



Short Pulse Reductive Activation of Pt/ceria for the Low-Temperature CO Abatement in Vehicles Operated with the Synthetic Diesel Fuel OME

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Abstract

The synthetic Diesel fuel oxymethylene ether (OME) is sulfur-free by nature, and due to the low soot formation, no active filter regeneration events are required, limiting the maximum temperatures seen by the exhaust catalysts to ~450 °C. These OME-specific ageing requirements will enable the application of new types of catalysts that cannot be used in conventional Diesel vehicles. Such new catalytic solutions will allow ultra-low emissions at a much-reduced cost and will hence contribute to the overall efficiency of the OME approach. In this contribution, we focus on CO abatement from OME exhaust. To enable an efficient evaluation of new catalysts under practically relevant conditions, a test bench was set up that can reproduce the transient temperature-, mass flow- and concentration profiles measured during real driving tests. In a first step, the transient test bench was used to compare CO oxidation over a commercial Diesel oxidation catalyst for OME- and conventional Diesel conditions. The same low-load cold-start drive cycle run with OME showed slightly lower raw emissions, but the CO emissions downstream of the catalyst increased by a factor of ~2. The main reason for the lower CO conversion is the lower temperature of the OME exhaust. In a second step, we investigated short-pulse reductive activation of Pt/ceria as a promising new technology that benefits from the OME-specific low ageing requirements. A Pt/ceria catalyst activated by a short 5–10 s reductive pulse achieved virtually 100% conversion even at exhaust temperatures below 80 °C. With one 5 s reductive activation pulse per 30-minute drive cycle, a CO conversion of > 99.9% is demonstrated over the low-load cold-start OME drive cycle, compared to 59% obtained with a standard commercial Diesel oxidation catalyst. To our knowledge, this is the first published demonstration of short pulse reductive activation of Pt/ceria for CO oxidation using realistic transient drive cycles.

Keywords OME aftertreatment · Pt/ceria · Reductive activation · Driving cycle · Lab-scale test rig

Abbreviations

OME	Oxymethylene ether
DC	Driving cycle
CO	Carbon monoxide
CO ₂	Carbon dioxide
NO	Nitric oxide
NO ₂	Nitric dioxide
HC	Hydrocarbons
CH ₄	Methane
C ₃ H ₆	Propene

DOC	Diesel oxidation catalyst
SCR	Selective catalytic reduction

1 Introduction

1.1 Exhaust Aftertreatment for OME Fueled Diesel Engines

The transition to a zero CO₂ economy is one of the major challenges for our generation. For road transport, besides batteries, synthetic fuels such as oxymethylene ether (OME) offer a promising route towards carbon neutrality [1]. E-fuels are produced based on CO₂ as a carbon source and renewable electricity as an energy source, for example from photovoltaics or wind energy. The net CO₂ balance for synthetic fuels is zero since the CO₂ released during combustion has been extracted from the air before [2].

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The overall well-to-wheel energy efficiency of e-fuels is significantly lower (~ factor 5–7) than the efficiency obtained by direct use of electricity in battery-electric vehicles [3]. But this lower efficiency is to a large extent compensated by the fact that renewable electricity can be produced in regions where photovoltaics or windmills operate most efficiently [4]. Furthermore, in a fully regenerative scenario, energy production and demand will not be synchronized, so that energy needs to be stored.

Since synthetic fuels are synthesized starting from CO₂, the chemical structure can be designed to optimize combustion performance. OME is an attractive synthetic fuel to replace Diesel, mainly due to its significantly reduced tendency to form soot. The low soot formation results from the molecular structure of OME, with no directly connected carbon atoms, thus preventing the formation of soot precursors [5–9]. Due to the low soot formation, OME engines can be operated at high exhaust gas recirculation rates (EGR), allowing for a significant reduction in NO_x formation [10–14], without the known NO_x-soot trade-off. Furthermore, the reduced soot formation will eliminate the need for high-temperature regeneration of the particulate filter.

Further, as a synthetic fuel, OME is sulfur-free by nature [15–17]. Current Diesel exhaust gas systems use high-temperature regenerations to remove soot from the filter and to regenerate sulfur-poisoned SCR catalysts. The ageing requirements of current Diesel exhaust systems are to a large extent determined by these regenerations. In the absence of thermal regeneration events, the maximum temperature seen by a catalyst is ~ 450 °C, resulting in a strongly reduced thermal stress.

OME exhaust treatment also poses new challenges. Compared to conventional Diesel operation, the main challenge is the reduced exhaust temperature that results from the lower energy density of the OME fuel and the corresponding increase in thermal mass of the exhaust [17, 18]. Due to the structure of OME with no direct C-C bonds, the expected hydrocarbon emissions are mainly C1 species, especially methane, and formaldehyde. The formation of both species has been experimentally observed, especially during cold-start [18, 19]. Formaldehyde formation has also been shown to increase with higher exhaust gas recirculation, resulting in a formaldehyde-NO_x tradeoff [20]. A similar tradeoff has been observed for methane-NO_x. Methane conversion is a big challenge in OME exhaust treatment, especially in combination with low exhaust temperatures. Formaldehyde is relatively easily converted on platinum catalysts. For air cleaning applications significant formaldehyde conversion is achieved at room temperature [21]. However, formaldehyde oxidation in vehicle exhaust is more challenging since the reaction is inhibited by CO such that the formaldehyde conversion can only be obtained after CO has been fully converted [22].

