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Formation of NH$_3$ and N$_2$O in a modern natural gas three-way catalyst designed for heavy-duty vehicles: the effects of simulated exhaust gas composition and ageing

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Graphical abstract

Highlights:

- NO and CH$_4$ concentrations in exhaust gas affect NH$_3$ and N$_2$O formation.
- Increasing temperature restricts NH$_3$ and N$_2$O formation with fresh catalysts.
- Ageing changes the structure of oxygen storage material, influencing the formation of NH$_3$ and N$_2$O.

Abstract

An increasing number of heavy-duty vehicles are using liquefied natural gas (LNG) as a fuel due to the expanding refuelling station network for LNG and lower overall emissions compared to diesel vehicles. The latest EURO VI regulation or natural gas fuelled vehicles set a limit for NH$_3$ of 10 ppm, and N$_2$O exhaust is expected to be restricted in Europe in the near future. Poisonous and corrosive NH$_3$ and the greenhouse gas N$_2$O are formed as by-products in a three-way catalyst used to minimize the emissions of stoichiometric heavy-duty engines. In this work, we studied how high temperature NH$_3$ and N$_2$O formed in modern, fresh and aged bimetallic Pd/Rh three-way catalysts in simulated exhaust gas. More precisely, the exhaust gas composition and temperature were examined. Decreases in NO concentration
and increases in temperature lowered the formation of NH$_3$ and N$_2$O, whereas a decrease in CH$_4$ concentration reduced only NH$_3$ formation. According to Raman and powder X-ray diffraction experiments, the structure of the catalyst changed during the ageing, and this reputedly affected the function of cerium-zirconium mixed oxides and thus the formation of NH$_3$ and N$_2$O. Temperature programmed reduction (H$_2$-TPR) measurements showed changes in cerium-zirconium mixed oxide performance after ageing supporting Raman spectroscopy findings. Catalyst ageing in oxidizing conditions increased the formation of N$_2$O. This study showed that exhaust gas composition plays an important role in the formation of undesired NH$_3$ and N$_2$O emissions.

**Keywords:** NH$_3$, N$_2$O, Natural Gas, Stoichiometric engine, Ageing

1. **Introduction**

An increasing number of heavy-duty vehicles are using liquefied natural gas (LNG) as a fuel due to the successful development of a LNG refuelling station network. LNG is composed almost entirely of methane, which contains four C–H bonds and only one carbon—the high H/C ratio forms less CO$_2$ per unit of produced energy than any other fossil fuel.[1] Interest in natural gas (NG) is growing enormously due to low overall exhaust emissions. NG engines are commonly divided into two categories: lean-burn engines and stoichiometric engines. Stoichiometric natural gas engines equipped with a modern three-way-catalyst (TWC) are comparable in terms of emissions to lean-burn diesel engines.[2, 3]

Currently, stoichiometric NG engines equipped with a TWC after-treatment system meet stringent Euro VI emission limits.[4] However, the use of TWC in vehicles has rapidly increased over the past three decades, and at the same time, undesired NH$_3$ and N$_2$O emissions into the atmosphere have also increased. [5] Thus, some researchers suggest that vehicles equipped with catalytic converters are partially responsible for increased NH$_3$ and N$_2$O emissions into the atmosphere, and vehicles with TWCs, which use low-sulfur fuels, have especially increased NH$_3$ formation.[5, 6]

According to the European dangerous substances directive (67/548/EEC), NH$_3$ is a poisonous and corrosive gas. NH$_3$ is a secondary pollutant that is formed in a TWC process during NO conversion under rich conditions. [7] NH$_3$ also acts as a precursor to form secondary atmospheric aerosols,[8] and its reaction with nitrogen and ammonium nitrate forms particulate matter, which causes severe health threats.[9] The latest EURO VI regulation for heavy-duty vehicles has set a limit of 10 ppm for NH$_3$ formation.[4] N$_2$O is rated as a strong greenhouse gas, and its greenhouse potential is 300-times greater than that of CO$_2$. The N$_2$O emission of vehicles in the US and China [10] is regulated, and N$_2$O emissions would potentially be regulated in Europe soon, based on the latest knowledge. Ravishankara et al. suggested that N$_2$O gas has had the greatest impact on ozone depletion in the 21st century. [11]

