Short Communication

Operando XANES study of simulated transient cycles on a Pd-only three-way catalyst

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ABSTRACT

A model Pd-only three-way catalyst has been subjected to simulated driving conditions of natural gas and gasoline operation in an operando reactor cell for X-ray absorption spectroscopy that included alternated, but longer than real oscillations, rich and lean periods and a high temperature surge (850–900 °C). The X-ray absorption near edge structure (XANES) spectra indicated that metallic palladium is observed in the whole temperature range investigated (up to 900 °C) and irrespective of the air/fuel ratio. In both natural gas and gasoline cycles, the XANES data show that the PdO reduced in the rich periods cannot be restored in the lean periods. With this background, activity for methane abatement in the high temperature regime is greatly affected by the oxidation state of palladium rather than by the change of air/fuel ratio. In the case of propene oxidation, while Pd also remains predominantly in the reduced state, activity is dictated by the oxygen concentration in the feedstock. Comparison between the two hydrocarbons demonstrates that the oxidation state of Pd may be responsible for observed methane emissions under realistic operating circumstances. Moreover, the experiments demonstrate that reduced Pd may be continuously present during operation in agreement with observations on real catalytic converters. Although this may be the average oxidation state of Pd, more advanced probes are certainly necessary to capture variations of oxidation state under the fast oscillatory conditions needed to imitate real operation.

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1. Introduction

Natural gas receives increasing public awareness as an alternative to gasoline and diesel fuels. The advantages of natural gas (>90% methane, CH_4) are numerous, including the lowest CO_2 emission per unit energy and the low toxic emissions. However, CH_4 slip from the engine needs to be treated catalytically because of the large global warming potential of CH_4. Precious metals, e.g. Pd and Pt, are the most active for CH_4 oxidation [1]. The oxidation activity of palladium is greatly hampered at temperatures higher than 700 °C because of the spontaneous reduction of active PdO to metallic Pd [2,3]. Such temperatures are periodically attained upon motorway operation as a consequence of increased catalyst load. For close coupled catalytic converters, high temperatures belong to regular operating conditions.

Under realistic driving conditions of stoichiometric engines, CH_4 slip is often observed during transient engine operation at higher speed

and temperature than average operation (Fig. 1). Total hydrocarbon emissions are also higher for natural gas operation than for gasoline operation [4]. Additionally, it is known that CH_4 conversion in catalytic converters also decreases for fuel lean engine operation ($\lambda > 1$), thus reflecting NO_x emissions, that is contrary to the typical behavior of higher hydrocarbons [5–7]. The difference with respect to hydrocarbon emissions between natural gas and gasoline operation could be related to the state of the precious metal(s), among other possible effects that are difficult to disentangle [6,8]. The state of precious metals of three-way catalyst (TWC) formulations has been rarely studied under simulated reaction conditions of λ oscillations and in a wide temperature range [9–11]. Recently, time-resolved methods have provided deeper insight into the dynamic behavior of metal nano-particles under oscillating conditions close to TWC operation [12–14]. In this respect, X-ray absorption spectroscopy is a powerful tool to elucidate structure–activity relationships of working catalysts [15]. In this work we subjected a model Pd-only TWC to simulated driving cycles of natural gas and gasoline engines while recording operando X-ray absorption near edge structure (XANES) spectra in order to correlate catalytic activity for CH_4 and propene (C_3H_6) oxidation under TWC conditions with the oxidation state of palladium. Our discussion is confined to hydrocarbon conversion

