

Vanadium-Based SCR Systems: Release of Vanadium and Tungsten during Operation and Possibilities for Reducing Vanadium Emissions

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ABSTRACT

Data on the release of vanadium and tungsten during operation from a vanadium-based Selective Catalytic Reduction catalyst and a newly developed product with advanced thermal stability are presented. The effect of the ammonia slip catalyst as a vanadium trap is highlighted and the implications of the vanadium and tungsten release are briefly discussed.

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INTRODUCTION

Catalysts based on the use of V_2O_5 and WO_3 supported on a TiO_2 carrier provide a fundamental solution to effectively reduce NO_x emissions from Diesel fueled vehicles by means of the Selective Catalytic Reduction (SCR) with ammonia [1, 2, 3]. Compared to alternative strategies for NO_x emission control like exhaust gas recirculation (EGR) [4,5] and zeolite-based catalysts [6], a great advantage of vanadium-based SCR catalysts (V-SCR) is its fuel efficiency, robustness to sulfur and/or price. All of these are key parameters to establishing acceptance for regulations leading to cleaner air also in BRIC countries. On the other hand, V_2O_5 as an essential component of the catalyst is toxic [7] and indeed its use in catalyst production requires stringent safety routines. Reports in the literature suggest that bulk V_2O_5 has a significant vapor pressure at temperatures relevant to the catalyst operation [8], and both V and W compounds react with water to form species with increased vapor pressure [9, 10, 11, 12]. EPA has hence expressed its concerns over the release of toxic V_2O_5 to the environment during operation of V-SCR systems [13,14]. Chapman [12] has shown that measurable amounts of vanadium are first released at temperatures of $\sim 550^\circ C$, which is around the highest applicable working temperature of these systems. Additionally, an important conclusion was that the extent of vanadium release greatly depends on the specific nature of the V-SCR catalyst. It is thus the catalyst manufacturers' responsibility to investigate to which extent vanadium release from their products can occur.

In this study the extent of vanadium and tungsten release from V-SCR catalysts is presented and compared to the release of a newly developed thermally stable V-SCR product.

EXPERIMENT

The testing procedure followed the general recommendations by EPA [15] with some deviations regarding sample size and instrumentation. Most investigations were made on a catalyst ("catalyst A") with a nominal V_2O_5 content of 3.0 wt-% and a WO_3 content of 7.0 wt-% supported on non-stabilized TiO_2 . Some experiments were made with a catalyst using a stabilized TiO_2 as support with improved thermal stability ("catalyst B"). The sample was cut to a volume of 0.13 L (~ 60 g). The release of V and W from the V-SCR catalysts was investigated with a Diesel fueled aging unit containing three sample cells in parallel of which one was always a blank and the two other cells were V-SCR catalysts (usually measured as doublets). Type K thermocouples were placed in the catalyst sample. The catalysts were treated at temperatures between $450 - 750^\circ C$ in a Diesel exhaust gas with a composition of:

5-10 wt % H_2O
0.8-1.0 wt % CO_2
7-10 wt % O_2
5 ppm HC
50 ppm NO_x
Balance N_2 .

The linear velocity of the gas passing through the catalyst was 1 m/s corresponding to a NHSV of $50000\ h^{-1}$. The duration of the test was at least 50 hours after reaching the temperature set point.

Vanadium released from the monolithic catalyst was captured by two alumina traps downstream of the catalyst, i.e. a hot capture bed of high surface area alumina situated directly after the catalyst, a downstream quartz glass condensation column and a cold capture bed ($\sim 200^\circ C$) of high surface alumina.

(Figure 1). The capture beds contained a specific amount of $\gamma\text{-Al}_2\text{O}_3$ (5.0 g, size fraction 150-300 μm) in a cylindrical container ($\varnothing$ 50 mm, height 10 mm) having affinity for V_2O_5 [12].

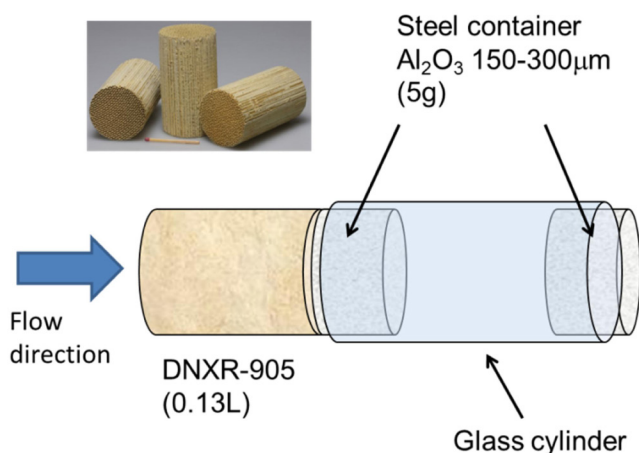


Figure 1. Schematic representation of the configuration of the downstream alumina traps with a downstream quartz cylinder (not true to scale).

