

# Technical Advantages of Vanadium SCR Systems for Diesel NOx Control in Emerging Markets

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## ABSTRACT

Selective catalytic reduction (SCR) is a promising technology for diesel aftertreatment to meet NOx emissions targets in several countries. In established markets such as the US and Europe, zeolite SCR systems are expected to be used due to their ability to survive the exhaust gas temperatures seen in an active diesel particulate filter regeneration. In emerging markets where the fuel sulfur level may be as high as 2000 parts per million, zeolite SCR catalysts may have durability issues. In these markets, low sulfur fuel is needed overall to meet emissions standards and to avoid high sulfate emissions, but the aftertreatment system must be durable to high sulfur levels because there is a risk of exposure to high sulfur fuel. Also, emissions standards may be met without a DPF in some applications, so that the exhaust system would not see temperatures of 600°C or higher. If a zeolite SCR system were used in this application, a diesel oxidation catalyst would be needed to regenerate the SCR after exposure to high sulfur fuel, adding cost to the system. Thus, a vanadium SCR system has several advantages for this application. This work shows experimental comparisons of state of the art vanadium SCR catalysts with base metal zeolite SCR catalysts. NOx conversion performance after exposure to sulfur is examined, as well as NOx conversion in the presence of hydrocarbons. Improvements in durability and performance of vanadium SCR catalysts are shown. Also, modeling results are presented demonstrating the ability of a vanadium SCR system to meet the NOx emissions targets for a Euro IV or Euro V standard. The thermal durability of current vanadium SCR catalysts is also evaluated. Based on these tests it is concluded that in markets where there is a risk of exposure to high sulfur fuel, vanadium SCR is the recommended technology.

## INTRODUCTION

With increasingly stringent automobile exhaust emissions regulations, aftertreatment systems for the control of oxides of nitrogen (NOx) are expected to be needed soon in many emerging markets. In these markets, the availability of low sulfur diesel fuel may not be guaranteed, so any NOx control system must be

robust to high levels of fuel sulfur. The fuel sulfur level may be as high as 2000 ppm or more in fuels for these markets. For such applications, a vanadium SCR catalyst system may be ideal to meet NOx emissions standards when low sulfur fuel is used and to survive exposure to high sulfur fuel. Vanadium containing SCR catalysts ( $V_2O_5$  supported on  $TiO_2$ , see, e.g., Twigg [1]) are very robust to sulfur poisoning and very active for selective catalytic reduction of NOx. Vanadium SCR catalysts have low thermal durability in comparison with state of the art zeolite-based SCR catalysts, but in applications where the SCR catalyst will not see elevated temperatures, this concern is avoided. An example might be a system without a diesel particulate filter (DPF). In Europe vanadium SCR catalysts are common in systems where a DPF is not needed to meet the emissions requirements.

Emissions standards are difficult if not impossible to meet when high sulfur fuel is used, due to the potential formation of ammonium sulfate if urea is used at low temperatures with high sulfur fuel. Also, use of high sulfur fuel can lead to higher fine particle emissions due to sulfate formation, as is shown in Figure 1 [2]. Thus, the goal for finding a system to work in developing markets is to meet emissions standards when using approved low sulfur fuel, and to survive possible exposure to high sulfur fuel.

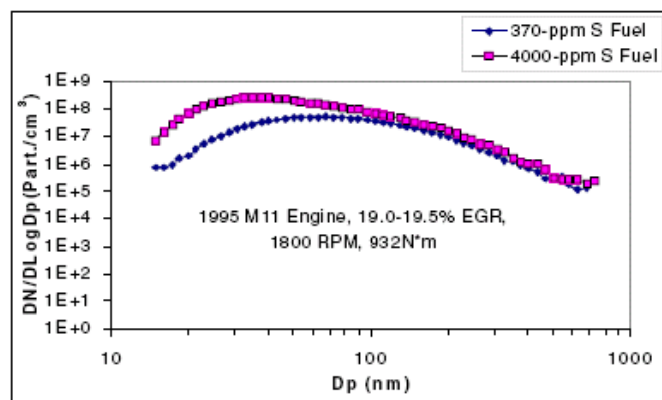


Figure 1: Change in number density of diesel particulate matter with fuel sulfur level [2]

This paper provides a comparison of state of the art vanadium SCR catalyst formulations, and characterizes them in terms of thermal durability, NOx conversion activity and tolerance to sulfur and hydrocarbons. Modeling results are included based on laboratory flow reactor data demonstrating that a vanadium SCR-based aftertreatment system can achieve Euro V NOx emissions targets. Furthermore, configurations in which a vanadium SCR system is practical are discussed.

