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Effect of SiO₂ on co-impregnated V₂O₅/WO₃/TiO₂ catalysts for the selective catalytic reduction of NO with NH₃

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Graphical Abstract

Highlights:

- Co-impregnation of V and W on TiO₂ generates low temperature active SCR catalysts.
- Co-impregnated V-based catalysts with SiO₂ are stable after aging at 650°C.
- Addition of 4wt% SiO₂ preserves the low temperature activity after aging at 650°C.
- Polymeric SiO₂ entities inhibit the inter-particle contact of anatase TiO₂ units.
- SiO₂ prevents TiO₂ sintering but causes the formation of crystalline WO₃.

Abstract

Co-impregnation of vanadia and tungsta on titania produced highly active catalysts for the reduction of nitrogen oxides with ammonia but showed aging tendencies at temperatures around 600°C. In order to preserve their low temperature activity after hydrothermal aging up to 650°C, the catalysts were enriched with Si during the co-impregnation process using different SiO₂

precursors and amounts. The optimized catalyst composition comprised ca. 4 wt% SiO₂, was stable after aging at 650°C, could preserve the low temperature activity and was more active than the catalysts prepared from commercially available silica-stabilized TiO₂ supports. The origin of the effect of SiO₂ was investigated by XRD, BET, TEM, STEM and ²⁹Si MAS NMR. SiO₂ remained amorphous at all temperatures and 2-4 wt% SiO₂ hampered the anatase crystallite growth at 600°C and 650°C. In contrast to WO₃, SiO₂ was unevenly distributed over the TiO₂ particles and ca. 60-70% of Si was present as bulky amorphous SiO₂ agglomerates after aging at 650°C. Small and extended SiO₂ polymeric entities were identified to be essential for delaying the offset of the catalyst sintering. With the addition of a small amount of SiO₂ in the co-impregnation process, the low temperature activity of these catalysts could be preserved up to an aging temperature of 650°C.

1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia (NH₃) is the most efficient after-treatment technology for reducing NO_x emissions from stationary and mobile sources. In the standard SCR reaction, gaseous NO and NH₃ react over a solid catalyst according to eq. 1 [1, 2]:

The current catalysts used in stationary applications are composed of vanadia-tungsta supported titania (VWT). Anatase TiO₂ acts as the support material, around 10 wt% WO₃ is added as a promoter for surface acidity and catalyst stability and ca. 1-3 wt% V₂O₅ is needed as the redox-active component [3]. For mobile applications, SCR catalysts have to operate under dynamic conditions and need to be thermally stable at least up to 650°C due to the particulate

filter located up-stream of the SCR catalyst that undergoes periodic regeneration at deliberately generated high exhaust gas temperatures [4, 5]. VWT catalysts usually show aging tendencies already at ca. 600°C, which is manifested by the loss of NH_3 selectivity at high reaction temperature and the loss of activity at low reaction temperatures [6, 7]. The deactivation can be partly retarded by lowering the vanadium loading which, however, negatively affects the low temperature activity and is therefore an unsatisfactory solution to gain stability [6]. The stability issue is crucial because SCR catalysts in mobile sources have to be low temperature active due e.g. to more stringent governmental regulations, cold starts and short city driving.

Silicon was proposed to be a valuable promoter for tackling the stability concerns because it delays the TiO_2 sintering [4, 8-15]. The stabilization effect is considered to originate from the distortion of the anatase lattice, the formation of solid solutions, the substitution of Ti^{4+} by Si^{4+} or from the inhibition of molecule diffusion and the reduction of anatase inter-particle contact [16]. All these phenomena possibly hinder the growth of anatase crystallites and the subsequent phase transformation to rutile that is unwanted due to its smaller surface area and lower vanadium dispersion capacity [17]. Chapman et al. tested the stability of various $\text{SiO}_2\text{-WO}_3\text{-TiO}_2$ materials using various precursors and loadings of SiO_2 and WO_3 [8]. After impregnation with 2 wt% V_2O_5 , a support with ca. 5 wt% SiO_2 and 6 – 8 wt% WO_3 was found to be optimal for the catalyst stability. A sol-gel and co-precipitation approach used in other studies and the effect of SiO_2 loading in $\text{V}_2\text{O}_5\text{-SiO}_2\text{-TiO}_2$ catalysts were tested [10, 12]. The catalysts stabilized by 10 – 20 wt% SiO_2 exhibited higher overall stability, lower SO_2 oxidation activity and increased vanadia dispersion reflecting the enhanced SCR activity. Similar observations were also found for catalysts prepared by co-precipitation of V, Mo, Ti and 7 – 13 wt% SiO_2 . Due to the high V loading (8 wt% V_2O_5), the catalyst was active at low temperature and the vanadia species were

