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Natural Gas Engine Emission Reduction by Catalysts

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Abstract In order to meet stringent emission limits, after-treatment systems are increasingly utilized in natural gas engine applications. In this work, two catalyst systems were studied in order to clarify how the catalysts affect, e.g. hydrocarbons, NO_x and particles present in natural gas engine exhaust. A passenger car engine modified to run with natural gas was used in a research facility with possibilities to modify the exhaust gas properties. High NO_x reductions were observed when using selective catalytic reduction, although a clear decrease in the NO_x reduction was recorded at higher temperatures. The relatively fresh methane oxidation catalyst was found to reach reductions greater than 50% when the exhaust temperature and the catalyst size were sufficient. Both the studied catalyst systems were found to have a significant effect on particulate emissions. The observed particle mass reduction was found to be due to a decrease in the amount of organics passing over the catalyst. However, especially at high exhaust temperatures, high nanoparticle concentrations were observed downstream of the catalysts together with higher sulphate concentrations in particles. This study contributes to understanding emissions from future natural gas engine applications with catalysts in use.

Keywords Natural Gas · Engine emissions · Methane oxidation · NO_x reduction · Nanoparticles

1 Introduction

Natural gas (NG) engines are used worldwide in energy production, vehicle applications and increasingly also in marine applications. The increased availability of natural gas (e.g. extraction of shale gas), increasing fuel prices as well as the ever more stringent emission legislations boost the use of natural gas. Furthermore, and importantly, the use of natural gas can lead to lower CO_2 emissions compared to conventional liquid fossil fuels. This is due to the chemical properties of NGs, with their high H/C ratio, as natural gas is primarily composed of methane (CH_4; e.g. [6]).

Although NG combustion applications have clear benefits when compared to conventional liquid fossil fuels, NG engines also produce emissions that have adverse environmental and health effects. In general, the formation of NO in combustion processes occurs mainly at high temperatures. When compared, e.g. to diesel engines, in NG engines, lower levels of NO_x can be achieved (in lean burn conditions with premixed combustion) due to the relatively low temperature of combustion of NG engines. On the other hand, lean burn conditions of an NG engine can lead to relatively high CO and HC emissions if the emissions are compared with stoichiometric combustion. Several studies have shown that NG engines have higher CO and HC emissions compared with liquid fuel engines (e.g. diesel engines; see, for example, [1, 6, 11, 19]). Methane is the principal hydrocarbon species emitted by NG engines. Since methane is a potential greenhouse gas, its emissions should be minimized. Another important emission component found in NG engine emissions is formaldehyde, a toxic compound which is hazardous even in low concentrations.

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Formaldehyde can be emitted from NG engines as a product of incomplete combustion, mostly due to partial oxidation events in the engine [23, 27].

Particle emissions from NG engines are known to be low, e.g. when compared to conventional diesel engines. This is because of the lower soot particle formation in combustion. However, recent studies indicate that particle number emissions of NG engines, especially nanoparticle emissions, are not necessarily low [2, 12]. Particle emissions are known to have a negative impact on human health, and especially the smallest particles (nanoparticles) can penetrate into the lungs and blood-vascular system (e.g. [32]).

In order to diminish the environmental and health effects and to comply with tightening emission limits, exhaust aftertreatment systems will, in future, also be increasingly utilized in natural gas engine applications. The oxidation catalysts for lean burn natural gas engines have mainly been designed to oxidize CO and non-methane hydrocarbons (and formaldehyde). In order to oxidize methane, a highly efficient catalyst is needed. One significant challenge in the development of methane oxidation catalysts for lean NG applications is the catalyst deactivation since, e.g. both sulphur and water have been found to inhibit the oxidation of methane (e.g. [16, 30]). To the best of the authors' knowledge, no commercially available methane oxidation catalysts for lean conditions currently exist.

One option to further reduce NO_x from NG engines is a selective catalytic reduction (SCR) method which has been proven to be very effective in many applications (vehicles, ships and stationary applications). The SCR uses a catalyst and ammonia to reduce NO_x. Several chemical reactions can occur in the SCR system, the dominant one involving nitrogen monoxide, ammonia and oxygen reacting to produce nitrogen and water (e.g. [20]). Due to the toxicity and handling problems associated with pure ammonia, an aqueous solution of urea is widely used as an ammonia source. Typically, urea is injected into the exhaust gas well upstream of the catalyst itself in order to have enough time for the urea to decompose into ammonia before entering the catalyst.

In the present study, we investigated the efficiencies of two different catalysts with real NG engine exhaust gas in a facility with possibilities to adjust the exhaust gas temperature, flow and composition independently. For catalyst studies, we see this as a relevant intermediate step, between the catalyst laboratory tests with synthetic gases and the actual target real application test. We examined two different catalyst systems (combinations of oxidation catalyst and SCR) to determine how they affect gaseous and particle emissions from a natural gas engine in different operating conditions. The experiment for the decomposition of urea in the exhaust is included in the study. A methane oxidation catalyst, still under development, was also studied.

2 Experimental

The research facility included a passenger car gasoline engine that was modified to run with natural gas. The selection of driving conditions was based on the emission levels. The target was to mimic the emission levels of a relevant power plant engine. Acceptable carbon monoxide and nitrogen oxide levels were achieved with engine adjustments. However, in order to achieve acceptable hydrocarbon levels, HC additions into the exhaust gas were also made. The engine with the test facility was presented in detail in Murtonen et al. [24]. The engine was operated with a lean air-to-fuel mixture.

For the present study, two different engine driving modes were utilized. These are presented in Table 1 along with the engine out O_2, CO and NO_x levels. The exhaust gas flow and temperature (measured upstream of the catalysts) were adjusted independently, and therefore, it was possible to keep these constant even when changing the driving mode.

Natural gas from the Nord Stream pipeline has high methane content. In the present study, the gas analysis results were: 97.2% methane, 1.37% ethane, 0.17% propane, 0.07% other hydrocarbons, 0.9% nitrogen and 0.2% carbon dioxide. The sulphur content of the gas was below 1.5 ppm. The lubricating oil sulphur content was 1760 mg/kg, density was 852.3 kg/m^3, and viscosity at 100 °C was 12.0 mm^2/s.