A modern TWC, including noble metals such as Pt, Rh and Pd, was coated over ceramic or metallic substrates. Different noble metal combinations have been studied in after-treatment systems of NG vehicles.[12-15] In general, Rh reduces NOx, [16] whereas Pd or Pt oxidizes CO and CH$_4$ emissions. Interest in Pd in TWC converters has increased due to the increased use of NG as a fuel. [16] In the after-treatment systems of stoichiometric NG engines, Pd is the most widely used noble metal because it has the best ability to convert CH$_4$ emission.[17, 18]
The catalyst active metal composition, air-to-fuel ratio, and operation temperature play important roles in the formation of NH$_3$ and N$_2$O. Catalysts that have Pd/Rh or Pt/Rh as active metals produce more NH$_3$ under rich conditions than the Rh-only catalyst.[19, 20] The largest N$_2$O formation was observed to occur for monometallic Rh-only TWC [21], but emission decreased with increasing temperature, and with Pd-only TWC, N$_2$O formation continued up to 500 °C.[22]

The durability of the catalyst is an important topic because catalytic converters must tolerate high temperatures during operation. High temperature laboratory ageing simulates the conditions that the catalyst undergoes in real driving situations. TWC contains components that inhibit the sintering of the catalyst, such as CeO$_2$ and ZrO$_2$. These components also act as oxygen storage material by improving the ability of the catalyst to store and release oxygen when the engine is operating near the stoichiometric air-to-fuel point. [2, 23]

Salaün et al. [24] studied NG simulated exhaust gases with commercial TWC. They examined the exhaust gas composition on TWC operation. They also studied how changes in NO and CH$_4$ concentrations in simulated exhaust gas affect the catalyst performance. They concluded that NO is the main oxidising agent for CH$_4$ at higher temperatures. Bounechada and coworkers [23] studied the effect of the periodic lean/rich switch and stationary experiments on CH$_4$ conversion by simulating the exhaust of the NG vehicle using the Pd-Rh/Al$_2$O$_3$/Ce-Zr catalyst. They concluded that the reduction of NO and CH$_4$ steam reformation and the water gas shift reaction occur in the rich side, and there are different kinds of chemistry involved on the lean side. Klingsted et al. [25] studied how fresh and aged Ba promoted Pd/Al$_2$O$_3$ and Pd/Ce/Al$_2$O$_3$ catalysts for natural gas vehicle (NGV) with simulated exhaust gas by completing sweeping tests from lean-to-rich and back from rich-to-lean. According to sweeping tests from lean-to-rich and rich-to-lean at 450 °C, a hysteresis effect was detected in CH$_4$ and NO conversions. The researchers supposed that it was caused by phase changes occurring in the surface of the Pd species. We also observed this hysteresis behaviour in our measurements. However, none of the aforementioned studies considered the effect of exhaust gas composition on the formation of NH$_3$ and N$_2$O. Our aim is to study this with modern, aged and fresh bimetallic (Pd/Rh) TWCs, including how concentration changes of NO and CH$_4$ in simulated natural gas engine exhaust gas affect NH$_3$ and N$_2$O formations when water is present. We demonstrate NH$_3$ and N$_2$O formation at 440, 490, and 530 °C with the fresh and aged catalysts when the oxygen concentration is varied stepwise from lean-to-rich and back from rich-to-lean conditions. At higher temperatures, methane acts as a reducing agent for NO, which is why we concentrated on higher temperatures. Our hypothesis is that lower exhaust gas concentrations of NO and CH$_4$ directly reduce NH$_3$ and N$_2$O formation and that aged and fresh catalysts show differences in NH$_3$ and N$_2$O formations because ageing affects Ce-Zr mixed oxides, thus oxygen storage function. The study provides valuable knowledge on the formation of NH$_3$ and N$_2$O emissions in NG heavy-duty vehicles and offers a one way to the engine operators to tailor their engines to achieve lower emissions by modeling the exhaust gas composition.

