



Methane Abatement and Catalyst Durability in Heterogeneous Lean-Rich and Dual-Fuel Conditions

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Abstract

Natural gas is an alternative fuel to replace partly conventional liquid fuels like diesel or gasoline to improve fuel economy (less CO₂) and decrease pollutants (particulates). Mixed stoichiometric–lean combustion has been introduced as a potential way to manage without secondary diesel fuel. This study focused on catalytic methods to oxidize methane, HCs, CO and NO in lean-stoichiometric NG and lean diesel–NG exhaust gases in heavy-duty applications. Lean methane oxidation is the most challenging condition and only methane oxidation catalyst (MOC) developed for lean conditions was able to reach low methane light-off temperatures. MOC was almost as good as three-way catalyst (TWC) in stoichiometric conditions but the heavier ageing and λ oscillating conditions cause problems for MOC (no oxygen storage materials). Diesel oxidation catalysts (DOC) were very poor in TWC reactions but Pt-rich DOC is important to reach in lean higher NO₂ utilized in DPF regeneration and SCR. In TWC + MOC, DOC + MOC combinations, the MOC part dominated methane oxidations due to that significant difference in their base activity for methane oxidation. The combinatory systems showed also in deactivation–regeneration cycles promising and interesting results, which can be utilized in transient, heterogeneous exhaust conditions.

Keywords Natural gas · Methane · Oxidation · Catalysts · Nitrogen oxides

1 Introduction

Natural gas (NG) is an alternative fuel to replace partially conventional liquid fuels to improve fuel economy (less CO₂) and to decrease pollutants (particulates). NG combustion is quite pure without producing more toxic, heavier hydrocarbons (HC), but methane (CH₄) has a green-house gas factor 25 higher than CO₂ and thus methane emissions are also limited by the latest international regulations. Lean combustion of natural gas has been applied in stationary applications but it is challenging in mobile applications, where dual-fuel (NG–diesel) lean and bi-fuel (NG–gasoline) stoichiometric engines have been the main commercial

solutions. Mobile diesel and dual-fuel heavy-duty engines have Non-Methane HC (HCs excluding CH₄) limits of 0.13 g/kWh in ESC (European Steady Cycle) and 0.16 g/kWh in ETC (European Transient Cycle) but gas engines have also a methane limit of 0.50 g/kWh in ETC [1]. The emissions in stoichiometric NG or bi-fuel (NG–gasoline) engines are purified with a three-way catalyst (TWC). Therefore, the combustion is more controlled and after treatment system (ATS) simpler in stoichiometric combustion, which has also been a practical solution to avoid diesel particulate filter (DPF) and selective catalytic reduction (SCR) units of lean engines in Euro VI [2]. However, fuel consumption is lower in lean than in stoichiometric and therefore lean combustion is a development target in mobile heavy-duty applications.

Catalytic methane oxidation is challenging when the exhaust gas conditions are lean on average. The stable methane molecule is the most difficult HC to be activated for oxidation reactions, which require temperatures above 400 °C and are also very sensitive to catalyst poisoning [2]. Therefore, a high amount of active metals (loading, catalyst volume) is necessary. Particular high loaded (> 100 g/cft), palladium-rich methane oxidation catalysts

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(MOC) have been developed to catalyse methane oxidation in lean [3–6]. Pd/Al₂O₃ with varying additives is the known composition for MOC [7–10]. The high Pd loading and larger particle size are associated with lower Pd-support interaction and Pd–O bond strength, which variation promotes methane oxidation [11]. In lean NG applications, exhaust temperatures and thermal deactivation are much lower but the sulfation tendency of catalysts is higher than in stoichiometric applications. Sulfur oxides (SO_x) form sulfates with palladium and support materials like alumina, ceria and other metal oxides. Many metal sulfates are stable in lean conditions but decompose naturally under stoichiometric or rich atmosphere. Sulfur durability and regeneration strategies have been the main development focus for MOCs [12–14]. A periodic sulfur regeneration (desulfation) of catalysts is possible at elevated temperatures, usually in the presence of reducing agents like hydrogen or hydrocarbons. In desulfation, metal sulfates are decomposed back to gaseous SO₂, active sites and support.

In dual-fuel lean applications, a full diesel ATS is necessary including the diesel oxidation catalyst (DOC), DPF and SCR units. As separate designs, TWC and MOC require both roughly the volume of an engine displacement but DPF about 2× and SCR about 3× engine displacement volume [2].

Mixed lean-stoichiometric NG combustion is a way to manage without secondary diesel fuel and avoid a DPF in heavy-duty applications (Fig. 1). This study is focused on catalytic methods to oxidize CH₄, non-methane HCs, CO and NO in lean-stoichiometric NG and lean diesel–NG exhaust gases. MOC differs from NG–TWC and DOC by properties and it is a target in this study to find the integration potential. The proper optimization of integrated systems, to reach target emissions and promotions (NO₂), should be based on deactivated catalysts.

