

Dynamic Properties of Vanadium and Zeolite Catalysts

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ABSTRACT

The Selective Catalytic Reduction (SCR) catalyst with ammonia as reducing agent plays a central role in today's exhaust after-treatment systems for heavy-duty vehicles and there is a wide selection of possible catalytic materials to use. In order to facilitate the design of future catalysts, several aspects of the materials must be evaluated both in steady-state and transient operation. To this end, this paper presents a methodology for comparing the dynamic properties of different catalysts using full-size engine testing. The studied characteristics include the ammonia storage capacity, the effect of starting with an empty catalyst, the transient response to temperature gradients and changes in the urea dosing level. The temperature response is of particular importance in transient operation, where temperature increases may lead to substantial ammonia slip. A vanadium catalyst is compared to a Cu-SAPO-34 catalyst, and they show significant differences in their dynamic response.

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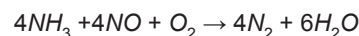
INTRODUCTION

Selective Catalytic Reduction (SCR) of nitrogen oxides using ammonia as reducing agent [6] plays a central role in today's exhaust after-treatment systems for heavy-duty vehicles in order to meet the more stringent emissions standards. A modern after-treatment system typically consists of several units besides the SCR: a Diesel Oxidation Catalyst (DOC) intended to remove unburned hydrocarbons and CO and producing NO₂ to facilitate soot oxidation and fast SCR reaction, a Diesel Particulate Filter (DPF) for trapping particulate matter, and an Ammonia Slip Catalyst (ASC) for removing excess ammonia leaving the SCR catalyst. For each unit, there is a wide selection of possible substrates and catalytic materials to use. In order to facilitate the design of future after-treatment systems, several aspects of the materials must be evaluated. Since the certification of new systems is performed using both transient and steady-state tests, the catalyst evaluation must take both of these factors into account [12].

Among the possible categories of SCR catalysts are vanadium-based catalysts and zeolite type catalysts. In this study, the vanadium catalyst is represented by a V₂O₅/WO₃/TiO₂ catalyst, a type of catalyst with good sulfur tolerance, high NO_x conversion performance, and good durability [1, 9, 13]. The zeolite type of catalyst is here represented by the zeolite-like Cu-SAPO-34 (Silica Alumina Phosphate, i.e. technically it is not a true zeolite) [10, 11, 13]. The tolerance for high temperatures (above 600 °C) is considerably better for Cu-SAPO-34, which is of importance for instance in connection with an active

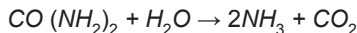
regeneration of the particulate filter. The motivation for studying these two catalysts is that their respective appealing features make them relevant candidates for design of current and future aftertreatment system. A performance comparison of SCR on DPF using vanadium and Cu-SAPO-34 was presented in [13] and demonstrated comparable performance using the coated filters as with a similarly sized flowthrough catalyst. In [1], a steady-state comparison of a V₂O₅/WO₃-TiO₂ catalyst with the iron and copper exchange zeolites Cu-ZSM5 and Fe-ZSM-5 was presented. Dynamic modeling studies of both vanadium and Cu-SAPO-34 catalysts include [7, 8].

The main reactions involved in the NO_x reduction are the "standard", and "fast", SCR reactions:



The SCR reactions occur with ammonia adsorbed on the active sites of the catalyst. Since the available ammonia storage capacity of the catalyst decreases with increasing temperature, transient operation presents several challenges. If a temperature increase occurs while the catalyst is operated with a high relative coverage ratio, there is a risk of tail-pipe ammonia slip when the excess ammonia is desorbed. Conversely, after a temperature decrease, the greater ammonia storage capacity requires an increased urea dosing rate in order to achieve the desired NO_x conversion level. In automotive applications, a urea solution is often used as a

reducing agent. The urea is then converted to ammonia through decomposition and hydrolysis reactions, which can be described globally as



This conversion requires a certain minimum temperature of around 180-200 °C in order to occur, which introduces an effective lower temperature limit for the reducing agent in order to avoid urea deposits in the exhaust system.

In this paper, the World Harmonized Transient Cycle (WHTC), which is used for current emissions legislations for heavy-duty road vehicles in the EU [12], is used as a starting point for discussing the differences in the transient behavior of the vanadium and zeolite catalysts. The dynamic properties are then highlighted through various dedicated experiments consisting of transients in the urea dosing level and exhaust gas temperature.

EXPERIMENTAL SETUP

Engine

The experiments were performed using a 13 liter 6 cylinder 480 horsepower Scania DC13 heavy-duty diesel engine. It was equipped with unit injectors and waste gate turbo and run without exhaust gas recirculation.