2. Experimental

2.1 Catalyst texture

Dinex Ecocat Oy provided the studied commercial bimetallic TWC (Pd and Rh 16:1 200 g/cft). Catalysts consist of a Al$_2$O$_3$ support material and a Ce-Zr mixed oxide as oxygen storage material. The catalyst was designed for heavy-duty applications. To simulate durability of the catalyst, it was aged under air at 1000 °C for 3 hours. BET surface area for the fresh Pd/Rh TWC was 113 m$^2$g$^{-1}$ and for the aged Pd/Rh TWC 66 m$^2$g$^{-1}$. In addition, to investigate the role of noble metals after ageing, the fresh
and aged catalysts without noble metals were prepared and studied. BET surface areas of fresh and aged catalysts without noble metals were 113 and 63 m$^2$g$^{-1}$, respectively.

2.2 Characterization

Surface areas were measured for the fresh and aged Pd/Rh TWC and for noble metal free catalysts with Quantachrome Autosorb-iQ device. Prior to experiment, the catalyst were removed from metallic foil to measure its surface area in powder form. Sample weight of 150 mg was used in the measurements. All the samples were degassed under vacuum at 350 °C for 150 min to remove moisture and air residuals before surface area measurement. The measurement was carried out at temperature of liquid nitrogen -196 °C and the surface areas were calculated according to Brunauer-Emmett-Teller theory.

The performance of the catalysts and the formation of NH$_3$ and N$_2$O were studied with a laboratory scale reactor equipped with a Gasmet FTIR on-line device. A packed small-scale TWC reactor which had the monolithic structure (500 CPSI), with diameter 1.0 cm, length 1.8 cm, and volume 1.4 cm$^3$, was placed inside a metallic tube. The catalyst weight of 300 mg was used in each experiment. Reactors were rolled into cylindrical shape by using flat and corrugated metal foils coated with the catalyst. Simulated exhaust gas was used in the experiments with a flow of 1180 ml min$^{-1}$, resulting in a gas hourly space velocity of 50 000 h$^{-1}$. The composition of the simulated exhaust gas was as follows: NO 500/1500 ppm, CH$_4$ 700/1400 ppm, CO 4200 ppm, CO$_2$ 6 %, H$_2$O 10 %; O$_2$ 0.50–0.18 % and balanced N$_2$. The TWC was heated with a programmed electric furnace, and the temperature of the catalyst were precisely recorded inside the reactor above the monolith. The catalysts were pretreated at 600 °C in reaction conditions for 1 hour. A peristaltic pump was utilized to feed H$_2$O in the reactor. Measurements for the fresh and thermally aged TWC reactors were carried out at constant temperatures 440 °C, 490 °C or 530 °C. The oxygen concentration of the exhaust gas was varied stepwise from lean-to-rich and rich-to-lean to obtain full NO conversion. In the stoichiometric engine, the TWC cycle between the rich and lean conditions varied rapidly, with a frequency of approximately 1 Hz. In our measurements, we wanted to illustrate factors that affect the formation of NH$_3$ and N$_2$O. Thus, we operated the lean-to-rich and reverse rich-to-lean cycle more slowly than occurs in a real operation. The oxygen concentration of the exhaust gas was changed stepwise. After oxygen concentration change, the CH$_4$ and NO concentrations were always allowed to stabilize. The oxygen concentration was decreased until at least 98 % conversion of NO was achieved. Temperature was kept constant during the measurements, and the range of the constant temperature was ±3 °C.

Phase changes of the catalyst after thermal ageing were determined with powder X-ray diffraction (XRD). The catalysts were removed from the metal foil with a spatula. Analyses were conducted with the Bruker-AXD D8 Advance device, using Cu Kα as a radiation source. The diffraction patterns were collected at the 2θ scale from 17° to 90°.