in polymeric form [18]. Co-impregnation of V and W on $\text{SiO}_2\text{-TiO}_2$ and TiO_2 showed that both the presence of SiO_2 and the preparation method have a significant effect on activity and stability [13]. In presence of SiO_2 , the support sintering as well as the formation of crystalline WO_3 and V_2O_5 started at higher temperatures. Incipient wetness impregnation of Si and V (1 wt% V_2O_5) on TiO_2 revealed a limited interaction between the two elements, hence the structure of the surface vanadium oxide was not altered by the presence of SiO_2 [19]. SiO_2 in flame-made VWT did not only exhibit improved thermal stability but also prevented the crystallization of tungsten oxide and increased the NO_x reduction efficiency at high temperatures. The low temperature SCR activity was however inferior compared to that of the SiO_2 free catalyst [14]. Summarizing, SiO_2 plays a major role in changing the properties of SCR catalysts such as stability and activity. This seems to be a typical drawback of V-based catalysts using SiO_2 stabilized supports, whose low temperature activity becomes inferior compared to state-of-the-art VWT catalysts [20]. The selection of the appropriate preparation method is thus crucial to tackle the issues of stability and low temperature activity [21-26].

In this study, first we show that co-impregnation of W and V is beneficial to the low temperature activity of VWT catalysts. Because the hydrothermal stability of VWT is still not guaranteed above 600°C , the main focus of this study was to induce stability to the co-impregnated VWT catalyst upon addition of SiO_2 . As a result, the low temperature activity could be preserved up to the aging temperature of 650°C . The stabilization effect of SiO_2 was evaluated using different silicon precursors and by varying the SiO_2 loading systematically at constant loadings of V_2O_5 and WO_3 . The origin of the stabilization effect was addressed using XRD, BET, TEM and NMR.

2. Experimental

2.1 Catalyst preparation

The catalysts were prepared following a wet co-impregnation procedure approach [13, 27-29], thereby using commercial low sulfate containing TiO_2 (DT-51-D, 0.6 wt% SO_3 , Cristal Global), ammonium vanadate (AMV, NH_4VO_3 , Sigma Aldrich) and ammonium metatungstate hydrate (AMT, $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$, Sigma Aldrich). For the Si-containing catalysts, tetramethylammonium silicate (TMA-Si, 17 wt% SiO_2 in aqueous solution, Sigma Aldrich), tetraethyl orthosilicate (TEOS, Sigma Aldrich), colloidal silica (Ludox AS30, ca. 200 m^2/g , Sigma Aldrich) or fumed SiO_2 (particle size 7 nm, Sigma Aldrich) were used as precursors. The resulting samples are abbreviated as SiVW-Ti (TMA-Si), Si-TEOS-VW-Ti (TEOS), Si-col-VW-Ti (colloidal silica) and Si-fumed-VW-Ti (fumed SiO_2). AMV (eq. to 2.0 wt. % V_2O_5 , dissolved in 20 ml H_2O) and AMT (eq. to 10 wt. % WO_3 , dissolved in 10 ml H_2O) were added to an aqueous slurry of TiO_2 ($\text{H}_2\text{O}/\text{TiO}_2$ ratio 5/1) and stirred for 30 min followed by addition of the Si precursor (according to Table 1). Reference catalysts 2 wt% $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ (V-WTi), 2 wt% $\text{V}_2\text{O}_5\text{-SiO}_2/\text{WO}_3/\text{TiO}_2$ (V-SiWTi) and 2 wt% $\text{V}_2\text{O}_5\text{-SiO}_2/\text{TiO}_2$ (V-SiT) were obtained from commercial DT-52, DT-58 and DT-S10 (Cristal Global) by impregnation with AMV, respectively. After stirring for 60 min, the mixture was ultra-sonicated for 5 min followed by water evaporation under reduced pressure and drying at 120°C for 2 h. The dried sample was grinded and calcined at 450°C for 3 h in a muffle oven. For washcoating, the powders were suspended in water (4 eq. of sample), sonicated for 10 min in an ultrasonic bath and homogenized with a disperser (Micra D-8, 25000 rpm, 5 min). The honeycomb monoliths (cordierite, 400 cpsi, ca. $12 \times 17 \times 50$ mm) were dip coated by repeated immersion in the slurry and drying with an air blower until a loading of the active material of around 1.30 g (130 g/L)