The main focus of previous work was to demonstrate that the requirements of OME exhaust aftertreatment can be met with currently established technology. This is important to guarantee a swift introduction of OME using the existing Diesel vehicles and fueling infrastructure. However, the specific low ageing requirements of OME operation open new degrees of freedom, far beyond the catalytic technology currently established for the aftertreatment of conventional Diesel vehicles. In the past, many of the promising catalytic concepts discussed in the academic literature could not be transferred into practical application due to problems with thermal stability or sulfur resistance. In the search for an optimal OME exhaust aftertreatment system, many of these concepts will need to be reevaluated. The promise is not only to meet the above-mentioned specific challenges of OME exhaust aftertreatment, but such systems might also fulfill the requirements at a much-reduced cost, for example, due to greatly reduced precious metal requirements and due to overall reduced catalyst volumes. In this way, the more efficient aftertreatment systems will contribute to the overall economic competitiveness of the OME approach.

To illustrate the opportunities for new types of catalysts arising from the reduced aging requirements of OME, in this paper, we focus on the CO aftertreatment of OME exhaust. CO conversion is not only relevant because CO is a regulated pollutant, but also because CO inhibits other reactions like formaldehyde- and NO oxidation, such that the corresponding reactions only process after CO is fully converted.

In a first step, we will investigate CO conversion on a commercial Diesel oxidation catalyst (DOC) during OME- and conventional Diesel operation. It will be shown that due to low exhaust temperatures, CO conversion is more challenging for OME exhaust. We will then demonstrate a new strategy for CO removal from OME exhaust, using short pulse reductive activation of platinum supported on ceria. This is an example of a new catalytic approach that shows promise for OME exhaust aftertreatment but was difficult to apply under conventional Diesel operating conditions.

1.2 Short Pulse Reductive Activation of Pt/ceria as a Promising Approach for CO Removal from OME Exhaust

It is known that Pt/ceria catalysts can be activated by reductive pretreatments and that very high CO- and hydrocarbon oxidation rates can be achieved [23]. Even room-temperature CO oxidation has been demonstrated [24]. The mechanism responsible for the extraordinary catalytic activity of Pt/ceria after rich activation is currently the subject of intensive investigations. It is well established that metallic platinum is catalytically more active than oxidized platinum and that the reductive pretreatments convert platinum back into the more active metallic state [25, 26]. Also, the Pt-ceria interface

plays a crucial role, and the activity of the interface processes is controlled by the platinum oxidation state [27, 28].

Although impressive CO/hydrocarbon oxidation activity has been demonstrated using reductive activation of Pt/ceria, this approach is not directly applicable to automotive catalysis, since usually reductive treatments were applied for several minutes, which would be associated with considerable CO and hydrocarbon emissions. Furthermore, so far, the focus is primarily on the ultra-high activity achieved with the reductive activation, and less attention is paid to the fact that the activated catalysts lose their activity quickly once the exhaust temperature exceeds ~ 230 °C. Due to this deactivation, in real vehicle operation, the reductive treatments would need to be repeated regularly, so that the CO emissions during the frequent activations would be higher than the CO emissions avoided by activation.

We have recently demonstrated that under certain conditions Pt/ceria catalysts can be activated by short 5–10 s reductive pulses, similar to the pulses applied to regenerate NO_x storage catalysts, and that CO conversions of $> 90\%$ at 100 °C can be reached in this way [29, 30]. As the catalyst deactivates once the exhaust temperature exceeds 230 °C, the catalyst needs to be regularly reactivated. Due to the short duration of the reductive activations, the frequent regeneration does not pose severe emission problems, since the rich pulses are fully absorbed by the oxygen storage, and negligible CO emissions are observed during the regenerations. Furthermore, the fuel penalty caused by the short reductive pulses is minimal. The short pulse activation scheme can be well combined with a NO_x adsorber functionality on the same catalyst since in this case, the rich pulses can regenerate the NO_x adsorber at the same time. Ceria itself acts naturally as a low-temperature NO_x adsorber. Additional barium-based storage compounds can be added to improve high-temperature NO_x storage.

Unfortunately, in the aftertreatment of conventional Diesel engines, the practical application of the short pulse activation strategy is not straightforward. One fundamental problem is the notorious tendency of ceria to be poisoned by SO_2 or SO_3 [31]. Another complication is that at ageing temperatures of > 650 °C usually observed in Diesel exhaust systems, platinum particles disperse into single platinum ions on the ceria surface [32]. These single-atom Pt/ceria catalysts are relatively inactive for CO- and hydrocarbon oxidation.

Once the catalyst has been deactivated at temperatures > 650 °C, the formed single atom Pt/ceria catalyst cannot be activated by short reductive pulses. In this case, a more intensive reduction for 30 min at 400 °C is needed. Such intense regenerations are feasible with Diesel engines and are applied already today for the sulfur regeneration of NO_x storage catalysts, although the fuel penalty is significant. After the regeneration at 400 °C, the catalysts again

show high CO oxidation activity and can be regenerated by short pulses, if the exhaust temperature exceeded ~ 230 °C.

Based on these observations, we have proposed a two-step activation scheme, where repeated short reductive pulses are applied each time the catalyst has been exposed to higher temperatures [29, 30]. These short pulse regenerations have to be applied at ~ 230 °C and before the catalyst temperature falls below 200 °C. In rare cases where the exhaust temperature has exceeded 650 °C, the more intense regeneration at 400 °C needs to be carried out. The two-step activation strategy can be combined with the application of NO_x storage catalysts since these catalysts periodically require an intense reductive treatment for desulfurization. The repeated short pulse activations between the rare desulfurization events serve as a regeneration of the NO_x storage.

For conventional Diesel exhaust aftertreatment, the short pulse activation strategy has not yet been applied in practice, mainly due to the emissions and fuel penalty associated with the intense regeneration events, but also due to the complexity introduced by the two-stage activation. The situation will be different for the exhaust control of OME. Due to the absence of soot- and sulfur regenerations, exhaust temperatures stay below 450 °C, such that it is unlikely that Pt/ceria will transform into the inactive single atom state. Platinum will thus remain in a particle size that allows a short pulse regeneration. In this way a relatively simple operation strategy can be applied, where the catalyst is periodically regenerated by short 5–10 s reductive pulses. The application of the reductive activation pulses will be further simplified by the ability of fuel-rich OME combustion without significant soot generation.

