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Engineered Sulfur-Resistant Catalyst System with an Assisted Regeneration Strategy for Lean-Burn Methane Combustion

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Catalytic combustion of methane, the main component of natural gas, is a challenge under lean-burn conditions and at low temperatures owing to sulfur poisoning of the Pd-rich catalyst. This paper introduces a more sulfur-resistant catalyst system that can be regenerated during operation. The developed catalyst system lowers the barrier that has restrained the use of liquefied natural gas as a fuel in energy production.

Transportation, including the road, aviation, and marine sectors, is responsible for over 20% of greenhouse gas emissions in Europe. Big steps have already been taken towards alternative fuels to reduce the emissions of the road-transportation sector. However, in a development of lean-burn engines for heavy-duty vehicles one should keep in mind the aftertreatment of exhaust gases. In general, the fuel itself and its quality together with operation conditions (lean or stoichiometric) affect the design, operation, and durability of the aftertreatment system.

Natural gas, which consists of mainly methane, will potentially be increasingly adopted as a fuel for the on-road transportation sector during the next years, because it is one way to reduce CO₂ emissions. On the contrary, the greenhouse gas warming potential of methane is ~30 times higher than that of CO₂, and thus, its emissions need to be prevented over the value chain.[1] The most active catalyst for methane combustion is palladium supported on alumina and promoted with a small amount of platinum.[2] However, the catalyst suffers from water inhibition[3] and sulfur poisoning,[4] both of which inhibit its low-temperature activity in methane combustion. The latest experiments performed under simulated exhaust gas have actually shown that sulfur makes the catalyst more vulnerable to water inhibition.[5]

Robustness of the aftertreatment system including sulfur poisoning of the aftertreatment system is one reason why natural gas has not been adopted widely in the road-transportation sector. Lean-burn engines are running at low temperature owing to high efficiency, which further increases the challenge. To regain the activity of the catalyst, a variety of regeneration methods have been suggested.[6] The latest studies have shown that regeneration under realistic operation conditions is possible, but a decrease in methane combustion activity has always been observed as a result of the formation of inactive metallic Pd.[5,7]

The paper presents a methane oxidation catalyst system that is less prone to sulfur poisoning and has the ability to be regenerated at reasonably low temperatures. The developed catalyst system is possible to implement in real lean-burn natural gas vehicles to reduce low tailpipe emissions. The system can control methane emission and, hence, decrease the overall greenhouse warming potential of the transportation sectors.

The lean-burn natural-gas engine of a heavy-duty vehicle operates at lower temperatures than a stoichiometric engine. Low exhaust gas temperatures together with stringent emission regulations set a great challenge for aftertreatment systems. In general, the temperature of the exhaust gas stream is most of the time between 400 and 500 °C. Recent laboratory experiments have shown that this temperature range is too low to achieve the desired 90% methane conversion with a sulfur-poisoned catalyst. Currently, a maximum methane conversion of 60% at 500 °C can be achieved with the present commercial technology in the absence of a regeneration strategy.[8]

The methane conversion activities of the examined catalyst systems are presented in Figure 1 after each aging cycle. The fresh-state performance of each catalyst was recorded in the presence of SO₂ in exhaust gas stream during the first light-off. All the catalyst systems, except TWC₁₅₀₀₀₀, showed the same performance, as can be seen in Figure 1a. The target of 90% methane conversion could be achieved with systems in their fresh state. TWC₁₅₀₀₀₀ alone did not show significant methane...
conversion in the light-off measurements, and hence, its activity is not further discussed in the comparison.

After the first aging and regeneration cycles, the second light-off was measured (Figure 1b). Sulfur poisoning could be observed as a decrease in methane conversion at 400 °C and beyond for all of the catalyst systems, except for the three-way catalyst/methane oxidation catalyst (TWC + MOC) system. For MOC + TWC and MOC_{50,000}, deactivation was the most apparent. It can now be stated that good methane conversion activity of the TWC + MOC (TWC_{10,000} + MOC_{50,000}) system cannot be connected to the noble-metal content of the catalyst system.

This statement can be made because typically the most active MOC_{25,000} catalyst (MOC_{50,000} + MOC_{50,000}), which was designed to convert methane under lean-burn operation conditions, suffered from sulfur-originated deactivation, whereas the performance of the TWC + MOC system remained the same as that of the fresh state and the noble-metal loading of the systems was the same.

The second aging cycle decreased the methane conversion activities of the conventional catalyst systems further, but again the TWC + MOC system still showed the same, good performance as the fresh system. A reason for the significant improvement in methane conversion activity after heavy sulfur poisoning was better sulfur storage ability of the TWC, which hindered deactivation of the downstream MOC. Sulfur content analysis, shown in the Table 1, confirmed the role of the upstream TWC on the TWC + MOC system.