was reached. The monoliths and the remaining slurry were dried and calcined at 450°C for 10 h in a muffle oven (fresh catalyst). After the catalytic test in the fresh state, the catalysts were consecutively hydrothermally aged at 600°C, 650°C and 700°C for 16 h each in a lab scale reactor in 10 vol% O₂, 5 vol% H₂O in N₂ at a gas hourly space velocity of 10,000 h⁻¹ (GHSV = volumetric gas flow/coated monolith volume).

2.2 Catalytic measurements

In order to mimic exhaust gas composition, a feed of 10 vol% O₂, 5 vol% H₂O, 500 ppm NO, 0–600 ppm NH₃ with balance N₂ (total gas flow ca. 500 L/h, GHSV of 50,000 h⁻¹) was used to test the washcoated monoliths on a dedicated laboratory test reactor [30, 31]. The maximum NO_x reduction efficiency was measured by varying the NH₃ dosage from 0 to 600 ppm. Under the assumption of a zeroth kinetic order with respect to NH₃ and pseudo-first order with respect to NO, the mass specific rate constant (k_{mass}) for the maximum NO_x reduction efficiency was calculated according to eq. 2 [32],

$$k_{mass} = -\frac{V^*}{A} \cdot \ln(1 - X_{NO_x}) \quad (\text{eq. 2})$$

where V^* is the total flow rate at reaction conditions, A the loading of the active component and X_{NO_x} the fractional NO_x conversion. The first order SCR reaction with respect to NO is justified despite the adsorption of both NH₃ and NO at low temperature because NH₃ adsorption dominates on acidic SCR catalysts resulting in virtual NH₃ excess at the active sites [2]. The independence of the rate constant from the washcoat loading is essential for monoliths where small loading deviations are unavoidable. The NO_x reduction efficiency was calculated according to eq. 3 [32],

$$NO_x \text{ reduction efficiency} = \frac{C_{NO}^{in} - C_{NO_x}^{out}}{C_{NO}^{in}} \cdot 100\% \quad (\text{eq. 3})$$

where $C_{\text{NO}}^{\text{in}}$ is the NO concentration upstream of the catalyst and $C_{\text{NOx}}^{\text{out}}$ the NO and NO₂ concentrations downstream of the catalyst. A calibrated FT-IR spectrometer (Nexus Thermo Fisher) equipped with a heated gas cell was used for the online gas analysis of the exhaust gas.

The activity of the catalysts was screened at three reaction temperatures, *i.e.* 250, 350, and 550 °C [33]. The low temperature regime is represented by 250°C, where the reaction rate constant (k_{mass}) can be calculated with accuracy. At the intermediate temperature of 350°C, V-based catalysts exhibit their optimal working conditions. The high temperature activity was tested at 550 °C, which provides indications about catalyst selectivity.

2.3 Physicochemical 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 15 to 60° 2 θ using a step size of 0.03°/2 θ s acquisition time. The phases were identified with the X'Pert HighScore Plus software and crystallite size of TiO₂ was determined by the Scherrer equation using the peaks at 25.4° and at 48.0°. The BET specific surface area (SSA) was measured by N₂ adsorption at -196 °C on a Quantachrome Autosorb I instrument. Prior to the measurement, the samples were outgassed at 350 °C for 5 h. Transmission (TEM) and scanning transmission electron microscopy (STEM) images were taken with a Talos F200X (FEI) microscope operated at an acceleration voltage of 200 kV. Elemental mappings were recorded by four energy-dispersive X-ray spectrometers (EDX) mounted on this microscope. Magic angle spinning (MAS) solid-state ²⁹Si NMR spectra were recorded on a Bruker 400 NMR spectrometer using a 7 mm CP/MAS probe. The single pulse experiments were recorded at 79.5 MHz using the following parameters: 4500 Hz MAS rate, ca. 10,000 scans, 10 s relaxation delays applying high powered SPINAL 64 proton decoupling during the data acquisition. The ²⁹Si chemical shifts

were referenced to an external sample of tetramethylsilane (TMS). The observed resonances were analyzed using the Q^n classification, where a SiO_4 tetrahedron is connected to n neighboring SiO_4 tetrahedra ($n=0-4$) [34].