Two different catalyst setups were utilized in the present study. Both utilized urea for NO_x reduction, but the oxidation targets were different. The first setup consisted of a combination of a separate oxidation catalyst and an SCR catalyst. The oxidation catalyst, placed upstream of the SCR (and upstream of the urea injection), was targeted for methane oxidation (methane oxidation catalyst, MOC). The MOC utilized platinum–palladium (1:4) as active metals on a tailored coating developed for lean NG applications and supported on a metallic substrate. The volume of MOC was 1.69 dm^3. The SCR catalyst was a stabilized TiO_2–WO_3-based vanadium catalyst supported on a metallic substrate with a volume of 5.5 dm^3. The other setup consisted of only one catalyst reactor (OXICAT-x, placed similarly to the SCR in the first catalyst setup; see Fig. 1), which targeted to the oxidation of carbon

Table 1 Driving modes

	Mode 1	Mode 2
Torque (Nm)	70	35
Speed (rpm)	2700	3100
Power (kW)	20	12
O_2 (%)	6.0	6.3
NO_x (ppm)	190	50
CO (ppm)	400	430
Hydrocarbon additions	No	Yes

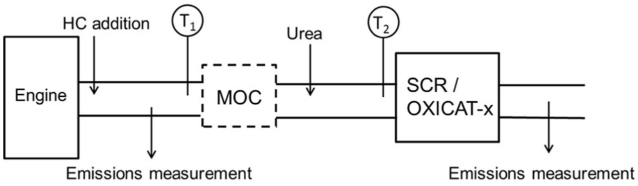


Fig. 1 Test setup

monoxide and formaldehyde and at the same time could utilize ammonia for NO_x reduction. This OXICAT-x utilized a fibre-reinforced noble metal–vanadium–tungsten–titania catalyst. The volume of OXICAT-x was 5 dm^3.

In order to study the performance of catalysts, the exhaust gas temperature and the space velocity are essential parameters. In the test facility of the present study, the exhaust gas temperature and the exhaust gas flow were adjustable [24]. Studies were conducted in an exhaust gas temperature range of 350–500 °C and with two exhaust gas flows (80 and 40 kg/h). The higher temperatures are needed for methane oxidation and would also mean that the catalyst placement in any real application would be first in line downstream of the engine, even pre-turbocharger. The utilized flows result to space velocities (1/h) of 8600 and 4300 for the MOC + SCR system and 12,400 and 6200 for the OXICAT-x system. A minimum of three test repetitions were made for each test condition in order to obtain reliable results.

Before conducting any actual tests, the catalysts were preconditioned by ageing for 48 h in mode 1 (with an exhaust gas temperature of 400 °C and exhaust flow of 80 kg/h; Table 1), without any urea feed. After the preconditioning, preliminary tests were performed for both catalyst setups in order to determine the urea feed to be utilized in subsequent tests. Aqueous 32.5% urea solution was used. The urea feed was selected to have a condition in which no (or only minor, i.e. below 5 ppm) ammonia slip was formed in the catalyst and the NO_x reduction was still clearly above 90%. The used NH_3/NO_x ratios were 1.12 and 1.17 in mode 1 and mode 2 (see Table 1), respectively. This preliminary test was made only at an exhaust temperature of 400 °C, and in further tests in different exhaust temperatures, the urea feed was kept the same. It should be noted that this most probably did not result in the SCR's best possible performance in all the selected temperature modes.

The emission measurement setup consisted of a chemiluminescence detector, used to measure the NO_x (NO and NO_2) and a non-dispersive infrared analyser to measure CO and CO_2. A Fourier transform infrared spectroscopy (FTIR) analyser was used to measure water, methane, NH_3 and HNCO concentrations. The FTIR as well as the sampling line and the filter prior to the FTIR spectrometer were heated to 180 °C. In addition, the methane, ethane, propane and ethylene components were measured from a diluted exhaust gas sample with a gas chromatograph (GC). Aldehyde samples were collected from diluted exhaust gas by using the dinitrophenyl hydrazine cartridges. In the cartridges, aldehydes form hydrazine derivatives which are then analyzed by high-performance liquid chromatography. The sample for GC and aldehyde measurement was taken from the FTIR output, utilizing a T-branch diluter and a tracer (sulphur hexafluoride, SF_6) to define the exact dilution ratio. This was observed to be 9–13. All these measurements of gaseous emissions were made upstream and downstream of the catalyst setups.

For the measurements of particle number, size distribution and composition, the exhaust was sampled using a sampling system consisting of a porous tube diluter (PTD), a residence time tunnel and an ejector diluter (Dekati Ltd.) [22, 25]. The system was the same as in the study of [2], but now the exhaust sample was taken from two different positions, as indicated in Fig. 1 (upstream and downstream of the catalyst). Residence time in the primary dilution system, i.e. in the PTD and the residence time tunnel, was 2.6 s, and the dilution ratio in the PTD was as low as 6 (to ensure concentration levels high enough for the EEPS and the Nano-SMPS). The secondary dilution ratio over the ejector diluter was 4, resulting in a total dilution ratio of 24 after two dilution stages. Both the primary and secondary dilution ratios were calculated from CO_2 measurements conducted for undiluted exhaust and diluted exhaust samples. After the secondary dilution, the particle size distribution of the exhaust sample was measured using the Engine Exhaust Particle Sizer (EEPS, TSI Inc.), the scanning mobility particle sizer (Nano-SMPS, consisting of DMA 3085 and CPC 3025, TSI Inc.) and the electrical low pressure impactor ELPI+ (Dekati Inc.), and the chemical composition of the particles was measured using a soot particle aerosol mass spectrometer (SP-AMS, Aerodyne Research Inc., USA). SP-AMS is a combination of two instruments: an Aerodyne high-resolution time-of-flight aerosol mass spectrometer and a single-particle soot photometer (SP2; Droplet Measurement Technologies, CO, USA), and it is capable of measuring refractory and non-refractory particulate materials [29]. In this study, the SP-AMS was operated in V-mode with a time resolution of 1 min. Both the laser and tungsten vaporizer were used and the concentrations of chemical species were calculated by using a default collection efficiency of 0.5. Particle number concentration measurements were conducted by the CPC 3776 (TSI Inc.) and the Particle Size Magnifier (PSM, Airmodus Ltd.) combined with the CPC 2775 (TSI Inc.). The exhaust sample was further diluted by a factor of 36. PSM was also used for sub-5-nm particle size distribution measurements in scanning mode (saturation flow scanning between 0.1 and 1 lpm). Volatility measurements for particle emission were made using a thermodenuder that was designed for nanoparticle measurements [10]. In the thermodenuder, aerosol sample is heated up to 265 °C in order to evaporate the volatile fraction of the particles and then led through an active charcoal section where the evaporated particulate matter is absorbed and cooled. When total particle number emission was measured, the thermodenuder was bypassed.