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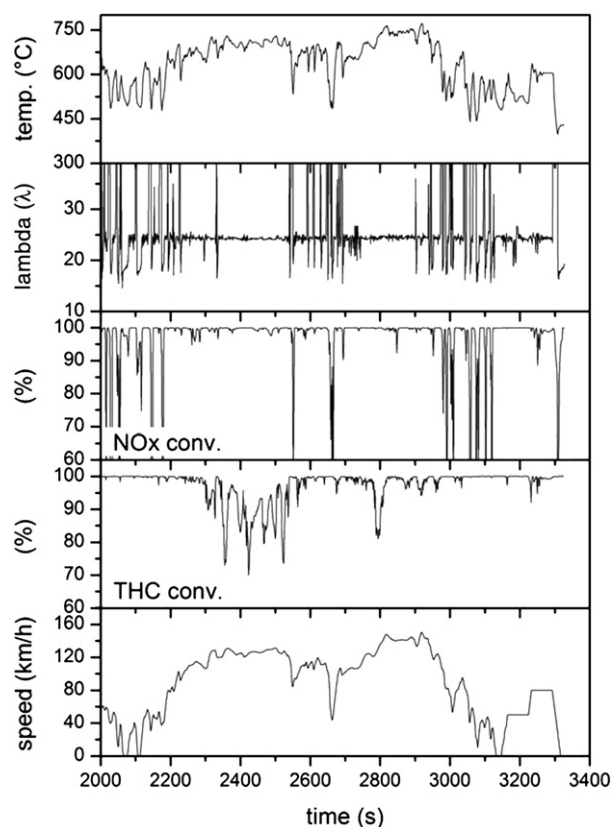
Fig. 1. Total hydrocarbon and NO$_x$ conversion efficiency of a natural gas driven mid-size passenger car during a Common Artemis Driving Cycle (CADC). Lambda (λ) does not have any influence on the observed changes of pollutants conversion. CADC is a highly transient driving cycle with urban, extra-urban and motorway segments. λ is the raw electric signal.

and will not discuss the effect of other species (e.g. H$_2$O) and of the complex reaction network and conditions that are involved in TWC operation [8,16–18].

2. Experimental

The powder alumina and alumina–ceria–zirconia supported Pd samples (hereafter Pd/A and Pd/ACZ, respectively) with 1.6 wt% Pd were kindly provided by Umicore as model Pd-only three way catalysts. Operando XANES spectra were recorded in the transmission mode at the Pd K-edge (E$_0$ = 24.35 keV) at the beamline X1 of Hasylab (DESY, Hamburg). The electrically heated quartz reactor cell (d$_i$ = 20 mm) was connected to a gas-feeding system with mass-flow controllers and was interfaced to a mass spectrometer [19,20]. The sample (400 mg, sieved 150–200 μm) was firmly placed between two plugs of quartz wool, one end being placed against a quartz frit. The reactor was mounted in the furnace so that the X-ray beam passed axially through the reactor tube and the optical pathlength coincided with the catalyst bed length (ca. 2 mm). After pre-treatment at 300 °C for 30 min in 5 vol% O$_2$/He (400 ml/min), the oxidation state of Pd species was monitored under varying conditions of λ = 0.97, 1.01 and 1.1 and in a wide temperature range (100–900 °C) using a simulated exhaust composition of a stoichiometric natural gas engine (7000 ppm CO, 1300 ppm CH$_4$, 1600 ppm NO, 5012–5396 ppm O$_2$, bal. He; GHSV = 76,000 h^{-1}). The MS signal for oxygen (m/z 32) was used to confirm that the air/fuel ratio effectively changed. High temperature was targeted to simulate the acceleration section of the driving cycle. In the case of a gasoline engine, 150 ppm C$_3$H$_6$ were used together with 2650–3025 ppm O$_2$. Pd/ACZ was also subjected to two consecutive heating–cooling cycles under stoichiometric conditions (7000 ppm CO,

1300 ppm CH$_4$, 1600 ppm NO, 5300 ppm O$_2$, bal. He; GHSV = 76,000 h^{-1}) in the temperature range of 100–850 °C, as described elsewhere [21]. XANES spectra were recorded continuously during the heating, dwell and cooling segments. The raw data were analyzed using the WINXAS 3.1 software package [22]. Room temperature k^3-weighted FT-EXAFS data were obtained in the k ranges of 2–16 Å^{-1}, 2–13 Å^{-1} and 2–12 Å^{-1} for the reference Pd foil, fresh Pd/ACZ and used Pd/ACZ, respectively.

Experimental exhaust emission and catalytic conversion efficiency investigations with a Euro-4 natural gas vehicle were performed on a chassis dynamometer using the real-world based driving cycle from the EU project ARTEMIS (Common Artemis Driving Cycle) [23].