In this paper, we demonstrate the feasibility of short pulse reductive activation of Pt/ceria catalysts for efficient CO removal from OME exhaust, using reductive pulses similar to those applied today for the regeneration of NO_x traps [33]. We will show that despite the reduced temperature of OME exhaust, CO conversions of more than 99.9% can be achieved in a low-load transient real driving cycle, where a commercial DOC achieves $\sim 60\%$ conversion.

2 Methods

2.1 Engine Measurement of raw Emissions for Conventional Diesel and OME Operation During Cold Start

To investigate catalyst performance under practical operating conditions, the raw emission profiles of two cold-start transient real drive cycles were implemented on a new lab-scale test bench. The route profile of a real driving cycle described in [34] was simulated with a low-load velocity/time profile on an engine test bench.

These engine tests were carried out on a 4-cylinder engine with 2 l displacement and were run with OME and Diesel fuel. For the engine operation with OME, only the injection duration (comparable load) and the start of injection (comparable center of combustion) were adjusted to guarantee the highest possible comparability with conventional Diesel. The resulting raw emissions were detected using a Fourier Transform Infrared Spectrometer (SESAM i60 FT) and a Flame Ionization Detector (FID i60) both provided by AVL. For the tests at the lab scale test bench, only the first 30 min of the engine experiments were used as this work focuses on the cold-start behavior. See [14] for a more detailed description of the implementation of transient cycles for the operation with OME at the engine test bench.

2.2 Implementation of Driving Cycles on a Transient Lab-Scale Test Bench

As the optimization of OME engine operation strategies is ongoing, the search for new catalytic solutions needs to proceed in parallel with the engine development.

To enable such parallel development of engine hardware, operating strategies, and catalytic aftertreatment, we developed a lab-scale test bench that can emulate transient engine out emissions. In this way, realistic dynamic lab tests can be implemented based on engine tests, single-cylinder studies, or even simulations, so that new catalysts can be tested efficiently under OME-relevant conditions before engines become available for catalyst testing.

The transient profiles of catalyst inlet temperature, mass flow, and exhaust composition were implemented on a lab-scale test rig. The layout of the test rig is similar to the one used in [35] and [36]. Exhaust gases were dynamically dosed using fast flow controllers provided by Bronkhorst® and Alicat®. Water is added to the exhaust using an evaporator system provided by Bronkhorst®. Temperature profiles measured on the engine could be reproduced with high time resolution using a low heat capacity electrical heating element. Concentrations of CO, NO, NO₂, CH₄, and C₃H₆ downstream of the catalyst were analyzed with a MultiGas™ 2030 FTIR provided by MKS.

For the experiments shown in this paper, the raw emissions measured on an engine bench were reproduced on the lab test bench as follows: Concentrations of CO, NO, NO₂, O₂, CH₄, H₂O, and CO₂ were dosed as measured on the engine bench, using N₂ as balance. For test cycles reproducing conventional Diesel operation, all non-methane hydrocarbons (obtained as the difference of the total hydrocarbons measured at the engine by a flame ionization

detector and the separately measured CH₄) were represented as C₃H₆, with the dosed concentration computed on a C1 basis. If not stated otherwise, methane was added as the only hydrocarbon in the OME test cycles. The concentration profile for each species of the Diesel and OME driving cycle can be found in S1, respectively S2.

2.3 Reductive Activation Pulse

The application of short-term-rich operation on Diesel engines is well-established for the regeneration of NO_x storage catalysts [33]. Here, we propose to apply similar short rich pulses for the activation of the Pt/ceria catalyst. To mimic such a regeneration event, the catalyst is heated to 230 °C and then a 5–10 s reductive pulse is applied by the flow controllers at a space velocity of 28 kh⁻¹. The exhaust composition during the rich pulses was 2% CO, 0.5% O₂, 2.5% H₂O, and a balance of nitrogen. The 0.5% oxygen during the rich phase are applied since this is the typical minimum oxygen concentration observed in Diesel exhaust, even during net-rich operation. The details of the regeneration procedure are provided in the supplementary material S4.