3. Results and discussion

3.1 Catalytic tests

3.1.1 Benefits and limitations of co-impregnated VW-Ti catalysts

The activity of two different catalysts comprising both 2 wt% V_2O_5 and 10 wt% WO_3 on a commercial TiO_2 support is compared after different aging temperatures in Figure 1. For V-WTi, a commercial tungsta-titania support (DT-52) was impregnated with V, while for VW-Ti, commercial TiO_2 (DT-51-D) was co-impregnated with V and W (Table 1). It is evident that the co-impregnated catalyst (VW-Ti) exhibited a much higher activity compared to the reference catalyst (V-WTi), especially in the lower temperature regime (below $300^\circ C$). At $250^\circ C$ the conversion difference was ca. 35% in the fresh state (catalyst calcined at $450^\circ C$ for 10 h). After hydrothermal aging at $600^\circ C$ (Figure 1b), the NO_x reduction efficiency of both catalysts was nearly identical (ca. 53 % at $250^\circ C$), hence VW-Ti slightly deactivated while V-WTi was activated by aging. The activation of V-based catalysts with such a support is a known phenomenon and has been addressed in earlier works [6, 35]. By increasing the aging temperature to $650^\circ C$ (Figure 1c), the co-impregnated catalyst showed more pronounced aging tendencies over the whole temperature range while V-WTi mainly deactivated at high reaction temperatures ($> 400^\circ C$). It appears that co-impregnation of V and W on TiO_2 is advantageous to

obtain a highly active catalyst after moderate calcination at 450°C. To this end, the synthesis route is simple and less time consuming, which brings advantages in lowering the production cost of potential applications. The precise origin of the enhanced low temperature activity cannot be resolved solely by these measurements and is out of the scope of the present work. The characterization is further hampered by the presence of sulfate groups, which are inherently present in these commercial supports. Nevertheless, the reducibility of the two catalysts measured by temperature programmed reduction (Figure S1) was different in the fresh state but very similar after aging at 600°C in line with the catalytic behavior shown in Figure 1. It suggests a different interaction between V, W and Ti depending on the preparation method, which becomes comparable upon aging [36-38].

Despite the promising low temperature activity, the co-impregnated VW-Ti catalyst already started deactivating after hydrothermal aging at 600°C and even more severely at 650°C compared to V-WTi (Figure 1c). In order to preserve the benefit of the low temperature activity of co-impregnated VW-Ti but to gain temperature stability, VW-Ti was modified by SiO₂ (SiVW-Ti), because of its known promotion effect towards increasing the temperature stability of VWT catalysts [4, 8-16, 18, 19]. Various co-impregnated SiVW-Ti catalysts with different SiO₂ contents and precursors were synthesized according to Table 1 and were investigated with respect to the effect and the origin of their thermal stabilization. The remarkable low temperature activity of co-impregnated catalysts is worth mentioning but is not being further investigated in this work and will be the focus of an upcoming study.

3.1.2 Si-stabilized vanadia-tungsta-titania catalysts

The SiVW-Ti catalysts were synthesized identically to VW-Ti but additionally comprised various loadings of SiO₂ (0 – 10 wt%, precursors TMA-Si) added during the co-impregnation

process (e.g. 5 wt% SiO₂, 2 wt% V₂O₅, 10 wt% WO₃ on TiO₂ is labelled as 5SiVW-Ti, Table 1). To simplify the comparison of the activity of all catalysts with different SiO₂ contents and aging temperatures (450°C, 600°C, 650°C and 700°C), only three crucial temperatures for each catalyst, i.e. 250°C, 350°C and 550°C were tested and are shown in Figure 2a-2c, respectively. The activity of the catalyst after calcination at 450°C in the low temperature regime (Figure 2a) reveals that a higher amount of SiO₂ is increasingly detrimental for the activity. Already with 5 wt% SiO₂ (5SiVW-Ti), the NO_x reduction efficiency decreased from 60% to ca. 40%. At 350°C (Figure 2b), the activity decreased only for SiO₂ contents larger than 5 wt% while for the high temperature activity (Figure 2c) the increasing SiO₂ content increased the NO_x reduction efficiency.