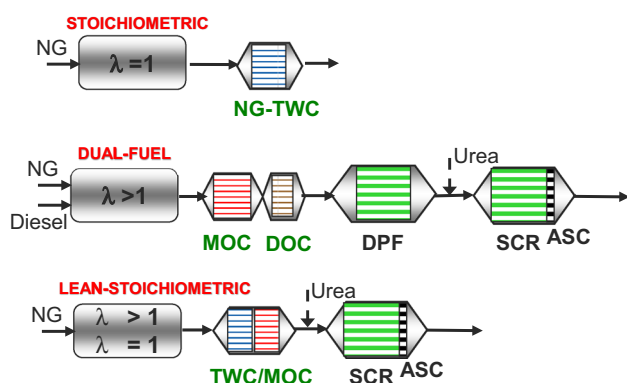


Fig. 1 ATSs for the NG engine solutions

2 Materials and Methods

The small-scale, metal substrated (500 cpsi, foil thickness 50 μm) catalyst samples were prepared for experimental activity and durability simulations. Palladium (Pd on all catalysts), platinum (Pt on MOC and DOC) and rhodium (Rh on TWC) were used as active metals. The coatings were developed for each application including the metal oxide based support with tailored thermal stabilizers and promoters. The ageing was conducted in tube reactors in the presence of static air, hydrothermal ageing (HT) conditions (10% water in air for 20 h) or sulfur accumulation (sulfation, 25 ppm SO₂ with water and air for 20 h at 400 °C) [11]. The activity of structured TWCs (PdRh (16:1) as 150–200 g/cft), DOCs (Pt, PtPd (4:1) as 50–60 g/cft) and MOCs (PtPd (1:4) as 100–200 g/cft) was evaluated in metallic tubular reactors (diameter 14 mm, length varied) by simulated exhaust gases (Feed: HCs, CO, NO_x, O₂, CO₂, H₂O, H₂, SO₂, bal. N₂) with relevant concentrations and space velocities (SV, mainly 50,000 h^{−1}) (Table 1). Oxygen feed concentration oscillated in stoichiometric experiments simulating λ control effects. The compositions were analysed by a set of single analysers (IR for CO and CO₂, chemiluminescence for NO_x/NO, FID for HC/CH₄, paramagnetic analyser for oxygen) and also with FTIR (Gaset CR 2000) equipped with heated (180 °C) sampling lines. The combinatory catalyst systems (screening by 1:1 of volume ratio) were investigated in mixed lean-stoichiometric conditions by their combined activity and selectivity. The main focus

Table 1 Feed gas mixtures in experimental simulations

| Compound | Stoichiometric | Lean NG | Diesel |
|------------------------------------|-----------------------------|---------|--------|
| NO (ppm) | 600 | 500 | 200 |
| CH ₄ (ppm) | 1800 | 1500 | – |
| Ethane (ppm) | 100 | 300 | – |
| Propane (ppm) | – | 100 | – |
| Propene (ppm) | – | – | 80 |
| Toluene (ppm) | – | – | 15 |
| Decane (ppm) | – | – | 15 |
| Acetaldehyde (ppm) | – | 150 | – |
| H ₂ (ppm) | 3800 | – | – |
| CO (ppm) | 8000 | 1200 | 1500 |
| Oxygen (%) | 0.4–1.1 ± 0.11 ^a | 10 | 14 |
| Water (%) | 10 | 8 | 6 |
| CO ₂ (%) | 9 | 7.5 | 6 |
| Nitrogen | Bal | Bal | Bal |
| λ | 0.96–1.01 | 1.78 | 2.50 |
| SV ^b (h ^{−1}) | 50,000 | 50,000 | 30,000 |

^a 1 Hz, ^b varying in reaction studies

was on the CH_4 oxidation activity, which is challenging in lean and sulfating conditions (dual-fuel).

Total oxygen storage capacity (OSC) of catalysts was measured by CO-O_2 exchange experiments at 450 and 600 °C in the presence of argon and helium in a small tube quartz reactor (diameter 10 mm), where the consumption and adsorption of O_2 and CO in dry gases were determined by fast mass spectrometer (Thermostar GSD 320) responses. Feed gas mixtures containing 0.5% CO and 0.5% O_2 were switched by 420 s intervals to integrate the total reactant adsorptions and the formation of CO_2 .

3 Results and Discussion

3.1 Activity of Single MOC, TWC and DOC in Lean and Stoichiometric Conditions

The cross-checking of single catalysts showed their abilities to compensate other catalyst's functionality in varying lean-stoichiometric NG and dual-fuel conditions. That compensation makes possible to decrease single catalyst volumes. The pre-treatment of HT700/20 h ageing covered all the conditions resulting in stabilized catalysts in the comparison. The main focus was on the demanding lean THC performance, including methane oxidation.

3.1.1 Lean NG Feed Gas

A PtPd(1:4)–MOC was developed for these conditions and showed clearly the lowest light-off performance for HCs with methane as a main HC in feed (Fig. 2). Pd-rich PdRh(16:1)–TWC with a 200 g/cft loading was also better for HCs than DOCs, which had a very low activity ($T_{50} > 600^\circ\text{C}$). The MOC showed also a low light-off even with 100 g/cft. CO was best oxidized on MOC but DOCs with a lower total loading showed also a good performance. Pt-free TWC had the highest CO light-off temperature in lean conditions. NO_2 formation was clearly highest on Pt-only and Pt-rich DOCs. Even the total loading was four times higher and the absolute Pt loading (40 g/cft Pt) on the same level, PtPd(1:4)–MOC catalysed less NO_2 formation than DOCs (max. 60% vs. 25%). The high amount of Pd inhibited the Pt's ability to catalyse NO_2 formation. NO_2 is utilized in passive DPF regeneration (dual-fuel) and SCR reactions in lean NO_x removal.

