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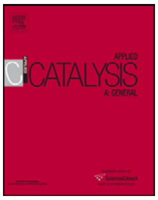

# Behavior of titania-supported vanadia and tungsta SCR catalysts at high temperatures in reactant streams: Tungsten and vanadium oxide and hydroxide vapor pressure reduction by surficial stabilization

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ABSTRACT

In order to meet impending regulations for soot and $NO_x$ reduction from mobile diesel engines, advanced emission control systems may require SCR catalysts with substantially improved thermal durability. State of the art vanadia-based SCR catalysts are composed of vanadia, tungsta, and possibly silica, present at relatively low mass fraction and supported on high-surface-area titania. Concern over the possible emission of metals such as vanadia from diesel vehicles fitted with vanadia-based catalysts limits their potential utility. Vanadia and tungsta oxide and hydroxide vapor pressures over the bulk oxides under conditions relevant for the simulated lifetime exposure of catalysts in the mobile SCR application were estimated on the basis of literature data, and the vapor pressures can be consequential. For the bulk tungsta and vanadia, the most volatile component is $WO_2(OH)_2$, formed from the reaction of tungsta with water, followed by $V_4O_{10}$ and then $VO(OH)_3$, also a reaction product. An experimental method was developed to measure the vapor-phase transport (a manifestation of vapor pressure) of such inorganic components over real catalysts in representative gas streams by collection on high-surface-area alumina at exposure temperature. In the absence of water at 750 °C, only $V_4O_{10}$ was anticipated as the volatile species. However, no V was observed downstream of the catalyst, so that the vapor pressure of titania-supported vanadia was strongly suppressed relative to the bulk oxide. In the presence of water, the results depended on the support. In the case of a support that underwent substantial loss of surface area during exposure, amounts of W were collected consistent with equilibrium vaporization as $WO_2(OH)_2$. However, the amounts of V collected were below the amount expected based on equilibrium vaporization as either $V_4O_{10}$ or $VO(OH)_3$. Thus, the reaction of titania-supported vanadia with water at high temperatures was also suppressed. The vapor pressures of the vanadia and tungsta, and the extent of their reaction with water, can be reduced by varying degrees by reducing loss of the surface area of the titania support during exposure and by minimizing the mass fractions of the surficial oxides. New, highly stable titania supports with optimized compositions were found to virtually eliminate the loss of vanadia and tungsta.

## 1. Introduction

Emission standards for mobile diesel engines are becoming increasingly stringent. The selective catalytic reduction (SCR) of $NO_x$ with urea is currently employed on a commercial basis, and the technology is expected to become even more widespread in the near future [1,2]. Vanadia-based SCR catalysts are approved for on-road mobile applications on heavy-duty diesel trucks in Europe to meet Euro IV (2005) and Euro V (2008) regulations. However, the vanadia-based catalysts are not approved for on-road use in the U.S. by the Environmental Protection Agency, or in Japan. This lack of approval stems from the concern over the potential toxicity that might arise from exposure to vanadia emitted from the tailpipe [3]. Furthermore, impending regulations for soot and $NO_x$ (e.g., Euro VI and U.S. 2010) may necessitate the use of a diesel particulate filter (DPF) in tandem with an SCR catalyst, and possible configurations include combining the SCR catalyst together with, or immediately downstream of the DPF [4]. Regeneration of the DPF, which involves the combustion of collected soot, can cause high temperature exhaust gas to pass over the SCR catalyst. Thus, there has been much emphasis in the industry on developing SCR catalysts with improved thermal durability [5]. Cavataio et al. [6] developed a bench-scale accelerated aging protocol to simulate the useful lifetime exposure (120,000 miles of on-road use for light- and medium-duty vehicles) of an SCR catalyst positioned downstream from a regenerating DPF. These test

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conditions are $t = 670\,^\circ$C, time = 64 h, with a water partial pressure of 5 vol%.

Commercial vanadia-based SCR catalysts for mobile applications consist of intimate mixtures of $V_2O_5$, $WO_3$ and possibly $SiO_2$ supported on relatively high-surface-area anatase-phase titania. Since the melting point of pure bulk vanadia ($V_2O_5$) is 670 °C, it is not unreasonable to expect that this oxide may have appreciable volatility at comparable temperatures. One goal of this work was to determine if the vapor pressures of the relevant catalyst components, vanadia and tungsta, are appreciable under conditions similar to those of accelerated aging tests. A second goal was to explore the impact of experimental parameters on the volatilities of the catalyst components, and a third goal was to develop catalyst materials that exhibit negligible vanadia and tungsta volatilities. Towards the first goal, literature studies on the vaporization of bulk vanadia and tungsta were reviewed in order to determine the nature of the vaporization reactions and their equilibria.

### 1.1. *Vapor pressures of bulk $WO_3$ and $V_2O_5$*

The melting point of pure bulk monoclinic tungsta ($WO_3$) is 1472 °C. The vapor pressure of this oxide has been previously measured at elevated temperatures by Blackburn et al. [7] over the temperature range 1068–1308 °C, and Meyer et al. [8] over the temperature range 1127–1227 °C, with reasonably good agreement. $WO_3$ sublimes according to the equilibrium:

$$3WO_3(s) \rightarrow (WO_3)_3(g) \tag{1}$$

Investigation of the vapor in equilibrium with $V_2O_5$ over the temperature range of 730–932 °C by Farber et al. [9] revealed the following equilibria:

$$2V_2O_5(l) \rightarrow V_4O_{10}(g) \tag{2}$$

$$2V_2O_5(l) \rightarrow V_4O_8(g) + O_2(g) \tag{3}$$

The equilibrium constant for reaction (3) is orders of magnitude lower than for reaction (2), and the equilibrium will be suppressed by the presence of oxygen in an exhaust stream.

