significant differences were observed in the presence of CO (**Figure 3c**). The peak was asymmetric and shifted clearly from $2.771 \text{ \AA}^{-1}$ at $\phi^{\text{PSD}} = 60^\circ$ to $2.706 \text{ \AA}^{-1}$ at $\phi^{\text{PSD}} = 210^\circ$, corresponding to ca. 2.4% lattice expansion, which was larger than with CH_4 or H_2 . This difference was amplified at demodulation frequency 2ω . Also in this case the shape of the Pd(111) reflection was similar for the two CH_4/O_2 and H_2/O_2 modulation experiments while **Figure 3d** shows the existence of a clear bipolar reflection in the $\text{CH}_4+\text{CO}/\text{O}_2$ modulation experiment that exemplifies the reversible shift of the Pd(111) reflection.

Figure 4 shows that the temporal behavior of the signal maxima confirmed this shift and that the low levels of d lattice change corresponding to maximum 1.4% were mirrored by small intensity changes. In the $\text{CH}_4+\text{CO}/\text{O}_2$ modulation experiment, the intensity of the signals corresponding to the low-Q ($2.69 \text{ \AA}^{-1}$) and high-Q ($2.79 \text{ \AA}^{-1}$) lobes of the Pd(111) reflection (indicated in the PSD data of **Figure 3d**) and to the position of the same reflection in the time-resolved data ($2.74 \text{ \AA}^{-1}$, **Figure 1a**) increased quickly within 5 s in the CH_4+CO reducing pulse (**Figure 4b**) indicating a fast reduction of oxidized Pd. The intensity of the reflection at $2.79 \text{ \AA}^{-1}$ passed through a maximum and returned to close to the value obtained before the reduction pulse. On the contrary, the signal at $2.69 \text{ \AA}^{-1}$ continued increasing after 5 s but at a diminished rate reflecting the decrease of the signal at $2.79 \text{ \AA}^{-1}$. The intensity change at $2.74 \text{ \AA}^{-1}$ after 5 s was less

significant because this point corresponds to the inflection point between the two lobes at 2.69 and 2.79 Å⁻¹ (**Figure 3d**). The decrease of the high-Q signal after ca. 5 s agrees with the lattice expansion but is not easily visible in the time-resolved patterns without the aid of the phase sensitive analysis shown above. In the CH₄/O₂ (**Figure 4a**) and H₂/O₂ (**Figure 4c**) modulation experiments, the three signals stabilized after 20 s and 10 s, respectively. Thus, their behavior was significantly different from that in the presence of CO confirming that addition of CO is needed in order to observe a large extent of lattice expansion.

The reversible increase in the d spacing of Pd nanoparticles in Pd/Al₂O₃ was associated previously with the dissociation of adsorbed CO species in the CO pulses of CO-NO modulation-type measurements.²⁰ The formation of carbide-like species explains the increase in the lattice parameters and the larger extent of expansion observed with the addition of CO.³⁸ The CH₄/O₂ modulation experiment demonstrated lesser extent of expansion likely as a consequence of the weaker interaction of CH₄ with Pd. The expansion observed in the H₂/O₂ modulation experiment is tentatively assigned to the formation and observation of Pd-hydride species, causing Pd-Pd bond distance expansion in Pd nano-particles.³⁹

Finally, **Figure 4** also shows that the decrease of the Pd(111) reflection in the O₂ pulse occurred in two steps.²⁵ The first step was faster than the initial intensity growth in the reduction pulse but the second step was much slower, thus corroborating the PSD data discussed above (**Figure 1** and **Figure 2**). Pd⁰ formation was also clearly faster in the presence of CO, requiring as mentioned 5 s in the CH₄+CO/O₂ modulation experiment and ca. 20 s in the absence of CO.