## EXPERIMENTAL SETUP

Experimental work was performed on catalyst cores 2.54 cm in diameter and ranging from 1.60 to 3.81 cm in length. Simulated diesel exhaust gas (a mixture of bottled gases) was flowed over the catalyst cores in a bench reactor where the catalyst temperatures were controlled using tube furnaces. Gas analysis was performed using a Midac FTIR.

Three different performance metrics were used to evaluate the different SCR washcoat formulations: thermal durability, resistance to hydrocarbon poisoning, and resistance to sulfur poisoning. For each of these performance characteristics, the metric for performance is conversion efficiency of NOx to N<sub>2</sub>. Table 1 gives the details of gas composition and flow rates for the thermal durability evaluations. The aging conditions are also given in Table 1. The thermal durability aging for the vanadium catalysts was intended to represent time at temperature for a full load condition on a diesel truck.

**Table 1: Aging and evaluation conditions for thermal durability testing of vanadium SCR catalysts.**

| <u>Hydrothermal Aging</u>            | <u>Steady State Evaluation</u>          |
|--------------------------------------|-----------------------------------------|
| 14% O <sub>2</sub>                   | 350 ppm NO                              |
| 5% H <sub>2</sub> O                  | 350 ppm NH <sub>3</sub>                 |
| 5% CO <sub>2</sub>                   | <b>alpha = 1.0 (NH<sub>3</sub>/NOx)</b> |
| 0 ppm SO <sub>2</sub>                | 14% O <sub>2</sub>                      |
| bal N <sub>2</sub>                   | 4.5% H <sub>2</sub> O                   |
| <b>S.V. = 30,000 hr<sup>-1</sup></b> | 5% CO <sub>2</sub>                      |
| <b>Baseline Aging:</b>               | 0 ppm SO <sub>2</sub>                   |
| <b>75hrs 550°C</b>                   | bal N <sub>2</sub>                      |
| <b>High Temperature Aging:</b>       | <b>S.V. = 30,000 hr<sup>-1</sup></b>    |
| <b>50 hrs 600°C</b>                  | <b>T = 150 - 600°C</b>                  |
| <b>Zeolite SCR Catalyst Aging:</b>   |                                         |
| <b>64hrs 670°C</b>                   |                                         |

Measurements of vanadium and titanium were also taken for green samples and compared to those aged hydrothermally. These measurements were performed to estimate potential loss of vanadium or titanium from thermal exposure. X-ray fluorescence (XRF) was used for this elemental analysis.

Hydrocarbon tolerance was evaluated by measuring NOx conversion performance in the presence of representative hydrocarbon species. Table 2 gives the details of the hydrocarbon tolerance test conditions. Propylene and decane were among the hydrocarbon species used for these evaluations. The testing was done at relatively low temperatures, since the SCR

catalyst is expected to oxidize hydrocarbons at higher temperatures and therefore no NOx conversion performance impact is expected.

**Table 2: Evaluation conditions for hydrocarbon tolerance testing of vanadium SCR catalysts.**

| <u>Steady State Evaluation</u>            |
|-------------------------------------------|
| 350 ppm NO                                |
| 350 ppm NH <sub>3</sub>                   |
| <b>alpha = 1.0 (NH<sub>3</sub>/NOx)</b>   |
| 14% O <sub>2</sub>                        |
| 4.6% H <sub>2</sub> O                     |
| 5% CO <sub>2</sub>                        |
| 0 ppm SO <sub>2</sub>                     |
| <b>700 ppm C<sub>3</sub>H<sub>6</sub></b> |
| bal N <sub>2</sub>                        |
| <b>S.V. = 30,000 hr<sup>-1</sup></b>      |
| <b>T = 200°C and 300°C</b>                |