3. Results and discussion

Fig. 2a shows the behavior of the MS signals corresponding to NO, CO (N$_2$), CH$_4$, CO$_2$, H$_2$, H$_2$O and O$_2$ when subjecting the Pd/ACZ catalyst to a simplified transient cycle for natural gas catalyst operation in the XAS reactor cell. The cycle consisted of heating to 500 °C under reducing conditions (λ = 0.97), dwelling at 500 °C, heating to 900 °C under reducing conditions, cooling to 500 °C under slightly lean conditions (λ = 1.01) and dwelling at 500 °C. At 500 °C, both prior to heating to 900 °C and after cooling, λ was varied between 0.97 and 1.01, which is a common λ-variation for stoichiometric engine operation. At 500 °C at the rich end of the stoichiometric λ-window (λ = 0.97), CH$_4$ reforming occurs as it is evident from the evolution of hydrogen and CO. That a change of the λ value effectively occurs is confirmed by the next switch to the lean end of the stoichiometric λ-window (λ = 1.01) that results in the increase of CH$_4$ and CO conversions and a decrease of H$_2$ concentration, as well as by the reversed switch to λ = 0.97. Upon heating to 900 °C at the rich end CH$_4$ conversion increases; this is mirrored by NO depletion and by an increase of outlet H$_2$ and CO (signal influenced by possible N$_2$ production) as a result of CH$_4$ reforming. Above 700 °C, H$_2$ production decreases. The CH$_4$ conversion is almost complete above 700 °C. Upon switching to the lean end at 900 °C, the effect of increased oxygen concentration is evident from the quick drop of both CO and H$_2$ signals. During cooling, the CO signal reaches the level obtained at 500 °C under λ = 1.01 prior to heating. CH$_4$ conversion decreases as well but attains a lower level at 500 °C than prior to heating under rich conditions indicating less favorable reaction conditions. The last λ switch from 1.01 to 0.97 at 500 °C causes a further decrease of CH$_4$ conversion. It is clear from Fig. 2a that the behavior of the NO signal closely follows that of CH$_4$ confirming a close relationship between the abatement of the two pollutants [8,24]. This is not the case for C$_3$H$_6$ (Fig. 2b). NO concentration increases in the cooling segment under lean conditions after exposure to high temperature while C$_3$H$_6$ conversion remains unaltered.

