Thermal activation and aging of a $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ catalyst for the selective catalytic reduction of NO with NH_3

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Graphical Abstract

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Highlights

- 2 wt% $V_2O_5/WO_3/TiO_2$ calcined at $450^\circ C$ activated after aging under various conditions
- Low temperature SCR activity was maximum after hydrothermal aging at $550^\circ C$
- Low temperature SCR activity was maximum after thermal aging at $600^\circ C$
- Activation was attributed to change of V coverage and surface acidity

Abstract

Real-world vanadium-based catalysts for the selective catalytic reduction (SCR) of NO with NH_3 are occasionally exposed to high temperatures, which can induce catalyst aging. In this work, a 2.0 wt% V_2O_5/WO_3-TiO_2 catalyst based on commercial WO_3-TiO_2 was lab aged at different time lengths, temperatures, dry and wet feed. Aging carried out in static atmosphere or in flow only marginally influenced its performance, while e.g temperature and water in the feed heavily affected the SCR activity. The low temperature NO conversion ($\leq 300^\circ C$) increased after aging up to $600^\circ C$ for 16 h and was more pronounced after hydrothermal aging compared to thermal aging, which was associated with the increased surface coverage of the SCR-active vanadyl groups. Measurements of vanadium volatility in the temperature range selected for the aging temperatures revealed the high mobility of V species induced by the (hydro-)thermal treatments. The onset of catalyst deactivation, observed at lower aging temperature for the hydrothermally aged catalyst compared to the thermally treated one, is possibly due to a larger amount of mobile V and W species and the concurrent loss of specific surface area. The set of catalytic and characterization data showed that water is an essential component in aging protocols because it heavily affects the structure and the resulting catalytic activity of the SCR catalyst. Removal of residual sulfate groups present on the commercial support above $550^\circ C$ also contributed to catalyst activation as a result of structural changes evidenced by surface area measurements and by IR and Raman spectroscopy, including rearrangement of V species and apparent increase of Lewis acidity.

Keywords: SCR, Vanadium, V_2O_5 , aging, V volatility, activation

1. Introduction

The selective catalytic reduction (SCR) reaction is exploited to convert gaseous NO_x to water and dinitrogen with the addition of NH_3 over a solid catalyst. The most efficient and industrially widespread SCR catalysts are based on vanadium oxide, which is deposited on TiO_2 or $\text{WO}_3\text{-TiO}_2$ [1, 2]. For decades, $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ (VWT) catalysts have been installed in stationary plants and lately also applied in heavy-duty diesel vehicles, where a urea solution is used as a harmless source of NH_3 [3].

In this type of catalysts, the TiO_2 support material is generally present in its anatase polymorph and ca. 10 wt% WO_3 is introduced as a promoter [1, 4-6]. The highly dispersed and redox-active vanadium oxide species [4, 7, 8], usually reported as V_2O_5 , are responsible for the SCR activity and a loading of ca. 1 – 3 wt% V_2O_5 is recommended [2, 9]. Besides the harmful NO_x , the combustion of Diesel fuel generates mainly CO_2 , H_2O and particulate matter. Especially the large amount of water (ca. 10 vol%) influences the performance of the SCR catalysts because of its inhibiting character in the low temperature regime [10, 11]. It is also responsible for improved selectivity at higher reaction temperature [11, 12]. When exposed to high temperatures (above 600°C), a VWT catalyst starts deactivating within hours, an effect that is typically reproduced at lab scale either under thermal [5, 12-14] or hydrothermal [14-18] conditions. A detailed study of the influence of water to the aging at different temperature of V-based catalysts is therefore of importance.

Recently, Kompio et al. [5] investigated the impact of time and temperature during aging in a dry environment on catalyst structure and performance. It was shown that a VWT catalyst (V_2O_5 loading of 0.5-1.5 wt%) can be thermally activated/deactivated at aging temperatures between $600\text{-}750^\circ\text{C}$, depending on the aging time. At 600°C , the VWT catalysts were found to be more active after longer aging times than in the pristine state. At higher aging temperatures, VWT deactivated heavily after 1000 min. An increase of SCR activity upon thermal or hydrothermal aging for low V-loaded VWT was also observed by others [12, 13, 18]. This effect vanishes with higher V loading, but also leads to deactivation effects at low reaction temperatures and selectivity loss at elevated reaction

temperatures. The increased activity upon aging of the catalyst was explained by the morphology change and the formation of bulk WO_3 and polymeric VO_x species, which are often reported as inherently more active than isolated VO_x sites [4, 19-21].

A crucial and disadvantageous property of V-based SCR catalysts is the potential V volatility because of its hazard to human health and the environment [22]. While V itself is not considered toxic, V_2O_5 is listed as a harmful chemical [23, 24]. Increasing amounts of V are typically measured in the offgas downstream of hydrothermally aged V-based catalysts with increasing SCR reaction temperatures, while none is detected in case of dry aging conditions. The overall small amount of released V was justified by the strong V interaction with titania [25]. Similar behavior is also encountered in engine-based volatility tests with the difference that volatilization of small amounts of V occurs already at 500°C under SCR conditions [26].

