Fundamental chemistry of V-SCR catalysts at elevated temperatures

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ABSTRACT

Understanding the structural properties of vanadium at high temperatures for vanadia-based SCR at nearly monolayer coverage is an important topic, which has influence on e.g. automotive applications. Nowadays, improved, stabilized Anatase combined with profound technical insights makes high and low temperature behavior of V-SCR significantly better. However, the equilibrium between surface anchored $V^V = O$ and interstitial V^{4+} species intercalated into the TiO_2 matrix is changed during a thermal runaway of the catalytic system in question, and vanadium catalyzes Rutilation of the Anatase. Hydrothermal aging of the V-SCR catalyst is not related to vanadium evaporation, but to changes of the surface chemistry. Our observations were achieved by using in-situ Raman spectroscopy at relevant temperatures and gas conditions, showing that the vanadia-tungsta catalyst is stable under hydrothermal conditions at 550 °C and that a $V_XTi_{1-X}O_2$ phase is formed during thermal runaway of the catalyst, exemplified by exposure of an excess monolayer vanadia titania model catalyst to 750 °C. These observations, combined with new achievements at low temperature for corrugated monolithic catalysts at 200 °C reveal that vanadium based catalysts remain a robust, cost efficient and sulfur tolerant solution for automotive exhaust gas cleaning meeting future demands.

1. Introduction

The implementation of catalysts for off-gas treatment, e.g. exhaust from automotive sources, is carried out by adding catalytically active materials to a monolithic structure, whereby diluted contaminants can be cleaned due to the efficient gas to solid contact combined with acceptable low pressure drops. In this work, we focus on the application of catalysts based on vanadia-titania systems for the Selective Catalytic Reduction (V-SCR) reaction:

$$4NO + 4NH3 + O2 \rightarrow 4N_2 + 6H2O \qquad (1)$$
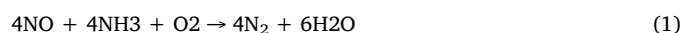
Supported V- based catalysts have a long history and have been studied extensively in many contexts [1]. In general for SCR, the catalyst works by reacting ammonia adsorbed on Lewis and Brønsted acid sites with loosely bound or gas phase NO in a de-facto Eley-Rideal type of mechanism [2,3].

V-SCR has many favorable attributes when compared with other technologies such as Cu-zeolites. V-SCR catalysts are sulfur- tolerant, which is an advantage particularly for countries such as China along with Brazil, Russia, India and Mexico (the so-called BRIM countries) where ultra-low S-diesel is not yet readily available [4–6]. Cu-based zeolite catalysts suffer significant deactivation due to even low concentrations of S exposure and require high temperature (T > 500 °C) regeneration in order to regain initial activity [7–9]. Additionally, at

low temperatures, zeolite-based SCR catalysts generate significantly more N_2O than V-SCR catalysts [10]. N_2O is a strong greenhouse gas and Greenhouse Gas (GHG) emissions mandates are already in place in many places including the US and EU [11]. The low cost of V-SCR catalysts compared with the very expensive zeolite catalysts makes them more accessible in areas where economics may be a concern. Previously, Cu-zeolite based catalysts have had the advantage of a very high activity for NOx conversion at low temperatures (200 °C). However, new developments in V-SCR catalysts show them to be closing in on the low temperature activity gap as shown below. Vanadium based catalysts were originally developed for medium temperature stationary applications, where high temperature stability and low temperature activity were of less importance. Therefore, new fundamental and applied research have been necessary in order to transform vanadium-based systems into an attractive solution also for automotive catalysis. In this work we report on modern V-SCR catalysts with improved carriers that, as seen by in situ Raman spectroscopy, are stable in hydrothermal conditions at 550 °C. Furthermore, we revisit the phenomenon of vanadium's tendency to catalyze sintering and Rutilation at high temperatures by intercalation forming the black $V_XT_{1-X}O_2$ phase, [12,13] and put in the context of explaining the fate of vanadia during a thermal runaway of a catalytic system. Raman spectroscopy is essentially the most useful method for acquiring structural information on the surface of e.g. V-SCR catalysts at the molecular level [12,14–17]. It