3.2 X-ray absorption spectroscopy (XAS)

Figure 5a shows the Pd K-edge X-ray absorption near edge structure (XANES) region of the averaged time-resolved QuickEXAFS spectra obtained in the CH₄/O₂ modulation experiment at the end of the O₂ and CH₄ pulses. The first evident information from inspection of the whiteline region is that the catalyst exhibited mainly variations of the oxidation state around the reduced state. It appeared completely reduced in CH₄ and re-oxidized partially in the presence of O₂. Analogous behavior was obtained in the CH₄+CO/O₂ modulation experiment. These results are consistent with previous investigations. Measurements of similar nature carried out on 2 wt% Pd/Al₂O₃ by changing repeatedly between reducing and oxidizing conditions every 300 s showed the complete oxidation of Pd nanoparticles in the lean pulse at 350°C and 400°C.²⁸ At 300°C, Pd was not fully oxidized. Pd nanoparticles in 2 wt% Pd/Al₂O₃ were found to completely reduce in CH₄ pulses of 60 s at 500°C, while they only partially re-oxidized in the CH₄/O₂ pulses.²⁹

Figure 5b compares the XANES spectra obtained at the end of the reduction period in the two concentration modulation experiments. In presence of CO, the apparent broadening and shift to higher energy of the first whiteline peak at 24370 eV (**Figure 5c**) suggests the formation of a palladium carbide-like phase.⁴⁰⁻⁴² The insertion of carbon atoms within adjacent Pd atoms generates an expansion of the lattice and causes an increase in the Pd-Pd distance by 1.1-1.2% that is visible in the Fourier transform XAS data.⁴⁰⁻⁴² Therefore, a curve fitting analysis of the extended X-ray absorption fine structure (EXAFS) data collected during the reduction period was carried out. **Tables S1-S2** report the results of the EXAFS fit. **Figure S2** compares selected experimental and fit data obtained from this analysis. Only the first Pd-Pd shell was considered, because the data quality did not allow the fit of more than one shell (**Tables S2-S4**). **Figure 6** compares the temporal evolution of the Pd-Pd bond length (R) during the reduction period in the two modulation experiments. When CH₄ was the only reducing agent, the Pd-Pd bond length was ca. 2.72-2.73 Å

and did not change significantly during the pulse. In the presence of CO, the Pd-Pd bond length was similar at the beginning of the reduction pulse, but increased visibly in the first 20 s reaching a mean value of 2.75 Å at the end of the pulse. This result is consistent with EXAFS data showing an increasing Pd-Pd bond length from 2.73 Å to 2.76 Å as a consequence of CO dissociation on Pd and the subsequent storage of atomic carbon within Pd nanoparticles.⁴³ **Figure 6b** shows that simultaneous to these changes, the Pd coordination number increased within 20 s to a value of 9 in both modulation experiments, in line with the likely complete reduction of the Pd nanoparticles covered by the layer of PdO_c observed by XRD, and did not change further.

Both XANES and EXAFS analysis show the formation of Pd carbide species in the presence of CO, whereas no evidence for such Pd carbide was found when CH_4 was the only reducing agent. These results compare qualitatively with the expansion of the lattice parameters by ca. 2.4% in the presence of CO obtained from the phase-resolved XRD data. However, the relative changes induced by the formation of a carbide-like phase are larger in XRD than those probed by EXAFS (ca 1.1%). This discrepancy can be explained by recalling that XRD and EXAFS of supported nanoparticles do not necessarily yield identical values of nearest neighbor distances.²⁰ Whereas EXAFS is equally sensitive to all metal atoms composing the nanoparticles (surface and bulk), the diffraction measurement only sees those that are arranged in an ordered phase. In a similar work to this,²⁰ XRD probed a larger variation in the lattice constant of Pd by ca. 0.45% than that obtained by EXAFS. In addition, the larger expansion measured in the XRD (**Figure 3b-4b**) can be justified by considering that EXAFS analysis was carried out on the averaged time-resolved data; given that EXAFS is a bulk technique, an average information on all Pd atoms present in the catalyst is obtained, i.e. between the fraction of atoms (ca. 30%) that responded to the external redox stimulation and the fraction (ca. 70%) that did not react. In the case of the XRD data, information

on the possible presence of Pd-carbide species was obtained only after inspection of the phase-resolved data, thus an unusual set of data for this type of experiments, which shows information only on the fraction of palladium responding to the periodic stimulation.

