SCR for marine applications

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Abstract

This paper presents results regarding the influence of SO_2 on the activity of a marine SCR catalyst for NO_X reduction. It is demonstrated that increasing SO_2 concentrations in the exhaust can enhance the SCR activity under certain conditions. However, in the presence of water and at temperatures below ca. 230°C, the presence of SO_2 is negative for the SCR reaction.

Introduction

Shipping is a major source of emissions of nitrogen oxides (NO_X). In Europe emissions of NO_X from shipping is expected to become larger than all land-based sources together by 2020. These emissions cause significant problems with acidification and eutrophication and contribute to the exceedance of the environmental quality levels in many port cities. NO_X from shipping also contribute significantly to concentration levels of particulate matter.

The NO_X emissions from ships, i.e. marine diesel engines, must follow the IMO regulation which will be tightened in special NO_X emission control areas (NECA) by 2016. The allowed emission levels for new ships (Tier III) are then between 3.4 and 2.0 g/kWh depending on engine speed (rpm). For new engines today, and outside the NECAs in the future, allowed emissions of NO_X are between 14.4 and 7.7 g/kWh. To accomplish the Tier III standards, ships will need to install and operate some kind of NO_X abatement technology.

There are different ways to reduce the emissions of NO_X from marine engines. Engine measures include use of exhaust gas recirculation. The introduction of water in the engine through, e.g. direct injection or the use of fuel-water emulsion will reduce the NO_X formation. At present, the most effective method to reduce the NO_X emissions from ships, and a method that can accomplish the Tier III standards, is to use selective catalytic reduction, SCR. In SCR the nitrogen oxides are reduced over a catalyst, normally containing vanadia and titania, through reactions with a reducing agent, urea or ammonia, which is introduced into the exhaust gases.

SCR has successfully been used on a number of ships for a few decades. However, there are some issues that should be looked into. These relates to the low temperature activity and to deactivation of the catalyst. The problems with low temperature activity means the SCR system often is inactive at low engine loads. This is a situation often occurring during manoeuvring and at berth, i.e. where the ship is close to or in port. Problems with deactivation can be either reversible or permanent and the latter often leads to high costs as catalysts may need to be replaced. Deactivation can occur as a result of erroneous operation (too high temperatures), or poisoning by impurities in the fuel or in the urea. These issues are at least in part associated with the low quality of the fuel normally used at sea: residual fuel oil with a sulphur content of 1-3 wt%.

In this paper the influence of sulphur on the SCR activity of a commercial SCR catalyst is discussed. Data from laboratory experiments with a commercial marine SCR catalyst are presented.

Methods

The SCR catalyst samples in the present study were cut from a commercial vanadia-based washcoated urea-SCR catalyst for marine applications.

The flow reactor used consisted of a horizontal quartz tube heated by a heating coil. The inlet and sample temperatures were measured by thermocouples (type K), approximately 15 mm

before the sample and inside the monolith sample (just before the rear end), respectively. The inlet gas composition was controlled by mass flow controllers (Bronkhorst High-Tech) and the outlet gas composition was analyzed by an MKS MultiGas 2030 HS FTIR instrument. For the experiments with both water and SO_2 in the feed gas, a Horiba PG-250 instrument was used to analyze the outlet gas composition. The PG-250 uses non-dispersive IR detection for CO, SO_2, and CO_2; chemiluminescence (cross-flow modulation) for NO_x; and a galvanic cell for O_2 measurements.

Prior to all flow reactor experiments the samples were pre-oxidized in 8 % O_2 (Ar bal.) at 550°C (or 350°C when the Horiba instrument was used) for 1 hour. The inlet gas composition consisted of 500 ppm NO, 500 ppm NH_3, 8% O_2, with varying concentrations of SO_2 (0-1000 ppm) and H_2O (0-6%), balanced with Ar.