This work focuses on the influence of the experimental protocols that can be exploited to thermally age a SCR catalyst on the structure and catalytic activity of 2.0 wt% $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ prepared by impregnation of a commercial $\text{WO}_3\text{-TiO}_2$ support [18]. Aging was performed in a muffle furnace (herein termed static aging) and in a plug-flow reactor (dynamic aging) both in the absence and presence of water. After comparing the performance of the aged catalysts and measuring the corresponding V volatility, the catalysts were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller specific surface area measurements (BET), temperature programmed reduction ($\text{H}_2\text{-TPR}$), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and Raman spectroscopy.

2. Materials and Methods

2.1 Materials and catalyst preparation

TiO_2 (CristalActive DT-51D, 0.6 wt% SO_3) and $\text{WO}_3\text{-TiO}_2$ (WTi, CristalActive DT-52, 10 wt% WO_3 and 90 wt% TiO_2 ; 1.35 wt% SO_3) were kindly provided by Cristal Global. Ammonium metavanadate was purchased from Sigma Aldrich (NH_4VO_3 ; assay $\geq 99.0\%$).

The catalyst was prepared by wet impregnation of commercial WO₃-TiO₂ labelled as WTi (10.0 g) with NH₄VO₃ (eq. to 2.0 wt. % V₂O₅) dissolved in H₂O (20 mL), which was added to an 80 mL aqueous slurry of WTi. After the slurry was sonicated for 10 min in an ultrasonic bath and stirred for 60 min, water was evaporated under reduced pressure and the sample was dried at 120°C for 4 h. The sample was ground thoroughly and was calcined at 450°C for 3 h in a muffle furnace. For washcoating the honeycomb monoliths (cordierite, 400 cpsi, ca. 12 × 17 × 50 mm), the powders were suspended in a mixture of water (3 eq. of catalytic material) sonicated for 10 min in an ultrasonic bath and homogenized with a disperser (Micra D-8, 20000 rpm, 5 min). The monoliths were repeatedly immersed in the slurry and dried with an air blower to reach a loading of the active material of around 130 g/L. The monoliths and the remaining slurry were dried and calcined at 450°C for 10 h in a muffle furnace (V-WTi, fresh catalyst).

2.2 Catalytic measurements

The washcoated monoliths were tested on a laboratory test reactor [27, 28] under a feed of 10 vol% O₂, 5 vol% H₂O, 500 ppm NO, 0 - 600 ppm NH₃ with balance N₂ (ca. 500 L/h at STP), in order to mimic realistic exhaust gas composition. The gas hourly space velocity (GHSV = volumetric gas flow/coated monolith volume, STP) was 50,000 h⁻¹, which is typical of SCR converters of Diesel vehicles [27]. The NO_x conversion was calculated according to eq. 1 [29, 30]:

$$NO_x \text{ conversion} = \frac{C_{NO}^{in} - C_{NO_x}^{out}}{C_{NO}^{in}} \cdot 100\% \quad (1)$$

where C_{NO}^{in} is the NO concentration upstream of the catalyst and $C_{NO_x}^{out}$ the sum of the NO and NO₂ concentrations downstream of the catalyst. Online gas analysis of the exhaust gas was performed with a Fourier transform infrared spectrometer (Nexus 670 ThermoNicolet, ThermoFisher) equipped with a heated gas cell. The maximum NO_x conversion was measured by optimizing the NH₃ dosage (NH₃/NO_x = 0 - 1.2). The excess of NH₃ is utilized

to achieve a maximum NO_x conversion that is not affected by possible side reactions of NH_3 . It further ensures a maximum NH_3 surface coverage at elevated reaction temperatures [31]. In order to obtain a more practice-oriented value for SCR systems, the NO_x conversion at 10 ppm NH_3 slip was measured as well [2, 28, 32]. The mass-specific rate constant (k_{mass}) for the maximum NO_x conversion was calculated according to eq. 2, under the assumption of a pseudo-first order of the SCR reaction with respect to NO and zeroth order with respect to NH_3 [2, 30, 31],

$$k_{mass} = -\frac{V^*}{A} \cdot \ln(1 - X_{\text{NO}_x}) \quad (2)$$

where V^* is the total flow rate at reaction conditions (in cm^3/s), A the washcoat loading (in g) and X_{NO_x} the fractional NO_x conversion. Although adsorption of both NH_3 and NO occurs at low temperature [2], NH_3 adsorption dominates on acidic SCR catalysts thus justifying the first order SCR reaction with respect to NO. The rate constant is independent of the catalyst loading, which is particularly important for coated monoliths where small loading deviations are unavoidable. It should be noted that k_{mass} is a parameter used for the sake of comparison of the catalysts and not to derive kinetics quantitatively. Only k_{mass} values at 250°C were used for the comparison. Above $250 - 300^\circ\text{C}$, diffusion limitations and NO_x conversion close to 100% hinder the use of this parameter. The k_{mass} normalized by the BET specific surface area is provided as k_{BET} (k_{mass}/BET).