2.4 Temperature Ramp Experiments

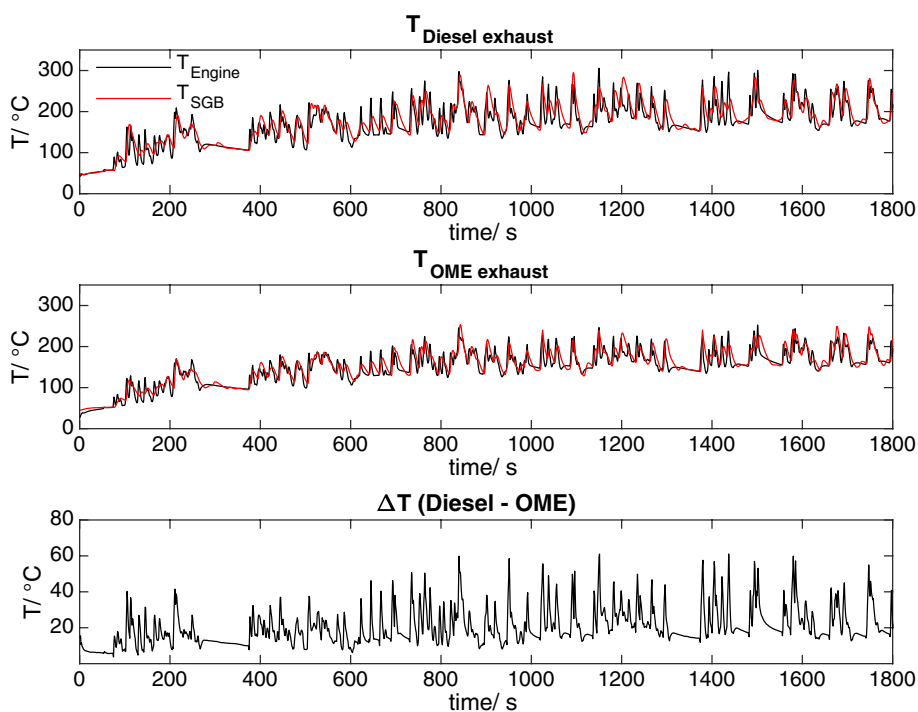
Temperature ramp experiments were performed to further investigate the activity of the Pt/ceria catalyst. For this purpose, the catalyst was first deactivated at 450 °C for 30 min in 10% O₂ and 10% H₂O. Following the pretreatment, a first temperature ramp test was performed with the deactivated catalyst, ramping the inlet temperature from 50 to 200 °C in a typical Diesel exhaust (1000 ppm CO, 100 ppm NO, 30 ppm NO₂, 10% O₂, 5% H₂O, balance N₂, space velocity 23 kh⁻¹). After the first temperature ramp, the catalyst was activated by a 10 s reductive pulse, using the procedure described in Sect. 2.3. Then a second temperature ramp identical to the first one was performed on the activated catalyst. Details of the test procedure are described in the supplementary material S5.

2.5 Catalysts

2.5.1 Reference Diesel Oxidation Catalyst

A commercial DOC supplied by Umicore was used as a reference. The Pt:Pd ratio was 2:1, and the platinum loading was 28 g per cubic foot. The cell density and wall thickness of the cordierite substrate were 400 cells/inch² and 4.3 milli-inch, respectively. The used catalyst core had a volume of 0.1544 l. No aging procedure was applied to the catalyst, reflecting the low ageing requirements of OME operation. Before each test, oxidative pretreatments were applied that are described together with the test procedures.

Fig. 1 Top: Temperature profile for the cold-start driving cycle at Diesel operation run at the engine (black) and the lab-scale test bench (red). Center: Temperature profile for the cold-start driving cycle at OME operation run at the engine (black) and the laboratory test bench (red). Bottom: Difference in the exhaust gas temperature during Diesel and OME operation



2.5.2 Pt/ceria Model Catalyst

A platinum/ceria model catalyst was prepared as follows: A high surface area ceria (BET 140 m²/g) was impregnated with an aqueous solution of Bis(ethanolammonium) hexahydroxoplatinum(IV) using the incipient wetness method, such that a Pt loading of 1% by weight was obtained. The material was dried and treated for 2 h in a reductive atmosphere (2% H₂ in N₂) at 500 °C. The Pt/ceria powder was then suspended in water together with a high surface area alumina oxide (BET 140 m²/g, 50 g Al₂O₃ per 100 g of the impregnated ceria). The resulting slurry was applied on a cordierite monolith with a cell density of 400 cells/inch² and a wall thickness of 4.3 milli-inch, using a standard dip-coating procedure. This resulted in a catalyst loading of 150 g/l, corresponding to a platinum loading of 28 g per cubic foot. Finally, the coated monolith was dried and then calcined for two hours at 550 °C in air. The used catalyst core had a volume of 0.1544 l and was used without further ageing.

3 Results and Discussion

3.1 Implementation of Transient real Driving Cycles in a Lab Experiment

To obtain raw emission profiles, a real driving test cycle was first run on an engine bench, using Diesel and OME as fuel, see Sect. 2.1 for details on the engine measurements. The

transient catalyst inlet conditions were then reproduced on the lab-scale test bench. Figure 1 compares the catalyst inlet temperatures measured on the engine and on the lab-scale test bench. The CO concentration inlet profiles are compared in Fig. 2. All other concentration profiles, as well as the mass flow, are compared in S1-S3 in the supplementary material. Obviously, all profiles can be accurately reproduced on the lab bench.

3.1.1 Temperature Profiles: Diesel vs. OME Operation

Figure 1 compares the temperature profile for the Diesel- (top) and OME operation (center) as well as the difference curve (bottom). A major difference between Diesel- and OME exhaust is the temperature level. Especially at the start of the test cycle, the temperature difference reaches ~20–30 °C. This will cause the catalyst to achieve light-off more slowly during OME operation.

3.1.2 Performance of a Commercial DOC for Conventional Diesel- and OME Exhaust Gas Aftertreatment

Figure 2 (top) shows the CO concentration profile of the cold-start driving cycles for Diesel- (left) and OME (right) operation which were operated at the lab-scale test rig. The blue curves depict the raw pre-catalyst CO emissions, which were obtained with a dummy test. The red curves show the post-catalyst CO emissions for OME and Diesel operation. Figure 2 (bottom) shows the cumulative CO mass over the time upstream (blue) and downstream (red) of the catalyst.