After aging at 600°C, a small deactivation of the catalyst without SiO₂ was obvious at 250°C and 550°C. The low temperature activity in Figure 2a reveals that the addition of 3 – 10 wt% SiO₂ produced a slightly more active catalyst than in its corresponding fresh state. At the reaction temperature of 350°C, all catalysts showed full conversion (Figure 2b) after aging at 600°C. At high reaction temperature (Figure 2c), the NO_x reduction efficiency increased predominantly up to a loading of 4 wt% SiO₂. Comparison of the fresh and aged catalysts with different SiO₂ loadings revealed that the optimal SiO₂ content is around 3 – 4 wt%. Figure 2 demonstrates that this amount of SiO₂ guarantees high catalytic activity already in the fresh state and aging resistance up to 600°C.

Major differences between the co-impregnated catalysts with and without SiO₂ stabilization can be observed after hydrothermal aging at 650°C. VW-Ti heavily deactivated in the low and high temperature regime (see also Figure 1c) but a low amount of SiO₂ contributed to stabilize the catalyst. The low temperature activity of VW-Ti could be fully preserved with a loading of

4wt % SiO₂ (4SiVW-Ti). The NO_x reduction efficiency at intermediate temperatures was only affected for SiO₂ loadings up to 2 wt%, while a higher SiO₂ content was beneficial for the conversion in the high temperature regime.

Summarizing, the optimized 4SiVW-Ti showed high NO_x reduction efficiency at low temperature in the fresh state, similar to the catalyst without TMA-Si stabilization (VW-Ti). While the SCR activity of VW-Ti and the V-WTi were considerably affected by aging at 650°C over the entire reaction temperature regime (Figure 1c), it was not affected for 4SiVW-Ti in the low and medium temperature regime (Figure 2 and Figure 3b) and was only partly lost in the high temperature regime. The reaction rate constant k_{mass} (Table 1) is a useful parameter to compare the activity of different catalysts and is a suitable descriptor of the effect of SiO₂ loading. The highest k_{mass} value after calcination at 650°C was found for 4SiVW-Ti (142 cm³g⁻¹s⁻¹) while a lower or higher SiO₂ content decreased the k_{mass} values. Figure S2 additionally displays the k_{mass} values as a function of SiO₂ loading and all aging temperature. It is clear that k_{mass} decreases with increasing aging temperature and that 4SiVW-Ti preserves the highest k_{mass} value after aging at 650°C.

Based on the loading study using TMA-Si, three additional SiO₂ precursors (TEOS (4Si-TEOS-VWT), fumed silica (4Si-fumed-VWT) and colloidal silica (4Si-col-VWT)) were also tested at a fixed loading of 4 wt% SiO₂ (Table 1) in order to investigate the influence of the nuclearity of the silicon precursor on the activity and stability of the catalysts. While TEOS is a molecular silicon precursor, the silicon nuclearity increases from TMA-Si to fumed silica and colloidal silica. SiO₂ in TMA-Si is mainly structured as cubic octamer nuclei, which can however slightly vary depending on the concentration and alkyl-ammonia used [39, 40]. The mean particle size of fumed silica and colloidal silica used in this work is ca. 7 nm and 20 nm,

respectively [41]. Figure 3a shows that hydrothermal aging at 650°C affected all tested catalysts more significantly compared to that prepared from TMA-Si. There was no noticeable correlation between catalyst aging and nuclearity of the silicon precursors and the highest k_{mass} value was obtained with TMA-Si (4SiVW-Ti), followed by 4Si-TEOS-VWT, 4Si-fumed-VWT and 4Si-col-VWT (Table 1). Hence, the best SiO₂-stabilized catalyst was obtained from the TMA-Si precursor and with a loading of ca. 4 wt% SiO₂. Figure 3b compares the NO_x reduction efficiency of the optimized 4SiVW-Ti catalyst with that of a silica stabilized reference catalyst which was designed for high temperature stability (V-SiWTi, support with 10% SiO₂, 9 wt% WO₃ and TiO₂, DT58 from Cristal Global) with identical vanadium loading. It is evident that 4SiVW-Ti is more active in the fresh state and, below 450°C, also after hydrothermal aging at 650°C. A co-impregnated catalyst using a commercial Si-stabilized Ti support VW-SiT_i (Figure S3, 10 wt% SiO₂, DT-S10) also exhibited a lower NO_x reduction efficiency and a lower k_{mass} value (Table 1) than 4SiVW-Ti. This was not the case after hydrothermal aging of 4SiVW-Ti at 700°C (Figure 2). Nevertheless, 4SiVW-Ti seems to be the best catalyst with respect to simultaneous low temperature activity and hydrothermal stability up to 650°C.