3.3 DRIFTS

Infrared spectroscopy delivers molecular level information on adsorbates under reaction conditions and is thus a powerful complementary tool to X-ray based methods probing the catalyst structure directly. **Figure 7** shows selected averaged time-resolved DRIFT spectra collected during the CH₄/O₂ modulation experiment at 320°C in the reduction and oxidation pulses. The overall spectral intensity decreased above ca. 1500 cm⁻¹ during the CH₄ pulse (**Figure 7a**) and returned to the original level during the O₂ pulse (**Figure 7b**). This reversible change has been associated to the reversible reduction and oxidation of the catalyst.⁴⁴ The baseline changes and the presence of signals of gaseous CO₂ (ca. 2383-2307 cm⁻¹) and water (ca. 4000-3600 cm⁻¹ and 1750-1000 cm⁻¹) from atmospheric air complicate the identification and the extraction of the temporal evolution of the IR signals. The broad band extending between ca. 3700 cm⁻¹ and 2600 cm⁻¹ appearing in the reduction pulse and attenuating in presence of O₂ is due to the presence of adsorbed water molecules (the product of CH₄ oxidation) and to perturbed hydroxyl groups of Al₂O₃.⁴⁵ After ca. 2 s from CH₄ admittance, a major signal appeared at ca. 1895 cm⁻¹ that was accompanied by a second one at ca. 2044 cm⁻¹, both being due to CO bridged-bonded to (100) planes of the metallic Pd particles (CO_B) and linearly adsorbed on edge sites (CO_L), respectively.⁴⁶ Within the reduction pulse, signals also appeared at ca. 2907 cm⁻¹ (weak) and ca. 3550 cm⁻¹ that are assigned to the C-H stretch mode of formates coordinated to Al₂O₃⁴⁷⁻⁴⁹ and to hydroxyls on both Al₂O₃⁵⁰ and Pd,⁵¹

respectively. The signals of adsorbed CO rapidly vanished in the O₂ pulse, while the intensity of the latter two bands adjusted to lower levels.

Figure 7c shows selected phase-resolved spectra for the same experiment. PSD removes the static signals due to atmospheric CO₂ and vapour, thus greatly improving the signal-to-noise ratio and the spectra quality facilitating the identification of relevant features. However, the phase-resolved spectra are equally strongly affected by the large change in baseline due to Pd reduction and oxidation. The signals at 3758, 3722 and 3673 cm⁻¹ of the hydroxyl groups of Al₂O₃ can be clearly distinguished in the phase-resolved spectra. The signal of the CO₂ product is also clearly visible at ca. 2345 cm⁻¹.⁵² The CO_B signal at ca. 1895 cm⁻¹ reveals a low energy shoulder (ca. 1825 cm⁻¹) that was assigned to CO bridged bonded to 3-fold sites (CO_{3B}).⁴⁶ A weak feature is visible at ca. 1575 cm⁻¹, which is likely associated with the asymmetric OCO stretch mode of formate ions on Al₂O₃ consistent with the presence of the C-H stretch mode at 2907 cm⁻¹.^{47, 53-55}

Based again on the notion that signals possessing fast kinetics in the time-domain possess phase-angles that shift to higher ϕ^{PSD} (**Figure S7**),²⁵ the discussion of the phase-resolved spectra is made on decreasing values of ϕ^{PSD} . The baseline (the extended region above 1500 cm⁻¹) became positive at ϕ^{PSD} ca. 240°, reached maximum intensity at ca. 150°, and returned to negative values at ca. 60°. The CO_B signal (1895 cm⁻¹) became positive at 82°, whereas all other visible signals had negative sign, and intensified upon decreasing ϕ^{PSD} . The CO_L signal (2041 cm⁻¹), the perturbed hydroxyls (broad band at ca. 3600 cm⁻¹), physisorbed CO₂ (2345 cm⁻¹), hydroxyls on Al₂O₃ (3758, 3722 and 3673 cm⁻¹) and on Pd (3550 cm⁻¹), and formates (2907 cm⁻¹) assumed positive sign at 74°, 64°, 60°, 54° and 48°, respectively. Hence, the phase-resolved data suggest that CO adsorption occurred first and was followed by the appearance of CO₂ and in a second stage by the formation

of formates. Therefore, adsorbed CO was an intermediate species in CH₄ oxidation to CO₂, whereas formates were likely not involved in the reaction, rather a final product (vide infra).