Results and discussion

At high temperatures, around 350°C, an enhancement of the SCR activity can be observed. This is shown in Figure 1 where the SCR activity is presented as a function of the SO_2 content in the gas for a synthetic gas mixture of NO, NH_3, O_2 and SO_2. Also shown is an increase in the formation of N_2O with increased SO_2 content. Thus, the high sulphur content in marine fuels does not seem to have a negative impact, in the absence of water, on the SCR activity at temperatures that are in the range of what can be expected at engine loads for typical operation of a marine engine, i. e, at design speed. On the contrary, the presence of SO_2 results in an increase of the activity. The reason for this increase in activity is not clear but has been attributed to the formation of acidic sites due to sulphate formation over the catalyst surface (Zhu, 2001) for other types of SCR catalysts. These acid sites may enhance the adsorption of ammonia and thereby the SCR reaction rate. Activity for SO_3 formation over marine SCR catalysts has been reported earlier (Magnusson, 2012).

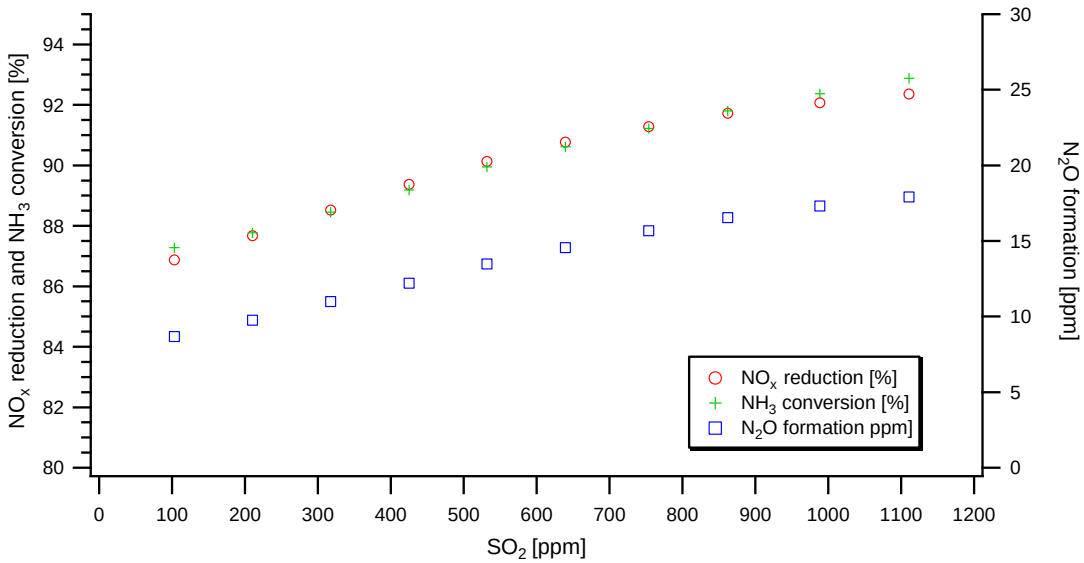

Figure 1. NO_X reduction performance as a function of the SO_2 concentration over a marine SCR catalyst. Feed gas composition: 500 ppm NO, 500 ppm NH_3, 8 % O_2 and 100-1100 ppm SO_2 (350°C and 12200 h^{-1})

At lower temperatures, below about 250°C, the effect of SO_2 in combination with water has a detrimental effect on the SCR activity. In this temperature range there is a slow decrease in the activity as the catalyst is exposed to a flue gas containing SO_2 and water. This is illustrated in Figure 2 which shows the NO_X reduction activity as a function of time for two exhaust gas temperatures (300 and 250 °C) and two SO_2 concentrations (750 and 250 ppm). At the higher temperature the SCR activity is stable for both sulphur levels. However at the lower temperature the activity decreases with time for the higher of the two SO_2 concentrations. This decrease indicates poisoning of the catalyst in an exhaust gas with high concentration of SO_2. The

formation of ammonium sulfates may be a likely candidate for poisoning the reactive sites (Magnusson, 2012).