In the treatment of exhaust gases, water is present in the vapor phase, and both tungsta and vanadia may react with it at high temperatures to form volatile hydroxides. The vapor pressure of tungsta in the presence of water vapor at high temperatures was studied by Glemser and Ackerman [10] over the range 400–900 °C, and Meyer et al. [11] over the range 1121–1246 °C. Tungsta reacts with water vapor according to:

$$WO_3(s) + H_2O(g) \rightarrow WO_2(OH)_2(g) \tag{4}$$

Glemser and Ackerman [10] identified the hydrous oxide product using mass spectrometry.

Finally, the vanadia–water system over the temperature range 639–900 °C and water partial pressure range from 13 to 100 vol% was studied in detail by Yannopoulos [12]. While this temperature range is relevant for the mobile application, it should be noted that the water partial pressure range is higher than that (5 vol%) typically used in accelerated aging protocols for SCR catalysts [6]. Vanadia reacts with water to form a volatile hydroxide according to:

$$V_2O_5(s) + 3H_2O \rightarrow 2VO(OH)_3(g) \tag{5}$$

Equilibrium constants for the reactions in (4) and (5) are given in Eqs. (6) and (7), respectively, where $p_{(x)}$ is the partial pressure of compound $x$:

$$K_{(WO_2(OH)_2)} = \frac{p_{(WO_2(OH)_2)}}{p_{(H_2O)}} \tag{6}$$

**Table 1**
Coefficients for Eq. (8).

| Species | Ref. | $A$ | $B$ | T. Range[a] |
|---|---|---|---|---|
| $(WO_3)_3$ | [7] | 23590.5 | 11.830 | 1314–1581 |
| $(WO_3)_3$ | [8] | 24585.0 | 15.640 | 1400–1500 |
| $V_4O_{10}$ | [9] | 5109.6 | −0.891 | 1003–1205 |
| $V_4O_8$ | [9] | 24505.0 | 9.042 | 1003–1205 |
| $WO_2(OH)_2$ | [10] | 8399.0 | 3.760 | 673–1173 |
| $WO_2(OH)_2$ | [11] | 5630.0 | 1.833 | 1121–1246 |
| $VO(OH)_3$ | [12] | 9619.1 | −0.225 | 912–1173 |

[a] K.

$$K_{(VO(OH)_3)} = \frac{p^2_{(VO(OH)_3)}}{p^3_{(H_2O)}} \tag{7}$$

The equilibrium constants for reactions (1) through (5) as a function of temperature have the form:

$$\text{Log}\, K_{(x)} = \left(\frac{-A}{T(K)}\right) + B \tag{8}$$

The values for the parameters $A$ and $B$ obtained from the literature are given in Table 1.

The calculated values for the equilibrium vapor pressures of $(WO_3)_3$, $V_4O_{10}$, $V_4O_8$, $WO_2(OH)_2$ and $VO(OH)_3$ for conditions of interest ($T = 650$–$850\,^\circ$C, 5 vol% $H_2O$) are given in Fig. 1, below.

The following observations can be made. First, the vapor pressure of anhydrous tungsta is several orders of magnitude lower than that for anhydrous vanadia. Second, the vapor pressure for the vanadium hydroxide is lower than that for the anhydrous vanadia, and lastly, the vapor pressure for the tungsten hydroxide is orders of magnitude higher than that for the anhydrous tungsta. The results of Meyer et al. [11] for tungsten hydroxide are extrapolated to lower temperature here, and are higher than those actually measured by Glemser and Ackerman [10] at these temperatures. Glemser and Haeseler [13] also measured the vapor pressure at higher temperatures, and at a temperature of about 1100 °C, the results agree with those of Meyer. However, the slopes of the curves are different, resulting in the noted disparity at lower temperatures. For the present work, the values of Glemser and Ackerman [10] are used for reference as a worst case scenario. Nonetheless, it can be concluded that in a system containing both tungsten and vanadium oxides in the presence of water at high temperatures, $WO_2(OH)_2$ and $V_4O_{10}$ are the predominant vapor species followed by $VO(OH)_3$, while $(WO_3)_3$ and $V_4O_8$ are negligible. In this work, an experimental investigation of the volatility of vanadia and tungsta supported

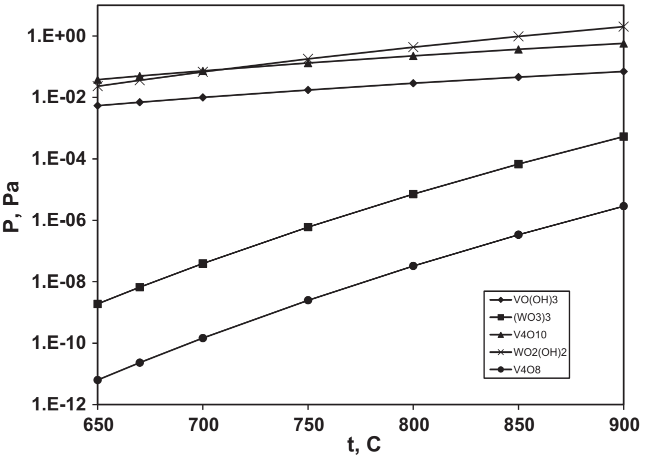

**Fig. 1.** Vapor pressures of various species over the bulk oxides with 5 vol% $H_2O$ and $O_2$, balance inert gas: crosses, $WO_2(OH)_2$; triangles, $V_4O_{10}$; diamonds, $VO(OH)_3$; squares, $(WO_3)_3$; circles, $V_4O_8$.