Figure 8 shows the molecular aspects of CO addition to the modulation experiment. In the selected phase-resolved spectra, the signal of adsorbed CO reached its maximum intensity at higher ϕ^{PSD} values (360°; equals 0°) in the presence of CO than when CH₄ was the only reducing agent (ϕ^{PSD} 346°; -16°). These values suggest that the adsorption of CO on reduced Pd was faster when CO was present in the feed. The spectra obtained during CH₄+CO/O₂ and CO/O₂ modulation experiments display similar features. The signals of adsorbed CO grew and shifted to higher energy as a result of increasing CO coverage. The CO_B signal exhibited a broader envelope resulting from at least two contributions. The one assigned to CO_B on Pd(100) shifted to ca. 1920 cm⁻¹, while a second signal detected at ca. 1945 cm⁻¹ only in presence of CO was attributed to bridged-bonded CO on Pd(111) planes.⁴⁶

These results indicate that while CO adsorbs everywhere on the Pd nanoparticles, CH₄ activation occurs only on definite Pd sites at the same temperature. Density functional theory (DFT) calculations have shown that the activation energy of CH₄ decomposition is higher on Pd(111) than on Pd(100),⁵⁶⁻⁵⁸ in agreement with the observation that CO_B forms predominantly on (100) facets upon CH₄ oxidation under reducing conditions. Two types of bridged bonded CO were identified on Pd/Al₂O₃ used for CO₂ hydrogenation.⁵⁹ The high frequency one (1960-1945 cm⁻¹) corresponded to weakly bound CO desorbing to gaseous CO while the low frequency one (1850-1921 cm⁻¹) was more stable. Since CH₄ formation was associated only with the latter species whose signal shows similar energy to the one observed in the CH₄/O₂ modulation experiment, it is reasonable to presume that also the reverse reaction, adsorbed CO formation from CH₄ oxidation, occurred on the same site.

The involvement of formates in CH_4 oxidation on $\text{Pd}/\text{Al}_2\text{O}_3$ is a debated issue. Formates/carbonates (signal at ca. 1590 cm^{-1}) were shown to be produced from the interaction of CO with Al_2O_3 , a reaction catalyzed by palladium.^{55, 60} However, the emergence of formate species was also associated with intermediate species of CH_4 oxidation to CO_2 .⁶¹⁻⁶² Formates were proposed to originate from incomplete CH_4 oxidation and to further oxidize to carbonates when sufficient reactive oxygen species are supplied. Formates were not visible in the time-resolved spectra at the end of the CH_4 pulses and were detected only after data averaging (**Figure S9a**). They were also not visible at the end of the first CH_4+CO pulse, but their features intensified significantly at the end of the last pulse suggesting a continuous formate production along the modulation experiment (**Figure S9b**) but also a fluctuating formate surface coverage induced by the modulation. The larger amount of formates produced in the presence of CO suggests that CO was their precursor. These modulation results seem to exclude the participation of formate species to CO_2 production from CH_4 oxidation. Nevertheless, the data of **Figure 7** and **Figure S9** suggest that two types of formates were present. While the signal at 2907 cm^{-1} did not completely disappear in O_2 , indicating that a fraction of formates was produced at the beginning of the modulation experiment and did not further react, the intensity of the signal slightly increased during reduction and decreased during oxidation, thus revealing that a fraction of formates was reversibly produced and consumed during the CH_4/O_2 modulation experiment. This fraction appeared in the phase-resolved spectra. When CH_4 was the only reducing agent, formates were produced and consumed; in the presence of CO they were produced and accumulated over the course of the experiment. Formates could be involved in side-reactions^{55, 60} and could be produced from the interaction of adsorbed CO with Al_2O_3 . On the other hand, it cannot be excluded that formates are also involved

in CH₄ oxidation in absence of O₂ or under strongly reducing conditions, i.e. when Pd is fully reduced. Further experiments are needed to clarify this point.

3.4 Combination of techniques

The advantage of the spectroscopic cell used in this work relies on the possibility to conduct identical experiments with different spectroscopic/diffraction methods. In the case of transient experiments as those reported here, this allows correlating the kinetics of features belonging to physically and chemically different components of the catalytic material. **Figure 9** combines the time-resolved information delivered by XANES, XRD and DRIFTS with the catalytic activity obtained from the analysis of the gas concentration at the outlet of the reactor cell using the online mass spectrometer for the CH₄/O₂ and CH₄+CO/O₂ modulation experiments (**Figure 9a-c**).