3.1.2 Stoichiometric NG Feed Gas

In lean-stoichiometric engine calibrations, ATS needs to manage also in stoichiometric and rich conditions, which are demanding when planned to be applied at low temperatures. λ values are oscillating (e.g. by frequency of 1 Hz) around the value of 0.98, which is nominally slightly in rich side and requires oxygen buffering properties created by oxygen storage compounds/capacity (OSC). Even

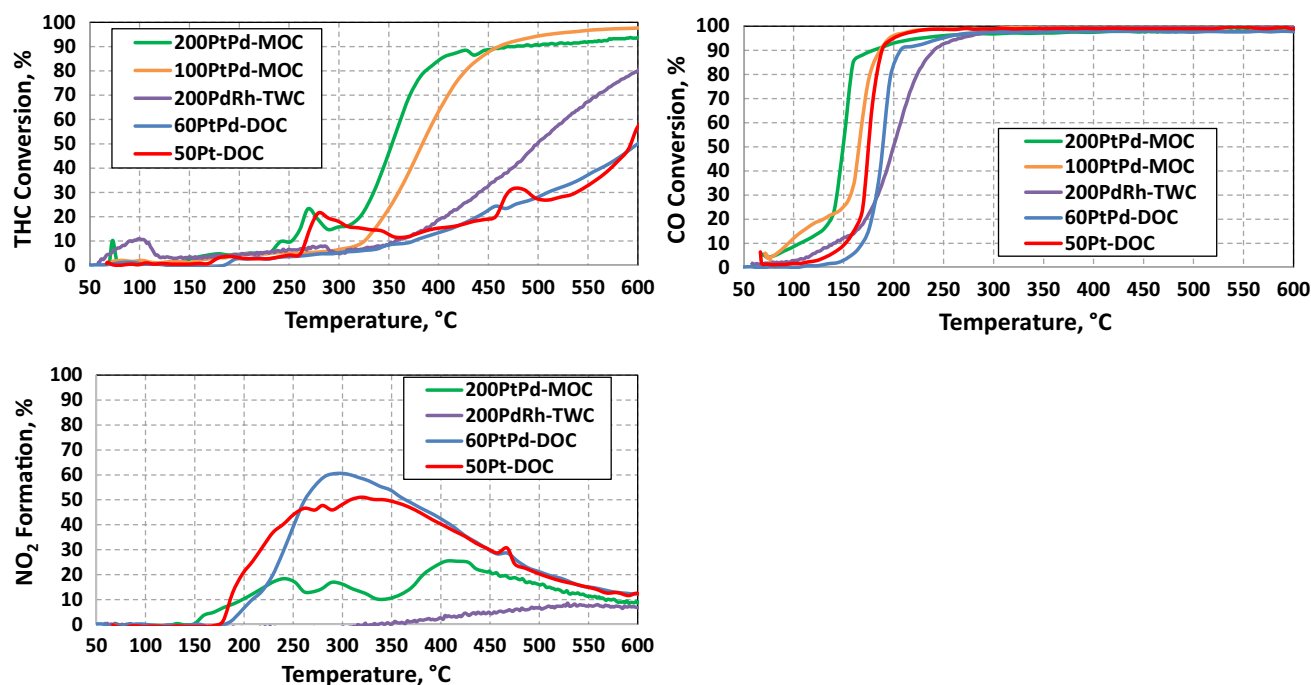


Fig. 2 THC/ CO conversion and NO_2 formation on HT700/20 h aged catalysts in lean NG feed gas ($50,000 \text{ h}^{-1}$). Legends include loading as g/cft

if catalysts are not sulphated under stoichiometric conditions and maintain stable reaction rates, methane oxidation is still demanding with a light-off temperature over 300–350 °C. PtPd–MOC was as good as TWC by HC light-off after HT700/20 h ageing (Fig. 3). OSC on TWC enabled to reach the higher end conversions at higher temperatures. TWC showed the highest conversions when λ varied in the range of about 0.97–1.00. CO light-off was low in stoichiometric NG conditions, because saturated HCs did not inhibit the CO oxidation like HCs in gasoline exhaust gases. Methane and other light HCs can be understood almost as inert like nitrogen much below their adsorption and light-off temperatures. DOCs were quite poor due to wrong PGMs and low loadings, to activate methane in stoichiometric mixture. CO conversions dropped above 350 °C due to the competition of CO and methane oxidation with limited oxygen sources (O_2 and NO). PtPd–DOC showed clearly a lower initial NO_x light-off for CO reduction than Pt–DOC but a lower end NO_x

conversion above 300 °C. High Pd loadings on the stable TWC support with OSC materials are necessary to reach a low light-off temperature and high end conversion.

Results after air ageing at 1000 °C, simulating deactivation in stoichiometric applications, showed the same orders of activity by catalyst types but the light-off temperatures increased clearly. The THC light-off was about 415 °C on TWC and MOC with 200 g/cft and 50,000 h⁻¹. The THC conversion at 550 °C was 89% on TWC and about 80% on MOC.

Ceria-free MOCs have also OSC on palladium surfaces ($Pd \rightleftharpoons PdO$) at lower temperatures but that is lost more easily in thermal ageing than OSC based on stabilized ceria, which is also able to keep a higher OSC in driving conditions at higher temperatures (Fig. 4) [15]. Measured OSC related to the total capacity on fully reduced surface. In reaction conditions with a tight λ control only a part of total OSC is in active use.