After each test the alumina beds were analyzed for vanadium, tungsten and titanium. Titanium served as an internal marker for dust spill over. The quartz glass tubes were inspected for visual appearance of V_2O_5 (yellow stains) and washed in a mixture of oxalic and sulphuric acid in order to dissolve any traces of V. The wash was analyzed for V and W. The recovered alumina was homogenized and digested following recommendations from Herner *et al.* [16]. Two sample aliquots of 200 mg and 300 mg, respectively, were transferred to Teflon pressure vessels with a mixture of 12 mL of 16 N HNO_3 , 2 mL of 28 N HF and 1 mL 12 N HCl. The samples were heated in a microwave oven to 200 °C for 20 min. After cooling the sample was diluted to 100 mL with high purity 18 MQ water. The glass tube wash was analyzed directly. The digests were analyzed for vanadium, tungsten and titanium using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) from Agilent (720 series). Standard plasma condition was 1300 W using an Oneneb nebulizer. A NIST SRM 69b Standard Reference (7 analyses) was measured for every batch of 25 samples. The instrument detection limit (IDL) was determined from reagent blanks (7 analyses). For every batch of 18 samples, 6 samples were reactor blanks for determination of the method detection limit (MDL). The V-concentrations (as expected from previous experiments) were approximately 20 times the detection limit. Vanadium (and tungsten) release rates were calculated using Equation 1.

$$r_x = \frac{c_x \cdot m_{\text{Al}_2\text{O}_3}}{V_{\text{cat}} \cdot t_{\text{exp}}}$$

(1)

r_x is the release rate of V or W, respectively, c_x the concentration of V or W found in the alumina trap, $m_{\text{Al}_2\text{O}_3}$ the mass of the Al_2O_3 in the trap (5.0 g), V_{cat} the catalyst volume and t_{exp} the time at the specified temperature.

RESULTS AND DISCUSSION

In order to ensure full capture of the V and W containing fumes, the method described by Chapman [12] was extended to comprise a second Al_2O_3 trap and a quartz cylinder situated further downstream the first (hot) trap. This configuration both increases the reliability of the experiment, and simulates the effect of an ammonia slip catalyst (ASC) on the vanadium release, provided that the ASC does not contain vanadium itself. Additionally, an exhaust gas obtained from burning Diesel fuel was applied to obtain a more realistic gas atmosphere. Most investigations were made on a catalyst sample with a high nominal V_2O_5 content of 3.0 % (and 7.0 % WO_3) on non-stabilized TiO_2 (catalyst A). This will result in vanadium evaporation rates on the high end of the scale, should the evaporation depend on V content. It must be stated that the amounts of V and W released were small compared to the V and W content of the catalysts. Thus, their release is no significant factor in catalyst deactivation.

V and W levels in the cold trap and the glass cylinder were never significantly higher than the concentration measured in the blanks. Thus, trapping of both elements can be considered quantitative in the first alumina bed. Figure 2 shows the amounts of V and W recovered in the first (hot) Al_2O_3 trap, which increased linearly between 50 - 200 h, allowing vanadium and tungsten release rates, respectively, to be used in the following.

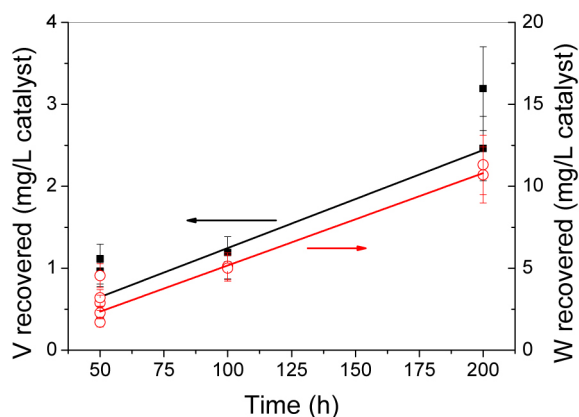


Figure 2. V and W recovered from the hot alumina trap after the VSCR catalyst (catalyst A) as a function of time at 550 °C.

The release of vanadium and tungsten greatly depended on the temperature (Figure 3). Significant release of both elements first commenced at temperatures of 550 °C after which the release rate increased approximately linearly with temperature. This finding is qualitatively in line with results presented by Ibiden [17]. Experimentally determined vanadium release rates at 600 °C were between 50 - 80 $\mu\text{g}/(\text{L}_{\text{cat}} \cdot \text{h})$ or as a concentration in the exhaust gas (after the catalyst) at 1-1.5 $\mu\text{g}/\text{Nm}^3$. The highest release rates reached at 750 °C were 100-150 $\mu\text{g}/(\text{L}_{\text{cat}} \cdot \text{h})$, and the corresponding V concentration in the exhaust gas (after the catalyst) was 2-3 $\mu\text{g}/\text{Nm}^3$.

Comparison of the experimentally determined V concentration (which are reached only directly after the catalyst and likely not