



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



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ABSTRACT

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

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1. Introduction

Natural gas plays a central role for the reduction of CO₂ road emissions, especially because of the growing importance of addition of bio-gas and synthetic natural gas to the existing distribution network. Vehicles fueled with natural gas and bio-gas are powered by either stoichiometric or lean burn engines depending on the size and purpose of the vehicle. Emissions of methane (CH₄), the major component of these fuels, remain a concern because of its global warming potential and are thus controlled efficiently by exploiting catalytic converters [1]. Three-way catalysts (TWC) represent the current technology in the case of the exhaust of natural gas passenger vehicles operating with stoichiometric engines [2,3]. The catalyst composition is adapted from the gasoline TWC counterpart by additional platinum group metals (PGM), mostly palladium (Pd), in order to improve the efficiency of CH₄ oxidation, which is

more difficult to activate than longer chain hydrocarbons representative of gasoline exhaust (propane, propene) [4]. A stoichiometric air-to-fuel ratio ($\lambda = 1$) is required for the TWC operation in order to remove simultaneously the three pollutants, CO, NO and hydrocarbons [5]. This type of operation is characterized by the point at which CO oxidation activity increases to full conversion and the NO reduction activity decreases simultaneously while moving towards lean conditions [6], the CO-NO crossover point [7]. Around this point, the conversion of the three pollutants is most efficient. It is known [7–10] that in the case of TWC for natural gas fuel this point does not correspond to stoichiometry ($\lambda = 1$) but is shifted into slightly rich of stoichiometry, essentially because of the low reactivity of CH₄. This practical observation reflects also the different chemistry of abatement of the exhaust pollutants between gasoline and natural gas. Despite the extensive knowledge on the chemistry of CH₄ oxidation on PGM based catalysts under lean conditions [11–17] that in the automotive sector pertains to lean burn engines of large vehicles, e.g. buses and trucks, a systematic investigation of the complex chemistry involved in CH₄ oxidation on TWC is rare. On the one side, this knowledge is crucial for the design of cat-

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alysts specialized on the abatement of emissions from natural gas fueled engines in contrast to catalysts for gasoline operation. On the other side, the knowledge should also be used to develop catalyst control strategies tailored for operation with this fuel. While little information is available on the behavior of simplified catalyst formulations, which are desirable in order to rationalize the involved chemistry, the majority of the studies in the open literature focused on the characterization of complex or even commercial TWC compositions. A rigorous derivation of the mutual effects of chemical and material components is difficult based on these premises. Subramanian et al. [10] were the first to subject a Pd/Al₂O₃ catalyst to various reaction environments with the aim to derive the essential chemistry of CH₄ oxidation on a TWC. Besides reporting higher CH₄ conversion under reducing conditions than under oxidizing conditions, critical observations revealed a substantial inhibition of CH₄ oxidation in the presence of CO under net oxidizing conditions. Moreover, CH₄ oxidation by NO was emphasized as a route for CH₄ removal under net reducing conditions, while steam reforming was considered negligible, in marked contrast to observations by others on commercial catalysts of complex composition [18,19] and on Pt-Rh/CeO₂-Al₂O₃ [20]. The presence of the oxygen storage component (Ce) and of rhodium may contribute to explain the beneficial role of steam on CH₄ conversion. Additionally, NO reduction by hydrogen (NO + H₂) and by CH₄ (CH₄ + NO) were identified at different temperature regimes [18,20]. Hence, it is important to underline that the typical reaction responsible for NO reduction on gasoline TWC, i.e. CO + NO, does not contribute appreciably when CH₄ is the hydrocarbon. These data were obtained predominantly under static reaction conditions exploiting temperature programmed ramps in either rich or lean feeds and lambda sweeps, where the air-to-fuel equivalence ratio is varied stepwise at various temperatures. Bounechada et al. [19] analyzed this chemistry on a commercial Pd-Rh-Al-Ce catalyst under periodic rich/lean reaction conditions that better mimic the operating conditions of the TWC. It was demonstrated that short rich pulses can sustain CH₄ oxidation at higher conversion levels than static experiments and that small amplitude oscillations of O₂ concentration around stoichiometry were more beneficial than large amplitude oscillations. Hence, these experimental conditions are favorable to CH₄ oxidation compared to either rich or lean conditions.

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

2. Experimental

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

2.1. Catalytic measurements

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

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

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

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

2.2. Spectroscopic measurements

Diffuse reflectance UV-vis (DRUV) and infrared Fourier transform (DRIFT) spectroscopy measurements were performed using the same gas feeding system described above for the catalytic measurements. For these measurements, the catalytic reactor was by-passed and the feed gas was directed either to the UV-vis spectrometer (Cary 4000, Agilent) or the FTIR spectrometer (Vertex 70, Bruker). The sample was cut from the full-size monolith and crashed to fine powder before mounting in the diffuse reflectance reactor cell attached to a Praying Mantis mirror unit (Harrick) fitting both spectrometers.

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

3. Results and discussion

3.1. Temperature programmed reaction

Periodic rich/lean reaction conditions are beneficial for the efficiency of a three-way catalyst (TWC) [23] also for aftertreatment of natural gas vehicles [19] and represent realistic operation conditions. The effect of oscillating reaction conditions was verified on the Pd-only honeycomb catalyst and compared to steady state reaction conditions. Methane (CH₄) conversion in continuous stoichiometric feed representative of the exhaust gas of natural gas fueled engines proceeded as shown in Fig. 1. Light-off occurred at ca. 350 °C but CH₄ conversion was not complete even at 600 °C and the maximum value was ca. 30%. Despite the impossibility to control the catalyst composition, meaning that possibly other catalysts could provide better performance, the data reveals the difficulty to remove CH₄ from exhaust gases under steady state stoichiometric conditions (λ = 1) questioning the suitability of this type of mea-

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