Sulfur tolerance testing was performed by exposing the SCR catalysts to varied levels of sulfur, then evaluating NOx conversion performance. The details of the sulfur exposure and testing are provided in Table 3. Sulfur levels were chosen to try to represent both high sulfur fuel, which may be available in some emerging markets, and low sulfur fuel. The sulfur levels and times of exposure were translated into estimated miles driven at a given fuel sulfur level

**Table 3: Aging and evaluation conditions for sulfur tolerance testing of vanadium SCR catalysts.**

| <u>Sulfur Exposure</u>                              | <u>SCR Evaluation</u>                |
|-----------------------------------------------------|--------------------------------------|
| <b>S.V. = 30,000 hr<sup>-1</sup></b>                | 14% O <sub>2</sub>                   |
| <b>T = 200°C</b>                                    | 4.6% H <sub>2</sub> O                |
| 14% O <sub>2</sub>                                  | 5% CO <sub>2</sub>                   |
| 4.6% H <sub>2</sub> O                               | 0 ppm SO <sub>2</sub>                |
| 5% CO <sub>2</sub>                                  | 350 ppm NO                           |
| <b>Sulfur Exposure 1:</b>                           | 350 ppm NH <sub>3</sub>              |
| <b>600 ppm SO<sub>2</sub> =&gt; 2000 ppm S Fuel</b> | bal N <sub>2</sub>                   |
| <b>Sulfur Exposure 2:</b>                           | <b>S.V. = 30,000 hr<sup>-1</sup></b> |
| <b>30 ppm SO<sub>2</sub> =&gt; 50 ppm S Fuel</b>    | <b>T = 175 - 600°C</b>               |
| bal N <sub>2</sub>                                  |                                      |

The newer vanadium based samples were fully formulated and washcoated on ceramic monolith substrates with 300 cells per square inch (46.5 cells per square cm) and 8 mil (0.21 mm) wall thickness. The previous generation vanadium based catalyst was an extruded vanadium titanium substrate having sinusoidal cell structure and 300 cells per square inch (46.5 cells per square cm) with 13.8 mil (0.35 mm) wall thickness.

## RESULTS AND DISCUSSION

### THERMAL DURABILITY

Vanadium SCR catalyst NOx performance vs. temperature results after long term hydrothermal aging at 550°C are given in Figure 2.

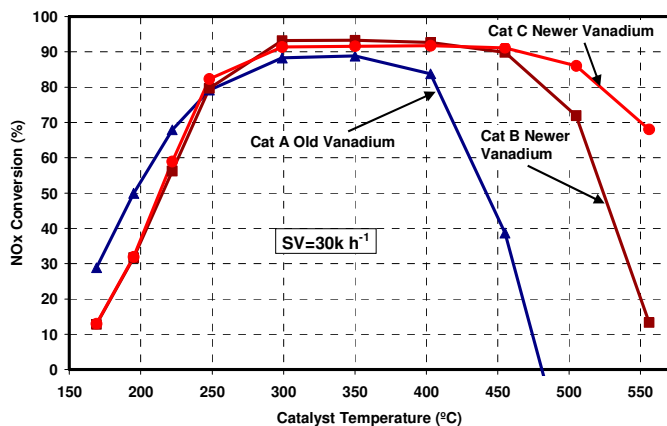


**Figure 2: NO<sub>x</sub> conversion performance of previous generation vs. state of the art vanadium SCR catalyst formulations. Catalysts aged 75 hrs at 550°C.**

As can be seen, the previous generation vanadium catalyst suffered deteriorated performance after the 550°C aging condition – the high temperature performance of the catalyst was lost and NO<sub>x</sub> production from NH<sub>3</sub> oxidation was observed at temperatures of 500°C and higher (negative NO<sub>x</sub> conversion cut off from Figure 2). The two newer technology vanadium SCR catalysts had very promising performance after long term aging at 550°C.

The N<sub>2</sub>O production for each of these catalysts is given in Figure 3, and was relatively low for all of the samples.