Heavy-duty vehicles can operate under steady-state conditions over long distances. Hence, aging and regeneration experiments were performed under lean steady-state operation at 400, 450, and 500 °C to study the durability of the catalyst systems. Figure 2a shows the methane conversions for each catalyst system at 400 °C before, during, and after regeneration. The methane conversion was the highest, over 60%, for the MOC_{25,000} and TWC + MOC systems, whereas the MOC_{50,000} and MOC + TWC systems showed only 35–40% methane conversion. During regeneration, the methane conversion decreased for the systems in which the TWC was absent. After regeneration at 400 °C, the methane conversion increased more if the TWC was in the system. Placement of the TWC into the upstream position with respect to the MOC was beneficial, because the TWC was designed to produce reducing agents under rich conditions to promote regeneration of the downstream-positioned MOC. Hence, it can be concluded that the contribution of the TWC is needed to improve the operation of the catalyst system despite its placement in the system.

![Figure 1. Methane light-off curves in the presence of SO\textsubscript{2}: a) first light-off as fresh, b) second light-off after one aging cycle at 400 °C, and c) third light-off after two aging cycles at 400 and 450 °C. The composition of the exhaust gas was 2000 ppm CH\textsubscript{4}, 2000 ppm CO, 500 ppm NO, 10 ppm SO\textsubscript{2}, 6% CO\textsubscript{2}, 10% H\textsubscript{2}O, and 10% O\textsubscript{2} balanced with N\textsubscript{2} and with a total gas flow rate of 70 800 cm\textsuperscript{3} h\textsuperscript{-1}.](image)

| System         | MOC sulfur content [%] | TWC sulfur content [%] |
|---------------|------------------------|------------------------|
| MOC\textsubscript{25,000} | 0.61                   | –                      |
| MOC\textsubscript{50,000} | 0.67                   | –                      |
| TWC\textsubscript{50,000} | –                      | 1.39                   |
| MOC + TWC     | 0.71                   | 1.14                   |
| TWC + MOC     | 0.41                   | 1.54                   |

[a] MOC_{25,000} corresponds to the MOC_{50,000} + MOC_{50,000} system.
Methane conversions for each catalyst system during the third aging regeneration cycles at 500 °C are represented in Figure 2c. The TWC + MOC system continued with high performance, and sulfur did not decrease the activity in methane combustion, whereas MOC_{25000} showed lower initial activity but after regeneration reached almost the same conversion together with the TWC + MOC system. Potentially, a temperature of 500 °C is high enough for the MOC to produce reducing agents, which thus assist with the regeneration of the catalyst. The MOC_{50000} and MOC + TWC systems showed methane combustion activity that was clearly lower than that of either the MOC_{25000} or TWC + MOC system, and the activity also decayed faster after regeneration. The fast deactivation was linked to poor regeneration of the active catalyst, as it was lower because of the absence of an upstream reducing agent promoter such as the TWC. During regeneration, the TWC provides reducing agents such as CO and H₂ that further promote the decomposition of metal sulfates of the downstream catalyst. Although H₂S formation was expected during the regeneration, the applied FTIR spectrometer was not capable of measuring H₂S. Only SO₂ release was detected during sulfate decomposition in the regeneration.

The average methane conversions during the steady-state operation under lean-burn conditions are shown in Table 2. Comparison of the methane average conversions revealed the promotional role of the upstream TWC on MOC performance in methane combustion. In the low-temperature region, the promotional effect was negligible relative to that observed for MOC_{25000}, but comparison with MOC_{50000} revealed a remarkable improvement in the conversion.

![Figure 2. Steady-state methane conversions of the aftertreatment systems during a) the first aging cycle at 400 °C, b) the second aging cycle at 450 °C, and c) the third aging cycle at 500 °C. 10 ppm SO₂ gas was present during the entire measurement. The composition of the exhaust gas was 2000 ppm CH₄, 2000 ppm CO, 500 ppm NO, 10 ppm SO₂, 6% CO₂, 10% H₂O, and 10% O₂ balanced with N₂ and with a total gas flow rate of 70800 cm³ h⁻¹. Regeneration was performed by replacing O₂ in simulated exhaust gas with extra N₂ and keeping conditions steady for 200 s.](image)

As a conclusion, it can be stated that clean energy with lower overall emissions than regular diesel fuel can be generated with lean-burn natural-gas engines operating together with a sulfur-tolerant aftertreatment system. The experiments performed revealed that the order of the exhaust gas converter in the aftertreatment system was significant in removing methane from exhaust gas streams. The upstream three-way catalyst (TWC) played a major role in hindering sulfur poisoning of the downstream methane oxidation catalyst (MOC). The developed system enables the use of natural gas in the transportation sector, controlling stringent emission and durability requirements as well as giving more opportunities to operate engines with higher lambda values. To be precise, the enhanced low-temperature durability of the aftertreatment system enables the lambda value for engine operation to be increased.