Raman spectra of the fresh and aged samples were measured using Renishaw inVia Raman Microscope with an Ar-ion laser at 785 nm. Raman spectra were also measured for the fresh and aged catalyst samples without the noble metals. Five parallel measurements were completed for each catalyst. Temperature programmed reduction (H$_2$-TPR) experiments were carried out with a Quantachrome Autosorb-iQ device equipped with a thermal conductive detector (TCD). Gas mixture of 10% H$_2$ in Ar was used as a reactive gas. Measurements were conducted for the fresh and aged Pd/Rh TWC and for the catalysts without the noble metals. The catalysts were removed from the metal foil with a spatula prior to experiments. The amount of catalyst used was 180 mg in all cases. The H$_2$-TPR experiment was carried out in a flow of 20 ml/min of 10% H$_2$/Ar at a heating rate of 10 °C/min up to a maximum temperature of 1000 °C.
3. Results and discussion

In stoichiometric engines, the air-to-fuel ratio has a significant influence on NH₃ formation, which occurs when NO starts to convert and the engine is operating slightly on rich λ-value; it increases even more in richer conditions. The formation of N₂O occurs under lean conditions, and it is bound to NO₂ formation. [26]

The majority of studies focus on the formation of NH₃ and N₂O in a TWC operation at low temperatures. However, at low temperatures (150–400 °C), CO converts to CO₂, which decreases NO conversion; above 400 °C, CO conversion does not affect NO conversion. Thus, we focused particularly on higher temperatures, 440 – 530 °C. All measurements were conducted with both fresh and the aged catalysts. Conversions of NO and CH₄ as well as the formation of undesired by-products NH₃ and N₂O during the lean-to-rich/rich-to-lean cycles are illustrated in Fig. 1.

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \quad (1) \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad (2) \\
2 \text{NO} + 4 \text{CO} + 2 \text{H}_2\text{O} + \text{H}_2 & \rightarrow 2 \text{NH}_3 + 4 \text{CO}_2 \\ 
2 \text{NO} + 5\text{H}_2 & \rightarrow 2 \text{NH}_3 + 2 \text{H}_2\text{O} \quad (4) \\
2 \text{NO} + \text{CO} & \rightarrow \text{N}_2\text{O} + \text{CO}_2 \quad (5) \\
2 \text{NO} + \text{H}_2 & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad (6)
\end{align*}
\]

The formation of NH₃ and N₂O requires H₂ according to Reactions (3)–(6). Fig. 1 shows that the formation of NH₃ and N₂O requires the same H₂ reserves. When the reaction conditions approach the rich regime, NO conversion started to increase, and N₂O formation simultaneously increased. N₂O reached its highest concentration right before NH₃ formation started. The same trend was observed when oxygen concentration was increased after the rich regime, and NH₃ concentration started to decrease. NH₃ formation was the most intense when NO conversion exceeded the 98 % limit. According to our results, NH₃ concentration reached the highest formation limit, and the formation did not further increase, although the oxygen concentration decreased more than necessary for 100 % NO conversion. In Fig. S1 oxygen concentration is decreased more than it is necessary to achieve 98% NO conversion limit, and as it shows, that NH₃ concentration is not increasing anymore and actually, it is decreasing.

**Fig. 1.** CH₄, NO, NH₃ and N₂O concentrations during the lean-to-rich and rich-to-lean operations and oxygen concentration at 440 °C with fresh TWC.
The primary reactions that occur during operation of TWC of NG vehicles that are responsible for NH₃ and N₂O formation in the rich side are presented in Reactions (1)–(6). The formation of H₂ in TWC is due to steam reforming (SR) Reaction (1) and the water gas shift (WGS) of Reaction (2).[27, 28] NO is converted in the presence of H₂, which is formed via Reactions (1) and (2). During NO conversion, the formation of the harmful by-products NH₃ and N₂O may occur in Reactions (3)-(6). [29]

The conversion of NO requires H₂ and CO to occur under rich conditions. However, the simulated exhaust gas does not contain any H₂; therefore, all H₂ originates from the WGS and SR reactions. Meija-Canteno and co-workers [30] studied the formation of NH₃ and N₂O with Pd-only TWC and a Pd model catalyst for diesel and gasoline vehicles with water containing exhaust gas, and they suggested that the majority of formed H₂ originated from the steam reforming reaction when the temperature was 300–500 °C; however, the water gas shift reaction was responsible for the production of H₂ above 500 °C.