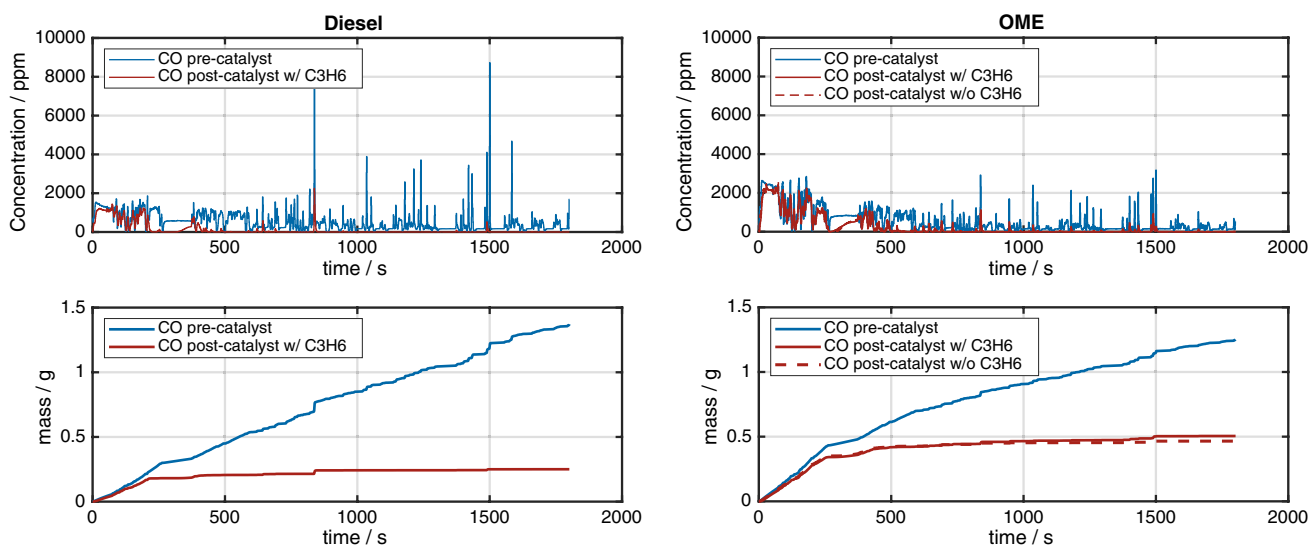


Fig. 2 Diesel conditions left, OME conditions (with and without C_3H_6) right: Pre- and post-catalyst CO emissions during the cold-start driving cycle for a lab-scale experiment with a commercial DOC

(top). Cumulated CO mass over the driving cycle before and after the catalyst (bottom). Both driving cycles were run with a commercial reference DOC

Both experiments were performed with the commercial reference DOC. The measured raw emissions are $\sim 10\%$ lower for OME compared to Diesel operation [34]. When comparing the post-catalyst CO emissions, a significantly higher CO conversion is observed for Diesel operation. At the end of the driving cycle, twice as much CO is emitted in OME operation compared to the Diesel case. This is attributed to the significantly lower exhaust gas temperature in OME mode.

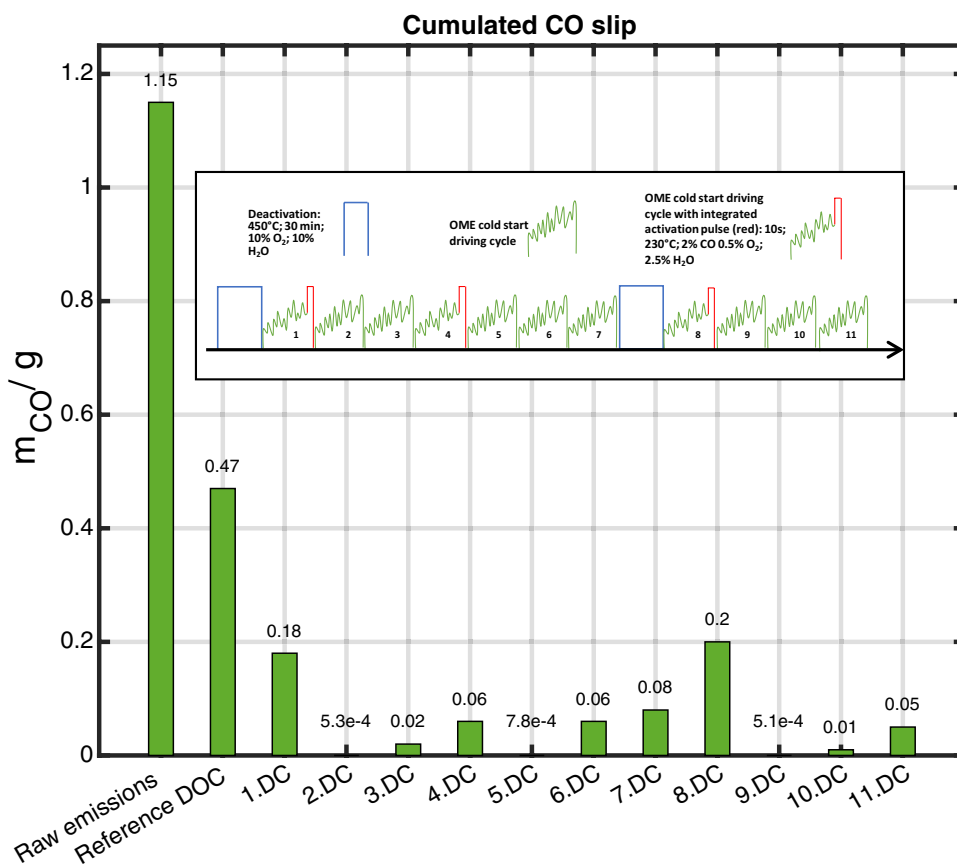
For the conventional Diesel exhaust, propene was used as a representative non-methane hydrocarbon with a concentration profile determined from the total hydrocarbon signal detected in the engine experiments. In OME exhaust, the primary hydrocarbon species are CH_4 and formaldehyde, which are expected to be much less inhibiting and deactivating than C_3H_6 . To investigate the sensitivity of the CO conversion to propene inhibition, for the OME case an additional measurement was performed without C_3H_6 . The CO emissions with and without propene are shown in Fig. 2 (right). Under these conditions, the effect of C_3H_6 is nearly negligible. This behavior can be explained on the one hand by the overall very low total hydrocarbon content in OME operation. The much larger factor, however, is the low temperature. At low temperatures, the inhibiting character of the propene plays a subordinate role, since the light-off temperature of the catalyst has not yet been reached. In order to keep the framework conditions as close as possible to the real OME conditions in the following experiments, propene is no longer used.