The operando XANES spectra recorded continuously during this transient cycle show that the state of Pd in Pd/ACZ prior to heating to 500 °C under λ = 0.97 corresponds to that of a supported PdO catalyst (Fig. 3a). While heating, the oxidation state of the catalyst does not change until 300 °C. Reduction occurs suddenly between 300 and 350 °C. The XANES spectrum at 500 °C is characterized by the typical EXAFS oscillations and is obviously different from that representing the initial state. In the case of simulated gasoline operation, Pd reduced ca. 50 °C earlier (Fig. 3b). For both hydrocarbons, the variation of the λ value from the rich to the lean end does not cause any visible spectral change. There is no tangible evidence that the oxidation state of Pd differs from the reduced one in the whole cycles of Fig. 2. Therefore, the catalyst remains predominantly in the reduced state independently from heating–cooling cycle and from λ switches. However, the static nature of the data does not allow concluding whether surface re-oxidation occurred upon λ switches [12,13]. At the end of the experiment of Fig. 2, λ = 1.1 (>6200 ppm O$_2$) was provided to the catalyst at 500 °C to induce further changes. Visible but partial re-oxidation of
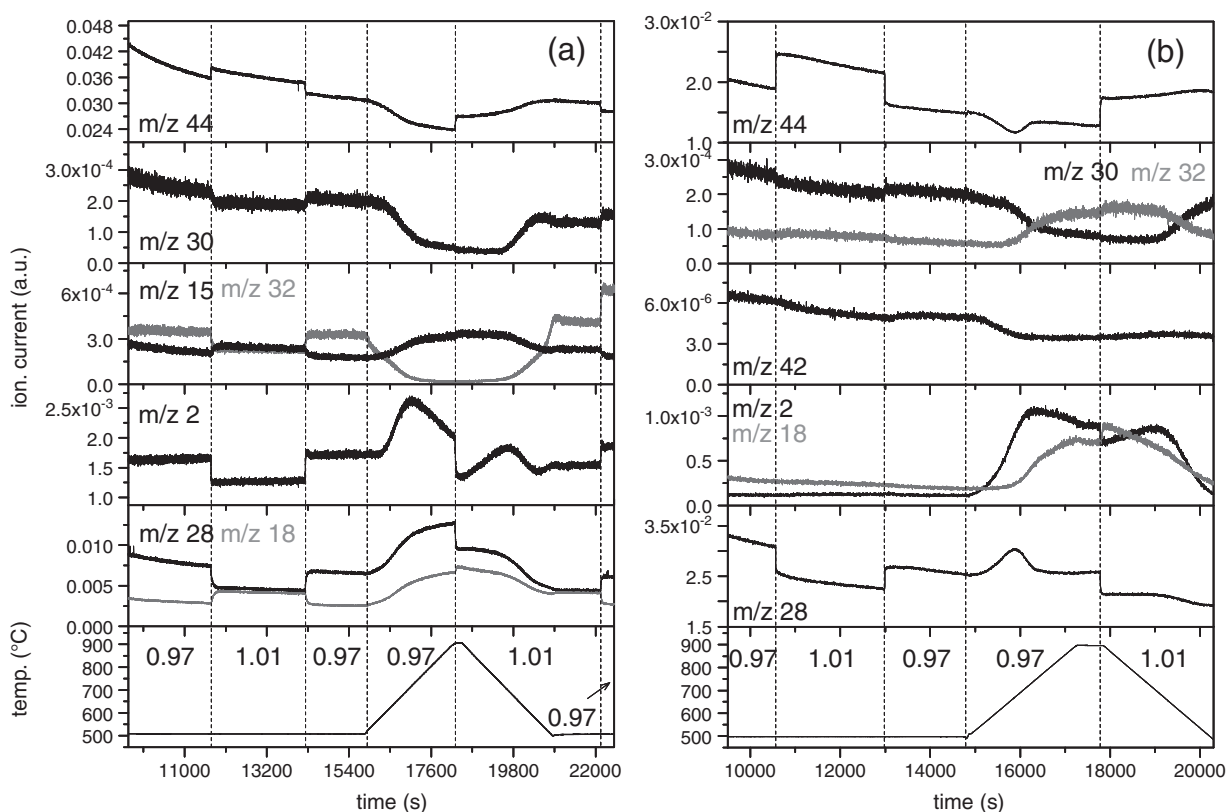
Fig. 2. MS profiles as a function of catalyst temperature during simulated cycle of (a) natural gas and (b) gasoline operation. During the measurement m/z values of 2 (H_2), 4 (He), 15 (CH_4), 18 (H_2O), 28 (CO, N_2), 32 (O_2) and 44 (CO_2) were followed. The λ values are indicated in the bottom panel. Heating–cooling rates were of 10 °C/min.
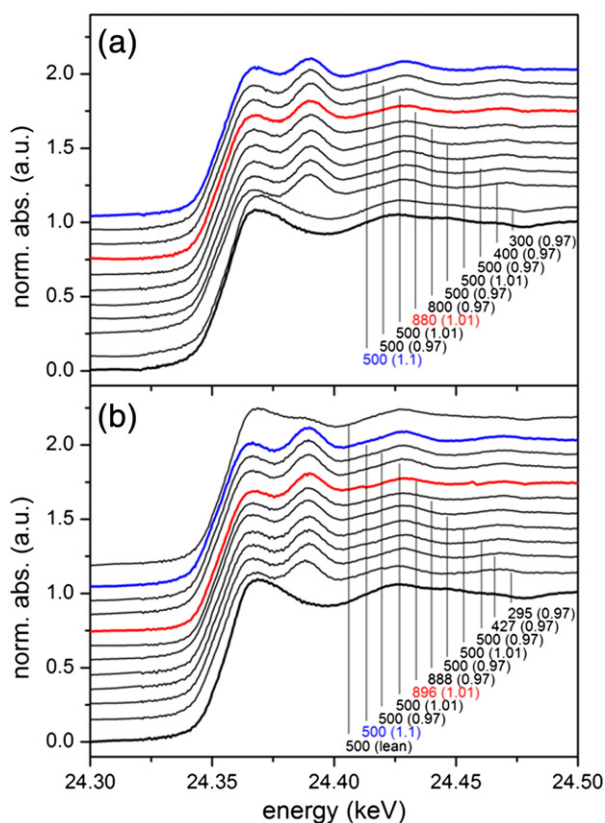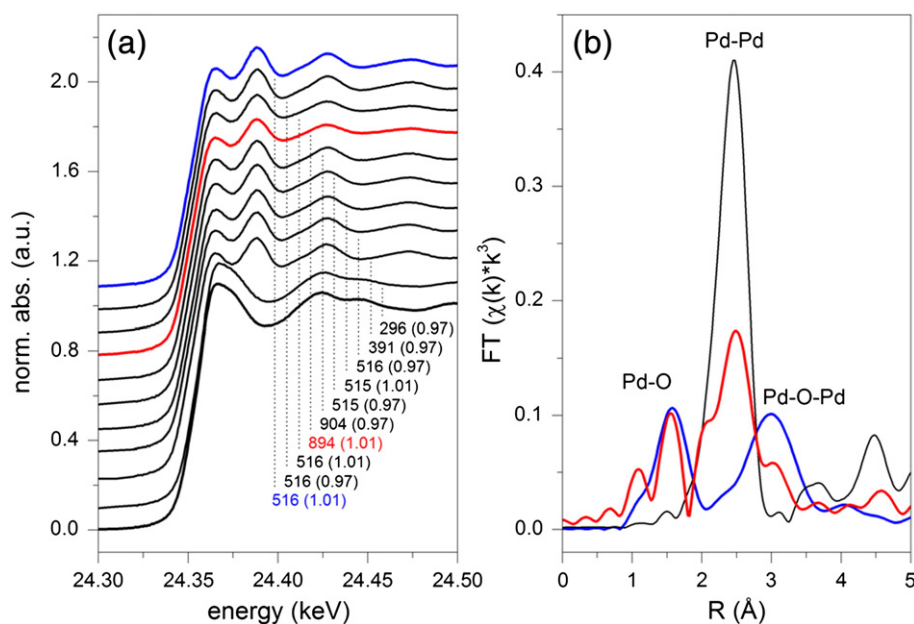