3.1 NO concentration effect on NH₃ and N₂O formation

Two NO concentrations, 500 and 1500 ppm, were used in measurements to study the formation of NH₃ and N₂O. Figs. 2 (a) and (b) clearly show that by increasing the NO concentration of simulated exhaust gas from 500 ppm to 1500 ppm, the formation of NH₃ and N₂O significantly increase over the fresh catalyst if the CH₄ concentration is 1400 ppm. Oh et. al. [31] showed that with Pd-containing TWC, the presence of CO and H₂O in the feed gas stream at temperatures above 400 °C and with higher NO concentration in the gas feed can cause an increase in NH₃ formation because extra H₂ is produced via WGS reaction (R2), which reacts with NO (R3 and R4).

NO conversion cycles are presented at different temperatures (Fig. S2). The results illustrate that NO concentration affects a conversion window of NO. According to our results, the fresh catalyst required richer conditions to convert all the NO; thus, NH₃ and N₂O concentrations increased.

Automobile catalyst are exposed to high temperatures during driving, which can reach up to 1000 °C. Thus, it is important to research catalyst durability to thermal ageing. In thermal ageing, the catalyst is pre-exposed to a high temperature, in our situation 1000 °C under air, and then, the catalyst undergoes different phase changes. Hietikko et al. [32] studied the different ageing conditions of Pd/Rh catalyst: reducing, oxidizing and inert in the laboratory and engine- and vehicle-aged. They discovered that oxidizing conditions at 1200 °C mostly correspond to the performance of a vehicle-aged catalyst.

Previously, high surface area has been suggested is generally related to good catalyst performance. [33, 34] Studies demonstrated ageing affects catalyst performance and morphology. Catalyst exposure to high temperatures in oxidising conditions decreases the surface area and sinters metal particles, especially Rh, and washcoat materials. [33] Especially with a laboratory scale catalyst, thermal ageing in oxidising conditions can decrease catalyst performance. [35] Lassi et al. [36] studied additive activity with gas composed of different concentrations of NO and CO and different catalyst structures for the Pd/Rh- catalyst with Ce- and La-oxides and CeₓZr₁₋ₓO₂ mixed oxides. They discovered that ageing under air at 1000 °C for 3 h affects the catalyst surface area and chemical state of the active metals. Neyestanakai et al. [37] discussed the influence in active metals in their review article about the catalyst deactivation. They concluded that PdO is the most active phase of Pd, which starts to decompose at 600 °C, even in oxygen-rich conditions, to form metallic Pd, which is less active in converting CH₄ than the oxidised form; the activity declines. Some researchers believe that there are differences in activity that depend on the form of the palladium oxide. [38]

The TWC support material, Al₂O₃, goes through phase changes during the ageing process. First, above 500 °C, alumina (bohemite) changes to γ-Al₂O₃; at 800–1000, alumina is δ-Al₂O₃; at 1000–1100 °C,
alumina is \( \theta - \text{Al}_2\text{O}_3 \); and when the catalyst reaches 1100–1200 °C, alumina changes to \( \alpha - \text{Al}_2\text{O}_3 \). However, commercial catalysts usually include the stabilizers \( \text{La}_2\text{O}_3 \) and \( \text{CeO}_2 \), which enhance \( \gamma - \text{Al}_2\text{O}_3 \) from sintering at high temperatures. The XRD results (explained later) confirmed that alumina maintained the \( \gamma - \text{Al}_2\text{O}_3 \) form, and the aged catalyst contained metallic Pd in addition to traces of PdO. Thus, in our case, aging at high temperatures could lead to loss of performance because of the metallic Pd or less active PdO. In addition, the sintering of Rh would also be apparent. Some researchers are conscious of morphology changes during the ageing, but they believe that effects on catalyst performance are minor. Fernandes et al. [39] studied the thermal deactivation effect on a commercial Pd/Rh catalyst, and they determined that catalytic propane conversion actually increased after ageing in oxidizing conditions at 1200 °C. Fig. S3 shows that CH\(_4\) conversion declined with the aged catalyst when NO concentration was 500 ppm, and it stayed somewhat the same or increased when NO concentration was 1500 ppm. With the fresh catalyst, CH\(_4\) conversion was almost the same at both NO concentrations. Based on the results, we assume that the NO concentration of the exhaust gas affects the performance of the aged catalyst.