2.3 Aging procedures

Monolithic catalysts were aged according to four different experimental protocols, namely static thermal, static hydrothermal, dynamic thermal and dynamic hydrothermal aging. Static aging was performed in a muffle furnace. For the static hydrothermal aging, ca. 10 vol% water was introduced into the muffle furnace by means of a saturated N_2 flow. The reactor for the dynamic aging was a quartz glass tube of 22 mm internal diameter similar to that used for SCR activity measurements, with a preheating section filled with steatite

pellets followed by a section comprising the catalyst sample. The reactor was divided into three independent heating sections controlled by separate heating coils. This ensured that the temperature remained constant over the entire length of the monolith. Dynamic aging was carried out under a continuous flow of 10 vol% O₂ (and 10 vol% H₂O for hydrothermal aging) in N₂ (GHSV= 10,000 h⁻¹). The same temperature ramp (10°C/min) and identical dwell time (16 h) were used for both protocols. Both aging set-ups were calibrated at each aging temperature in order to ensure that the two protocols were comparable.

2.4 Vanadium volatility

The vanadium volatility was measured on a new dedicated laboratory setup representing an evolution compared to that presented previously by our group [33]. The setup consists of a heated quartz glass reactor equipped with a sampling quartz tube (d_i = 6 mm) orthogonal to the flow direction and positioned directly after the honeycomb sample. The sampling tube allowed to pass 2 - 3 L/h at STP (total $\cong$ 3 - 4 m³ gas) of the feed to the catalyst through a γ -Al₂O₃ bed (Alfa Aesar 43823; 200 mg; grain size, 0.425 - 0.7 mm) firmly fixed between two plugs of quartz wool (10 mg at the inlet, 100 - 150 mg at the outlet). Vanadium vapors were collected on the alumina bed while exposing the honeycomb sample to a continuous feed of 10 vol% O₂, 500 ppm NH₃ and 500 ppm NO (bal. N₂; 690 L/h at STP; GHSV= 35,000 h⁻¹) at 550, 600 and 650°C for 24 h, which is equivalent to the experimental protocol for dynamic aging. Water (5 vol%) was added to reproduce wet conditions. The amount of vanadium trapped by alumina and the quartz wool plugs was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) upon digestion in HNO₃ (1 mL, 65 vol%)/HCl (1 mL, 30 vol%)/HF (0.16 mL, 40 vol%)/H₂O (2 mL) under shaking in boiling water bath for 2 h. After cooling, HCl (0.2 mL, 30 vol%) and water were added to a total volume of 10.0 mL prior to analysis.

2.5 Characterization methods

Powder X-ray diffraction (XRD) patterns were collected on a D8 ADVANCE (Bruker) diffractometer using Cu K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$). Data were recorded from 10° to 65° 2θ using a step size of $0.03^\circ/\text{s}$ acquisition time. The phases were identified with the X'Pert HighScore Plus software. The average crystallite size ($D_{p,XRD}$) of TiO_2 was determined by the Scherrer equation (eq. 3) using the peaks at 25.4 and at 48.0° [34],

$$D_{p,XRD} = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

where λ is the wavelength of X-ray, θ the diffraction Bragg angle and $D_{p,XRD}$ is the corrected peak width at half maximum.

The specific surface area (SSA) was measured by N_2 adsorption at -196°C on a Quantachrome Autosorb I instrument using the Brunauer-Emmett-Teller method (BET, [35]). Prior to the measurement, the samples were outgassed at 350°C for 4 h. For the calculation of the BET-SSA, eleven points were selected in the pressure range of 0.05-0.3 P/P_0 as it is generally applied in the case of mesoporous materials.

The surface density (ρ_v , V atoms/ nm^2) of the vanadium oxides covering the TiO_2 surface was calculated according to eq. 4 [36]:

$$\rho_v = \frac{\frac{N_A * x_V}{MW}}{SSA * 10^{18}} \quad (4)$$

where N_A is Avogadro's number, x_v the weight fraction of V_2O_5 , SSA the specific surface area and MW the corresponding molecular weight.