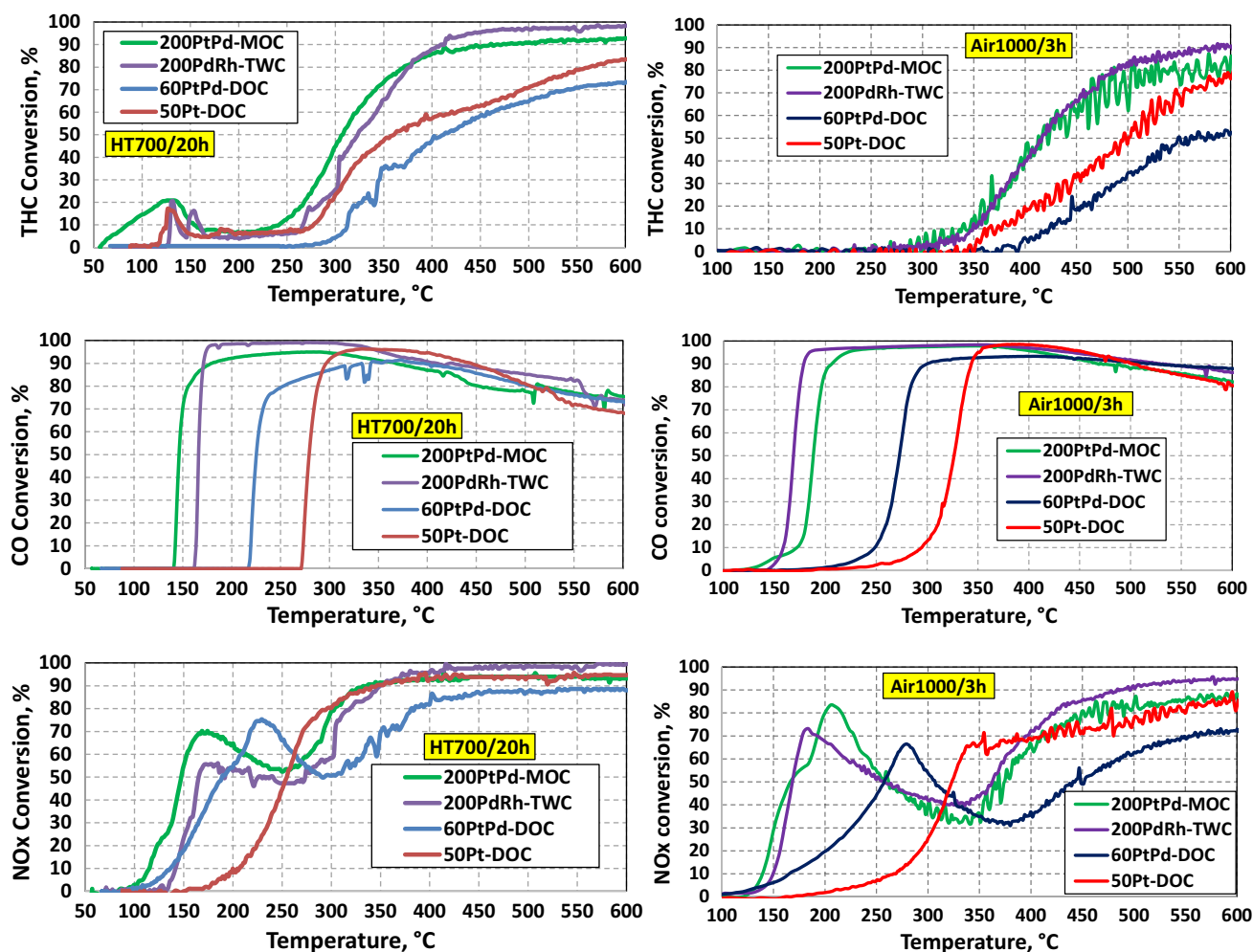


Fig. 3 THC/CO/ NO_x conversion on HT700/20 h and Air1000/3 h aged catalysts in stoichiometric NG feed gas ($\lambda \sim 0.98$, 50,000 h⁻¹). Legends include loading as g/cft

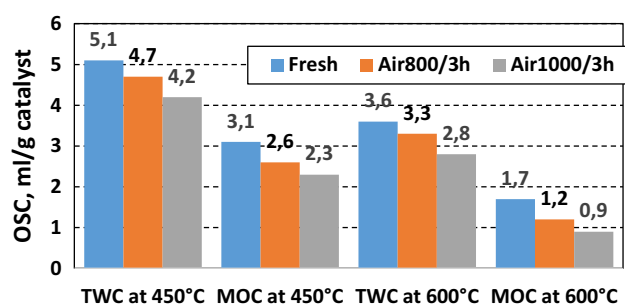


Fig. 4 Total oxygen storage capacity at 450 and 600 °C on TWC and MOC by ageing temperature

3.1.3 Lean Diesel Feed Gas

Catalyst functionality in diesel mode in dual-fuel conditions is required too. The functionality was evaluated in pure diesel feed gas even if the gas and diesel fuel are often injected concurrently into the engine by the latest technology. The first dual-fuel engines in past were based on gas or diesel injection by designed engine mapping. Usually diesel mode is applied in low temperature engine points, when gas ignition is hard. λ values vary also by the fuel type in dual-fuel engine mapping.

PtPd(1:4)–MOC with 200 g/cft was very efficient also in diesel exhaust conditions being on the same level with 60 g/cft PtPd(4:1)–DOC by CO and HC oxidation (Fig. 5). The oxidation of HCs was easier in diesel (propene, toluene, decane) than in NG exhaust gas (mainly methane). PdRh (16:1)–TWC with 200 g/cft showed a higher light-off and

a low NO_2 formation due to the absence of Pt, which is the main active metal in DOCs. PtPd–MOC catalysed reasonably NO oxidation, which can be utilized in dual-fuel ATSS too. Both DOCs contained also zeolite, which adsorbed HCs at low temperatures [16]. PtPd–DOC is a main stream in ATSS with active regenerated DPFs [17] and it was better for HC and CO but Pt–DOC was better for NO oxidation.