Emissions Measurement

Emissions of NO, NOx, CO, CO₂, O₂, HC, and N₂O were measured using two Horiba MEXA 7000 systems. The systems measure at 10 Hz. This setup allows for simultaneous measurements at sample points located before and after the studied catalyst.

Ammonia was measured using two separate systems. A Siemens LDS 6 is a diode laser spectroscopy system specifically tuned to detect ammonia in any environment [3]. The LDS is put in series after the after-treatment system, and can thus only measure tailpipe ammonia concentrations. It is an in situ measurement with excellent precision and response time. The second system used for ammonia measurements was a Gasmet DX-4000 [5] FTIR system (Fourier Transform Infrared Spectrometry) [4] equipped with a dedicated pump/filter combination. The FTIR system additionally gives measurements of NO, NO₂, N₂O, CO, CO₂, and H₂O, but at a slightly lower rate than the MEXA systems.

Table 1 lists the analyzer for each species and the corresponding measurement range.

In these tests, the MEXA units sampled the gas upstream and downstream of the SCR. The FTIR was mounted downstream of the SCR together with the LDS system.

Table 1. Emissions analysis instruments and ranges.

Emission	Analyzer	Range
HC	FID Horiba FIA-726D	0 – 50 000 ppm
CO (low)	NDIR Horiba AIA-721	0 – 5 000 ppm
CO / CO ₂	NDIR Horiba AIA -722	0 - 12 Vol% CO, 0 - 20 Vol% CO ₂
O ₂	MPD Horiba MPA-720	0 - 25 Vol% O ₂
NO / NO _x	CLD Horiba CLA-757	0 - 500 ppm or 0 – 10 000 ppm (automatic range)
N ₂ O	NDIR Horiba AIA-721	0 – 5 000 ppm
NH ₃ (ex situ)	FTIR Gasmet 4000DX	0 – 2 000 ppm
NH ₃ (in situ)	Diode Laser Siemens LDS 6	0 - 300 ppm

Catalysts

The tested catalysts were a commercial vanadium/tungsten catalyst and a Cu-SAPO-34 catalyst with a loading of approximately 180 g/liter. Both catalysts were washcoated. For an overview of SCR catalyst development ranging from vanadium to metal-exchanged zeolites, see [1]. The majority of the experiments were performed using catalysts washcoated on 10.5" diameter and 12" length substrates, corresponding to approximately 17 liters of SCR. A few experiments were performed using 6" length substrates to achieve even higher space velocities. The catalysts were run as single bricks with temperature sensors mounted engine out, before the catalyst, and after the catalyst.

TEST PROGRAM

The test program can be divided into three categories: transient test cycles, ammonia response tests, and temperature response tests.

Transient Test Cycles

In order to evaluate the transient performance of the catalysts in a transient cycle, the World Harmonized Transient Cycle (WHTC) was used. The tests were run with a fixed Ammonia-to-NO_x-ratio (ANR). The results were used to study the overall NO_x conversion as well as mean and peak ammonia slip levels. These tests were performed once with an empty catalyst, i.e. the catalyst had no ammonia stored at the start of the cycle, and once with a pre-conditioning. The tests with empty catalysts were performed by running the engine with high exhaust gas temperatures without urea dosing for an extended period of time. The engine and after-treatment system were subsequently cooled down before starting the test. The pre-conditioned tests were performed by running the cycle once with urea dosing, followed by a 10 minute soak period before repeating the cycle. The benefit of having ammonia present on the catalyst at the start of the cycle could then be evaluated.

The remaining test categories are aimed at highlighting specific aspects of the overall dynamic behavior studied in the test cycles.

Ammonia Transient Tests

In order to quantify the transient response to changes in the urea dosing level, tests were performed where pre-determined changes in the dosing level occurred. Studying the time until the expected steady-state conversion is obtained when starting from an empty catalyst is relevant to the results from the transient tests with and without pre-conditioning. It also gives a measure of the ammonia storage capacity of each catalyst. Additionally, changes between two different dosing levels are relevant for the in-cycle behavior of the catalyst, where the dosing level is typically varied rapidly in response to changes in the inlet conditions. The tests were performed at multiple temperatures, since the differences can be considerably smaller at high temperatures.

Temperature Transients

This test category consisted of transients between a low temperature operating point and a high temperature one. The same exhaust gas flow was maintained in both points. The urea dosing level was adjusted by selecting an ANR corresponding to a pre-defined ammonia slip level at the SCR outlet. The operating point was then changed to increase or decrease the engine out temperature, while maintaining the same ANR throughout the experiment. During such a temperature increase, a peak in ammonia slip is expected to occur, due to the reduction in ammonia storage capacity of the catalyst, which can be evaluated in terms of peak height and timing.