provides details about bulk as well as surface species, and when used correctly, Raman spectroscopy is among a few characterization tools that can provide this information about heterogeneous catalysts under in-situ reaction conditions. One major advantage for Raman spectroscopy is that it can detect the very weak signals of materials that are x-ray amorphous (e.g., metal oxide crystallites smaller than around 4 nm). This can provide fundamental knowledge of vanadia speciation and their relation to catalyst stability. Raman fingerprints of dispersed active metals, e.g. $(TiO)_X VO_3 H$ and promotors, e.g. $(TiO)_X-WO_3$ can be clearly identified alongside crystalline materials such as the carrier (TiO_2) or sintered, crystallized active metal oxides, such as $V_2O_5(s)$ and $WO_3(s)$. Here we present novel in situ aging studies of V-SCR catalysts using a recently developed new method to homogeneously fluidize particles inside a Linkam CCR1000 micro-reactor, such that they are monitored by in situ Raman spectroscopy without the drawback of laser heating or damage [12]. In this way temperature gradients and sampling issues were completely eliminated and a trustworthy analysis of the Raman could thus be carried out.

2. Materials and methods

2.1. In situ Raman spectroscopy

Around 20 mg sieved fractions (0.15–0.3 mm) of the samples were transferred to a Linkam CCR1000 reactor based on a 10 mm alumina tubular oven heated by enrolled kanthal wire (setup shown in Fig. 1 [18].)

The sample holder holds the sample by means of a quartz wool mat, and a controlled gas atmosphere of 1.3% H_2O and 10% O_2 balanced in He was passed through the fluidizing sample. The V-SCR catalyst sample used for the study was a corrugated monolith core 50 mm in diameter and 76 mm in length with a metal oxide surface density of around 3 V/nm^2 and 3 W/nm^2.

The sample was exposed for a total of 110 h to the hydrothermal conditions at 550 °C, while acquisition of Raman spectra was carried out with a 633 nm laser with 5 mW laser power at the sample focus. The fluidization caused the sample to be somewhat in and out of focus, and half hour sample times were used for each sampling point.

For the study of the non-promoted crystalline vanadia containing vanadia-titania sample, a 45 m^2/g 10% V_2O_5/TiO_2 sample was used, produced by impregnating TiO_2 with oxo vanadium oxalate incipient wetness method. The vanadium content corresponds to 2.5 monolayers of vanadia (20 V/nm^2). This sample was exposed to the hydrothermal conditions for 22 h at 550 °C with continuous acquisition of spectra. Thereafter the sample was heated to 750 °C and kept for an hour and

cooled to room temperature in the cell before acquisition of the last spectrum.

2.2. SCR activity measurements

The activities were measured in monolithic form with 5–10% H_2O, 14–20% O_2, balance of N_2, NHSV of 50000 h^{-1}, 500 ppm NO and an ANR (ammonia to NOx ratio) of 1.2. The relative apparent k-values given in Fig. 2, which are overall design parameters for the kinetics of the entire monolithic systems rather than intrinsic values, were elaborated from $k_{overall} = -GHSV \cdot \ln(1-x)$

3. Results

3.1. V-SCR activity evolution

As mentioned above, we are utilizing modern V-SCR catalysts with optimized carriers, in this case TiO_2, such that high temperature stability and access to high activities at low temperatures are achievable. This has led to an evolution of activity as can be seen in Fig. 2. This evolution means that V-SCR exhibits sufficient low temperature activities to work inside a EURO VI configuration, with e.g. passive regeneration. Note that the catalysts used here consist of sub-monolayer coverages of V_2O_5 and WO_3 and thus at 200 °C the selectivity is 100%.