In the CH₄/O₂ modulation experiment, oxygen breakthrough occurred immediately at the CH₄→O₂ switch (**Figure 9a**) and accompanied the rapid increase of the fraction of Pd²⁺ obtained from LCF analysis of the XANES spectra (**Figure 9d**). The partial re-oxidation of Pd occurred in two stages. Initially, ca. 20% of Pd oxidized within 6 s. A sharp peak of gas phase CO₂ (**Figure 9b**) was observed simultaneously that was likely due to the removal of the CO species deposited on the catalyst surface in the reduction pulse,²⁸ which were observed by DRIFTS. The CO₂ concentration reached a maximum before returning to negligible levels (**Figure 9b**). After this event, the oxidation of Pd (**Figure 9d**) proceeded more slowly through the rest of the O₂ pulse but did not reach steady state. After 60 s, ca. 32% of Pd was oxidized.

The two-steps re-oxidation process was confirmed by the corresponding experiment using time-resolved high energy XRD. Similar to the temporal profile of Pd²⁺ obtained from XANES, the intensity of the PdO reflection at 2.354 Å⁻¹ increased rapidly at the beginning of the O₂ pulse

(Figure 9f). Because XRD is sensitive to ordered phases, the development of the signal intensity in the second stage of the oxidation was enhanced compared to the evolution of the XANES signal. While quantitative information was obtained on the fraction of oxidized Pd with XANES, the phase-resolved XRD patterns suggest the initial formation of an amorphous oxidic phase followed by the development of a PdO phase of increased crystallinity. Considering that the Pd dispersion was ca. 21%, it is likely that all surface Pd atoms contributed to the formation of the amorphous oxide formed by chemisorbed oxygen on Pd. The second phase of the oxidation proceeded more slowly because the formation of the crystalline phase requires massive restructuring and diffusion limitations intervene as well.⁶³ The occurrence of this two-steps process agrees with experimental observations by others.²⁴ A monolayer of amorphous oxide was observed to form immediately during isothermal and temperature-programmed oxidation experiments when probing the oxidation dynamics of Pd/ZrO₂.⁶⁴ The initial amorphous oxide transformed into crystalline PdO and formed a shell of increasing thickness with increasing oxidation temperature around a metal core. Below 400°C the formation of a surface oxide on Pd(100) surfaces and its gradual transformation to bulk oxide was monitored also by in situ surface X-ray diffraction (SXRD).⁶³ A surface oxide was observed to form prior to the onset of the bulk oxide formation upon oxidation of a Pd(100) single crystal and Pd particles supported on SiO_x substrates by O₂ using in situ high-pressure X-ray photoelectron spectroscopy (XPS).⁶⁵ A surface oxide was observed to form by XPS, while cooling 5 wt% Pd/Al₂O₃ in air, which inhibited the nucleation and growth of bulk PdO.⁶⁶ If the proposed mechanism is consistent with previous investigations on single crystals and supported Pd particles, it is only the combination of time-resolved XANES and XRD with PSD that makes it possible to follow the details of the re-oxidation process on supported Pd nanoparticles of 2-5 nm of this low loaded catalyst.

Pd reduction occurred immediately at the beginning of the reduction pulse and Pd was completely reduced within 10 s (**Figure 9d**). Therefore, the reduction was faster than the overall oxidation process. However, both XANES and XRD revealed that reduction was slower than the first oxidation step, e.g. formation of disordered PdO, thus confirming the interpretation of the phase-angle dependence of the XRD signals (**Figure 6**). At the beginning of the CH₄ pulse, when a fraction of partially oxidized Pd was still present (**Figure 9d**), CO₂ production occurred (**Figure 9b**) as a result of CH₄ oxidation by oxygen (reaction 1; Table 1) but returned to low levels of ca. 70-40 ppm (**Figure S8**) after 10 s that were maintained throughout the whole CH₄ pulse. CH₄ evolution passed through a minimum coinciding with the maximum of CO₂ production (**Figure 9b**). The analysis of the phase-resolved DRIFT spectra suggested CO_B as intermediate species in CH₄ oxidation to CO₂. DFT calculations suggested that CH₄ oxidation proceeds through the reaction of CH fragments with adsorbed oxygen to formyl species,⁶⁷ which dissociates to adsorbed hydrogen and CO. However, no feature ascribable to formyl species was observed in the present DRIFTS data. The CO_B signal (**Figure 9g**) started increasing slowly from the beginning of the CH₄ pulse and stabilized after ca. 20 s. The formates, formed likely from the interaction of adsorbed CO with hydroxyls of Al₂O₃,^{55, 60} could be responsible for the CO₂ production when Pd was completely reduced. When XANES indicated that Pd was completely reduced (**Figure 9d**), CH₄ conversion decreased and H₂ production was observed (**Figure 9c**) to pass through a maximum before decreasing slowly until the end of the pulse. The presence of gas phase H₂ and adsorbed CO reflected the decomposition of CH₄ or the occurrence of steam reforming (reaction 2; Table 1) in the absence of O₂.²⁹ Nilsson et al.²⁸ attributed CO and H₂ production to the partial oxidation of CH₄ when oxygen was the limiting reactant. Water breakthrough was detected after ca. 16 s from the beginning of the reduction pulse. These reactions may cause the formation of