The effect of the catalysts on particulate matter (PM) was studied by sampling PM both before and after the catalyst with a sampling according to international standard ISO 8178-1:2006. According to this standard, the PM is measured as any material collected on a filter after diluting exhaust gas with clean, filtered air to a temperature higher than 42 °C and less than or equal to 52 °C, as measured at a point immediately upstream of the filter. A dilution ratio of 10 and a sampling time of 30 min were used. Samples were collected on TX40HI20-WW filters (Ø = 47 mm).

3 Results and Discussion

In order to determine how the injected urea is decomposed to ammonia, measurements were made upstream of the SCR, but downstream of the urea injection. These measurements were made using the FTIR. Urea decomposition occurs in phases (e.g. [14, 37]). First, the water from the urea solution droplets is evaporated. Then, the urea is thermally decomposed into ammonia (NH_3) and isocyanic acid (HNCO). Hence, 1 mol of urea produces 1 mol of ammonia and 1 mol of isocyanic acid. The isocyanic acid is quite stable in the gas phase, but readily hydrolyzes on the surface of a metal oxide catalyst, producing ammonia and carbon dioxide. The measurements showed that at a temperature of 350 °C, approximately 50% of the urea was decomposed to ammonia and isocyanic acid, whereas at higher temperatures, the decomposition rate was clearly higher: at 400–450 °C, almost 80% of the urea was decomposed (Fig. 2). This is clearly better than the results reported earlier for the decomposition of urea for automotive SCR systems by Koebel and Strutz [14], who found that only about 50% of urea decomposed at 400 °C when the residence time from urea injection to catalyst entrance was 0.09 s. In the present study, the residence time was longer: at 400 °C, the residence time was 0.13 s. The time available from the injection to the catalyst entrance is one of the key issues when discussing urea decomposition [14] and also one possible reason for the differences in urea decomposition between the present study and the study by Koebel and Strutz [14]. Other possible reasons could be a smaller droplet size or a better mixing of urea with the exhaust gas. One should also note that the accurate measurement of HNCO with FTIR can be challenging (e.g. due to interferences with other compounds existing in the exhaust gas). According to our experience, with the FTIR spectrometers we have utilized, especially the low HNCO levels (roughly below 30 ppm) cannot be measured accurately. In the present study, in the case of Fig. 2, the measured HNCO levels were between 64 and 100 ppm.

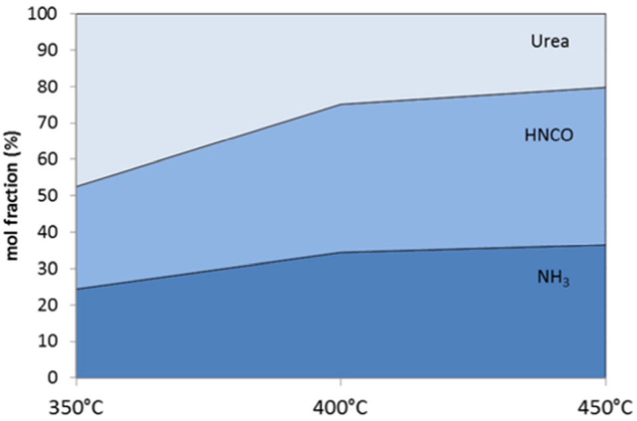


Fig. 2 Urea, isocyanic acid and ammonia measured upstream of the catalyst (downstream of the urea injection), i.e. at the catalyst entrance. The three measurement points (350, 400 and 450 °C) and the lines are to guide the eyes only

Good urea decomposition is a basis for efficient SCR operation and for avoiding misuse of the catalyst itself for water evaporation and urea decomposition.

Furthermore, the urea decomposition as well as the droplet size and mixing of urea with exhaust gas should be similar to those occurring in a real application case in order to make the present studies in an engine laboratory comparable with real application cases. For example, in the present study, the distance from the urea injection to the catalyst entrance and the nozzle utilized for urea injection were selected on the basis of the authors' knowledge of real application setups.

In the two different driving modes, the engine out NO_x levels were 190 and 50 ppm in mode 1 and mode 2, respectively. NO_2/NO_x was found to be 0.25 and 0.4 in modes 1 and 2, respectively. Exhaust from most combustion sources contains NO_x composed primarily of NO. However, leaner burn conditions tend to change the NO_2/NO_x ratio so that a higher fraction of NO_2 is emitted (e.g. [28]). In good correlation with the present results, significant fractions of NO_2 have earlier been reported for natural gas engines (e.g. [28, 33]).

The NO_x reduction, calculated from the NO_x measurements upstream and downstream of the catalyst, is presented as a function of temperature (measured upstream of the SCR or 'OXICAT-x', i.e. T_2 in the setup figure) in Fig. 3 at constant urea feed. The conventional SCR (placed downstream of the MOC) appears to operate similarly in both driving modes and the NO_x efficiency (in per cent) to depend rather little on the temperature between 350 and 450 °C.

The NO_x efficiency of OXICAT-x, however, was found to depend greatly on the temperature since a clearly lower efficiency was measured at the highest test temperature of 450 °C, especially in the case of mode 2. The lower NO_x reduction by 'OXICAT-x' was probably due to the competing reactions that actually oxidize the injected ammonia to NO rather than to the reaction between ammonia and NO resulting in N_2. It should

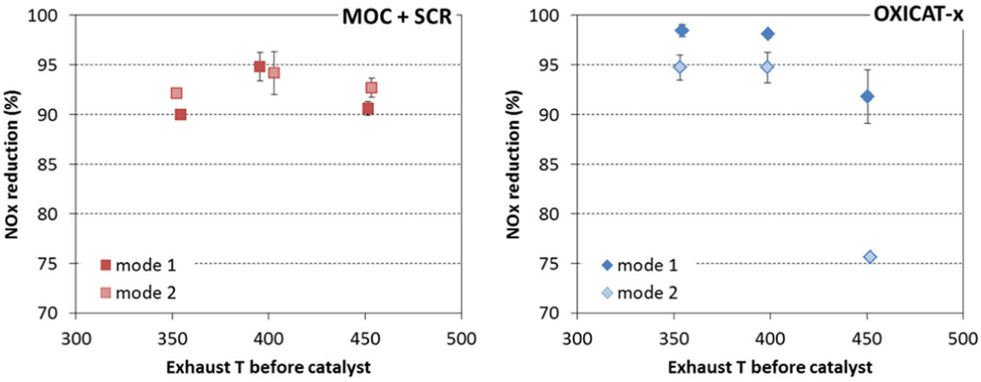


Fig. 3 NO_x reduction as a function of exhaust temperature. *Error bars* show the standard deviation of a minimum of three test repetitions

also be noted that the urea injection was not optimized for the different temperatures but was constant.

