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D4.2-3 Methane slip abatement by hydrogen addition

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Summary

The gas engines are good alternative as a peaking power, when the production of renewable energy is increasing. In the combustion of natural or biogas gas, unburned fuel, especially methane, is released in to the exhaust gas. Without a catalytic converter, the methane is going straight in to the atmosphere to worsen the greenhouse effect.

The Pd-Pt/Al_2O_3 catalytic converters are proven to be the best for methane conversion but they are easily poisoned by sulphur and water from the exhaust. Poisoned catalyst is inactive and methane conversion is low. By regeneration it might be possible to enhance the catalyst and in this work the regeneration by hydrogen (H_2) is studied. Literature review was performed at first and the engine experiments were performed according to the findings from the literature.

Helsinki, October 2016

CONTENTS

1. Introduction

While the production of renewable energy, wind and photovoltaic, is increasing, the need for energy sources for peaking power to keep the electricity network in balance is also increasing. Although the hydropower would be the primary solution, it is not available everywhere, in those cases the gas engine power plants could offer very flexible peaking power. They can be in stand-by mode and started rapidly in response to high power demand. Gas engines can also be stopped in only one minute.

During the very rapid transient loading situations and at low loads, methane emissions can grow. The unburned methane becomes a challenge, as it is a significant greenhouse gas and has proved to have a stronger impact on global atmosphere warming than carbon dioxide when their emission rates are equivalent. Oxidative catalytic converters can be used to block these methane emissions, but they are easily poisoned by sulphur. Exhaust gas contains always small amounts (~1-5 ppm) of sulphur compounds, which originate from the lubricating oil and the fuel gas itself.

Catalysts play an increasing role in achieving a cleaner environment, through the destruction of pollutants in the catalytic converters of the exhaust treatment systems of vehicles. The requirements for a successful catalytic process are: 1) the catalyzed reaction must be thermodynamically favorable and fast enough; 2) the catalyst must have an appropriate selectivity towards the desired product and 3) a lifetime long enough to be economical. (Atkins et al. 2006)

Supported palladium catalysts have shown to have good activity toward methane conversion. Although platinum based catalysts are commonly used for the elimination of non-methane hydrocarbons, they are not reported to have good activity for oxidizing methane. PdO is assumed to be the active species for methane conversion, which is then usually higher than 80 %. Pt/Pd mixtures are also used. Alumina has been reported to be the most active catalyst support for methane combustion, although it is not very durable. (Bank at al. 2015. Arosio et al. 2006. Gélin et al. 2002.)

The oxidation catalyst oxidizes HC and CO by using the oxygen present in the exhaust gas flow, and converts them to CO_2 and water vapor. The catalyst is activated at a certain temperature. Longer hydrocarbons start to oxidize at lower temperatures. Once the longer hydrocarbon chains start to oxidize, the heat release heats up the system and initiates the oxidation of methane. Catalyst performance can be up to 90 % and it is dependent on exhaust gas temperature. It increases linearly with the exhaust temperature until the temperature level is high enough. The catalyst also ages over time. (Lee et al. 1995)

In this work the regeneration of sulphur poisoned catalyst by H_2 in conjunction with a natural gas engine was studied. A bimetallic palladium-platinum catalyst with alumina support was used in the experiments. The first part of the work consisted of a literature review of methane catalysts. In the second part, the experimental setup is explained with the results, conclusions, and recommendations.

2. Catalyst regeneration with H_2 treatment

Results from various studies indicate that H_2 gas recovers the catalyst activity by removing the sulphite and sulphate groups. The H_2 treatments from the previous studies are compared in Table 1. In the table, there are two references (Hoyos et al. 1993 and Jones et al. 2003) which do not include as specific details from the H_2 treatment as the others. All the compared studies were performed in a laboratory scale, but Leprince et al. and Lampert et al. also included catalyst experiments on engines.

Table 1. Literature review of the hydrogen addition.