### Table 2. Average methane conversions during steady-state operation.

| System        | 400 °C Conversion [%] | 450 °C Conversion [%] | 500 °C Conversion [%] |
|---------------|-----------------------|-----------------------|-----------------------|
| MOC_{25000}   | 61.3                  | 82.6                  | 88.2                  |
| MOC_{50000}   | 28.6                  | 52.1                  | 69.6                  |
| TW_{50000}    | 4.8                   | 9.3                   | 6.3                   |
| MOC + TWC     | 37.3                  | 67.1                  | 76.4                  |
| TWC + MOC     | 64.5                  | 95.7                  | 93.7                  |
which improves the overall efficiency of the technology. This is due to the ability of the advanced TWC+MOC aftertreatment system to enable operation and regeneration at lower temperature. There is still a need for the development of methane combustion catalysts with low-temperature activity, independent of the sulfur-poisoning issue, even though the developed catalyst system lowers the sulfur-poisoning barrier.

**Experimental Section**

The miniature-scale catalyst systems were engineered for activity screening, and they consisted of a methane oxidation catalyst (MOC), natural-gas three-way catalyst (TWC), and their combinations (Figure 3 and Table 3). To engineer the catalytic converters, catalysts were placed on a metallic substrate (500 cps) with an open foil coating method by Dinex Ecocat. A total noble-metal loading of 7.06 g L⁻¹ was used in the experiments for all catalysts. Different noble-metal combinations were used for the catalysts: MOC Pt/Pd with a noble metal ratio of 1:4 and TWC Pd and Rh with a noble metal ratio of 16:1. Catalyst systems were examined under simulated exhaust-gas conditions. The composition of the exhaust gas was 2000 ppm CH₄, 2000 ppm CO, 500 ppm NO, 10 ppm SO₂, 6% CO₂, 10% H₂O, and 10% O₂, balanced with N₂, and a total flow rate of 70800 cm³ h⁻¹ was obtained. Regeneration was performed by replacing O₂ in the simulated exhaust gas with extra N₂ and keeping the conditions steady for 200 s. The catalyst system was heated with a rate of 7°C min⁻¹. Exhaust gas was analyzed every 20 s with a Gasmet Multigas FTIR analyzer DX-4000, which was calibrated for exhaust-gas measurements. The temperature was recorded with an interval of 20 s simultaneously with the FTIR result with a K-type thermoelement placed in front of the catalyst system.

The durability of the catalyst systems was tested by using a three-step sulfur-poisoning method, as shown in Figure 4. The exhaust gas temperature of a heavy-duty vehicle in a post-turbine position was most of the time between 400 and 500°C if the engine had been operated over the lambda range of 1.2 to 1.7. Hence, aging cycles were tailored to perform realistic conditions. Applied sulfur exposure corresponds to at least 150 h of operation under real exhaust gas of a lean-burn natural-gas engine. Sulfur analyses were done with an Elementar varioMICRO cube device. Sulfanilamide was used both to calibrate the device and as a reference compound for sulfur between experiments. A sample mass of 15 mg was used in the experiments.

![Figure 3. Designation of examined miniature-scale catalyst systems.](image)

![Figure 4. Combined aging and regeneration cycles for durability experiments performed at a) 400°C, b) 450°C, and c) 500°C.](image)

**Table 3. Studied catalyst systems and experimental details.**

| System | Gas flow rate [cm³ h⁻¹] | Reactor volume [cm³] | Space velocity [h⁻¹] |
|--------|------------------------|----------------------|---------------------|
| MOC₂₅₀₀₀ | 70 800 | 2.8⁴ | 25 000 |
| MOC₅₀₀₀₀ | 70 800 | 1.4⁴ | 50 000 |
| TWC₂₅₀₀₀ | 70 800 | 1.4³ | 50 000 |
| MOC + TWC | 70 800 | 1.4ₗMOC + 1.4ₗTWC | 25 000⁵ |
| TWC + MOC | 70 800 | 1.ₗMOC + 1.ₗTWC | 25 000⁶ |

(a) Reactor length was 3.6 cm with a diameter of 1.0 cm. (b) Reactor length was 1.8 cm with a diameter of 1.0 cm. (c) Space velocity over the system. Space velocity over the TWC or MOC was 50 000 h⁻¹.
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Conflict of interest

The authors declare no conflict of interest.

Keywords: emission conversion · green chemistry · low emissions · natural gas · sulfur

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