Since the two catalyst systems are different, e.g. in compositions, volumes and catalyst loadings, differences in NO_x reductions could also be anticipated. At an exhaust temperature of 400 °C, catalyst systems appeared to operate rather similarly (with the same urea feeds), reaching NO_x reductions close to 95% (OXICAT-x performs even better in mode 1), and as anticipated, differences were observed at the other test temperatures. In standard SCR catalyst, the optimal operation window depends greatly, e.g. on the catalyst (vanadium) loading (e.g. [8, 17, 18]). High vanadium loading increases NO_x reduction at low temperatures, but the higher the vanadium loading is, the more the SCR also oxidizes NH_3 at high temperatures. For example, in a recent study of differently loaded vanadium SCR performance (in heavy fuel oil application), a rather similar NO_x efficiency was observed with all the tested catalyst loadings at 350–450 °C, but at lower temperatures, the highest loaded catalyst gave significantly better NO_x removal efficiency than the lower loaded catalysts [17].

The oxidation catalysts most probably also have an effect on the NO_2/NO ratio. Both increase and decrease of NO_2 over an oxidation catalyst have earlier been reported [28]. In each test of the present study, the SCR method was utilized simultaneously with the oxidation catalyst, resulting in very low NO_x levels downstream of the catalysts. Practically no NO_2 was measured downstream of either of the catalyst systems.

The CO levels downstream of both catalyst setups in all test conditions were low. The highest value, 15 ppm, still implying a CO reduction of 96.5% over the catalyst, was recorded downstream of ‘OXICAT-x’ in mode 2 with the lowest test temperature (350 °C). At temperatures of 400 °C and higher, the CO reduction over both catalyst systems was 98–99%.

The measured methane concentrations (in mode 1) are shown in Fig. 4 as a function of the exhaust temperature measured upstream of the oxidation catalyst (T_1 for MOC and T_2 for OXICAT-x—see setup figure). For both catalyst setups, three different exhaust temperature modes were studied, as well as a lower exhaust flow mode in one selected temperature case. The OXICAT-x was not designed for methane oxidation and therefore was not expected to have any effect on the methane levels. This was found to be true on the basis of the measurement since the OXICAT-x had practically no effect on methane in either of the studied exhaust temperatures or flows. The MOC + SCR, with the methane oxidation catalyst, had a minor decreasing effect on the methane at ~400 °C, but at ~500 °C, approximately 50% methane decrease was observed. Furthermore, the lower exhaust flow studied at 450 °C increased the methane conversion from 38% (measured with 80 kg/h exhaust flow) to 65% (with 40 kg/h).

In order to have a fair idea of how the present results fit in with earlier published laboratory-based studies, we make here some comparisons. It should however be kept in mind that, e.g. the noble metal loading and catalyst sizing can have a significant effect on catalyst performance, making the comparison of different studies difficult. Ottinger et al. [30] reported light-off curves for CH_4 over Pd-based oxidation catalyst with an initial T_{50} (the temperature for 50% conversion) value of 480 °C, and some lower light-off temperatures were reported by, e.g. Corro et al. [7], Venezia et al. [36] and Gelin et al. [9]. By comparison, the methane conversion result of 50%

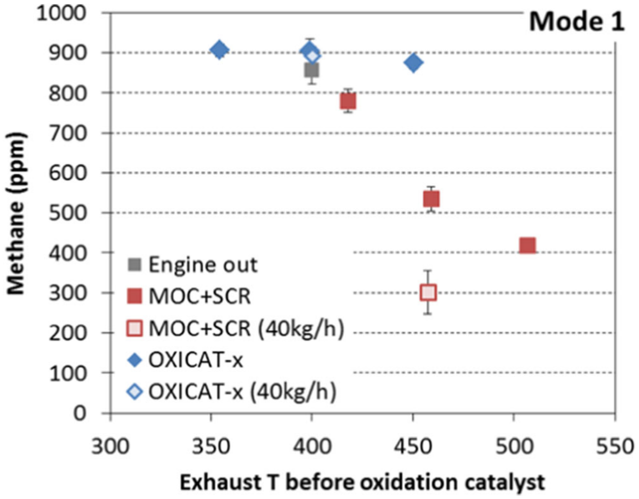


Fig. 4 Methane concentration as a function of exhaust temperature in mode 1

(present study, steady-state condition) required a higher temperature (i.e. 500 °C) than in the case of the T_{50} values reported earlier. However, the earlier studies have been carried out with simplified gas mixtures in laboratories and not with real exhaust gas as in the present study, which most probably had an effect on the results together with the differences in catalyst materials and amounts. Furthermore, the preconditioning procedure utilized in the present study (48 h) might have had a significant effect on the oxidation activity (the fresh catalyst was not measured in the present study).

The effect of sulphur on the methane oxidation catalyst performance can be crucial since as little as 1 ppm SO_2 present in the exhaust has already been found to inhibit the oxidation of methane (e.g. [16, 30]). In this study we did not observe any significant change in the catalyst performance during the tests. The possible SO_2 originates from the sulphur in natural gas and the lubricating oil. Assuming that all this sulphur (from gas and oil) ends up as SO_2, the SO_2 present in the exhaust gas would still be below 0.2 ppm in the driving modes of the present study. Furthermore, the test times in the present study were rather short, only tens of hours (after the 48-h preconditioning), which might be too short to observe any significant catalyst deactivation by the sulphur amount in the present study.