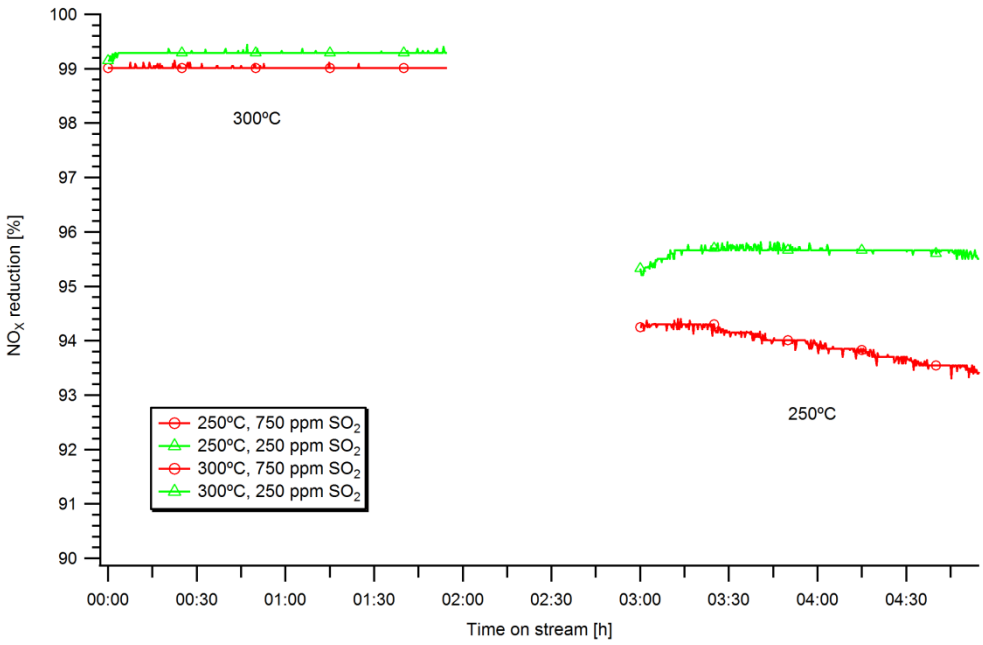

Figure 2: NO_x reduction at 300 and 250°C at varying SO_2 concentrations and in the presence of H_2O. Feed gas composition: 250 (Δ) or 750 ppm SO_2 (o), 500 ppm NO, 500 ppm NH_3, 8 % O_2 and 4 % H_2O (SV 6100 h^{-1})

The different impacts of SO_2 on the SCR activity in different temperature ranges will have some influence of the effect on NO_x emissions that can be expected from this technique. Many ships spend significant periods running their engines at low loads where the exhaust gas temperatures may not be high enough for the SCR to become active and this period may thus be prolonged in the case that a high sulphur fuel is used. Further, the low load periods are likely to take place close to the shore with the result that the emitted NO_x will impact the landside significantly. In addition to this, the testing if engines fulfil the Tier III regulations will likely be made in a testing schedule that includes a low load point, i.e., the SCR abatement equipment will have to operate also at this point. This put further focus on improving the low temperature activity of the catalyst. An alternative is to artificially increase the exhaust temperatures at low loads through injection of surplus fuel with the obvious disadvantage of a fuel penalty.

However, there are also regulations regarding the sulphur content in the fuel used in shipping being enforced in the coming years. In SECA areas (at present the Baltic Sea, the North Sea and the English Channel and the North American coasts) the maximum allowed sulphur content in the fuel will be 0.1%, down from today's 1%, from 2015 and in other seas it will be 0.5% from 2020 from a present maximum level of 3.5% (1% S in the fuel gives roughly 200 ppm SO_2 in the exhaust). Thus, the SO_2 content in the exhaust will be a much lesser problem in the future. However, there is another possibility to comply with the sulphur regulations where scrubbers are used to capture SO_2 from the exhaust allowing for the continued use of (the less expensive) high-sulphur heavy fuel oil. The possible combination of SCR and scrubbers can result in some problems. If the SCR unit is put closer to the engine than the scrubber unit, the SCR will be exposed to high SO_2 concentrations. On the other hand, after the scrubber the exhaust gas temperature will be much too low for an SCR to operate and such an arrangement would require reheating of the exhaust. Additionally, the future need for SCR-units on 2-stroke engines may require the unit to be placed upstream of the turbo charger, i.e. higher pressure and temperature, to allow for a sufficient NOx-reduction to take place. Likewise, may the combination of two-stage turbo charging and SCR, on 4-stroke engines, require the SCR to be placed between the two turbo charges to enable an appropriate working temperature for the catalyst. Conclusively, the need for reduced emission of CO_2, SOx and NOx may require a

holistic view point when considering the development and integration of the engine(-s) and the abatement systems.

At high temperatures the data presented here shows that high SO_2 concentrations in the gas are compatible with high activity of an SCR catalyst.

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References

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