3.2. In situ raman spectroscopy

The Raman spectra for the catalyst aging study at 550 °C is shown in Fig. 3. If significant changes with respect to vanadia over time at 550 °C should occur it is expected that the V = O stretch at 1025 cm^{-1} would vanish significantly, which would be a general sign of a deactivated catalyst. But both the V = O and the tungstanyl stretch, W = O at 1010 cm^{-1}, appear unchanged. The spectra were normalized to the TiO_2 band at 630 cm^{-1}, and apart from a small baseline shift during the first 10 h, probably due to a small initial sintering effect, no significant changes are observed. The spectral contributions around 940 cm^{-1}, where an increase would have suggested an increase of the V–O–M (M = W, V, Ti) bands appear stable. Furthermore, there is no formation of surface vanadates around 970 cm^{-1}. Other V–O–M, W–O–M and $WO_3(s)$ features expected around 800 cm^{-1} is observed relative to the TiO_2 signal. This implies strongly that the VO_X is stable on the surface at 550 °C, especially since the stretching frequency of the V = O stretch is sensitive to the vanadia surface density and thus a red shift (to lower frequencies) of the V = O band in the Raman spectra would imply lower surface density of vanadium due to loss of vanadia.
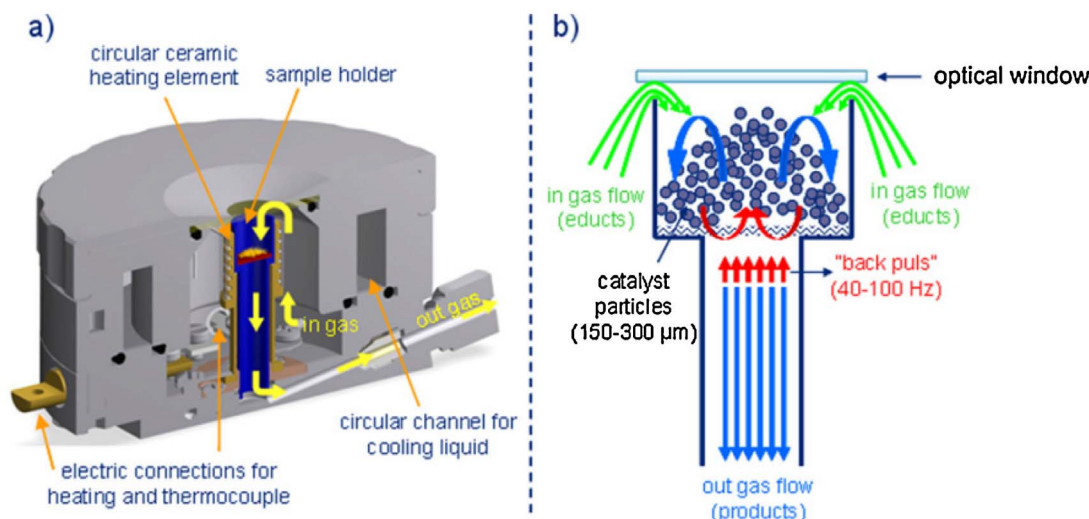

Fig. 1. (a) Linkam CCR1000 reactor (b) sample holder schematic drawing with flow directions illustrated. Reprinted with permission from [18].
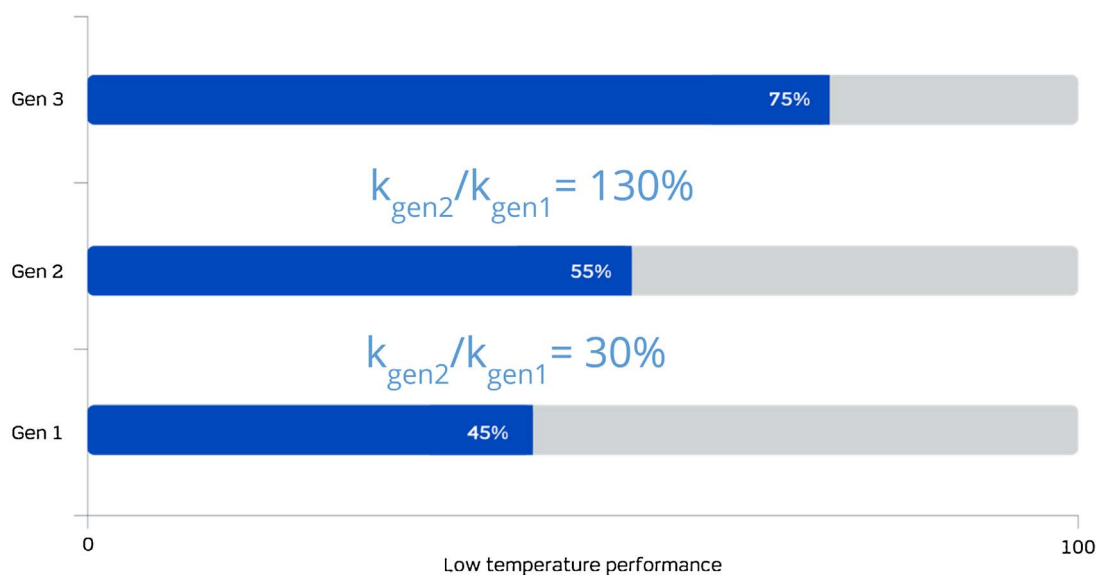
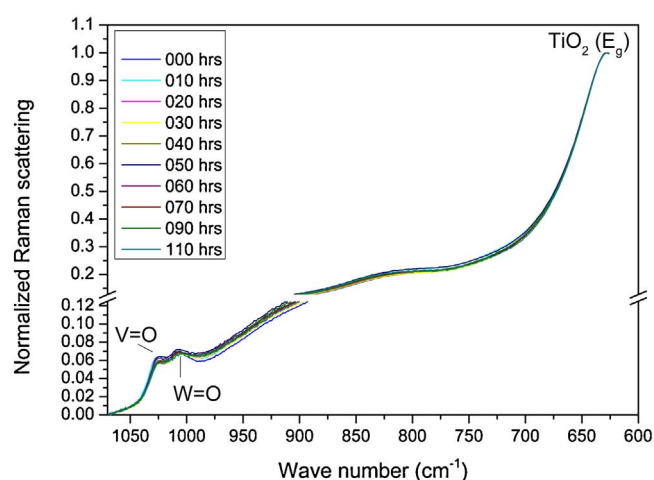Fig. 2. SCR conversion at 200 °C showing the activity evolution. SV: 50000 h^{-1}, 500 ppm NO, ANR 1.2.