In addition to methane, other hydrocarbon species, i.e. ethane, propane and ethylene, were also studied. The ethane and propane concentrations as a function of exhaust temperature in mode 2 are presented in Fig. 5. The OXICAT-x started to oxidize these hydrocarbon species at the exhaust T of 450 °C, whereas at lower temperatures, practically no effect was found. At the same temperature (450 °C), the MOC, as expected, oxidized ethane and propane more effectively than OXICAT-x, and the oxidation also increased with the temperature increase (500 °C). At 450 °C, the ethane conversions were 37% with OXICAT-x and 65% with MOC, and the propane conversions were 75% with OXICAT-x and 88% with MOC. Thus, the alkane reactivity proceeds in the order $C_3H_8 > C_2H_6 > CH_4$, which is as was expected and similar to the observations of, e.g. Lambert et al. [16] and Ottinger et al. [30]. Ethylene was the easiest to oxidize, and practically no ethylene was measured downstream of either of the catalyst setups.

The engine out formaldehyde concentration was ~50 ppm in both driving modes. Downstream of MOC + SCR, the measured formaldehyde levels were below 1 ppm in all test conditions. Downstream of OXICAT-x, the highest formaldehyde level was measured in mode 2 with an exhaust T of 350 °C, resulting in ~3 ppm, whereas at higher temperatures, the measured formaldehyde level was below 2 ppm. This 1–2 ppm was also rather close to the measurement accuracy of the aldehyde measurement in the present study. Since formaldehyde is hazardous even in small concentrations, these 1–2 ppm levels (or even below) will possibly need a relevant measurement method in the near future.

3.1 Particles

One standard (ISO 8178) method was utilized to study the particle mass emission. Since the PM method measures the total mass, larger particles can contribute to the result much more than smaller ones (nanoparticles).

Engine out PM results had a rather high variation of 17% (standard deviation of four to five samples; Fig. 6). The effect of the catalysts was however obvious, and both catalyst systems clearly decreased the total PM in all test conditions. The PM reduction was of the order of 45–73%. Since catalysts commonly have a decreasing effect only on the volatile (organic) fraction of the PM mass, this alone indicates that a large part of the engine out PM is some volatile material present in the gaseous phase at the catalyst temperatures.

However, the PM results measured downstream of the catalysts appeared to correlate with the exhaust temperature as higher PM levels were measured at higher exhaust temperatures (with 'the mode 1 and 500 °C' case forming an exception to this pattern; see Fig. 6). Sulphate formation contributing to PM increase is seen over many catalysts (ammonium sulphates in the case of SCR) and could be one explanation for the PM increase with temperature increase, although in the present study the total amount of sulphur available from the fuel and oil was very low.

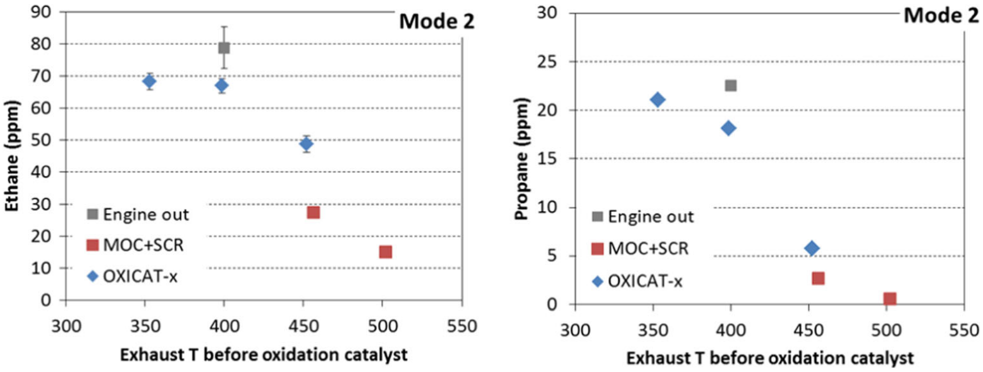


Fig. 5 Ethane and propane concentrations as a function of exhaust temperature (measured upstream of the oxidation catalysts) in mode 2

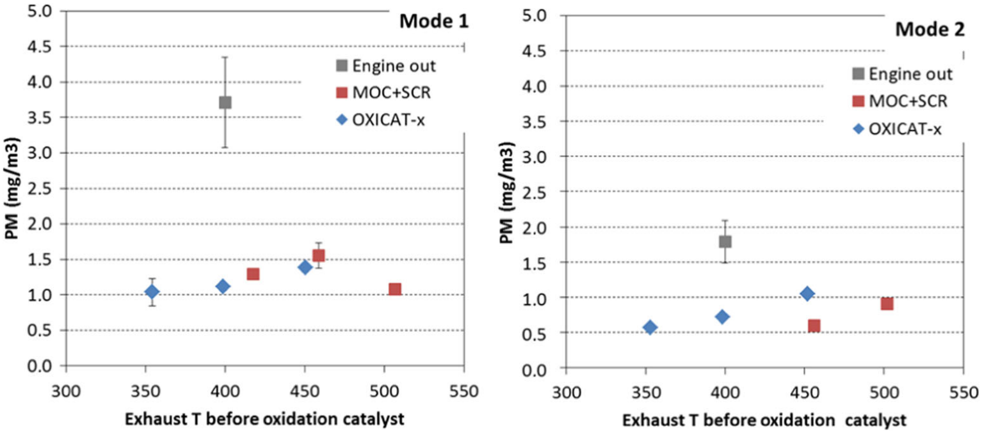


Fig. 6 PM emissions measured from engine out and downstream of the two catalyst systems in both driving modes and at all test temperatures

According to Alanen et al. [2], the particle number emissions of a natural gas engine are dominated by nanoparticles when the engine is not equipped with a catalyst or other exhaust after-treatment system. These nanoparticles, being even smaller than 5 nm in diameter, were reported to be initially formed already in high temperature conditions. In this study, the research engine was the same as in the study of Alanen et al. [2]. Only some very minor modifications were made to the engine. Engine out returned qualitatively similar results for particle number to those obtained previously (see Fig. 7); particle number size distribution was dominated by nanoparticles smaller than 10 nm, and especially the smallest particles were observed to be non-volatile. The thermodenuder treatment was observed to decrease the concentration of larger particles (diameter > 5 nm), shifting the mean particle size to a smaller level, which indicates that the particles also contained some semi-volatile compounds.