Fig. 2(a-d) shows differences in \( \text{N}_2\text{O} \) formation for the fresh and aged catalysts with two different NO concentrations: 500 ppm and 1500 ppm. The formation of \( \text{N}_2\text{O} \) was greater for the aged catalyst, and we observed precisely the same phenomenon in all measurements. S. Castillo et al.[41] investigated \( \text{N}_2\text{O} \) formation with three TWC (Pd, Rh and Pt) with different metal loadings, and they discovered that the aged TWC with a high loading of noble metals produced more \( \text{N}_2\text{O} \) than the fresh one. Zhao et al.[42] investigated the influence of mileage effects on gasoline vehicles, and they discovered that \( \text{N}_2\text{O} \) formation increases with increasing mileage. M. Odaka et al. [43] studied \( \text{N}_2\text{O} \) formation at high oxygen concentrations with aged and fresh low-Pd/Rh, high-Pd and high/low-Pt/Rh catalysts. They suggested that TWC decomposes \( \text{N}_2\text{O} \), but the ability of aged and fresh TWC to decompose \( \text{N}_2\text{O} \) differs, and declines in \( \text{N}_2\text{O} \) decomposition after ageing are due to changes in catalyst OSC (oxygen storage capacity). They also suggested that high metal loading fresh catalysts have larger \( \text{N}_2\text{O} \) concentrations and lower metal loading aged catalysts produce more \( \text{N}_2\text{O} \). Despite these results, a NG-tailored TWC was used, so we can substantiate some of those findings as reliable in our study because of oxygen storage material performance: catalyst ageing decreases the catalytic ability to decompose \( \text{N}_2\text{O} \). Our finding is that the aged catalyst produces more \( \text{N}_2\text{O} \) than the fresh catalyst. However, M. Odaka et. al.[43] did not test high loading Pd/Rh catalyst in their studies, which could explain the differing results.
Fig. 2. Formation of NH\textsubscript{3} and N\textsubscript{2}O during lean-to-rich and rich-to-lean operations for fresh catalyst at 440 °C with 1400 ppm CH\textsubscript{4} and NO concentrations of (a) 500 ppm or (c) 1500 ppm and for the aged catalyst with an NO concentration of (b) 500 ppm or (d) 1500 ppm.

Fig. 3 shows NH\textsubscript{3} formation for fresh (3a and c) and aged (3b and d) catalysts at three different temperatures. The effect of increasing temperature is obvious for the fresh catalyst, whereas in the case of the aged catalyst, increasing temperature has a minor effect. Slight differences in NH\textsubscript{3} formation with the aged catalyst at different temperatures can be explained by the performance of the oxygen storage material. It is clear that thermal ageing in an oxidising atmosphere can damage the catalyst, and thus, it is reasonable to assume that it affects also the oxygen storage material performance. Although the addition of zirconia to ceria should improve ceria thermal stability and enhance shielding against sintering and loss of surface area, it is shown that in some cases, TWC performance deteriorates due to thermal ageing [44]. Lambrou et al. [45] studied OSC containing a commercial Pd/Rh TWC function before and after ageing in a real driving situation, and they discovered that ageing affects OSC by changing the redox properties and decreasing operation. X. Zhang et al. [12] studied the CeO\textsubscript{2}-ZrO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} Pd-catalyst with and without La\textsubscript{2}O\textsubscript{3}, which was designed for NGV, and they discovered that after ageing at 1000 °C for 5 h, the OSC amount of the catalyst decreased. Kolli et al. [46] studied the performance of fresh and cyclic rich- and lean-aged catalysts at 925 to 1040 °C Pd-Ba-OSC/Al\textsubscript{2}O\textsubscript{3}, when activity was measured using only two-component gas mixture CO and NO, and they discovered that catalytic deactivation occurred during the ageing process, lowering the activity of the catalyst and OSC. Thus, OSC behaviour changed during the thermal ageing so that the ability to properly function decreased. Fig. 3(b) and (d) shows that with the aged catalyst, changes in NO concentration from 500 ppm to 1500 ppm increased NH\textsubscript{3} formation, similar to how it increased in the case of the fresh catalyst. Thus, ageing does not substantially affect NH\textsubscript{3} formation if the NO concentration is changed, but it equalizes NH\textsubscript{3} formation at different temperatures so that the formation stays more or less the same.
The size of the hysteresis loops decrease with increasing temperature, and at higher temperatures, CH₄ conversion increases (Fig. S3). According to Klingstedt et al. [25], hysteresis occurs due to changes on the surface of the Pd species. G. Bugosh et al. [14] studied methane oxidation in lean and rich conditions with a Pt/Pd/Al₂O₃ catalyst at temperatures 427, 482 and 538 °C. They obtained similar results concerning the temperature effect of CH₄ conversion; increasing temperature enhances CH₄ conversion. Nevertheless, their finding that hysteresis loops decrease with decreasing temperature is quite contrary to our findings for the Pd/Rh catalyst. According to our results, reactions that occurred at 440 °C had the widest hysteresis loops, and reactions that occurred at 530 °C had the narrowest hysteresis loops. Bugosh et al. [14] did not have oxygen storage materials in their catalyst, which explains differing results.

