

Methods for Quantifying the Release of Vanadium from Engine Exhaust Aftertreatment Catalysts

Z. Gerald Liu, Nathan A. Ottinger and Christopher M. Cremeens
Cummins Emission Solutions

ABSTRACT

Titanium dioxide supported vanadium oxide catalysts have been successfully utilized for the selective catalytic reduction (SCR) of nitrogen oxides emitted from both stationary and mobile sources. Because of their cost and performance advantages in certain applications, vanadium-based SCR catalysts are now also being considered for integration into some U.S. Tier IV off-highway aftertreatment systems. However, concern exists that toxic vanadium compounds, such as vanadium pentoxide, could be released from these catalysts as a result of mechanical attrition or high temperature volatility. An experimental study has been conducted to compare various techniques for measuring the release of particle and vapor-phase vanadium from SCR catalysts. Previous research has utilized a powder reactor-based method to measure the vapor-phase release of vanadium, but there are inherent limitations to this technique. A new method developed in this study utilizes a core reactor to measure the vapor-phase release of vanadium from commercially available SCR monolith cores in order to simulate real-world catalyst applications. The vanadium release results from this study were compared to engine-based measurements and previously published data from powder reactor experiments. Both reactor-based (i.e., powder and core) vanadium measurement techniques detected lower levels of vanadium than engine-based measurements. The increased level of vanadium release determined by the engine-based approach can be attributed to that method's ability to measure particle-phase and particle bound vanadium as well as the fraction of vapor-phase vanadium which was adsorbed onto particulate matter.

CITATION: Liu, Z., Ottinger, N. and Cremeens, C., "Methods for Quantifying the Release of Vanadium from Engine Exhaust Aftertreatment Catalysts," *SAE Int. J. Engines* 5(2):2012, doi:10.4271/2012-01-0887.

INTRODUCTION

Worldwide emission limits for nitrogen oxides (NO_x) from internal combustion engines continue to trend downward. As a result, a variety of NO_x reduction strategies are currently being utilized, with the most prevalent being selective catalytic reduction (SCR) and lean NO_x trap (LNT). Vanadium-based SCR systems are of particular interest in applications where ultra-low sulfur diesel fuel is not available and where the implementation of diesel oxidation catalysts is cost prohibitive. When used with non-ultra-low sulfur fuels, both zeolite-based SCR and LNT catalysts require high temperature desulfation [1,2], whereas vanadium-based SCR catalysts are more resistant to sulfur poisoning [3,4]. Furthermore, in applications where a DOC is not needed for active diesel particulate filter (DPF) regenerations, or where the additional cost of a DOC may be prohibitive, vanadium-based catalysts perform better than zeolite-based catalysts because they are able to obtain high NO_x conversion in the presence of hydrocarbons [3,4]. In addition, the lower NH_3

storage capacity of vanadium-based catalysts, specifically in comparison to zeolite formulations, means that an ammonia oxidation (AMOX) catalyst may not be required to suppress transient NH_3 slip. However, elevated temperatures associated with active DPF regeneration thermally degrade the NO_x conversion performance of vanadium-based SCR catalysts, hindering their widespread application. Nonetheless, vanadium-based SCR catalysts are currently being used in aftertreatment systems which require high NO_x conversion but where the risk of high temperature exposure is minimal.

In addition to the performance degradation associated with high temperature exposure of vanadium-based SCR catalysts, there is concern that toxic material could be released as a result of washcoat delamination [5] or volatilization [6]. The high temperature stability of vanadium-based SCR catalysts has been previously studied [3,4,6, 7, 8]. Ura et al. showed that V-based SCR catalysts have comparable low-temperature NO_x conversion performance to a Cu/zeolite catalyst after 600°C

hydrothermal aging [4]. However, particle and vapor-phase emissions of washcoat material were not measured during high temperature aging experiments in this study. Hu et al., in their study of metal emissions from vehicles retrofitted with PM and NO_x reduction aftertreatment, found that appreciable amounts of vanadium and titanium were released during cruise operation with a V-based SCR + DPF aftertreatment [7]. It was indicated that this material may have been derived from the washcoat of the SCR catalyst. Chapman, in a recent study, has measured the vapor-phase release of inorganic compounds from lab synthesized V-based SCR catalysts [6]. His experiments revealed that vanadium was released from commercial high surface area titania catalyst support material in the presence of H₂O at 670 and 750°C, but that it was possible to stabilize vanadium by modifying the support material. In contrast, Maunula et al. analyzed the thermal stability of pure V₂O₅, V₂O₅/TiO₂-WO₃, and a physical mixture of V₂O₅ with TiO₂-WO₃ and saw no evidence of vanadium release from any of these samples at temperatures up to 1000°C [8].