The fractional monolayer coverage (ζ) was calculated from the surface density (ρ_v) and the theoretical monolayer coverage (ρ_m ; $7.9 \text{ VO}_x \text{ nm}^{-2}$ [37]) according to eq. 5 [38].

$$\zeta = \frac{\rho_v}{\rho_m} \cdot 100\% \quad (5)$$

Diffuse reflectance Fourier transform infrared (DRIFT) spectra were measured using a Vertex 70 spectrometer (Bruker) equipped with a liquid N_2 cooled MCT detector and a Praying Mantis mirror unit (Harrick). The homemade DRIFT cell was equipped with a flat

CaF₂ window ($d = 25$ mm; 2 mm thick) and was connected to gas supply lines. The catalyst powder was finely ground and softly pressed in the sample holder of the cell. Prior to the experiments, the samples were dried *in situ* in 10 vol% O₂ (100 mL/min, bal. Ar) at 400°C for 1 h. After cooling to 250°C, a background spectrum was collected prior to admittance of ammonia. NH₃ adsorption was followed during exposure to a flow of 500 ppm of NH₃-5 vol% O₂ (100 mL/min, bal. Ar) at 250°C for 15 min. All spectra were collected by accumulating 100 scans at 4 cm⁻¹ resolution and a scanner velocity of 80 kHz.

Raman spectra were recorded with a Raman spectrometer (CW Raman RXN1, Kaiser Optical Systems) equipped with a 785 nm diode laser (Invictus 785 nm NIR Laser), a charge-coupled device detector (CCD, 1024 × 256 EEC MPP Type, Kaiser Optical Systems) cooled to -40°C and a PhAT-system probe-head (Kaiser Optical Systems) with collimated incident radiation and a sampling spot-size diameter of ca. 3 mm. The spectra were collected with an average laser power of ca. 300 mW by averaging 85 scans at 2 cm⁻¹ resolution and an exposure time of 2 s. Spectra were obtained at ambient conditions, at 250°C in 5 vol% O₂ and at 250°C in 5 vol% O₂-2 vol% H₂O (balance Ar) after dehydration in 10 vol% O₂ at 400°C for 1 h as described above.

3 Results and Discussion

3.2 Catalytic activity

Figure 1 shows the NO_x conversion of 2.0 wt% V₂O₅/WO₃-TiO₂ (V-WTi) after dynamic hydrothermal aging at 700°C for 0, 5, 10 and 16 h. The temperature was selected to ensure a severe deactivation of V-WTi [12]. In the fresh state (calcination only at 450°C, 0 h at 700°C), the activity increased between 200 and 300°C and over 90% NO_x conversion was found between 350 and 500°C. Above 500°C, the NO_x conversion started diminishing, which is a sign of loss of selectivity due to NH₃ oxidation [5, 13].

Aging at 700°C for 5 h caused the NO_x conversion to decrease substantially already above 400°C, whereas NO_x conversion was slightly but consistently higher in the low temperature regime. This activation at low reaction temperature is more evident in Figure 1b showing that the mass specific rate constant values, k_{mass} , for the catalyst aged for 5 h was larger than that of the one in the fresh state, a phenomenon that was recently proposed [5] to originate from the formation of polymeric V-O-V from isolated VO_x species.

Aging affected the NO_x conversion at 10 ppm NH₃ slip more than the maximum NO_x conversion. This is an indication that the overall NH₃ storage capacity and the related surface acidity decreased, thus lowering the capability of the catalyst to deliver NH₃ to the active sites for the SCR reaction [18]. Longer aging at 700°C (10 h) deactivated the catalyst severely in the entire temperature regime, an effect that was intensified by extending the aging to 16 h. It is evident from Figure 1 that the aging time at a given temperature should be selected carefully for the study of these catalysts because after too short aging times the maximum activity of an aged V-WTi catalyst may not have been developed. Consequently, an aging time of 16 h was chosen in this work for all aging protocols.

The impact of thermal and hydrothermal aging in a muffle furnace on the catalytic activity of V-WTi is compared in Figure 2. The four identically prepared monolithic catalysts exhibited virtually the same NO_x conversion in the fresh state (Figure 2a), confirming the consistency and reproducibility of the preparation method and the measurements with the lab scale test rig. The activity measurement was repeated for the four different aging protocols on V-WTi aged at 550, 600 and 650°C for 16 h (Figure 2b, 2c and 2d, respectively; Figure S1). The catalytic activity data are visualized again in Figure 2e using the corresponding k_{mass} values obtained at 250°C (including also the k_{mass} values after aging at 700°C). It is obvious from Figure 2b and Figure 2e that irrespective of the aging protocol, the catalysts exhibited higher maximum NO_x conversion and NO_x conversion at 10 ppm NH₃ slip after aging at 550°C than after calcination at 450°C. The presence of water during aging activated the catalyst to a larger extent. While hydrothermal aging in static or dynamic conditions equally affected the activity of the catalyst (Figure

S1), it is evident that aging at 550°C in wet conditions activated the catalyst to a greater extent than in the absence of water (Figure 2e). Hence, the presence of water in the gas environment during aging is critical for catalyst activation.