3.2 Demonstration of Low-Temperature CO Conversion by Reductive Pulse Activation of Pt/ceria

3.2.1 Performance of Pt/ceria Without Reductive Activation

In the first step, the performance of the Pt/ceria catalyst was tested without reductive activation. To this end, the catalyst was pretreated for 30 min under lean conditions ($10\% O_2$, $10\% H_2O$, space velocity 50 kh^{-1}) at 450°C , the maximum expected exhaust temperature for OME operation. Following the pretreatment, the OME drive cycle of Fig. 2 (right) was operated. Figure 3 compares the performance of the commercial Pt/Pd reference DOC and the Pt/ceria catalyst. With 0.18 g CO accumulated during the drive cycle, the Pt/ceria catalyst reduces the CO emissions to less than half the emissions obtained from the reference catalyst. At first sight, it might seem surprising that a Pt/ceria model catalyst outperforms the commercial DOC. However, one needs to consider that the reference catalyst has been optimized to withstand high ageing temperatures of $\sim 650^\circ\text{C}$, as well as sulfur poisoning. None of these properties of the reference catalyst are relevant for OME exhaust treatment, where temperatures are low, and sulfur is absent. The surprising performance of the nonactivated Pt/ceria catalyst is an illustrative example showing that the changed requirements of OME exhaust treatment allow for innovative catalytic solutions.

Fig. 3 Comparison of the cumulated post-catalyst CO mass for the 30-minute OME cold-start driving cycle (DC) in the Pt/ceria test series: 1. DC – 11. DC. The cumulated mass of the raw emissions and the test with a reference DOC are provided for comparison. The sequence of the test series: Deactivation of the catalyst (blue): 30 min, 450 °C, 10% O₂, 10% H₂O. OME cold-start driving cycle (green). Modified OME cold-start driving cycle with integrated CO reductive pulse at the end (10 s, 230 °C, 2% CO, 0.5% O₂, 2.5% H₂O) (red). The resulting CO mass also includes the unconverted CO during the pulse



3.2.2 Short Pulse Reductive Activation of Pt/ceria

To demonstrate the potential of reductive activation of Pt/ceria, a test sequence consisting of lean pretreatments at 450 °C, activation by 10 s reductive pulses, and repeated drive cycles were conducted. The sequence is shown in Fig. 3. It starts with a 30-minute deactivation at 450 °C simulating full load operation of an OME engine. The purpose of this 450 °C deactivation treatment is to initialize the catalyst in a nonactivated state. The pretreatment is followed by a first non-activated drive cycle which was discussed already in the previous section. A reductive activation pulse was applied at the end of drive cycle 1. The activation procedure involved heating the catalyst to 230 °C and then applying a 10 s reductive pulse (2% CO, 0.5% O₂, and 2.5% H₂O, space velocity of 28 kh⁻¹).

Figure 4 shows the CO emissions during the non-activated reference drive cycle (up to the dashed line) and the following activation procedure (starting from the dashed line). The 10 s reductive pulse significantly contributes to the CO raw emissions, but at 230 °C the catalyst activity is sufficient to fully convert the CO pulse. Thus, the CO emitted during the pulse is insignificant compared to the overall emissions. Following the activation procedure, three consecutive drive cycle measurements are performed without

further activation (Fig. 3, DC 2–4). Figure 3 summarizes the cumulated emissions during the drive cycle, including the emissions of the CO pulse, directly following the activation (DC 2). CO emissions are drastically reduced with the catalyst showing virtually full conversion from the start of the cycle, despite the low exhaust temperatures below 60 °C during this phase. Overall cumulated emissions of the second drive cycle are 5.3 10⁻⁴ g CO, which corresponds to an average conversion of 99.95% compared to 59% obtained with the commercial reference catalyst. During the two following drive cycles 3 and 4, the CO emissions gradually increase from cycle to cycle, resulting in a total conversion of 97.7%. The observed gradual deactivation implies that, as expected, the reductive activation must be repeated regularly. After cycle 4, the catalyst was activated by another 10 s reduction at 230 °C. Again, the drive cycle directly following the reductive activation (DC 5) shows virtually full conversion of CO. During the two following drive cycles without further activation (DC 6+7), the catalyst again gradually deactivates. Following the second activation, CO emissions increase slightly faster than after the first activation. The origin of this slightly faster deactivation after repeating the activation is not understood yet.

Previous work by Betz has shown that after short pulse activation, deactivation occurs particularly fast at