3.2 Thermal and Sulfur Deactivation and Regeneration of MOC, TWC and DOC in Lean-Stoichiometric NG Conditions

Thermal and sulfur deactivation have an important role in the comparisons of combinatory properties. The methane oxidation in lean is sensitive for sulfur deactivation and this is a key factor in MOC development. Thermal stress is harder in stoichiometric than in lean conditions. Air ageing at 1000 °C for 3 h simulated the thermal stress in stoichiometric conditions. Even if temperatures are not often above 800 °C in stoichiometric NG engine mapping, NG with a high heat capacity causes in fast λ control or even in small malfunction conditions a risk to temperature peaks up to 1000 °C. In lean-stoichiometric conditions sulfur and thermal deactivation can be reversible or irreversible, which was seen particularly in respect of methane oxidation. In lean-stoichiometric drive, sulfur compounds are accumulated in lean depending on the temperature but decomposed in stoichiometric and rich phases at least partially [18]. The lack of oxygen possesses by thermodynamics a strong decomposing force to sulfates.

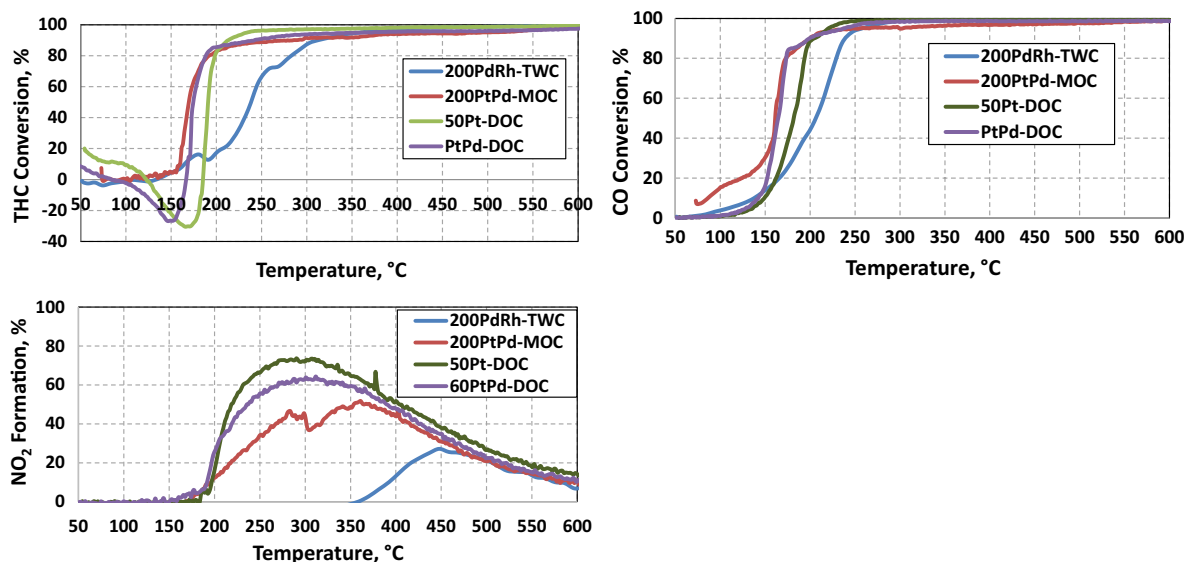


Fig. 5 THC/CO conversion and NO_2 formation on HT700/20 h aged catalysts in diesel exhaust gas ($30,000 \text{ h}^{-1}$). Legends include loading as g/cft

Sulfation was made for HT700 aged samples at 400 °C to focus on the sulfur effects on thermally stable catalyst surfaces. The light-off experiments made up to 600 °C, simulating common exhaust gas conditions, are powerful enough to remove the unstable deactivation but have also regeneration effects. It is possible that regeneration is also temporary after stoichiometric-rich treatment and it was necessary to repeat the light-off experiments at least twice. Reduced active sites might be very active in the first light-off ramp.

The catalyst performances were compared as HT700 aged, air1000 aged, HT700 + sulphated and after a stoichiometric light-off experiment (max. 600 °C) (Fig. 6). Sulfation for 20 h with 25 ppm SO₂ had a clear effect on MOC and T₅₀ of THC increased by 50 °C. The original activity of TWC was quite low and sulfation in fact slightly improved the THC performance. Sulfur deactivation of MOC is a known property, which resulted in an increase of T₅₀ of THC up to 400 °C. A short treatment (1 h at 100–600 °C) in a stoichiometric exhaust condition regenerated MOC by 30 °C as T₅₀. TWCs have often promoters which form stable sulfates causing fast deactivation in lean. However, PdRh–TWC was recovered almost to the same level with MOC in stoichiometric conditions. That is related to the presence of OSC materials, which are forming more active sites with palladium for methane oxidation in lean. Due to doubts about the stability of that regenerated state, the same lean experiment was also repeated and TWC lost the light-off by 30 °C in that second experiment. PtPd–DOC had almost no methane

oxidation activity (T₅₀ > 600 °C) in lean by any state but showed the highest NO₂ formation with that low noble metal loading (60 g/cft). PtPd–MOC stand well but PdRh–TWC lost the THC (CH₄) lean oxidation activity dramatically in air ageing at 1000 °C. MOC was also stable in thermal ageing and stoichiometric condition fluctuations. PdRh–TWC recovered from thermal ageing by stoichiometric treatment but that good activity stand only one light-off experiment and the second test resulted even in the lower activity than as air1000 aged. Therefore, after the oxidation of reduced PdRh-support phases, the temporary activation was lost. A recovery can be seen also by stoichiometric phase in CO and NO oxidation. Even if the TWC support structure is thermally more durable than the MOC support, thermal durability of Pd–Rh-support interaction in TWC was not planned to keep a good lean methane oxidation. That's also the original reason why particular MOC concepts have been developed.