carbide-like species on the Pd particles, whose oxidation also contributes to the CO₂ produced at the beginning of the oxidizing pulse.²⁹ DFT calculations suggested that the carbide species are intermediates of CH₄ oxidation on Pd nanoparticles supported on γ -alumina under O₂ deficient conditions.⁶⁸ Our XAS data provided no evidence of carbide formation when CH₄ was the only reducing agent while only PSD was able to identify slight expansion of the lattice in the XRD data, thus suggesting that the concentration of Pd carbide was negligible.

In the CH₄+CO/O₂ modulation experiment, the addition of CO did not modify significantly the oxidation period. The amount of evolved CO₂ was roughly doubled but otherwise adsorbed species at the end of the reduction pulse did not affect the oxidation process after 10 s. However, the presence of gas phase CO increased the rate of Pd reduction significantly as indicated by both XANES and XRD. The temporal evolution of the fraction of Pd²⁺ obtained from XANES during the reduction pulse can be fitted with a simple exponential decay (Table 2, see also supporting information). The decay constant C_{red} obtained in the experiment with the addition of CO was ca. twice the value obtained in absence of CO. The decay constant depends on the concentration of the reducing agent and on the kinetic constant of reduction. Because the concentration of the reductants doubles with the addition of CO by taking into account the concentration of the reducing agents, 0.25 vol% CH₄ and 1 vol% CO and the stoichiometry of their oxidation (reactions 1 and 5; **Table 1**), the increase in the reduction rate could be attributed to the increase in the concentration of the reducing agent. However, at the beginning of the reduction pulse more CO₂ was produced in the presence of CO but CH₄ conversion decreased significantly (**Figure 9b**). Hence, CO₂ was produced mainly by CO oxidation (reaction 5; **Table 1**) and the increase in the Pd reduction rate was also a result of the faster reduction of PdO by CO. The increase in the rate of PdO reduction in the presence of CO was also more evident in the time-resolved XRD data (**Figure 9f**). Complete

reduction of PdO was clearly anticipated in the presence of CO and PdO was reduced after ca. 17 s and 6 s in the CH₄ and CH₄+CO pulses, respectively.

The evolution of CO_B in the time-resolved DRIFTS data was identical in the CH₄+CO and CO pulses (**Figure 9g**). The signal increased immediately at the beginning of the pulse and reached steady state. As a consequence, the maximum of CO₂ production and the beginning of the decrease of the CO₂ concentration were anticipated by addition of CO (**Figure 9b**). Therefore, CO adsorbed immediately and inhibited CH₄ oxidation. The concentration of CO₂ produced in the presence of CO was larger than in its absence, and at the end of the reduction pulse the CO₂ concentration amounted to ca. 400 ppm. The observed hydrogen production (**Figure 9c**) was also anticipated, suggesting that the rapid reduction of Pd induced by CO and the inhibition of CH₄ oxidation preceded CH₄ decomposition. However, if we neglect the first 5-6 s of the reduction pulse CH₄ conversion was nil while hydrogen was still produced. H₂ production in the presence of CO can be attributed to the water gas shift (WGS) reaction (reaction 3; **Table 1**). In fact, the H₂ concentration in the presence of CO remained stable until the end of the pulse (ca. 150 ppm) and the signal of water did not increase, whereas it slowly decreased in the CH₄/O₂ modulation experiment. Considering the hydrogen balance (see Supporting Information), if CH₄ consumed at the beginning of the reduction pulse (first 5-6 s) was completely oxidized, the amount of water produced would have been sufficient to justify the H₂ production by the WGS reaction.