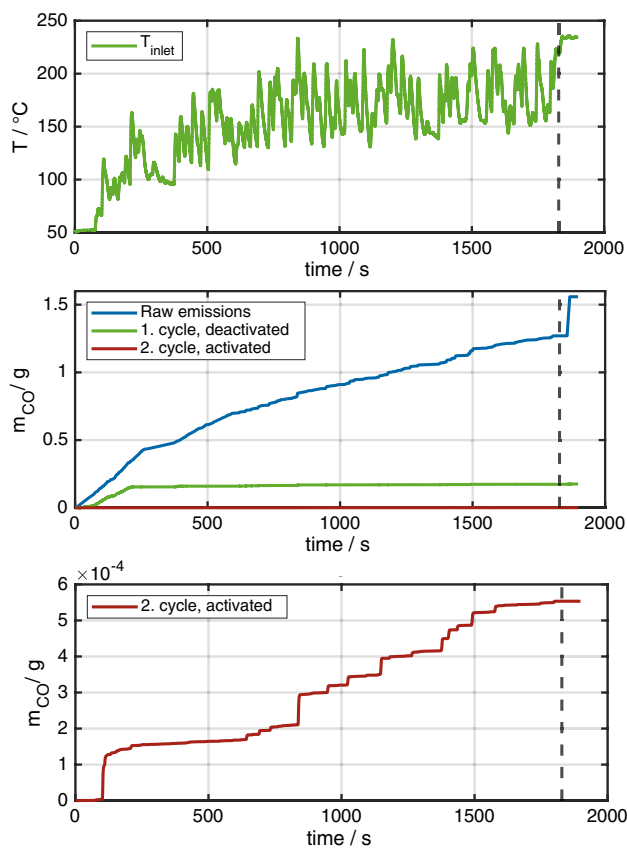


Fig. 4 Top: Temperature profile for the OME cold-start driving cycle at the lab-scale test bench with included period at ~ 230 °C for the reductive pulse which starts after the dashed line. Center: Cumulated CO mass over the driving cycle for the raw emissions (blue), the first driving cycle with the deactivated Pt/ceria catalyst (green), and for the reductively activated Pt/ceria (red) which is plotted in more detail at the bottom

higher temperatures [30]. This implies that an activation is required after each period of high-load operation of the engine. To mimic such a scenario, after DC 7 another 30 min deactivation was performed at 450 °C, followed by a drive cycle without activation (DC 8), a 10 s activation at 230 °C, and further three consecutive drive cycles with no further activation between the cycles (DC 9–11). The emissions in all four cycles closely follow the emissions in the four cycles after the first high-temperature treatment, demonstrating the repeatability of the activation procedure.

To further demonstrate the activity of the Pt/ceria catalyst after short pulse activation, temperature ramp tests were performed. Results are shown in Fig. 5. Under the conditions of the ramp test, 50% conversion was observed at 50 °C. Full conversion is achieved below 80 °C. This data confirms the high CO oxidation activity of the Pt/ceria catalyst after the short pulse activation procedure, also compared to previous studies on low-temperature CO oxidation [24, 29, 30].

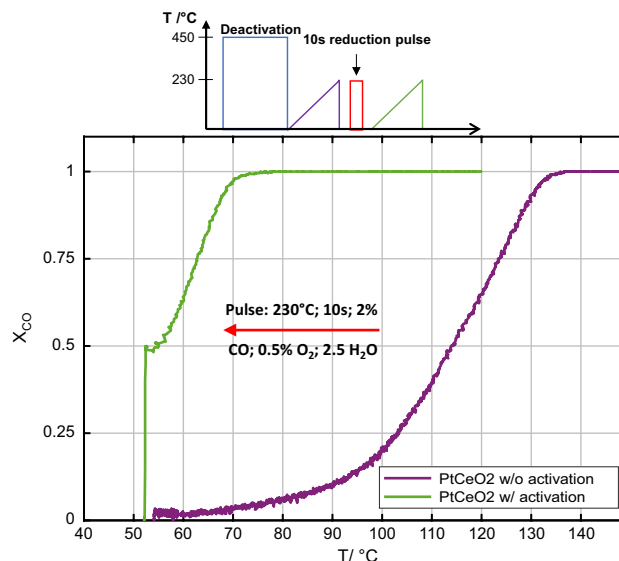


Fig. 5 Top: Used temperature profile for the deactivation of the Pt/ceria catalyst (blue), the first temperature ramp (purple), the activation pulse (red), and the second temperature ramp (green). Bottom: CO conversion after deactivation (purple) and after the activation pulse (green) against the temperature

Although 50% CO conversion at 50 °C is impressive, this conversion is below the conversion in the drive cycles, where virtually full conversion is observed at 50 °C. A potential explanation for the higher performance in the drive cycle is the extremely low space velocity of 13 kh^{-1} in the initial phase of the cycle, compared to 23 kh^{-1} in the ramp test.

The sequence with one activation every three drive cycles clearly demonstrates the gradual deactivation from cycle to cycle. Accordingly, compared to the first cycle directly after activation, emissions in the second and third cycles increased. A sequence with more frequent activation pulses thus allows for further lowering of the overall emissions. Therefore, we implemented an alternate sequence that applies a shorter 5 s rich reductive pulse prior to each drive cycle (Fig. 6, left). Due to the shorter activation pulse, CO emissions during the first drive cycle are slightly higher than after the 10 s activation. However, due to the repeated activation, very low CO emissions are obtained in all cycles (Fig. 6, right). Accumulated over the 5 activated drive cycles, a CO conversion of 99.87% is achieved, compared to 97.7% with the first sequence (Fig. 3, DC 2–4) and 59% with the reference DOC. Although very low emissions are obtained in all drive cycles, a slight decrease in CO conversion is observed from cycle to cycle, as shown in Fig. 6. The reason for this slow deactivation needs to be further investigated. Nevertheless, it has already been shown in Fig. 3 (sequence DC 7–9) that treatment at 450 °C under oxidizing conditions, combined with a short reductive pulse results