3.3 Performance of Catalyst Combinations

3.3.1 Binary MOC, TWC and DOC Combinations in Lean and Stoichiometric NG Feed Gases

It was seen by single catalyst studies that each particular property of MOC, TWC and DOC is needed in lean-stoichiometric and dual-fuel exhaust gas conditions. All catalysts have an activity in the other catalyst type's conditions but the differences were so significant that the optimum and a

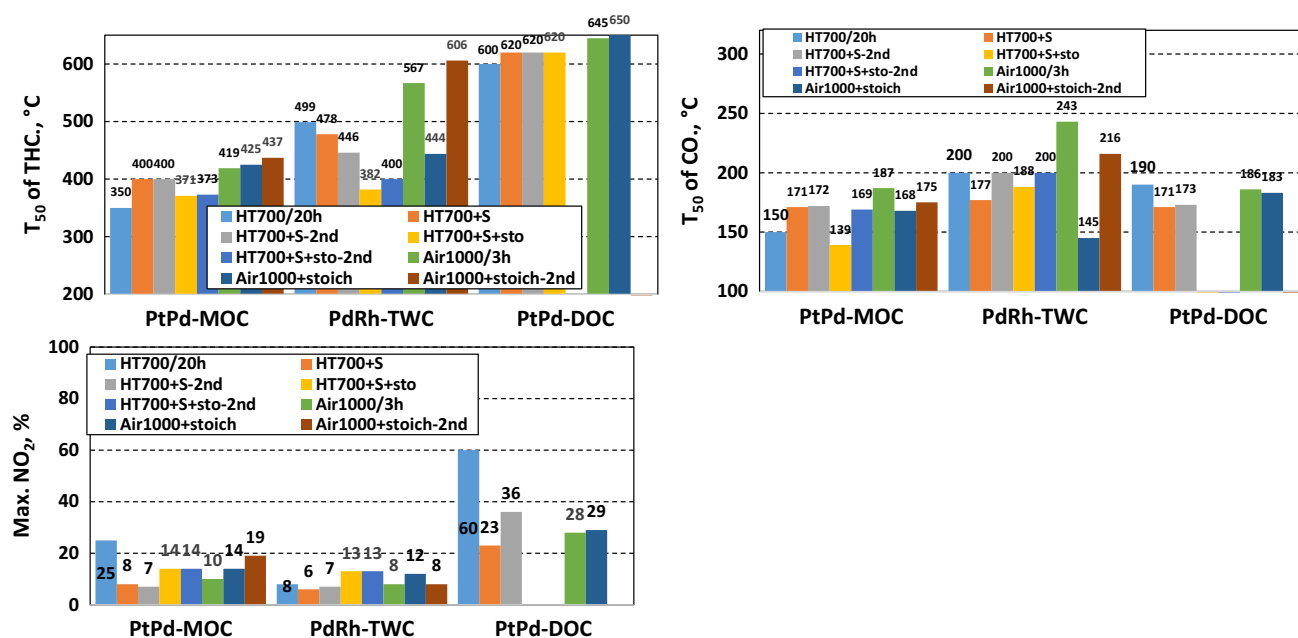


Fig. 6 Summary of THC/CO light-off temperatures (T₅₀) and maximum NO₂ formation on MOC, TWC and DOC in lean NG feed gas (50,000 h⁻¹) after ageing and regeneration history (HT700 hydrother-

mally aged/700 °C, Air1000 static air/1000 °C, S sulfation, sto stoichiometric light-off test)

minimum total catalyst volume (lower SV) is a combination of catalysts in flow directions. As mixed in the same catalyst coating layers, these chemical compositions usually disturb each other. Because CO is quite easy to remove with large catalyst volumes for methane reactions, the main focus was on methane oxidation in lean feed gas. It was clear that the highest activity for THC in lean was reached when MOC filled the all catalyst volume (Fig. 7). The single catalyst studies showed that TWC is not able to replace MOC properties in lean reactions. However, it was optimal for THC light-off if the MOC was located after TWC [19] or DOC, which were able to convert a part of NMHCs and CO when MOC will catalyse mainly methane oxidation. Even if kinetically MOC is more efficient in lean reactions, the additional TWC and DOC were able to enhance the efficiency in comparison to a single MOC with $100,000 \text{ h}^{-1}$ (37 mm). Partly the detected small differences can be also related to axial temperature gradients and heat generation in the first unit.

The same combinations in stoichiometric conditions showed that TWC, TWC + MOC and MOC + TWC had very similar properties but DOC + MOC was clearly the poorest, when not developed at all for those stoichiometric conditions (Fig. 8). A key difference is detectable at high temperature (end conversions), which is important in driving conditions and test cycles. MOC only was quite near to TWC or even slightly better by light-off but the end conversion above 400°C was poor. It was seen by single catalyst experiments that the light-off ability of MOC was lost in air 1000 ageing. The same high temperature conversion differences was also seen by stoichiometric CO and NO_x conversions.