Reference	Catalyst materials	Temperatures	H2 volume	H2 reaction time
Ordónes et al.(2005)	0.5% Pd/Al_2O_3	350 and 550 °C	10 % H_2 in Ar	n.a.
Leprince et al.(2004)	10 g/l 3:1 $Pd/Pt/Al_2O_3$	250 to 550 °C	1. 1%, balance N_2. 2. 0.25% H_2, 0.75% CO, balance N_2, 3. 70 ppm H_2, 200 ppm CH_4, 3ppm SO_2, 500 ppm CO, 6 % H_2O, balance N_2	30 min
Arosio et al. (2006)	2% $PdO/\gamma\text{-}Al_2O_3$	400 to 700 °C	2% H_2, 2% H_2O, balance He-Ar	30-60 min
Yu et al. (1998)	3 % $Pd/CeO_2/\gamma\text{-}Al_2O_3$	600 °C	5 %	56 min temperature program and 30 min hold
Lampert et al. (1996)	Pd/Al_2O_3	600 °C	10 %	n.a.
Jones et al. (2003)	Pd/Al_2O_3	400 °C	n.a.	0.5 h

Hoyos et al. (1993)	Pd/Al_2O_3 Pd/SiO_2	350 and 600 °C	n.a.	overnight
Xi et al. (2016)	$Pd/Pt/\gamma$-Al_2O_3	500 °C	1. 10 % H_2O, 7 % CO_2, 5000 ppm O_2, balance Ar, 5000 ppm CH_4, 2. 10 % H_2O, 7 % CO_2, 5000 ppm O_2, balance Ar, 2500 ppm CO, 5000 ppm H_2	5 min

Ordonés et al. (2005: 27-34) had the highest H_2 concentration, 10 %. They compared regeneration by H_2, vacuum, nitrogen, wet air and dry air. The H_2 was the most efficient treatment by comparison of the activity of recovery. The regeneration and deactivation was easier in samples deactivated at 350 °C than at 550 °C. As the regeneration temperature increased, the regeneration efficiency was also increasing.

Leprince et al. (2004: 1-5) studied three different H_2 concentrations and gas compositions. The mixture one, which contained the highest H_2 concentration, was the most efficient in catalyst regeneration. Though as the H_2 concentration was not the only changing component of the tested gas mixtures, the effect of H_2 concentration was not confirmed. For all gas mixtures, the regeneration at 600 °C showed better methane conversion than regeneration at 500 °C.

Arosio et al. (2006: 569-576) compared H_2 treatment to CH_4 reducing pulses and they stated that the CH_4 was more effective for palladium catalyst regeneration than H_2. They suggest, that this is due to the formation of surface sulfite species associated with the stronger reducing action of H_2, which was evidenced by notable H_2S production.

Results of Yu et al. (1998: 105-114) indicated that the activity of the catalyst regenerated by H_2 was mostly recovered. They claimed that reduction with 5 % H_2 from room temperature to 600 °C can remove most of the surface sulphide and sulphate groups.

Lampert et al. (1996:15-20) compared the regeneration of engine aged catalyst by H_2 reduction at 600 °C and thermal regeneration at 750 °C. With the H_2 inclusion, the catalyst activity was restored to some level, but not completely. No detectable changes in the catalyst sulphur content were acknowledged by XPS or microprobe. Effects to improve the activity were subtle. However, they proposed that poisoning may be prevented by periodical reduction of the catalyst at a relatively high temperature.

Jones et al. (2003: 589-601) did not give so specific information on the use of H_2. One part of the experiment was to compare poisoning and regeneration of palladium, platinum and rhodium catalysts. In their studies, they had the catalysts in flowing H_2 at 400 °C for 0.5 hours, but the concentrations remain unclear. All of the catalyst materials showed some regeneration, but the rhodium was little better than palladium. Platinum showed very slight recovery. They also studied the effect for particle sizes and they discovered very large areas of agglomerated palladium particles after the regeneration.