The release of vanadium from exhaust aftertreatment devices is a concern because of the possible risk this metal and its compounds could pose to human and environmental health [9,10]. The Occupational Safety and Health Administration (OSHA) has set exposure limits of 0.5 mg/m³ for V₂O₅ respirable dust and 0.1 mg/m³ for V₂O₅ fumes, both as ceiling values, and the National Institute for Occupational Safety and Health's (NIOSH) recommended exposure limit (REL) for vanadium dust or fumes is 0.05 mg/m³ as a 15 minute ceiling. Furthermore, the International Agency for Research on Cancer (IARC) has labeled vanadium pentoxide (V₂O₅) as a group 2B (possible carcinogen).

This study will develop and evaluate the effectiveness of a new method for measuring the vapor-phase release of vanadium from commercially available SCR monoliths. A core-reactor that is typically used for catalyst performance measurements was modified to measure vanadium released during high-temperature steady-state experiments. This new technique attempted to simulate diesel exhaust aftertreatment conditions by utilizing realistic monolith cores and gas hourly space velocity (GHSV). The method was further optimized to reduce the temperature gradient across the catalyst, maximize the amount of vanadium adsorbed, and minimize the vanadium concentration in blank measurements. Reactor-based vanadium emissions from this study were then compared to engine-based measurements and previously published data from powder reactor experiments, and possible reasons were offered to explain the differences in measured vanadium release levels among the methods.

CURRENT MEASUREMENT METHODS

Two testing methods have been used for collecting vanadium released from aftertreatment catalysts. The

particle-phase technique used by Liu et al. [11] and Hu et al. [7] has been extensively validated and vetted in the literature. This engine-based method uses a constant volume sampling (CVS) system to dilute raw exhaust gas and then a sampling device to trap particulate samples on quartz, polytetrafluoroethylene (PTFE), or PTFE impregnated glass fiber filters. The filters are then digested and the resulting solution is analyzed for metal content. This method has been used for measuring trace-metal emissions from engines and aftertreatment systems. In the case of vanadium emissions, which could be either particle or vapor-phase, this engine-based method will still have some sensitivity to vapor phase release since vanadium adsorption onto high surface area particulate matter can be expected. Garcia-Bodeje et al. have shown that a vanadium surface density on carbon of up to 1.78 V atoms per nm² is possible with high vanadium loadings [12].

The powder-reactor method recently developed by Chapman [6] measures the vapor-phase release of vanadium from a packed bed powder catalyst sample loaded in a quartz tube. Release experiments are performed by placing the quartz tube in a furnace heated to the desired temperature and flowing a suite of gases intended to simulate diesel exhaust through the packed catalyst bed. Directly downstream of the catalyst sample is another packed bed of gamma-alumina (γ-Al₂O₃) which is used to trap any gas phase vanadium that is released. As is seen in Table 1, γ-Al₂O₃ was chosen as the vanadium sorbent media in Chapman's as well as the present study because it has a high vanadium surface coverage in comparison to other high surface area, thermally stable oxide supports such as SiO₂ [13,14]. This reactor-based testing scheme, though it only marginally approximates real-world applications, is much simpler than the engine-based approach. It is possible with this technique to test for the release of vanadium in the washcoat development stage before the material has been applied to a substrate. However, there are inherent limitations to the powder reactor-based approach. Most importantly, it is not possible to measure the loss of vanadium containing particles due to attrition. Thus, this method is intended to only measure vapor-phase release. Furthermore, the applicability of vanadium release measurements with this technique to full-size, flow-through catalyst monoliths is unknown. This is a result of several factors. Gas hourly space velocities (GHSV) and exposed catalyst surface areas defined for packed-bed powder reactors are not directly comparable to similar definitions for cores and full-size catalysts. Also, the flow characteristics and the resulting convective and boundary layer mass and species transfer of a packed catalyst bed do not necessarily approximate those of a flow-through catalyst [15]. Finally, the sample size of a packed bed is generally small to minimize pressure drop across the sample, and this reduces the possible mass of released metal which challenges the detection limits of the analytical instrument.

Table 1. Maximum vanadium loading for SiO_2 and Al_2O_3 before the formation of crystalline V_2O_5 [13,14].