3.2 CH₄ concentration effect on NH₃ and N₂O formation

Fig. 4 shows that a decrease in concentration of CH₄ from 1400 ppm to 700 ppm affects NH₃ and N₂O formation with the fresh catalyst. Comparing Figs. 2(a) and 4(a), NH₃ and N₂O concentrations are quite similar in both situations, whereas in Figs. 2(c) and 4(c), there is a clear change in NH₃ concentration. We assume that the lower feed stream of CH₄ concentration decreases NH₃ formation, whereas N₂O formation seems to follow NO concentration via Reaction (5) rather than CH₄ concentration.
Fig. 4. NH$_3$ and N$_2$O formation and NO and CH$_4$ concentrations with the fresh catalyst, T = 440 °C, when CH$_4$ = 700 ppm and (a) NO = 500 ppm or (c) NO = 1500 ppm and with the aged catalyst when (b) NO = 500 ppm or (d) NO = 1500 ppm.

Decreasing CH$_4$ concentration from 1400 ppm to 700 ppm induces TWC to require richer conditions to convert NO, especially in the case of fresh catalyst. When CH$_4$ concentrations are lower, less H$_2$ and CO forms in SR (reaction 1), and this affects the NO conversion window.

When the simulated exhaust gas CH$_4$ concentration was 700 ppm, the CH$_4$ conversion rate increased (Fig. S4). It is interesting that CH$_4$ conversion (CH$_4$ = 700 ppm) was higher with the aged catalyst than with the fresh catalyst, which is a similar result to that which Fernandes et al.[47] determined for propane conversion. Overall, depending on feed gas composition, the ageing can affect the catalyst performance by increasing it.

3.3 XRD

The fresh and aged catalysts with the noble metal Pd/Rh and catalysts without the noble metals were analysed by powder XRD to determine the effect of ageing and the influence of noble metals. Fig. 5 shows the diffraction patterns for fresh and aged Pd/Rh catalysts and catalysts without the noble metals. Comparing fresh and aged diffraction patterns, the peaks become sharper after exposure to high temperatures, suggesting growth and sintering of crystallite particles. There are shoulders for the peak at 30° with both aged catalysts. Thus, Zr and Ce crystallinity increased after ageing, and some morphological changes occurred. With XRD, metallic Pd (40°) was detected with the aged catalyst, and PdO was also indicated. Comparing the aged catalyst with and without the noble metals to the fresh catalyst, the peak at 34° is shifted to a lower angle for the aged Pd/Rh catalyst; this shift is due to the formation of PdO. Rh could not be detect from the sample, but this can be explained by the low amount of Rh in the catalysts. Alumina retained the gamma phase during the ageing due to added stabilizers. The catalyst colour changed from brown to grey during the ageing with the noble metal catalyst, which also supports the conclusion that some morphological changes occurred. In addition, the catalyst without active noble metals also changed colour from light yellow to white. Ce$_2$(III)O$_3$ is gold-yellow,
and Ce(IV)O$_2$ is light yellow. This colour change during aging at high temperature could indicate that the Ce$^{3+}$ amount is reduced, which clearly affects oxygen storage material function.

Fig. 5. XRD patterns for the aged catalysts (a) with and (b) without the noble metals, together with the fresh catalysts (c) with and (d) without the noble metals. Highlighted area indicates shoulder formation (orange) of the peak with the aged catalyst and peak shift (yellow) due to PdO formation.