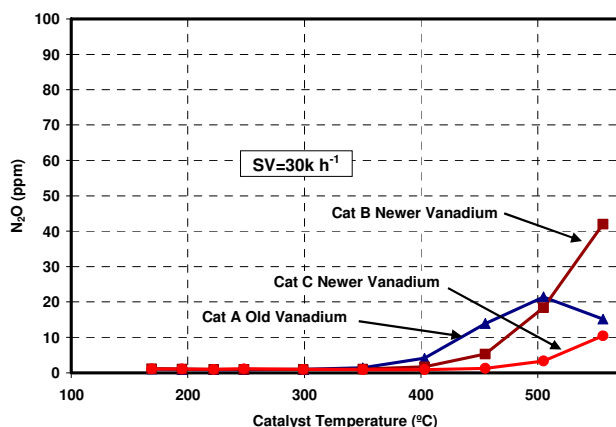


**Figure 3: N<sub>2</sub>O production of various vanadium SCR catalyst formulations. Catalysts aged 75 hrs at 550°C.**

The difference in performance between the previous generation vanadium SCR catalyst and the newer technologies is more pronounced at increased space velocities, as shown in Figure 4.

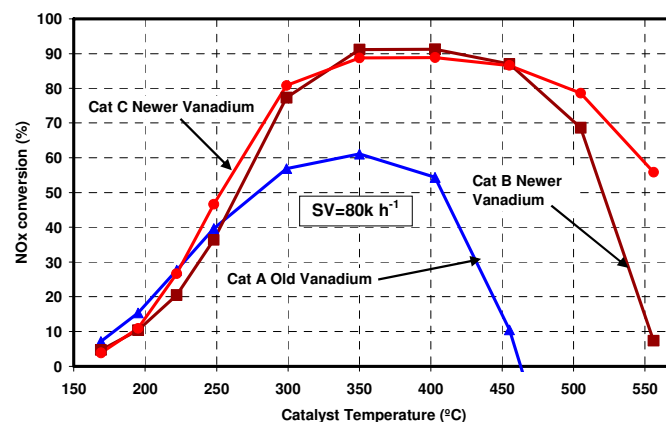


**Figure 4: NO<sub>x</sub> conversion at higher space velocities for vanadium SCR catalyst formulations. Catalysts aged 75 hrs at 550°C.**

Part of the difference in Figure 4 may be due to the difference in the catalyst structure. As mentioned previously in this paper, the older technology catalyst was an extruded titania vanadia catalyst, while the newer technology catalysts were washcoated on cordierite monoliths. As was the case for the lower space velocity (Figure 2), the older technology vanadium SCR catalyst begins to remake NO<sub>x</sub> from NH<sub>3</sub> at temperatures of 500°C and higher (negative NO<sub>x</sub> conversion cut off on Figure 4). The newer technology vanadium SCR catalysts still achieve 90% NO<sub>x</sub> conversion at temperatures from 350 to 450°C, but the light-off temperature for NO<sub>x</sub> conversion shifted higher by about 50°C vs. the 30,000 h<sup>-1</sup> result seen in Figure 2.

Based on the promising results seen after aging at 550°C, a second aging was performed under more severe conditions. Figure 5 shows the results of one of the newer technology SCRs after aging at 600°C for 50 hours.

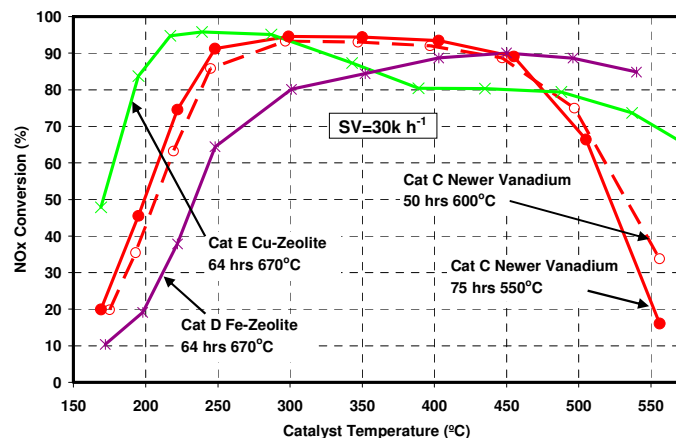


**Figure 5: Vanadium SCR Catalyst NO<sub>x</sub> conversion performance in comparison with state of the art copper zeolite and iron zeolite SCR catalysts.**

The performance of the newer technology vanadium SCR catalyst was only slightly worse after the 600°C