Support Oxide	Preparation Method	Surface area of support (m^2/g)	Maximum loading of vanadium (V atoms per nm^2 of support)
SiO_2	Chemical vapor deposition	203	3.9
Al_2O_3	Chemical vapor deposition	93	18.0

The analytical method for quantifying the collected vanadium is nearly independent of the sampling method. The filter and $\gamma\text{-Al}_2\text{O}_3$ samples are both digested in an aqueous acid solution and analyzed with high-resolution inductively coupled plasma-mass (ICP-MS) or emission spectroscopy (ICP-ES). This is discussed in more detail in the subsequent section.

EXPERIMENTAL SETUP

ENGINE-BASED SAMPLING PROCEDURE

Engine experiments were performed with a 15 liter 2010 Cummins ISX diesel engine rated for 500 hp (373 kW) at 1800 rpm. Controlled with a General Electric direct current dynamometer, the engine was fueled with ultra-low sulfur diesel. Aftertreatment components included a commercially available DOC consisting of platinum group metals (PGM) for the oxidation of CO, unburned hydrocarbons, NO, and the soluble organic fraction (SOF) of soot as well as a commercially available vanadium-based SCR catalyst for NO_x reduction. The vanadium-based SCR had a volume of approximately 13 liters and consisted of a proprietary washcoat applied to a cordierite substrate. Diesel exhaust fluid (DEF) was injected into a decomposition tube to ensure conversion of urea to NH_3 during all experiments, and the injection rate was automatically controlled by the aftertreatment control module. A DPF was not used in this study, and an empty tube with the same dimensions as the stock DPF holder was inserted in its place. The engine was run at a constant speed of 1562 rpm and a constant load of 1560 ft-lb (2115 N-m), and ultra-low sulfur diesel (ULSD) was dosed into the gas stream upstream of the DOC to obtain target SCR temperatures. During experiments without a SCR catalyst, a butterfly valve was used to maintain the same backpressure as the aftertreatment systems in order to simulate identical engine operating conditions.

To representatively simulate atmospheric conditions for mobile source applications, a full-partial-full source dilution sampling (SDS) system was incorporated for metal emissions measurements. Liu et al. have previously described the design considerations of the SDS system [11]. Briefly, it is intended to simulate atmospheric dilution and aging conditions, maintain proportional sampling during transient conditions, and reduce particle loss by minimizing thermophoresis, wall effects, and electrostatic forces. Figure 1 shows the schematic of the experimental apparatus. The main components of the

system consist of a primary dilution tunnel called the critical flow venturi-constant volume system (CFV-CVS), a secondary micro-diluter, a residence time chamber (RTC) for aging and atmospheric conditioning of the sample, and isokinetic sampling probes for the two sampling trains used in this study. The sampling probes were manufactured from thin walled stainless steel tubing, and the edges of the tubing were sharpened to minimize particle loss during sampling. Two-stage filter holders loaded with 47 mm Pall™ TX40 filter media were used for sample collection, and both primary and secondary filters were analyzed together for total metals content using the method described below. Diluted exhaust flow rate was controlled by Alicat™ mass flow controllers.

REACTOR-BASED SAMPLING PROCEDURE

A catalyst core-reactor was used for reactor-based metal emissions measurements and a schematic of the system is presented in Figure 2a. Briefly, the core-reactor used in this study consists of 12 MKS™ mass flow controllers (MFCs) for gas metering, two Waters™ high performance liquid chromatography (HPLC) pumps for water and liquid hydrocarbon (HC) injection, a Lindberg™ Blue M Mini-Mite tube furnace for reactor temperature control, and a MKS 2030 HS Fourier transform infrared (FTIR) spectrometer for gas analysis. All lines are heated to approximately 200°C to eliminate condensation of water and hydrocarbons and avoid the formation of undesirable low-temperature products such as ammonium nitrate. The quartz reactor tubes used in this study were 24 inches (61 cm) long with inner and outer diameters of 1.1 inches (28 mm) and 1.26 inches (32 mm), respectively. The inlet 10 inches (25.4 cm) of the reactor were filled with quartz beads to ensure that incoming gas is uniformly mixed and heated.

The same commercially available vanadium-based SCR catalyst formulation used for engine testing was also used for reactor-based testing. A core with dimensions of 1 inch (25.4 mm) diameter by 2 inch (50.8 mm) long was wrapped in non-intumescent mat to hold the sample in place and eliminate gas bypass. Gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) pellets (Alfa Aesar, aluminum oxide, gamma, catalyst support, high surface area, bi-modal) were used as a trapping media for released vanadium. Prior to use, the pellets were calcined for 6 hr at 800°C in air to ensure that changes in surface area did not occur during metal release testing. The $\gamma\text{-Al}_2\text{O}_3$ trapping media was placed at two locations in the reactor system, and