Thermally aged V-WTi was more active than hydrothermally aged V-WTi at 600°C (Figure 2c), which is opposite to the trend observed at 550°C. Aging in dry conditions further activated the catalyst and resulted in similar k_{mass} values to those obtained after hydrothermal aging at 550°C (Figure 2e). The hydrothermally aged sample started to deactivate when aged at 600°C. It seems plausible that water in the gas environment during aging accelerates the activation as well as the deactivation process of V-WTi. The enhanced mobility and diffusion of hydroxylated V and W species on the catalyst surface [25] can be considered the source of this phenomenon, which generates activated catalysts after calcination at higher temperature (550°C) than after synthesis (450°C) but causes also deactivation tendencies at 600°C.

Finally, aging at 650°C (Figure 2d) and 700°C (Figure 1a for hydrothermal aging, not shown for thermal aging) in the presence and absence of water deactivated V-WTi to a comparable extent. The catalysts started to deactivate in the low and the high temperature regime. Also, the NO_x conversion at 10 ppm NH₃ slip started to be reduced significantly, indicating the onset of loss of surface acidity [39].

3.3 Vanadium volatility

The V release of V-WTi at 550, 600 and 650°C in the presence and absence of water is presented in Table 1. At 550°C, the V release in wet conditions (2.1 µg/m³) was twice that measured in dry conditions but still very limited. At 600°C the value obtained in wet conditions increased significantly to ca. 50 µg/m³ confirming the remarkable effect of water on the V release [25]. This was even more evident at 650°C, where V-WTi released ca. 6 times more V at wet conditions (201 µg/m³) than at dry conditions. Despite these apparently large values, we note that the absolute loss of vanadium from the catalyst

remained below 0.8% of the overall V content and was thus very limited over the course of 24 h. While it is difficult to imagine that this low amount may have an influence on SCR activity, it strongly suggests that the enhanced V mobility with increasing temperature is responsible for the redeployment of surface species to eventually provide a different V speciation compared to the fresh catalyst. Hence, the very low level of V released at 550°C may be taken as indication for an initial change of the structure of V species that is more severe at higher temperatures and involves structural changes responsible for catalyst deactivation. The consequent activation and deactivation was thus further investigated by means of XRD, BET, H₂-TPR and infrared and Raman spectroscopy.

3.4 X-ray diffraction

The XRD patterns of the support material (WTi, Figure 3a), of V-WTi after thermal (Figure 3b) and hydrothermal (Figure 3c) aging are dominated by the anatase TiO₂ reflections, which sharpen with increasing aging temperature as a result of crystallite size growth. The V-WTi samples aged at 700°C also exhibited reflections of rutile TiO₂, whose amount was significantly larger after thermal aging than after hydrothermal aging.

The anatase crystallite size increased continuously up to 650°C, irrespective of the gas composition (Figure 4a), and the increase was steeper after thermal aging than after hydrothermal aging of V-WTi at 700°C. This agrees with the larger extent of phase transformation from anatase to rutile for the thermally aged catalyst. Besides the TiO₂ reflections, a WO₃ phase also appeared after thermal and hydrothermal aging of V-WTi above 550°C (Figure 3b and Figure 3c). Similar to TiO₂, larger WO₃ crystallites were formed after 700°C in the thermally aged catalyst. It is plausible that water partly hinders the WO₃ crystallite growth because of the formation of mobile WO_x species such as WO₂(OH)₂ [25]. No WO₃ reflections were detected in WTi even after aging at 700°C. These observations confirm that V promotes sintering of the support material [18] and the subsequent phase transformation from anatase to rutile [40, 41]. Finally, no reflection from

a V-containing phase was detected. This is generally the case for VWT catalysts because of the high interaction potential between V and TiO_2 , which leads to highly dispersed species [9, 42].

3.5 Surface area

The BET specific surface area of thermally and hydrothermally aged V-WTi decreased continuously with increasing aging temperature (Figure 4a). The surface area dropped notably from the value of the fresh catalyst ($97 \text{ m}^2/\text{g}$) to that of the sample thermally aged at 550°C ($71 \text{ m}^2/\text{g}$) and at 600°C ($53 \text{ m}^2/\text{g}$). Hydrothermal aging had an even more pronounced effect on the values measured after aging at 550°C ($62 \text{ m}^2/\text{g}$) and at 600°C ($45 \text{ m}^2/\text{g}$).

The surface area of V-based SCR catalysts is directly linked to the surface density of VO_x species and, as a consequence, to the catalytic performance [43]. As proposed earlier [18], V-WTi catalysts display optimal performance at a VO_x surface coverage of 25 - 50%. The calculated VO_x coverage for V-WTi in the fresh state was 17% (Table 1) and increased to 24% and 27% for thermally and hydrothermally aged samples, respectively. After aging at 600°C , the VO_x surface coverage increased to 32% (thermal) and 37% (hydrothermal), which are in the optimal coverage range as reflected by the increased activity at this aging temperature.