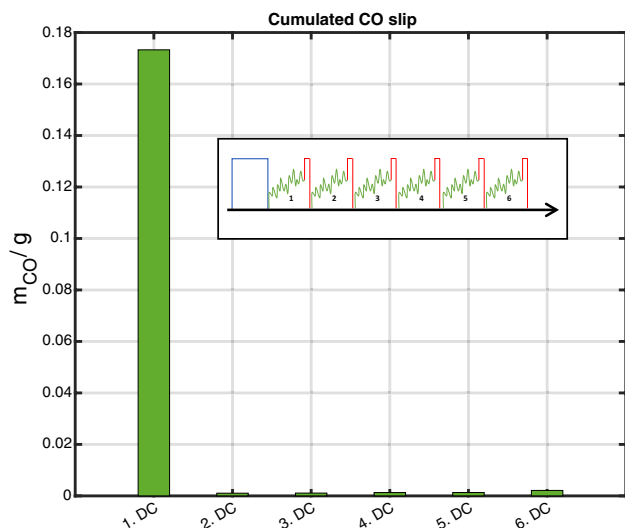
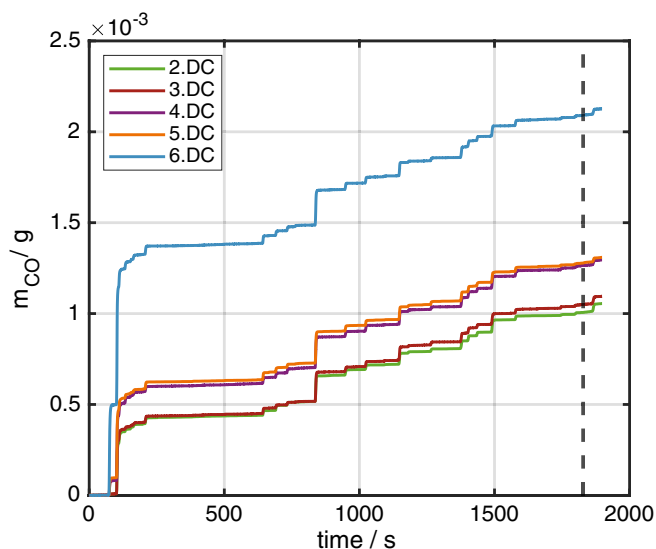


Fig. 6 Six consecutive cold-start driving cycles with an integrated 5-second reductive pulse after an initial deactivation. Left: Cumulated CO mass, measured after the catalyst for each driving cycle. Right:



Cumulated CO mass, measured after the catalyst for DC 2–6, against the time. The pulse was applied after the dashed line

again in a highly activated catalyst. This suggests that the initial activity can be restored in real operation.

In the drive cycle, after reductive activation virtually full conversion of CO is achieved at temperatures below 60 °C. In our previous work, 90% CO conversion was observed at 100 °C [29, 30]. There are several explanations for this difference:

Gas hourly space velocity: The real driving cycle applied in this work operates at an exceptionally low engine load, resulting in low space velocity. But space velocity alone unlikely explains the large difference in light-off temperature.

The catalyst: In the previous work the platinum was initially supported on alumina, and was transferred to the ceria by gas phase transport of PtO₂ during treatment at 800 °C as described in [32], resulting in atomically dispersed platinum on ceria. Only during a reductive treatment at 400 °C the catalytically active platinum particles were formed. In this work, the platinum was impregnated directly on the ceria.

Hydrocarbon inhibition: The previous work was performed in the context of Diesel exhaust treatment. Thus, C₃H₆ was added to the feed as a representative hydrocarbon. We have previously shown that cool-down in C₃H₆ containing exhaust deactivates a catalyst through site blocking by partial oxidation products, reducing the catalytic activity during the following heat-up [37–39]. In the current work, no hydrocarbons except methane were added to the feed. This is justified since the primary hydrocarbons in OME exhaust are the C1 species methane and formaldehyde, and unreacted OME [40]. Methane and formaldehyde are not expected to show significant pore blocking. OME has been

shown to hydrolyze on supported platinum to C1 hydrocarbon at 100 °C [41]. Nevertheless, in the future, the short pulse reductive activation should be studied with formaldehyde and OME in the feed. This will require a more quantitative specification of the hydrocarbon species in OME exhaust as well as an extension of our test bench so that formaldehyde and OME can be dynamically dosed.

For reference, we also applied the short pulse activation to the commercial Pt/Pd Diesel oxidation catalyst. The results are shown in S6. As expected, the short pulse activation has a negligible effect on the CO conversion in the following drive cycles. It is also seen that since the conventional oxidation catalyst has no oxygen storage, the rich activation causes a significant CO breakthrough.

4 Conclusion

With lower aging temperatures and no sulfur in the exhaust, catalysts for OME-fueled engines will have greatly reduced aging requirements, compared to current exhaust catalysts optimized for conventional Diesel fuel. This will allow the application of new types of catalysts which can achieve ultra-low emissions at reduced costs, hence contributing to the overall competitiveness of the OME approach.

In this paper, we focused on CO oxidation in OME exhaust. Using a laboratory test bench that can reproduce transient exhaust gas profiles measured during a low-load real driving cycle, we demonstrated that unprecedented CO oxidation activity can be obtained on a Pt/ceria model catalyst if the catalyst is activated by short reductive pulses

similar to the pulses commonly applied for the regeneration of NO_x storage catalysts. After the short pulse activation, virtually full conversion was obtained at temperatures as low as 80 °C. With a single 10 s reductive pulse applied during the 30-minute drive cycle, an average conversion of better than 99.9% was achieved, compared to 59% measured with a state-of-the-art commercial catalyst over the same low-load cycle.

The short pulse activation of Pt/ceria by fuel-rich operation has been investigated before for the exhaust treatment of conventional Diesel exhaust, but the practical application proved difficult due to catalyst deactivation occurring at temperatures above 600 °C and problems with sulfur poisoning. In this way, the short pulse activation of Pt/ceria is an example of a new catalyst principle that was difficult to apply under conventional Diesel conditions but shows promising potential for OME exhaust aftertreatment.

Besides CO, exhaust systems for OME will need to remove further pollutants including NO_x , methane, and formaldehyde. Especially methane abatement will be challenging at the extremely low temperatures of OME exhaust. In the literature, numerous new catalysis concepts have been proposed, for example, based on nano-design [27, 29]. Most of these sophisticated catalyst architectures do not sustain the aging requirements of conventional Diesel exhaust treatment. These approaches should be revisited for OME exhaust aftertreatment, providing interesting perspectives for further catalysis research.

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