In the following section, we try to rationalize the improved hydrothermal stability of the co-impregnated catalysts stabilized with TMA-Si by detailed physical characterization techniques such as powder X-ray diffraction (XRD), Brunauer–Emmett–Teller specific surface area measurements (BET), transmission electron microscopy (TEM), high-angle annular dark-field imaging TEM (HAADF-TEM) and ²⁹Si magic-angle spinning nuclear magnetic resonance spectroscopy (²⁹Si MAS NMR).

3.2 Physicochemical characterization

3.2.1 X-ray diffraction

The XRD patterns of SiVW-Ti catalysts and TiO₂ after aging at 650°C are displayed in Figure 4. All catalysts exhibited the anatase phase but the peaks broadened with increasing SiO₂ loading due to smaller anatase crystallites. The median size of these crystallites was calculated by the Scherrer equation (Table 1). The anatase crystallite size of commercial TiO₂ after calcination at 450°C and 650°C was ca. 20 nm and 30 nm, respectively (Table S1). After impregnation of 10 wt% WO₃ on TiO₂ (W-Ti), the crystallite size remained identical in the fresh state but was only ca. 25 nm after aging at 650°C. Therefore, WO₃ assisted the retardation of the sintering of the anatase phase [42-44]. By co-impregnating V and W (VW-Ti), the TiO₂ particle size grew to ca. 44 nm after aging at 650°C, confirming the promoting effect of V towards anatase particle growth [6]. Already 1 wt% SiO₂ could hinder particle growth to some extent (ca. 29 nm for 1SiVW-Ti). SiO₂ loadings of 2 to 5 wt% resulted in crystallite sizes of around 24 nm, which decreased to ca. 22 nm by increasing the SiO₂ loading to 7 and 10 wt%. SiO₂ in SiVW-Ti with loadings of 7 – 10 wt% is thus capable of preserving the crystallite size of TiO₂ after calcination at 450°C. Summarizing, a correlation between TiO₂ particle size and SiO₂ loading upon aging could be confirmed [12, 14].

No reflection was found at all SiO₂ loadings that could be attributed to SiO₂ or V₂O₅ crystallites, suggesting that VO_x and SiO₂ remained dispersed/amorphous or formed crystallites below the XRD detection limit. Besides TiO₂, clear WO₃ reflections were observed. The region at 23 – 24° comprehending the WO₃ reflections is enlarged in Figure 5 for all catalysts and aging temperatures. Figure S7 shows the WO₃ reflection intensities as a function of SiO₂ loading and aging temperature. From Figure 5a and Figure S7 it is obvious that the addition of SiO₂ promotes the formation of crystalline WO₃ after calcination at 450°C. The WO₃ peaks became visible

already with 2 wt% SiO₂ and were attributed to a monoclinic crystal structure with P2₁/n space group [45]. By increasing the SiO₂ loading, this WO₃ phase became more prominent, which is best visible in the alternative presentation of the data in Figure S7. After aging at 600°C and 650°C (Figure 5b and 5c, respectively and Figure S7), these reflections lost intensity with increasing SiO₂ contents. This suggests that crystalline WO₃ in e.g. 10SiVW-Ti calcined at 450°C partly decomposes with increasing aging temperature. Due to the increased surface diffusion, it is plausible that SiO₂ and WO₃ compete for anchoring positions on TiO₂. Because WO₃ is favored due to its higher acid strength [46, 47], WO₃ crystallites partly decompose with increasing aging temperature. For low loaded SiO₂ catalysts, no WO₃ was detected in the fresh state but the WO₃ reflections appeared with increasing aging temperature. The WO₃ crystallite formation of these catalysts is therefore dependent on the aging temperature. Because the WO₃ formation/decomposition upon aging is also influenced by the SiO₂ loading, an intermediate SiO₂ loading of 3 – 5 wt% results in WO₃ reflections that are similar at all aging temperatures (Figure S7).