The correlation between SCR activity and surface area is represented by k_{BET} , the surface normalized specific rate constant ($k_{\text{mass}}/\text{BET}$; Figure 4b). The hydrothermally aged V-WTi activated to a greater extent than the thermally aged V-WTi at 550°C . At 600°C , k_{BET} was highest for both aging gas compositions, slightly more for thermally aged V-WTi. It is interesting to compare k_{mass} (Figure 2e) and k_{BET} (Figure 4b) after hydrothermal aging of V-WTi at 600°C because the values decreased for the former and increased for the latter compared to the values obtained after aging at 550°C . Because the k_{BET} values increased, we conclude that the loss of activity (according to k_{mass}) after hydrothermal aging at 600°C

mainly originates from the loss of surface area, which can induce further changes in the structure of the V and W species. At 650°C, the k_{BET} values also started decreasing (Figure 4b), making it challenging to identify the exact origin of the decrease of catalytic activity. The activation event of V-WTi after aging at 550°C and 600°C can be conclusively correlated to the increase in VO_x surface coverage.

3.6 Spectroscopic investigations

In order to derive structure-activity relationships, spectroscopic methods such as infrared and Raman spectroscopy were applied. H_2 -TPR is an equally popular characterization method for this purpose but was not conclusive about the effect of activation and aging on these catalysts (Figure S2). We found that deconvolution and assignment of the reduction events in TPR is ambiguous and is further complicated by the presence of multiple oxides reducing at comparable temperatures. Spectroscopic methods provide direct indication of the molecular nature of adsorbates (IR) and of surface oxide species (Raman) that are perturbed upon increase of the calcination temperature.

3.6.1 Infrared spectroscopy

In situ DRIFT spectra of WTi in the fresh state and after calcination at 650°C and of V-WTi in the fresh state and after hydrothermal aging at 550°C were recorded during the adsorption of 500 ppm NH_3 at 250°C in O_2/Ar (Figure 5). While adsorbed NH_3 on Lewis and Brønsted acid sites produced positive signals, negative features were produced by the perturbation of the catalyst surface upon NH_3 adsorption. The signals were assigned according to literature [37, 44-49].

Peaks in the spectral region around 3600 cm^{-1} (Figure 5a) are caused by the stretch modes of metal-hydroxyl units ($\nu(M-OH)$). The stretch mode of W-OH groups of WTi consumed by NH_3 was vaguely visible at ca. 3650 cm^{-1} and was absent in V-WTi. Instead, an intense negative feature at 3642 cm^{-1} appeared in V-WTi, which was assigned to $\nu(V-OH)$ [50]. The absence of signals of W-OH groups could be due to interaction of W

with VO_x species or to signal overlap. Upon thermal and hydrothermal aging, a new feature appeared at 3588 cm^{-1} , which is absent in fresh WTi and after calcination at 650°C . The first plausible explanation for the formation of this new metal-hydroxyl group is the loss of surface area (ca. 28% for thermally aged and 35% for hydrothermally aged catalysts), which increases the surface coverages of V and W. Hence, V-(OH)-W bonds could form, which are depleted upon NH_3 adsorption, giving rise to the negative peak at 3588 cm^{-1} . This peak could also originate from hydroxyl groups of polymerized WO_x species. XRD showed that WO_3 agglomerates and forms WO_3 crystallites upon aging (Figure 3). This is more evident for the hydrothermally aged sample and could reflect the higher intensity of the signal at 3588 cm^{-1} in Figure 5a.

Figure 5b reveals the corresponding perturbation of the vanadyl ($2050\text{--}2044\text{ cm}^{-1}$; $2\nu(\text{V}=\text{O})$) and tungstenyl groups (ca. 2012 cm^{-1} ; $2\nu(\text{W}=\text{O})$) in V-WTi and of the tungstenyl groups in WTi. While the $2\nu(\text{W}=\text{O})$ signal did not shift noticeably after aging, the $2\nu(\text{V}=\text{O})$ signal red-shifted by ca. 10 cm^{-1} suggesting that the environment of the tetrahedral vanadyl species ($\text{O}=\text{VO}_3$) changed. Because of the increased vanadium mobility after aging at these temperatures, it is plausible that the O-atoms anchoring the vanadyl groups to the support formed new bonds. The absence of sulfates after aging V-WTi at 550°C as evident from TPR (Figure S2) and from the spectra in Figure 5c could be one reason for this structural change. Another possible reason is the formation of V-O-W bonds postulated above, which could produce the observed red-shift of the $2\nu(\text{V}=\text{O})$ mode. The presence of signals of tungstenyl species makes it difficult to fully disentangle the contributions of the various species in the IR region.

Removal of the sulfates was evident in the DRIFT spectra. The negative peak at ca. 1370 cm^{-1} ($\nu(\text{S}=\text{O})$) during NH_3 adsorption in Figure 5c corresponds to the consumption of the residual sulfate species present on the commercial support by NH_3 [51, 52] and was detected only for fresh V-WTi and WTi. This signal was still present in WTi calcined at 550°C (not shown) and nearly disappeared at 650°C , reflecting the H_2 -TPR profiles (Figure S2) where no reduction signal of sulfate species was detected after calcination at this

temperature. The absence of the negative feature at 1370 cm^{-1} in V-WTi already after aging at 550°C reveals that vanadium promoted the removal of the sulfates upon calcination at this temperature. The removal of sulfates likely affects the acidity of the catalyst. Because sulfated TiO_2 improves NH_3 adsorption [52], thus influencing the SCR activity [19, 53], the extent of the structural change induced by the removal of the sulfate groups should be matter of a systematic study.