EXPERIMENTAL RESULTS

Transient Test Cycles

Figure 1 shows the exhaust gas flow and temperature profiles of a WHTC test. The initial temperature is approximately 120 C and it takes almost 400 seconds until the temperature stays above 180 C, indicated by the black dashed line.

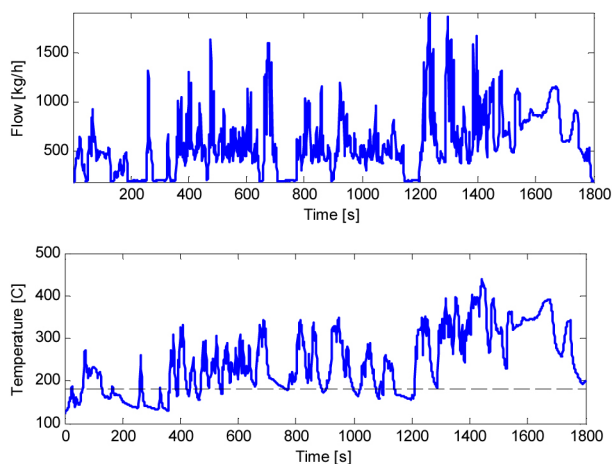


Figure 1. Exhaust gas flow and temperature of a WHTC test.

Figure 2 shows the results of WHTC tests with empty catalysts. The top plot shows the instantaneous NOx conversion for the vanadium and Cu-SAPO-34 catalysts in blue and green respectively. The data was downsampled by a factor of 10 to make the plots more readable. The bottom plot shows the SCR out NH3 for each catalyst. Note that the ammonia slip measurement saturated at 300 ppm. The urea dosing was disabled at temperatures below 180 degrees, and an ANR of 1.0 was used. The engine out accumulated specific NOx was approximately 10.5 g/kWh.

Clearly, both catalysts show rather low conversion levels during the first part of the cycle. The urea dosing system was only active at temperatures above 180 C, and there were only brief periods of urea dosing until approximately 400 seconds into the cycle. After that, the conversion levels are similar between the two with a slight advantage for the vanadium catalyst. A significant contribution to this is that the vanadium catalyst achieved high conversion levels faster than the Cu-SAPO-34 catalyst once dosing started. Since the dosing was ANR-based, the rate at which NH3 was added to the catalysts was the same in both tests. The vanadium catalyst also exhibited two early ammonia slip peaks, at approximately 400 and 600 seconds into the cycle, which were suppressed by the Cu-SAPO-34 catalyst. The second section where the vanadium catalysts showed higher performance was during the rapid temperature changes in the later part of the cycle. Here, the vanadium catalyst had a higher NOx conversion as well as lower ammonia slip.

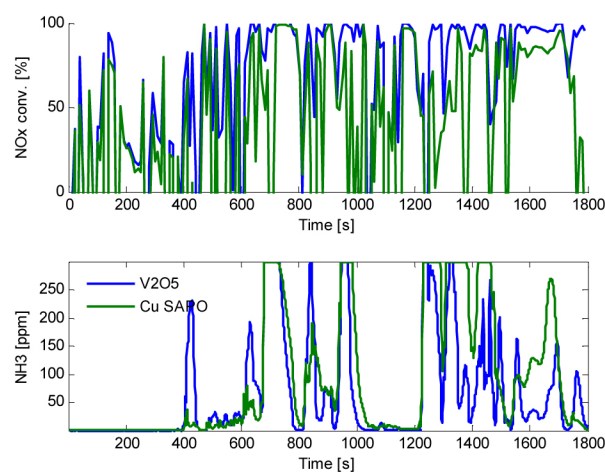


Figure 2. Results of WHTC tests with initially empty catalysts. The top figure shows the instantaneous NOx conversion of each catalyst (blue line for the vanadium catalyst and green line for the Cu-SAPO-34 catalyst), and the bottom figure shows the corresponding ammonia slip profiles.

The tests with empty catalysts were complemented by pre-conditioned tests where the catalysts had some initial NH3 coverage at the start. The test results are shown in Figure 3. In this case, the Cu-SAPO-34 catalyst showed a reduction in accumulated specific NOx of almost 10 %, from around 3.6 g/kWh to 3.25 g/kWh (corresponding to almost 70% overall conversion), while the corresponding reduction for the