Fig. 3. Operando XANES spectra at the Pd K-edge recorded on Pd/ACZ during the simulated driving cycle of (a) natural gas and (b) gasoline operation. The bottom spectrum in each panel corresponds to room temperature in λ = 0.97. Values in brackets indicate the λ value.

Pd could be observed (Fig. 3a). Only large excess of oxygen (λ >> 1.1) caused evident changes as demonstrated in Fig. 3b. The constantly reduced state of Pd in Pd/ACZ is justified by the persistent reducing conditions created by the presence of H_2 and by the non-complete conversion of CO and CH_4. Conversely, the lower CH_4 conversion values obtained at 500 °C at λ values of 0.97 and 1.01 after the high temperature segment reflect a negative effect of the presence of reduced Pd on activity and the difficult re-oxidation under these conditions [19].

Very similar behavior in terms of the oxidation state of Pd was observed for Pd/A. This measurement was performed only in the case of natural gas operation. The initial oxidized state of Pd vanished between 300 and 350 °C and was not recovered in the whole experiment similarly to Pd/ACZ, as indicated in Fig. 4a. Further, Fig. 4b shows the FT-EXAFS spectra obtained in situ before and after subjecting Pd/ACZ to two consecutive heating–cooling cycles under steady-state stoichiometric conditions up to 850 °C [21]. As mentioned above, the fresh catalyst exhibits 1st and 2nd coordination shells of PdO indicating that Pd is fully oxidized. After use, the appearance of strong and well-defined peak corresponding to the Pd–Pd first coordination shell at ca. 2.5 Å indicates that a considerable fraction of Pd is metallic and coexists with a fraction of PdO. Therefore, under the present experimental conditions ceria–zirconia is not able to buffer the reducing conditions likely as a consequence of the length of the rich periods. Nevertheless, the persistence of the metallic character of Pd confirms observations on TWCs aged under real driving conditions by XPS indicating that metallic Pd is a major species as a consequence of prolonged use [4].