Figure 5c also shows NH_3 adsorbed on Brønsted (B_{NH_3} , 1670 and 1430 cm^{-1}) and Lewis acid sites (L_{NH_3} , 1600 and 1270 cm^{-1}). Intensity differences between fresh and aged V-WTi are noticeable (increase of L_{NH_3} and decrease of B_{NH_3}). The L_{NH_3} signal of hydrothermally aged V-WTi ($\text{L}_{\text{NH}_3}/\text{B}_{\text{NH}_3}$ ratio = ca. 0.16) increased to a larger extent than that of the thermally aged sample ($\text{L}_{\text{NH}_3}/\text{B}_{\text{NH}_3}$ ratio = ca. 0.13). This suggests that more NH_3 coordinated to the Lewis acid sites after hydrothermal aging of V-WTi at 550°C . Despite the further structural changes involving surface area and V-coverage, the relative increase in Lewis acid sites was concomitant with the activation of the catalyst (Figure 2e) [54]. It is thus tempting to associate the two phenomena based on recent spectroscopic evidences on the role of Lewis acid sites in this SCR catalyst [55].

Hence, the DRIFT data indicate that a variety of structural changes such as anchoring of the vanadyl species, loss of the sulfates present in this commercial support and an apparent increase of density of Lewis acid sites are responsible for the catalyst activation upon aging of V-WTi at 550°C .

3.6.2 Raman spectroscopy

The Raman spectra of fresh V-WTi and after aging at 550°C are shown in Figure 6. The region between 1050 and 950 cm^{-1} is characteristic for the fundamental vibrational modes of metal-oxo groups of WO_x and VO_x species whose overtones are visible in the DRIFT spectra in Figure 5b. The signal at ca. 983 cm^{-1} in WTi and V-WTi (Figure 6a) was assigned to the $\text{W}=\text{O}$ stretch mode of hydroxylated WO_x [56]. The small blue-shift of this

signal in the V-containing samples is caused by the overlap of the signals of hydroxylated V=O and W=O groups [56, 57]. The band at ca. 1015 cm^{-1} with a shoulder at ca. 1030 cm^{-1} is the most prominent difference between the spectra of the fresh (WTi and V-WTi) and aged (V-WTi) samples in Figure 6a. These features appeared only after aging and were assigned to the W=O and V=O stretch modes of dehydroxylated species, respectively [56-58]. Catalyst aging at 550°C thus generated WO_x and VO_x units, which are less prone to hydroxylation under ambient conditions.

After dehydration at 400°C (Figure 6b), the signals of dehydrated species became visible in the spectra of fresh V-WTi recorded at 250°C in O_2/Ar and intensified in the case of aged V-WTi. The peak at ca. 985 cm^{-1} (hydrated metal-oxo groups) decreased simultaneously. Figure 6b suggests that aging at 550°C increased the density of W=O and V=O groups, which could be used to explain the higher activity measured after aging because of the increase in acidity (increased NH_3 adsorption, best observed by the enhanced NO_x conversion at 10 ppm NH_3 slip, Figure 2b), in surface coverage and in the amount of SCR-active sites (V=O) [54, 59]. However, it should be recalled that this occurred simultaneous to a decrease of surface area (Figure 4a). Since V=O units are crucial for the SCR reaction [1, 11, 54, 60, 61], it is likely that they are involved in the catalyst activation. The intensity of the V=O signal was slightly enhanced for hydrothermally aged V-WTi at 550°C , a further plausible explanation for the significant activation of this catalyst at 550°C (Figure 2b). Water vapor in the aging environment at 550°C is thus capable of restructuring the catalyst and the V=O sites, which is reflected by the higher surface VO_x surface coverage (Table 1). Finally, when water was added to the feed (Figure 6c), a large fraction of the V=O groups remained in the dehydrated form in the aged samples, which was not the case in the fresh V-WTi.

The data indicate that Raman spectroscopy can provide evidence that the activation of V-WTi upon aging at 550°C correlates with the enhanced accessibility of V=O groups through the presence of dehydrated V=O and W=O units and/or more active VO_x sites. The

precise role and structure of this dehydrated form of the vanadyl groups still remains to be studied particularly under reaction conditions.