3.4 Raman results

Structural changes during aging were determined by Raman spectroscopy. Aged and fresh Pd/Rh catalysts and catalysts without the noble metals were measured with Raman spectroscopy, see Fig. 6. According to the literature, the band located at approximately 465 cm$^{-1}$ of the Raman spectrum indicates the F$_{2g}$ mode of cubic fluorite CeO$_2$.[48] In our measurements, the equivalent bands have lower energy, approximately 420 cm$^{-1}$ for the fresh Pd/Rh catalyst, 424 cm$^{-1}$ for the aged Pd/Rh catalyst and 419 cm$^{-1}$ for the aged and fresh catalysts without the noble metals. After ageing the Pd/Rh catalyst, the F$_{2g}$ peak shifted to higher energies (from 420 to 424 cm$^{-1}$), whereas for the catalysts without the noble metals, the bands for fresh and aged catalysts stayed in somewhat the same position as for the fresh Pd/Rh catalyst. The energy band shift was not significant, but it indicates that morphological changes occurred after the addition of noble metals and ageing. Energy bands at ~ 612 cm$^{-1}$ and ~ 314 cm$^{-1}$ refer to the distortion of the oxygen lattice and the Ce–Zr mixed oxide pseudo cubic $\Gamma^7$ phase [12, 49], and those bands are shifted to higher energies during ageing and noble metal addition. We assumed that the metal addition changes the ceria lattice structure after exposure to ageing temperatures and thus affects oxygen storage material performance. The Raman results support the XRD and performance results.
Raman band shifts (190 – 790 cm⁻¹) for aged and fresh Pd/Rh catalysts and aged and fresh catalysts without the noble metals. The dashed red line shows where the aged Pd/Rh catalyst band shift occurs.

3.5 Temperature programmed reduction

To support Raman spectroscopy findings, H₂-TPR profiles are shown in Fig. 7 for the fresh and aged catalysts with and without noble metals. The fresh catalyst without the noble metals has three broad reduction peaks at 280, 520 and 660 °C. After ageing the lowest temperature reduction peak is missing and the highest temperature peak has shifted to higher temperature from 660 to 710 °C. According to the earlier studies, [45, 50-52] reduction peaks below 525 °C can be related to reduction of surface Ce-Zr oxides, whereas reduction of bulk Ce-Zr oxides occurred most likely over 600 °C. It is notable that the overall reduction of surface and bulk Ce-Zr does not change, even though BET surface area decreased from 113 m² g⁻¹ to 66 m² g⁻¹. Addition of noble metals (fresh Pd/Rh) shows three intensive peaks at 110 °C, 150 °C and 390 °C. After ageing (aged Pd/Rh) only one noble metal related peak can be observed at 110 °C and overall reduction of the catalyst decreases remarkably. As a summary, H₂-TPR results showed changes in reduction peak of Ce-Zr mixed oxide of noble metal catalyst. This observation is well in line with above shown Raman spectroscopy results.

Fig. 7. H₂-TPR profiles of the fresh and aged Pd/Rh TWC and catalysts without the noble metals. Effect of ageing has been highlighted in figure.
4. Conclusions

The study showed that the exhaust gas composition and the ageing of the catalyst have remarkable effects on catalyst performance and NH$_3$ and N$_2$O formation. To be more precise, performance experiments showed that lower NO concentration in the exhaust gas decreased both NH$_3$ and N$_2$O emissions, whereas decrease in CH$_4$ concentration reduced only NH$_3$ emission. In addition, increase in reaction temperature decreased both NH$_3$ and N$_2$O emissions with the fresh TWC catalyst. Ageing of the catalyst increased only N$_2$O emission. Characterization of the catalysts texture with powder X-ray diffraction, Raman spectroscopy and H$_2$-TPR techniques revealed that noble metals changed the ceria lattice structure during the ageing, which undoubtedly influenced oxygen storage material performance and thus the formation of harmful NH$_3$ and N$_2$O emissions. By tailoring CH$_4$ and NO concentrations at high temperature in the TWC of NG heavy-duty vehicles, harmful and dangerous NH$_3$ and N$_2$O gas formation can be diminished.

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6. References