3.3.2 Sulfur Effects in Combinations

The catalyst combinations were sulphated at 400°C for 20 h as the ready combinations of TWC + MOC, MOC + TWC, DOC + MOC and MOC + DOC. Then sulfur accumulation and regeneration proceed axially by the flow direction in

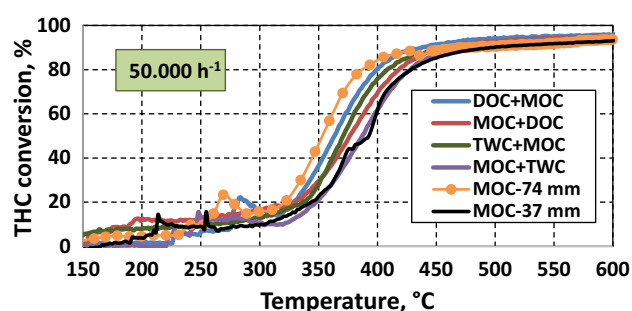


Fig. 7 THC conversion on HT700/20 h aged catalyst combinations (37 mm + 37 mm) in lean feed gas ($50,000 \text{ h}^{-1}$ by 74 mm). PtPd(1:4)–MOC and PdRh(16:1)–TWC with 200 g/cft, PtPd(4:1)–DOC 60 g/cft, the total catalyst volume fixed to 74 mm

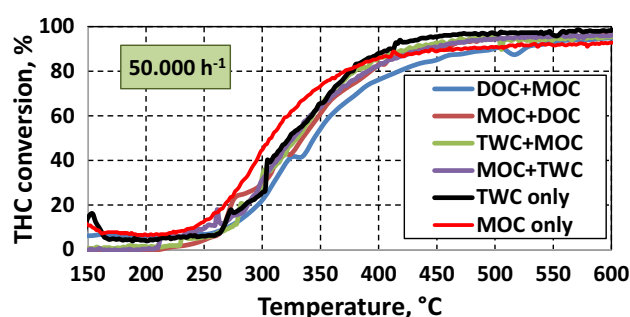


Fig. 8 THC conversion on HT700/20 h aged catalyst combinations in stoichiometric feed gas ($50,000 \text{ h}^{-1}$). MOC and TWC with 200 g/cft, PtPd–DOC 60 g/cft, the total volume by 74 mm

catalyst combinations. The unit orders might have effects on sulfation and desulfation tendencies. In results, MOC dominates still the THC efficiency and sulfation was partly recovered in combinations already in lean exhaust conditions (max. 600°C) and settled down near to the activity of non-sulfated level after stoichiometric exhaust gas treatment (max. 600°C) (Fig. 9). Because lean and stoichiometric testing conditions stand for a long time in these experiments, the order of units had a minor effect on the detected THC efficiency. In fast transients the sulfation–desulfation effects might be different, when sulfur accumulations are not stabilized but proceeds axially by flow conditions. Sulfur was recovered partly in lean conditions from noble metals and alumina. The stoichiometric conditions finally decomposed more stable sulphates from catalyst surface. Activity in stoichiometric feed was less examined but remained on the same level as HT700 aged and as sulphated.

Reactivity of HCs in lean NG feed gas was analysed also after sulfation and regeneration more in detail (Fig. 10). Methane dominates in real and simulated exhaust gases but it is important to remove also the traces of ethane, propane and aldehydes from these exhaust gases. The ethane (C_2H_6)

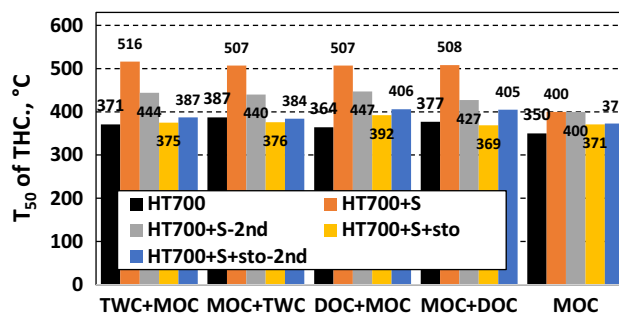


Fig. 9 Sulfur effects (Sulfation, *sto* stoichiometric pre-test) on THC conversions of HT700 aged combinations (37 mm + 37 mm) in lean feed gas ($50,000 \text{ h}^{-1}/74 \text{ mm}$). PtPd(1:4)–MOC and PdRh(16:1)–TWC with 200 g/cft, PtPd(4:1)–DOC 60 g/cft, the total volume by 74 mm

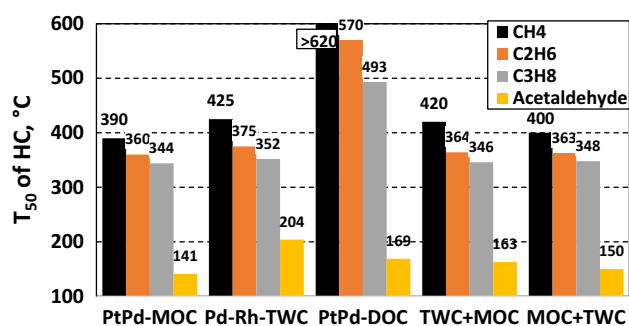


Fig. 10 Hydrocarbon light-off (T_{50}) temperatures in lean feed gas after HT700, sulfation and stoichiometric treatments. Combinations 37 mm + 37 mm (50,000 h⁻¹ by 74 mm). PtPd(1:4)-MOC and PdRh(16:1)-TWC with 200 g/cft, PtPd(4:1)-DOC 60 g/cft

and propane (C₃H₈) were also quite difficult to remove catalytically ($T_{50} > 340$ °C) but aldehydes are oxidized on all catalyst types below 210 °C and almost complete conversion was reached above 250 °C. This is important because NMHC emission limits are lower than methane limits e.g. in Euro VI legislation. NG exhaust gases consist solely of formaldehyde but acetaldehyde (C₂H₄O) has the same reactivity with the aldehyde functional group and it is easier to handle in laboratory reactors.