4 Conclusions

A 2 wt% V_2O_5/WO_3-TiO_2 catalyst was subjected to thermal and hydrothermal aging. While the aging in muffle furnace or in flow reactor did not produce substantial differences, water heavily affected the activity and structure of the catalyst. Aging also induced catalyst activation. Catalytic tests showed that the hydrothermally aged catalyst activated more readily at 550°C. Further increase of the hydrothermal aging temperature also produced deactivation tendencies at 600°C, while the activity of the thermally aged catalyst increased at the same temperature. Above this temperature, all catalysts aged similarly, which was especially visible in the NO_x conversion at 10 ppm NH_3 slip and the reaction rate constant. Differences in catalytic behavior may become evident at shorter aging time. Due to the presence of vanadium, the support material was heavily affected by aging, which was reflected by the increased TiO_2 crystallite size and the formation of crystalline WO_3 .

The activation of the catalysts could be correlated to various structural changes. Infrared and Raman spectroscopic data showed that the SCR activity correlated with changes in the type of surface acidity including removal of sulfate groups from the commercial support by calcination above 550°C and with an apparent increase in the amount of active vanadyl sites by decreasing specific surface area, which is essentially equivalent to an increase of loading of active species. To that end, the VO_x species were found to migrate to new anchoring sites on the catalyst surface. Water is an essential additive in the artificial aging process because it heavily affects the catalytic activity, the thermal stability, the mobility of VO_x and WO_x species, the surface species and the entire morphology of V-based SCR catalysts. Therefore, the structure of a V-based catalyst calcined at low temperature, e.g. 450°C, with the intention to avoid sintering and

restructuring of the V and W phases is not the final one responsible for SCR activity, it is rather its precursor.

Activation is likely the result of a delicate equilibrium between V surface coverage and surface area, which change in opposite directions upon aging. The increase of the former can enhance low temperature activity ($\leq 300^\circ\text{C}$). However, we speculate that the high temperature activity ($> 450^\circ\text{C}$) decreases at the same time, which can be explained by the decrease of selectivity and by the increasing importance of pore diffusion and film transfer limitations with decreasing surface area in the non-kinetically limited regime. It is thus recommended to thermally treat a washcoated SCR catalyst (2 wt% V_2O_5 , commercial $\text{WO}_3\text{-TiO}_2$ support containing low levels of sulfates) at 550°C to generate an activated SCR catalyst of 2 wt% $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ prior to use.

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Figure captions

Figure 1. (a) Maximum NO_x conversion (—) and NO_x conversion at 10 ppm NH₃ slip (---) of V-WTi after time-dependent dynamic hydrothermal aging. (b) Corresponding rate constants k_{mass} calculated at the reaction temperature of 250°C. The line is drawn to guide the eyes.

Figure 2. Maximum NO_x conversion (—) and NO_x conversion at 10 ppm NH₃ slip (---) of V-WTi (a) in the fresh state (for four identical monolith pieces), thermally and hydrothermally aged at (b) 550°C, (c) 600°C and (d) 650°C. (e) Corresponding k_{mass} determined at 250°C for the catalysts aged at the indicated temperature with the different aging procedures.

Figure 3. XRD patterns of (a) WTi and (b) V-WTi after thermal and (c) hydrothermal aging at various temperatures.

Figure 4. (a) BET surface area of WTi (Δ) and V-WTi after thermal ($\blacksquare$) and hydrothermal ($\bullet$) aging and the corresponding crystallite size of TiO₂. (b) k_{BET} at the temperatures indicated.

Figure 5. *In situ* DRIFT spectra of fresh WTi (450°C) and after calcination at 650°C and of fresh V-WTi and after hydrothermal aging at 550°C during adsorption of 500 ppm NH₃ at 250°C in O₂/Ar after 30 min. (a) $\nu(\text{O-H})$ and $\nu(\text{N-H})$ region; (b) $2\nu(\text{V=O})$ and $2\nu(\text{W=O})$ region; (c) deformation modes of adsorbed NH₃ at Lewis and Brønsted acid sites. Catalysts were dried *in situ* at 350°C in O₂/Ar for 1 h prior to NH₃ adsorption. Spectra of fresh V-WTi and WTi-450°C were scaled by 0.5.

Figure 6. Raman spectra of fresh V-WTi and after thermal and hydrothermal aging at 550°C (a) at ambient conditions, (b) in O₂/Ar at 250°C and (c) in H₂O/O₂/Ar at 250°C. A spectrum of fresh WTi

is also shown in (a) for comparison. Spectra recorded at 250°C after dehydration at 400°C as described in the experimental section.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table 1. Gas feed normalized V emissions and calculated VO_x surface coverage values (ζ) of V-WTi at 550, 600 and 650°C.

	gas feed	450°C	550°C	600°C	650°C
V release [$\mu\text{g}/\text{m}^3$] ^a	dry	-	1.0 ± 0.1	1.4 ± 0.1	34.2 ± 5.1
	wet	-	2.1 ± 0.2	49.3 ± 7.2	201 ± 30
ζ [%] ^b	dry	17	24	32	42
	wet	-	27	37	44

^a Measured by ICP-OES. ^b VO_x surface coverage (ζ) calculated according to eq. 4 and 5.