Fig. 3. Raman spectroscopic study of the stability of V = O, W = O, V–O–M, W–OM and WO$_3$ peaks after aging for 110 h at 550 °C in 1.3% H$_2$O/Air.

Fig. 4. Stability of the nanocrystalline V$_2$O$_5$(s)/TiO$_2$ model sample after 12 h at 550C.

On the other hand, a blue shift (to higher frequencies) would imply agglomeration of vanadium due to sintering, which would eventually form crystalline V$_2$O$_5$ (s), which is thought to be much more volatile than V-O-Ti anchored vanadia.

However, no shifts of the stretching frequencies are observed for V = O and W = O. Thus, it would be safe to conclude that during these conditions the catalyst surface is, in fact, stable. However, the extremely minor possibility exists that there is combined surface sintering and formation of V$_2$O$_5$(s) that evaporates so fast that Raman spectroscopy cannot detect its formation. Though this is highly unlikely due to the high Raman cross section of the VO band (995 cm^{-1}) of nanocrystalline vanadia we decided to further test the short term stability of a model system that in fact contains crystalline V$_2$O$_5$(s). The sample was exposed to identical conditions as the previous catalysts and spectra were acquired in a similar manner.

Even though the sample was intentionally designed to be a less stable model system with high V$_2$O$_5$(s) content without promoter, it is clearly seen that after an initial aging due to the sample being exposed to temperatures above its calcination temperature, the crystalline vanadia maintains its stability at these temperatures within the time frame of 22 h. What in fact is observed during the experiment is an initial sintering of the sample provoking an increase in the amount of
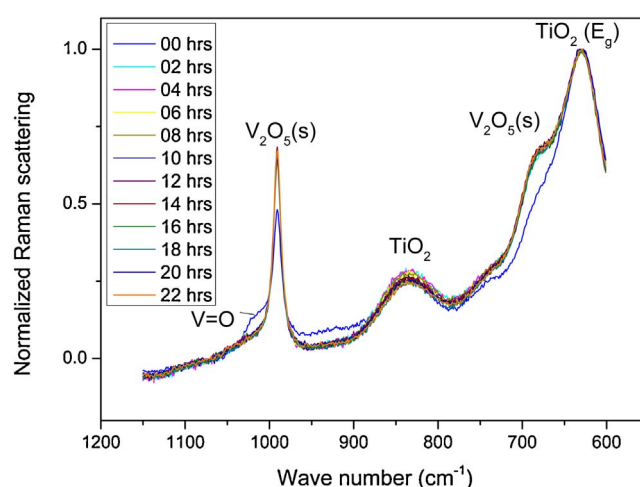
nano-crystalline V$_2$O$_5$(s). This is not surprising given the characteristics of such a non-stabilized model sample. It is, however, conclusive that nano-crystalline vanadia cannot be formed and evaporate quickly on the stabilized catalysts in Fig. 4.