Hoyos et al. (1993:125-138) treated the catalysts overnight in flowing H_2 at various temperatures between 350 and 600 °C. Palladium on alumina was compared to palladium on silica, the latter having a higher poisoning rate. Despite of the support material the number of active sites decreased in the same proportion. Regeneration after poisoning was performed only for silica supported palladium catalyst and the effect of H_2 and nitrogen were compared. Nitrogen was proven to be more effective in reactivating the conversion of methane after poisoning. IR spectroscopy showed a band at 1435 cm^{-1}, which is associated to sulphate species linked to palladium. After regeneration with H_2 at 600 °C this band had disappeared. However, it did not have any effect on catalytic activity. There are two hypotheses proposed what could cause the disappearing of sulphate groups and the lack of catalytic recovery. The first one is that the H_2 could induce a secondary reaction between palladium and the support at high temperatures. The second proposal is that the sulphate group could be reduced into a sulphide species linked to palladium, according to the reaction:

$$PdSO_4 + 4H_2 \rightarrow PdS + 4H_2O \qquad (1)$$

PdS is then oxidized into a sulphate group, which leads to a loss in the catalytic activity. Only a small portion of sulphide was removed by flowing H_2. Because the surface palladium sulphide coincides with the silica supports absorption range, it cannot be detected by infrared spectroscopy.

In the most recent research, Xi et al. (2016) tested the methane light-off and extinction after regeneration with two different reductive gas environments in 500 °C. The regeneration mixture which contained H_2 was simulating rich combustion exhaust, and it contained 5000 ppm CH_4, 2500 ppm CO and 5000 ppm H_2. The other regeneration gas contained 5000 ppm CH_4. In the study they noticed that the regeneration mixture containing H_2 was improving the light-off performance, but the effect was noticed only right after the regeneration. The regeneration mixture containing only methane did not have the same effect. They also noted that sulphur species started to release at about 500 °C under the regeneration mixture containing H_2, while the other regeneration mixture didn't have any effect below 600 °C. They proposed that more effective sulphur removal could be achieved by using the regeneration mixture containing H_2 and increasing the regeneration temperature.

3. Experimental setup

Engine tests were performed at VTT in Espoo from March to April 2016. Two exhaust gas temperatures, 380 °C and 500 °C, based on the possible real application exhaust gas conditions, were planned to be utilized in the catalyst studies.

The experimental study was performed utilizing a recently developed research facility to imitate the emission matrix of a large natural gas engine (Murtonen et al. 2016). The research facility included a passenger car gasoline engine that was modified to run with natural gas in lean mode. The exhaust gas temperature and flow could be independently adjusted with the research facility. The driving condition's selection was based on the emissions levels. In the selected driving mode, the engine out levels were: 220 ppm NO_x, 390 ppm CO, 6.9% O_2, and 1000 ppm CH_4.

The natural gas (from the Russian pipeline) has a high methane content (~ 97%).The sulphur content of the gas is below 1.5 ppm. The lubricating oil sulphur content was approx. 8000 ppm.

The catalyst sample used in this study was designed for oxidizing CH_4. The catalyst utilized platinum-palladium (1:4) as active metals on a tailored coating developed for lean natural gas applications and supported on a metallic substrate.

Prior to actual test, the catalyst was preconditioned for 50 h at the selected driving mode at an exhaust temperature of 400 °C. The test run itself included a 180 h at the same driving mode.

During the experiments 100 ml/min SO_2 was fed into the catalyst in 20 h periods from 16:00 to 12:00 and once over weekend (68 h). This SO_2 fed (together with the sulphur from the gas and oil) lead to an SO_2 level of 1.5 ppm in the exhaust gas. After each 20 h, at 12:00 (H_2) was fed into the catalyst for 0.5 to 1 h at concentrations of 1 – 2.5% in order to study how the catalyst regenerates.

The exhaust gas emissions were measured both up- and downstream of the catalyst sample (Figure 1.). SO_2 was measured downstream of the catalyst during the H_2 feed (regeneration). H_2 concentration was measured with MicroGC upstream of the catalyst during the H_2 feed.