When the exhaust was sampled for particle measurements downstream from the catalyst, the exhaust temperature was observed to significantly affect the particle number (see Fig. 8) and number size distribution (Fig. 7). First, at the lowest temperature, the measured particle numbers were lower than those in the sample from upstream of the catalyst. The catalyst was observed to affect all particle sizes. However, the particle number was also dominated by nanoparticles downstream from the catalyst. When the exhaust temperature was increased, both the mean particle size and the particle number concentration (measured downstream from the catalyst) increased. At the highest temperature point (500 °C), the particle size distribution was dominated by particles larger than 10 nm

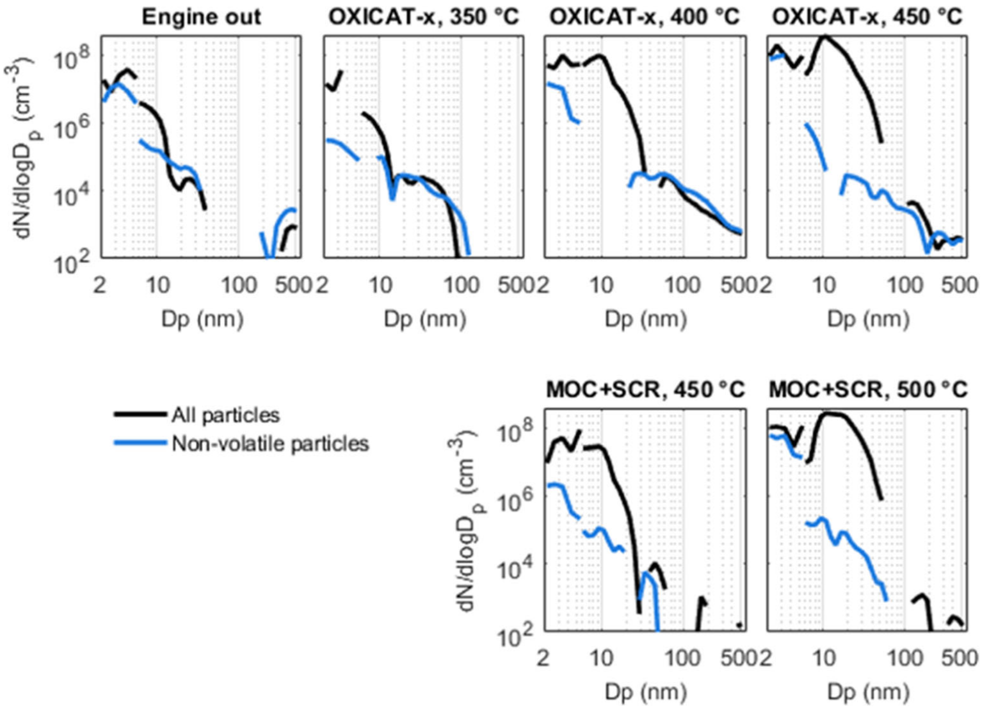


Fig. 7 Particle number size distributions upstream from the catalyst (engine out) and after the catalyst at different exhaust temperatures. Both the distributions measured without the thermodenuder (all particles) and with the thermodenuder (non-volatile particles) are shown. Size distributions were measured by the combination of PSM and CPC and by the EEPS in mode 2. Note: The discontinuity in the charts results from the low particle number concentrations and the subtracting of background levels, which can produce negative concentrations seen as a discontinuity in the logarithmic scale

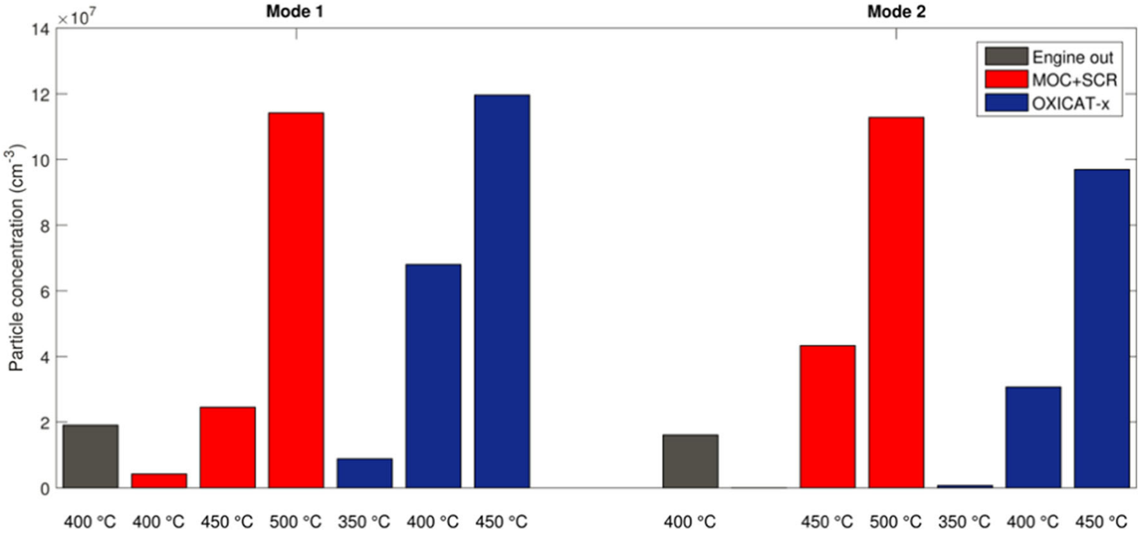


Fig. 8 Total particle number concentration of natural gas engine exhaust when the exhaust was sampled upstream from the catalyst (engine out) and after the catalyst. Particle concentrations were measured by the combination of PSM and CPC

and the total particle number (measured by PSM, particles larger than ~1 nm) was up to 20 times higher than the concentration at the lowest temperature point and more than five times higher than the particle number in the sample taken upstream from the catalyst.