Another point of interest for automotive applications is what happens during a thermal runaway of an exhaust cleaning system. In such a scenario the Diesel Particulate Filter (DPF) and any type of SCR catalysts placed thereafter would be severely harmed and unable to function. However, in the context of high temperature behavior of the V-SCR catalyst it is of interest to know whether vanadium will evaporate or melt into the catalyst itself (the melting point of V$_2$O$_5$ is 670 °C and its boiling point is 2030 °C). Fig. 5 compares the Raman spectra at 550 °C before and after the aging experiment with the spectra at room temperature after exposure to 750 °C. The latter spectrum was acquired at room temperature since black body radiation prevents in situ Raman spectra at this temperature with a 633 nm laser. The V$_2$O$_5$(s) crystals have gone into the TiO$_2$, promoting its conversion into the Rutile phase. A black V$_x$Ti$_{1-x}$O$_2$ phase is formed (confirmed by visual inspection) in combination with a broad band around 1045 cm^{-1}, either due to VO$_X$ dispersed on the hydrophobic Rutile surface or dehydroxylated VO$_X$ on remaining anatase. Alternatively, it cannot be ruled out that small contributions from Si-OH from objectives or quartz-based optics could interfere on this spectrum, especially since
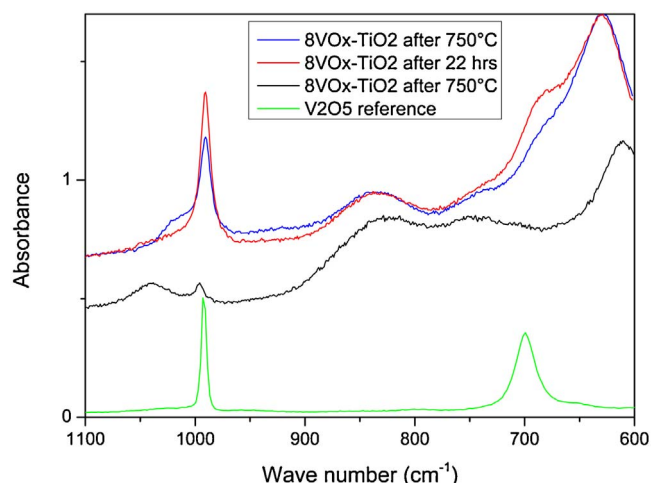
Fig. 5. Raman spectroscopy results of the nanocrystalline $V_2O_5(s)/TiO_2$ model sample, showing formation of $V_xTi_{1-x}O_2$ vanadium titanates in Rutile structure after exposure to 750 °C.

the sample is very dark and thus exhibits poor Raman scattering. In other words, the well-known Rutilation catalyzing effect of vanadia [12] can also be regarded as TiO_2 acting as a V_2O_5 scavenger during thermal runaways. This has been treated in details previously [19] for a similar V_2O_5/TiO_2 catalyst optimized for O-Xylene oxidation to Phthalic anhydride. In the latter study XPS was used to follow the V/Ti ratio on the surface and showed that a little amount of vanadium stayed on the surface, while the main part was intercalated into the Rutile structure via formation of penetrating V^{4+} ions. A weight loss was detected by TGA, which coincided with the loss of oxygen during the transformation of $(M-O)_X-V^V = O$ to V^{4+}. This fully supports our current observations regarding the scavenger effect of TiO_2 on vanadia during thermal runaway.

4. Conclusions

The capability of Raman spectroscopy to decipher surface phenomena for vanadia titania catalyst have been demonstrated. We observe no change in the surface chemistry of vanadia on a commercial type sample at > 100 h at 550 °C. Furthermore, $V_2O_5(s)$ crystals are stable for days under these conditions, so there is no removal of vanadium by the "Le Chatelier's effect". These results show that aging of any V-SCR catalyst is not due to vanadia evaporation. Finally, if suffering a thermal runaway vanadia is prone to disappear from the surface by going into the bulk TiO_2 (and catalyzing Rutilation), so in effect TiO_2 acts as a vanadia scavenger.

Acknowledgements

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