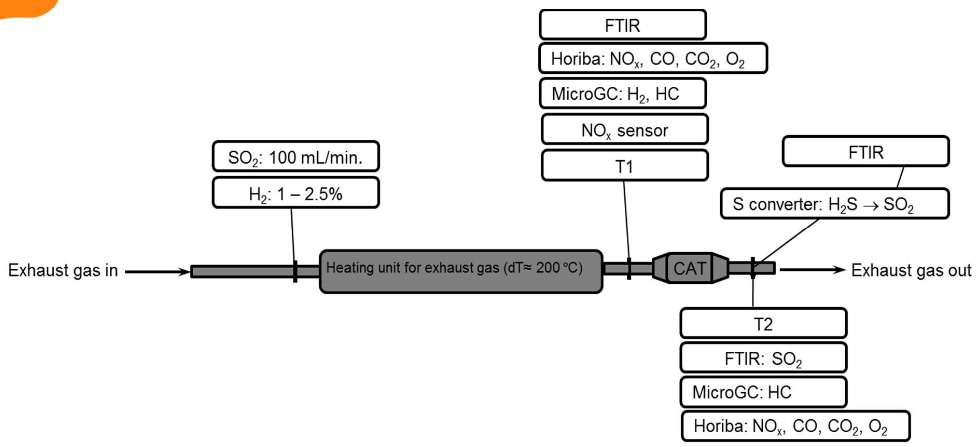

Figure 1. Catalyst set up and emission measurements of the exhaust gas.

3.1 Emission measurement equipment

NO_x, CO, CO_2, and O_2 were measured with a Horiba PG-250 analyzer. Analyzer uses non-dispersive infrared (NDIR) method for analyzing CO and CO_2 and chemiluminescence method for NO_x measurement. A paramagnetic measurement cell is used for O_2 measurement. For the Horiba analyzer the exhaust gas is dried with a gas-cooler.

Two Gasmet DX-4000 Fourier transformation infrared (FTIR) spectrometers (FTIR10 ja FTIR12) were used for measuring multiple gaseous compounds. One FTIR spectrometer was used to monitor the performance and stability of the engine and exhaust gases. Both FTIR spectrometers, as well as, their sampling lines and the filter prior to FTIR spectrometer were heated to 180 °C.

Rowaco FTIR Spectrometer was used for online measuring of SO_2. The instrument was Rowaco 2030 1 Hz FTIR spectrometer with FTIR Software MG2000 and Automated MEGA-1 (miniMEGA), sampling system.

TRS (Total Reduced Sulphur) Thermal Converter 891 was used in the measurement campaign in order to analyze the potential H_2S emissions during the H_2 feeds. The converter converts all reducible sulphur compounds to SO_2, which was then measured with FTIR after the converter.

MicroGC - The microGC used in these measurements was Agilent 490 MicroGC with the columns:

1. Molsieve, 10 m, Backflush, designed to separate H_2, CO, CH_4, N_2, O_2, and some noble gases
2. PoraPlot (PPU) 10 m, Backflush designed to separate ethane, propane, i-butane, and n-butane
3. Al_2O_3/KCl, Backflush designed to separate ethane, propane, i-butane, and n-butane

4. Results

As expected the methane conversion of the catalyst was very low at 380 °C (Figure 2.) In Figure 2 the methane conversion is presented as measured in the beginning (400 °C), after the ageing periods at 380 °C, and after each regeneration following the ageing period. Only in the beginning at 400 °C, a minor methane conversion was measured. After this, when the temperature was decreased to 380 °C and the first ageing period was done, the methane conversion was found to be near zero. Both the decreased temperature and the ageing period are believed to influence on the methane level. Immediately after the regenerations (regenerations 4, 5, 6 and 7 in the Figure 2) some improvements were seen in the conversion, but since the levels are low and rather difficult to separate from the measurement uncertainties, it is difficult to draw any final conclusions. At the end, the 400°C measurement was repeated and resulted to a lower level in methane conversion compared to what was measured in the beginning. This might reflect that the catalyst is really deactivated during the total ageing period of 180h and that the regenerations done between the 20 h periods were not sufficient to restore the efficiency. However, since the methane conversion also in the beginning was rather minor the meaning of the decrease over the ageing period is not clear.