It is of interest to compare the conversion profiles of CH_4 and C_3H_6 during the heating–cooling segments and to relate them to the oxidation state of the catalyst obtained from the XANES spectra. CH_4 conversion is already high at 500 °C under rich conditions and reaches ca. 100% at 750 °C (Fig. 5). During cooling to 500 °C at the lean end of the stoichiometric λ window, conversion substantially follows

Fig. 4. (a) Operando XANES spectra at the Pd K-edge recorded on Pd/A during the simulated driving cycle of natural gas operation. The bottom spectrum corresponds to room temperature in $\lambda = 0.97$. Values in brackets indicate the λ value. (b) FT-EXAFS data obtained in situ on Pd/ACZ before (blue line) and after (red line) two consecutive heating–cooling cycles under stoichiometric conditions. The spectrum of the reference Pd foil is shown for clarity (black line).

the same profile as during heating with a shallow conversion gain between 550 and 700 °C. On the contrary, C_3H_6 conversion slightly improves during heating; a significant hysteresis is observed between 650 and 500 °C during cooling that is expected from λ
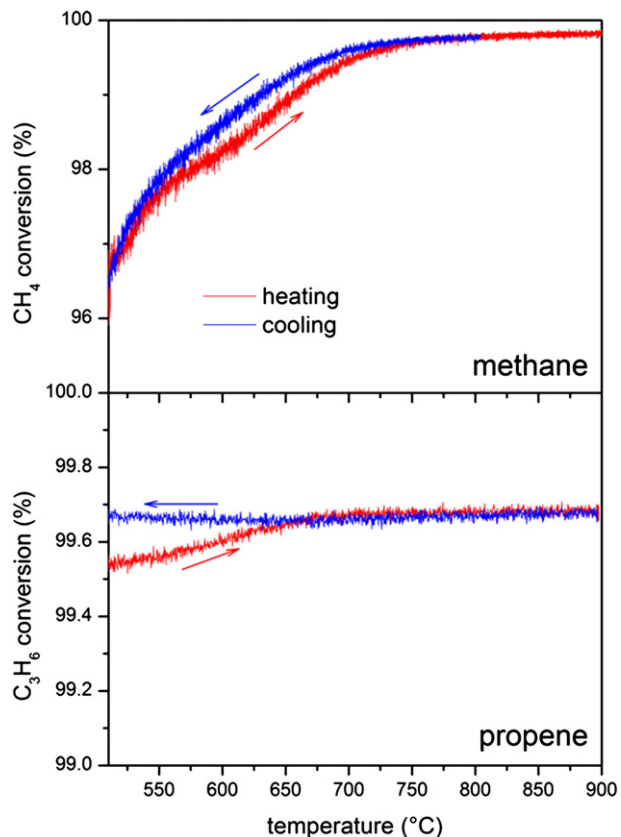
Fig. 5. Methane and propene conversion profiles during the heating–cooling segments 500 °C → 900 °C ($\lambda = 0.97$) and 900 °C → 500 °C ($\lambda = 1.01$) of Fig. 2.

sweep experiments, where hydrocarbon conversion is better under lean conditions than under rich conditions at a given temperature. Fig. 5 demonstrates that CH_4 slip can be expected in the temperature range explored in this work from operation of natural gas engines.