These experiments provide a molecular perspective of the inhibiting effect of CO on CH₄ oxidation on Pd. We had shown previously¹⁶ that Pd remains reduced until CO is present in the feed. At the moment CO is fully removed by oxidation, Pd re-oxidizes before CH₄ oxidation can start in line with the low reactivity of CH₄ in the temperature range where CO can be oxidized (<200°C). Moreover, we have also shown on a Pd-Al-Ce-Zr three-way catalyst¹⁸ that CH₄

abatement occurs efficiently only when CO oxidation is complete, which causes the air-to fuel ratio value for optimal abatement of CO, NO and CH₄ to shift to reducing reaction conditions compared to the case when propene is used as hydrocarbon. While the current results were obtained in the absence of steam in the feed, the observation of this inhibition in a more realistic feed¹⁸ makes us confident that our observations can be transferred to some extent to real exhausts. The effect of water in such type of experiments remains to be proved.

4. Conclusions

CH₄ abatement on Pd/Al₂O₃ and the influence of the addition of CO on the surface chemistry of the Pd nanoparticles were studied under dry redox cycling conditions. Operando and time-resolved X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) were combined to correlate the changes in the oxidation state and the structure of palladium with its activity, while infrared spectroscopy was employed to follow the evolution of the adsorbates on the catalyst surface. All spectroscopic and diffraction data were collected independently but with the same reactor cell and setup thus implying that the temporal evolution of species of different nature can be compared directly. Furthermore, performing the experiments under periodic redox conditions enabled to exploit phase sensitive detection (PSD) to obtain structural details of the chemistry of CH₄ oxidation on Pd/Al₂O₃.

Under these conditions, Pd exhibited variations of the oxidation state mainly around the reduced state; it was completely reduced in CH₄, and partially re-oxidized in the presence of O₂. Time-resolved XRD and XANES data revealed that Pd re-oxidation occurred in two stages. The fast formation of an amorphous oxidic phase likely at the surface of the palladium nanoparticles was followed by a slower evolution of an ordered PdO phase. PdO reduction was faster than the

overall oxidation process, but slower than the initial formation of the amorphous phase. CH₄ oxidation occurred on partially oxidized Pd at the beginning of the reduction pulse (**Figure 10a**), whereas a secondary reaction pathway of CH₄ decomposition occurred on fully reduced Pd after few seconds into the reduction pulse. DRIFT experiments showed adsorbed CO as possible intermediate in CH₄ oxidation to CO₂. While we exclude their participation to CH₄ oxidation, formate species could be involved in CH₄ decomposition in absence of oxygen. The observation from DRIFTS that CO generated by CH₄ activation coordinated predominantly at Pd(100) planes suggests that CH₄ decomposition may occur on these sites.

In the presence of CO in the feed (**Figure 10b**), CO oxidation was favored and inhibited CH₄ oxidation. CO was immediately adsorbed on metallic Pd and increased the rate of PdO reduction. The clear expansion of the Pd-Pd lattice only in presence of CO suggested the formation of carbide-like species that further confirms the stronger interaction of CO with Pd nanoparticles that may be at the origin of the inhibition of CH₄ activation.

The present study demonstrates that CO controls the surface chemistry of Pd/Al₂O₃ during CH₄ oxidation under redox conditions that could mimic TWC operation, thereby changing the activation of CH₄. From a practical perspective, the data suggest that a TWC for natural gas vehicles needs to convert CO completely before it can efficiently remove CH₄.

Supporting information

Linear combination fit of the XANES spectra; EXAFS fits; XRD patterns of the calcined and pretreated Pd/Al₂O₃; STEM images and particle size distribution of calcined and pretreated Pd/Al₂O₃; XANES and EXAFS of calcined Pd/Al₂O₃ at room temperature and after the

pretreatment; determination of particle size and dispersion; cumulative CO₂ production; DRIFTS spectra of formates accumulation; decay functions of Pd²⁺; H₂ balance in the CH₄/CO pulse.

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Competing interests

The authors declare no competing financial interest.