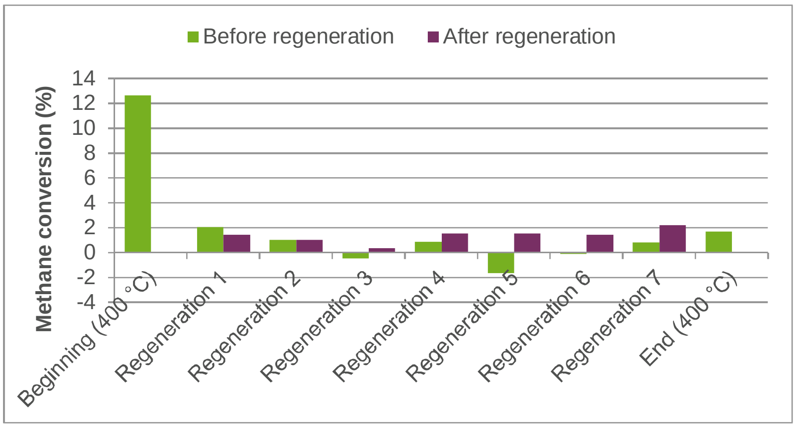

Figure 2. Average methane conversions during the experiments in 380 °C. The regenerations are done after 20h ageing periods with one exception, in which the ageing period was performed over the weekend (between regenerations 4 and 5).

Unfortunately, the experiment at higher temperature was stopped during the third ageing period. This was most possibly due to the operation of the control program of the engine test bench. Several improvements for the system were done following several catalyst tests restarts but it was not possible to conduct the total ageing period within this project. The methane conversion in the beginning of high temperature ageing (at 500°C) achieved a 50% level. After the first ageing period, this conversion was found to decrease to the level of 40% and immediately after the regeneration, the conversion of 48% was recorded. This motivates to continue the study in another project by the same partners.

During the regenerations, sulphur releases were recorded. Figure 3 shows the quick release of SO_2 from the catalyst straight after the H_2 injection. A temperature rise downstream of the catalyst can also be noticed. The analysis of these results continues and they will be published later on.

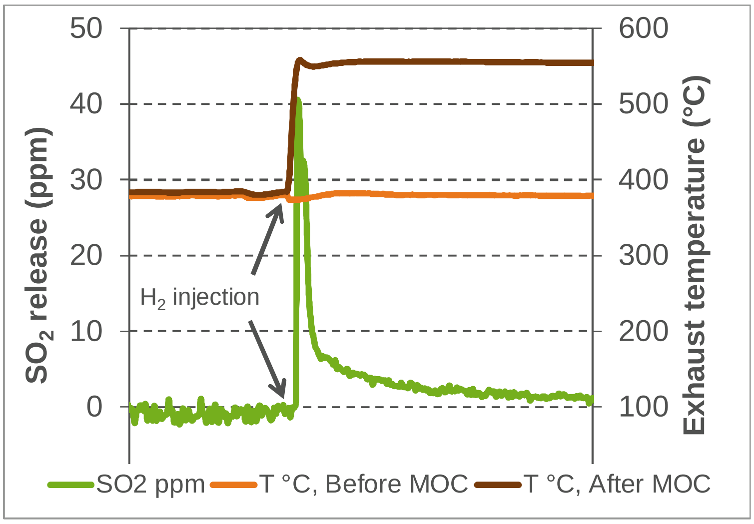

Figure 3. Effect of H_2 injection on the exhaust temperature up- and downstream of the catalyst and on the exhaust SO_2 content downstream of the catalyst.

5. Conclusions

Based on the literature review of catalyst studies involving H_2 addition for regeneration, it seems that the effect of H_2 is very dependent on the operation conditions. In the reviewed articles, the concentrations, temperatures and reaction times of the H_2 treatment varied very much, and not to mention the effect of the catalyst and support materials. The most successful results were obtained with high H_2 concentrations of 5 – 10 % and at higher temperatures 500 – 600 °C.

In the practical engine experiments performed at VTT, the used temperature (380 ºC) was too low for the methane conversion and the catalyst regeneration was too low, to be able to draw any reliable conclusions from the tests. In the upcoming tests, a higher temperature, e.g. 500 ºC, will be utilized.

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consortium consists of 17 industrial partners and 10 research organisations. The programme is coordinated by CLIC Innovation Ltd. www.clicinnovation.fi

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