The increase in particle number as a function of exhaust temperature was caused by volatile particles; the thermodenuder treatment for the exhaust sample totally removed the particle mode at 10 nm (Fig. 7). Based on previous studies, conducted mostly for diesel engines, the volatile exhaust particles have

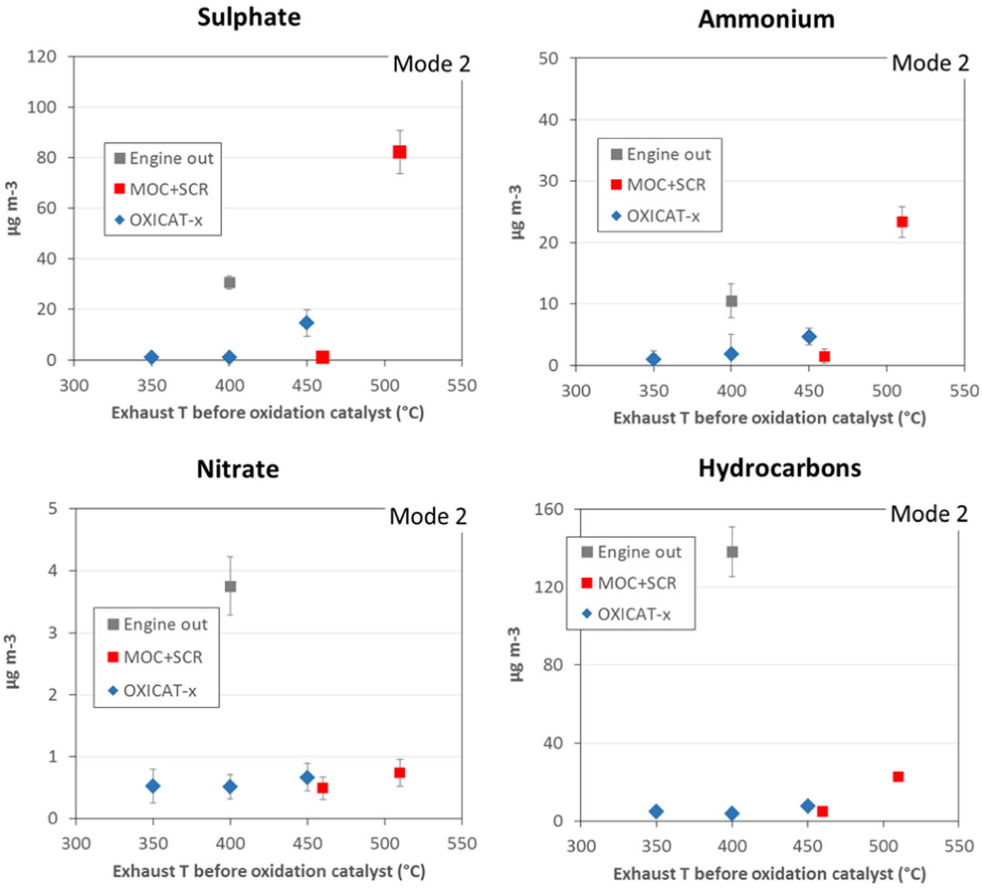


Fig. 9 Sulphate, ammonium, nitrate and hydrocarbon concentrations as a function of exhaust temperature (measured upstream of the oxidation catalysts) for mode 2

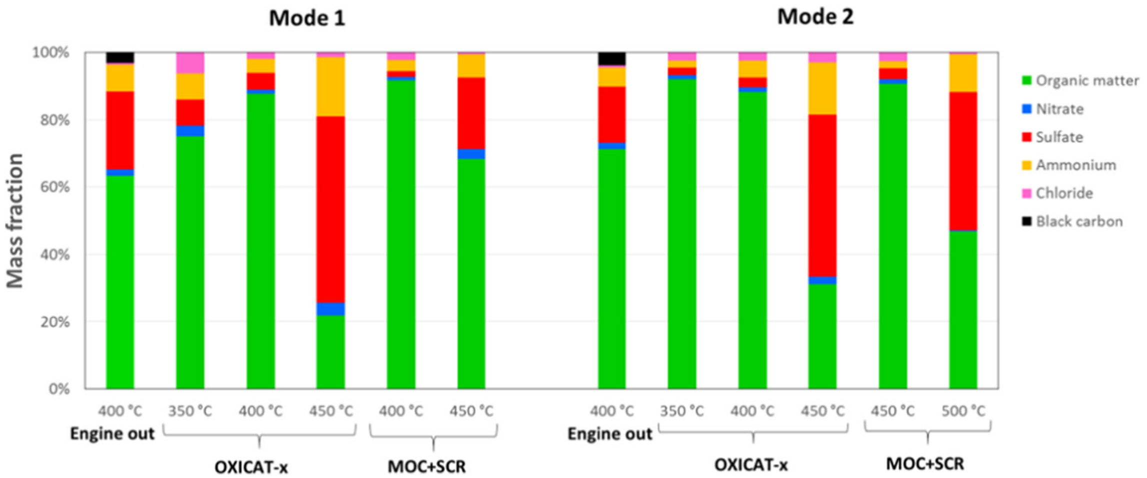


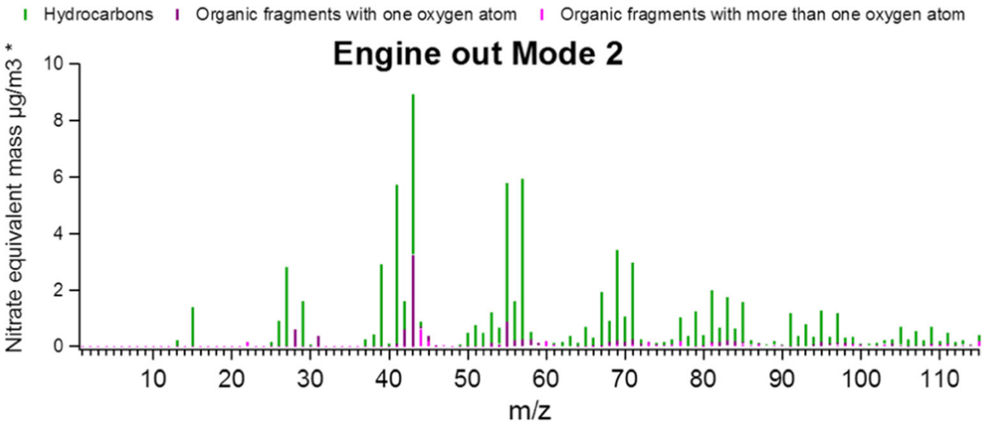
Fig. 10 Chemical compositions of particles at various measurement points

been observed to be formed during cooling and dilution of exhaust [15, 34], especially when the engine is equipped with an oxidative exhaust after-treatment device [13, 15, 21, 35]. One possible precursor for nanoparticle formation is sulphuric acid, which is present in the gaseous phase at typical exhaust temperatures and tends to nucleate in exhaust sampling systems (see, e.g. [26, 31]), forming new particles. However, organic acids have also been proposed to participate in this process [3]. The observations of this study are qualitatively similar to those of studies in which the role of sulphuric acid in particle formation has been measured; nanoparticles are volatile, they exist in the sample taken after the catalyst, and an increase of exhaust temperature increases particle concentration and size. The particle composition measurements (see the text below) support the notion that sulphur compounds may explain these observations.