It is also reasonable that exposure for long time, longer than the real high-frequency lambda oscillations, under rich conditions and to temperature as high as 900 °C causes Pd particle growth. We had observed that this occurs under lean conditions [18]. Given the well-developed signal of the Pd–Pd coordination shell, the FT-EXAFS of Fig. 4b confirm that particle growth has occurred also for Pd/ACZ after repeated reaction cycles under stoichiometric conditions. However, these structural changes did not affect the light-off characteristics for methane oxidation [21], in agreement with the observation that particle size was not a crucial parameter in determining the activity of a series of differently loaded Pd/Al$_2$O$_3$ catalyst [25]. Therefore, though particle growth may have occurred in the experiments of this work, it should have occurred in a comparable manner in the case of natural gas and gasoline operation because of the identical treatment the two catalysts have been subjected to. Hence, we do not interpret the different behavior of Pd in Pd/ACZ with respect to oxidation of CH_4 and C_3H_6 as being affected by Pd sintering. We consider that the different behavior observed in the heating–cooling segments of the cycle is determined by the different reactivity of CH_4 and C_3H_6 and by the different influence of the state of Pd on their reactivity [26]. The XANES data show that under these conditions Pd remains predominantly in the reduced state. In the case of CH_4, the oxidation activity of Pd is strongly coupled to the thermodynamic PdO–Pd equilibrium [27]. Reduction of PdO at high temperature (>750 °C) causes a reduction of oxidation activity in the cooling segment, metallic Pd being likely active at these temperatures [19]. Activity drop is typically observed also under lean burn conditions [2,19]. Therefore, cooling under lean conditions does not improve catalytic activity because the activity is dictated mainly by the reduced state of Pd rather than by changes in oxygen concentration in the feed. The fact that no substantial difference of activity is observed between heating (rich end of λ-window) and cooling (lean end) segments reveals that reduced Pd is not very efficient. This point is still source of debate and recently data have been reported that were interpreted by considering

metallic Pd as the active phase [28]. Also, we have shown on the same Pd/ACZ catalyst used in this work that though oxidized Pd may be responsible for activity on a fresh catalyst, a mixed PdO/Pd phase needs to be considered at work on the used catalyst, as also shown in Fig. 4b [21]. Though the present experimental conditions are static rather than real λ oscillations, the initial oxidized state of Pd cannot be recovered even under periodic feedstock fluctuations at 500 °C [29]. Moreover, full conversion is obtained only above 750 °C (Fig. 5) contrary to measurements conducted on oxidized samples under lean conditions [19]. Therefore, the CH_4 emissions observed in real transient cycles and with λ > 1 [5–7] could be partly ascribed to the effect of the oxidation state of Pd thus pointing to lower CH_4 oxidation activity of extensively reduced catalysts. This issue still deserves a more systematic study. The debate on the nature of the active sites for CH_4 oxidation, e.g. the role played by metallic Pd or PdO, and the observation of predominantly metallic Pd obtained from this work suggest that advanced structural probes are required to be able to assess the effective role of the species present on a working catalyst. This study shows that under the applied reaction conditions transmission XANES detects predominantly metallic Pd. However, X-ray absorption spectroscopy is not able to capture a surface re-oxidation when for example changing from rich to lean conditions because the method is sensitive to the bulk structure. Therefore, it cannot be excluded that under these experimental conditions surface re-oxidation occurs or that the reduction observed above 300 °C is not complete. A number of works have described the structure and the role of different Pd oxide layers or adsorbed oxygen for methane oxidation [30–32]. These species would not be detected under the present experimental conditions because of the nature of XANES. We consider that working under pulsed conditions is a better approach to obtain information on the active palladium species because even for a bulk sensitive technique such as XANES it becomes possible to extract information from surface processes [10,13,29,33].

In the case of C_3H_6 taken as model hydrocarbon for gasoline, the reduced state of Pd does not appear to play such a critical role as in the case of CH_4 and the increase of oxygen concentration in the feed causes the expected increase of oxidation activity.

4. Conclusions

We have shown that the oxidation state of Pd in a Pd-only TWC strongly influences hydrocarbon oxidation activity under simulated operation conditions. CH_4 abatement is mainly influenced by the reduced state of Pd. On the contrary, C_3H_6 oxidation activity is not affected by the reduced state of Pd and largely depends on the oxygen concentration of the feed. Although not conclusive on the role played by adsorbed oxygen and surface re-oxidation that can occur during operation under faster oscillatory conditions, the observed effects could contribute to rationalize observations on real catalytic converters.

Acknowledgments

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