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Table 1. Possible reactions occurring in the reduction pulse.

methane oxidation	$\text{CH}_4 + 4 \text{ PdO} \rightarrow \text{CO}_2 + 2 \text{ H}_2\text{O} + 4 \text{ Pd}$
steam reforming	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{ H}_2$
water gas shift (WGS)	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$
reverse water gas shift (RWGS)	$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$
CO oxidation	$\text{CO} + \text{PdO} \rightarrow \text{CO}_2 + \text{Pd}$

Table 2. Results of the fit of the temporal evolution of the fraction of Pd²⁺ obtained from the LCF of the XANES spectra during the reduction pulse with simple exponential decay (see Supporting Information). C₂ is the fraction of Pd²⁺ that does not reduce, C₁ + C₂ is the fraction of Pd²⁺ at the beginning of the reduction pulse, C_{red} is the decay constant.

	in CH ₄	in CH ₄ +CO
C ₁	0.31 ± 0.01	0.29 ± 0.03
C _{red}	0.38 ± 0.03	0.8 ± 0.2
C ₂	0.016 ± 0.002	0.042 ± 0.004

Figure captions

Figure 1. (a) Time-resolved XRD patterns recorded at the end of the CH₄ and of the O₂ pulses of the CH₄-O₂ modulation experiment. Arrows indicate position of faint but visible changes. (b) Selected phase-resolved XRD patterns. Symbols: (+) Pd, (O) PdO.

Figure 2. Phase angular dependence of the signals of (a) PdO (2.360 Å⁻¹), amorphous PdO (2.136 Å⁻¹), crystalline PdO, and of (b) Pd(111), Pd(200), and Pd(220) obtained from the phase-resolved XRD patterns collected during the CH₄-O₂ modulation experiment. (c) Phase angular dependence of the inlet concentration of O₂ and CH₄. The inset shows the pulse sequence in the time domain.

Figure 3. Selected phase-resolved XRD patterns collected during (a,b) CH₄/O₂, (c,d) CH₄+CO/O₂, and (e,f) H₂-/O₂ modulation experiments and obtained with demodulation frequency equal to (a,c,e) ω and (b,d,f) 2ω .

Figure 4. Temporal evolution of selected peaks corresponding to relevant contributions to the Pd(111) reflection of Figure 3d and Figure 1a during (a) CH₄/O₂, (b) CH₄+CO/O₂, and (c) H₂/O₂ modulation experiments. See text for peak assignment.

Figure 5. (a) XANES region of the averaged time-resolved QuickEXAFS spectra (1 spectrum/s time resolution) obtained at the end of the O₂ and of the CH₄ pulses. (b) XANES region of the averaged time-resolved QuickEXAFS spectra (averaged every 4 s in order to further improve the signal to noise ratio, 4 s/spectrum time resolution) obtained at the end of the CH₄ and the CH₄+CO pulses. (c) Magnification of the spectra indicated in (b) by the rectangle.

Figure 6. Temporal evolution of (a) the bond distance of the 1st Pd-Pd shell and (b) of the Pd coordination number during the reduction pulse of the CH₄/O₂ and CH₄+CO/O₂ modulation experiments.

Figure 7. Selected averaged time-resolved DRIFT spectra collected during (a) CH₄ and (b) O₂ pulses of the CH₄/O₂ modulation experiment. (c) Selected phase-resolved DRIFT spectra. Vertical dotted lines indicate the features discussed in the text.

Figure 8. Selected phase-resolved DRIFT spectra obtained from CH₄/O₂, CH₄+CO/O₂ and CO/O₂ modulation experiments where the intensity of the band of adsorbed CO is maximum. Vertical dotted lines indicate the features discussed in the text.

Figure 9. Temporal evolution of the concentration of gas components at the outlet of the reactor cell obtained from the analysis of MS data during CH₄/O₂ (black) and CH₄+CO/O₂ (grey) modulation experiments: (a) CO (dashed line) and O₂ (solid line), (b) CH₄ (dashed line) and CO₂ (solid line), (c) H₂. Temporal evolution of (d) the fraction of oxidized palladium obtained from the linear combination fitting of the XANES spectra, (f) the reflection PdO(002) (2.354 Å⁻¹), and (g) the DRIFT signal of CO bridged bonded during CH₄/O₂ (○), CH₄+CO/O₂ (●), and CO/O₂ (+) modulation experiments. (e) Magnification of the temporal evolution of the fraction of oxidized palladium at the beginning of the reduction indicated in (d) by the rectangle.

Figure 10. Scheme of CH₄ oxidation reaction on Pd/Al₂O₃ when switching from O₂ to (a) CH₄ and (b) CH₄+CO. The decreased area indicated with Pd²⁺ in (b) is used to indicate that CO reduced Pd²⁺ faster.

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22 Pd^{2+} faster.
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