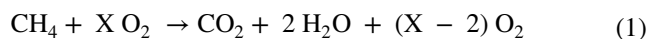
3.3.3 Catalytic Reactions in Cruising

Lean-Stoichiometric-Rich NG Exhaust Gases

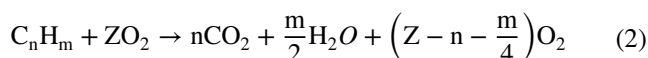
Reactions are mainly the same in lean and stoichiometric conditions but the amount of oxygen has a crucial role, which is the oxidation state of active sites and when they are active. The active sites are on noble metal surfaces, where Pd and Pt are here the main metals. TWC contained ceria, which acted as OSC but its pure catalytic activity is known to be negligible in comparison Pt and Pd. In stoichiometric conditions, oxygen and NO are competing in CO and HC oxidations, when these oxidizing and reducing compounds are about in balance and after catalysts almost completely consumed. In lean feed conditions oxygen is present as a high excess and remains as a high concentration in outlet mixture. This difference in oxygen balance has also a crucial effect on catalytic reaction rates. The thermal and sulfation ageing had also detected effects on the activity and selectivity of active sites. The oxygen partial pressure and temperature have effects on the oxidation state of Pd-Pt (8 and 9), where PtO₂ is thermodynamically less stable in lean than PdO, which is the main reason to the Pt's goodness in DOC reactions [20]. In rich, noble metals are mainly metallic but oxygen is able to dissociate on surface and maintain 3-way reactions. The oxygen on noble metals has a key part in reaction cycles but also in oxygen inhibition. That is the reason why palladium is easily forming quite stable sulfates, which

are regenerated thermally or in low oxygen conditions [20]. Water gas shift reaction (6) explains simply the hydrogen formation from CO and water. It can be assumed that HCs react always through CO, which reacts to CO₂ or reduces NO. The active sites on noble metals are more oxidized in lean but the metallic centre is the same. High Pd loadings are also resulting in larger noble metal clusters which have more reactive oxygen on surface. Pt has a promoting role in lean methane oxidation. Rh is known to promote NO_x performance in stoichiometric conditions (TWC). The optimal support composition is depending on the support- metal interaction in target reaction and ageing conditions. Thus the most active supports are not the same in lean and stoichiometric applications. The surface reactions are more complicated but main rich-lean reactions can be presented by joint equations as follows:

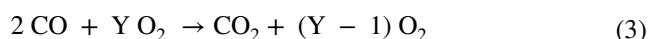
Stoichiometric if $X = 2$, Lean if $X > 2$



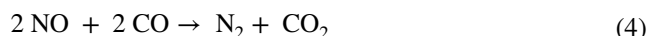
Stoichiometric if $Z = n + \frac{m}{4}$, Lean if $Z \gg n + \frac{m}{4}$



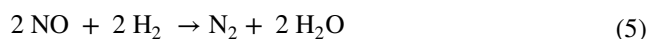
Stoichiometric if $Y = 1$, Lean if $Y \gg 1$



Stoichiometric-rich, NO reduction



Stoichiometric-rich, NO reduction



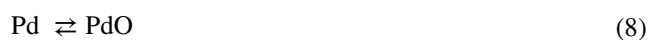
Stoichiometric-rich, Water-gas shift



Lean (on Pt), NO₂ formation



Rich/stoichiometric \rightleftharpoons Lean



Rich/stoichiometric \rightleftharpoons Lean



Rich \rightleftharpoons Lean (OSC on TWC)



4 Conclusions

The combined lean-stoichiometric natural gas combustion is an alternative for stoichiometric or dual-fuel applications, when lean NG-only combustion is difficult to adjust to heavy-duty mobile applications. Due to varying λ in lean-rich operation, combined TWC-MOC as well as SCR

catalysts are necessary to reach latest emission limits. In dual-fuel applications, MOC and DOC have joint properties too. Therefore, the combinations of TWC, MOC and DOC were investigated after varying ageing treatments in oxidation and 3-way reactions to find the optimal combinations by exhaust gas and ageing conditions. Each reaction required the right, tailored support to Pd and Pt to have efficient methane oxidation, 3-way reactions and NO oxidation. In lean phases, a larger MOC is necessary to keep high methane oxidation activity after demanding ageing. MOC was able to promote light-off of TWC in stoichiometric phases and stand quite well even the high temperatures up to 1000 °C. TWC was necessary to reach high HC, CO and NO_x conversions above 400 °C but it lost clearly activity in lean methane oxidation after ageing in air at 1000 °C. Pt-rich DOC had a key role to catalyse the formation of NO₂, which is further utilized in methane oxidation, SCR and dual-fuel-DPF. Formaldehyde formed in lean methane combustion is a harmful compound in lean NG exhaust gases but it was removed efficiently on investigated catalysts above 200–250 °C.

Lean-stoichiometric operation gives a natural way to maintain a high lean methane oxidation activity over MOC and combined systems. Short stoichiometric phases desulfated catalyst combinations periodically and the activity was recovered almost to the S-free level. These results clarified the ATS designs focusing on methane abatement in varying stoichiometry and a down-sizing is possible, when particularly TWC and MOC were both active for 3-way, lean methane and NMHC/CO oxidation reactions. Urea-SCR system after TWC/MOC/DOC will remove NO_x in lean phases. A more detailed system design will be the next step in the scale-up of ATSs for these applications.

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