Based on the SP-AMS results, the concentration of sulphate increased with higher catalyst temperature (Fig. 9). Sulphate was clearly higher at 450 °C for OXICAT-x and MOC + SCR in mode 1 and at 500 °C for MOC + SCR in mode 2. At an exhaust temperature ≤450 °C, the sulphate concentration measured downstream from the catalyst was lower than that measured upstream of the catalyst, but at 500 °C (MOC + SCR), it was more than double that measured upstream of the catalyst. Ammonium had similar temperature dependence to that of sulphate. Sulphate appeared to be mostly neutralized with ammonia as their ratio was close to that calculated for ammonium sulphate. Only at the highest catalyst temperatures (and sulphate concentrations) was there excess sulphate, suggesting that a part of the sulphate was in the form of sulphuric acid in particles. The amount of sulphuric acid ranged from 12 to 27% of the measured sulphate, corresponding to sulphuric acid concentrations of 2–22 μg m^{-3}. However, it should be noted here that the SP-AMS can detect particles only above ~50 nm in size, meaning that only the tail of the particle mode shown in the particle number size distributions of Fig. 7 was measured by the SP-AMS. In addition to sulphate and ammonium, nitrate concentration also increased with the catalyst temperature increase, although the catalysts decreased the concentration of nitrate by as much as 87% on average.

In addition to sulphate, ammonium and nitrate, particles contained organic matter, chloride and black carbon (Fig. 10). Excluding the measurement points with high sulphate concentrations, most of the particle mass consisted of organic matter. The concentration of organic matter had no clear dependence on the catalyst temperature, but the catalysts

Fig. 11 Mass spectra for particulate organic matter measured without the catalysts in mode 2



reduced organic matter by, on average, 86% (OXICAT-x) and 55% (MOC-SCR). This is in good correlation with the PM results, showing that the total mass was clearly reduced by the catalysts. Chloride also showed no trend with the catalyst temperature, and the concentration of chloride was only slightly lower with the catalysts. Black carbon was observed to exist in the exhaust only in engine out measurements.

Organic matter in the gas engine emission particles was mostly composed of hydrocarbon fragments (Fig. 11). The largest hydrocarbon fragments according to the mass spectra (MS) of organic matter were $C_3H_5^+$ (at *m*/*z* 41), $C_3H_7^+$ (at *m*/*z* 43), $C_4H_7^+$ (at *m*/*z* 55) and $C_4H_9^+$ (at *m*/*z* 57), typical for, e.g. vehicle emissions (e.g. [4, 5]). Similar to sulphate, ammonium and nitrate, the sum of hydrocarbon fragments increased with the catalyst temperature (Fig. 8), but the catalyst decreased the concentration of hydrocarbons much more than those of inorganics. As well as the hydrocarbon fragments, there were some oxidized organic fragments, e.g. $C_2H_3O^+$ (at *m*/*z* 43) in the MS. In general, no change in the oxidation state of organics was observed as a result of the catalysts.

4 Conclusions

The growing trend in the use of natural gas (and also biogas) as energy sources enhances the sustainable use of natural resources and can lead to lower CO_2 levels. However, gas combustion is not emission-free. Emissions such as hydrocarbons, especially methane, and formaldehyde, NO_x and particles, all known to have effects on the environment and on human health, are found from natural gas exhausts. In order to deal with the more stringent emission legislation, after-treatment systems, such as catalysts, are increasingly utilized in natural gas applications. In the present study, we made a comprehensive emission study from a natural gas engine exhaust both upstream and downstream of two different catalyst systems in order to determine the effects of the catalysts on different emission components.

The SCR was found to be effective in reducing NO_x. In the present study, the SCR was utilized in two different ways: as a separate catalyst reactor downstream of an oxidation catalyst and integrated into an oxidation catalyst. For the integrated system, the oxidation reactions and NO_x reduction reactions were suggested to be competing with each other, resulting in lower NO_x efficiencies at high temperatures. This might imply limitations for utilization; however, this greatly depends on the required NO_x reduction as well as on the possibilities to further optimize the behaviour in different temperature windows. In real applications with, e.g. limited spaces and the need to control the expenses of the catalyst systems, this kind of system can be more attractive compared to two separate catalysts.

The results indicated that the oxidation catalyst developed for methane reduction can reach methane reduction levels better than 50% in real natural gas engine exhaust gas applications if the temperature is high and the catalyst sizing is correct. However, further studies are needed to solve the long-term performance and the possible deactivation by sulphur.

The particle emission studies indicated that nanoparticles dominate the particle number size distribution. Catalysts were found to have a significant influence on particle emissions. Downstream of the catalyst, the particle formation was found to depend greatly on the exhaust temperature. At higher temperatures, higher numbers of volatile nanoparticles were found, indicating that sulphur compounds are involved in the particle formation. The composition studies support this interpretation as more sulphate was observed at higher catalyst temperatures. Both the studied catalyst systems had a clearly decreasing effect on total particle mass emissions, which, together with the composition study results, indicates a decrease in the organics (hydrocarbons). This might be one more relevant issue in the future, with the growing environmental and human health concerns of particle emissions. Future research needs to include solving the origin of the particles (e.g. lubrication oil versus the natural gas) and the possibilities to control these particle emissions.

In addition to the present results, studies in real natural gas combustion applications, both vehicle and power plant applications, are needed in order to confirm the emission levels and the catalyst operation in real-world conditions. In addition to pure natural gas combustion applications, the results of the present study may also be important when planning biogas utilization, which is expected to grow significantly in the near future, and when considering the emissions from biogas engines. Further studies are needed in order to be able to develop suitable systems for biogas emissions since, e.g. biogas impurities may play a major role in the catalyst performance.

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