It should be noted that VW-Ti and 1SiVW-Ti aged at 650°C displayed an additional WO₃ reflection at 23.1 and 24.1° from a different WO₃ phase (WO₃-B, Figure 5c). We tentatively assign this phase to a monoclinic crystal structure with Pc space group [45]. This phase became more prominent at 700°C (Figure 5d) where a clear SiO₂ loading dependence was observed: VW-Ti exhibited a major fraction of the WO₃-B phase, which decreased with increasing SiO₂ content and was no longer detectable in 7SiVW-Ti and 10SiVW-Ti.

The XRD data reveals that SiO₂ hinders the dispersion of WO₃ on the TiO₂ surface and consequently promotes the formation of crystalline WO₃ for SiVW-Ti catalysts. On the contrary, SiO₂ does not interact with vanadium species [19]. The observation that WO₃ crystallites

formation depends on SiO₂ loading can be explained with the fractional surface coverages of VO_x, WO_x and SiO_x (Figure S4a-c), which were calculated according to eq. S2 using the BET surface area and the theoretical saturation values for the monolayer coverage, i.e. 7.9 VO_x nm⁻², 4.2 WO_x nm⁻² and 10.5 SiO_x nm⁻² [6, 20, 48, 49]. For VW-Ti, a fractional monolayer coverage of 0.22 VO_x and 0.79 WO_x was obtained in the fresh state, which yields a total fractional monolayer of ca. one (Tf_m, eq. S3). Tf_m exceeded the monolayer value already for a loading of ca. 3-4 wt% SiO₂ (ca. 1.2, Figure S4d) in the fresh catalysts, which most likely accounted for the formation of the crystalline WO₃ units observed by XRD (Figure 5a). Tf_m was ca. 1.6 for 10SiVW-Ti, thus the formation of WO₃ crystallites was facilitated to a greater extent due to blocking SiO_x units on TiO₂ interaction sites. Because of the multiple total monolayer fractions at all loadings (Tf_m of 2 – 4), the presence of WO₃ crystallites was less dependent on the SiO₂ content (Figure 5c) after aging at 650°C. The catalysts with low SiO₂ content started sintering severely at this temperature, which was reflected by the decrease of the BET surface area (Table 1) and Tf_m above 2.5. It is likely that sintering induced the formation of the second WO₃ phase, which was mainly observed for VW-Ti and 1SiVW-Ti.

It should be mentioned that it is difficult to find a correlation between the WO₃ crystallite formation and the corresponding activity/stability of the catalysts. 2SiVW-Ti, 3SiVW-Ti and 10SiVW-Ti revealed lower WO₃ diffraction intensities than 4SiVW-Ti (Figure 5c) but their k_{mass} values (Table 1) were lower than that of 4SiVW-Ti after aging at 650°C. Also, catalysts with the identical composition and activity after aging at 600°C, i.e. V-WTi and VW-Ti (Figure 1b), exhibited very different XRD reflections of WO₃ (Figure S5 and Figure S6b, respectively).

The comparison of the different SiO₂ precursors at fixed loading (4 wt% SiO₂, Figure S8) revealed that crystalline WO₃ was formed in all samples. In the fresh state, the largest amount of

crystalline WO_3 was detected in 4SiVW-Ti, while it was only poorly visible for other catalysts. After aging at 650°C (Figure S8b), 4Si-fumed-VWT and 4Si-TEOS-VWT showed smaller WO_3 reflections than 4SiVW-Ti and 4Si-col-VWT. Similar to the SiO_2 loading study, no obvious correlation between the stability of the catalyst and the formation of WO_3 could be found. In order to address the origin of the stabilization effect by SiO_2 in SiVW-Ti more specifically, the optimized catalyst 4SiVW-Ti was further characterized by electron microscopy and NMR.

3.2.2 TEM/STEM

Figure 6 displays the transmission electron microscope images of VW-Ti and 4SiVW-Ti after aging at 600°C and 650°C . In all images, TiO_2 particles are visible, which mainly differ in size depending on the catalyst and the aging temperature. Similar particle sizes are evident from TEM of VW-Ti (Figure 6a) and 4SiVW-Ti (Figure 6c) after aging at 600°C . In contrast, the TEM images of the same catalysts after aging at 650°C (Figure 6b and 6d, respectively) showed a clear difference. The TiO_2 particles grew to a larger extent for VW-Ti than for 4SiVW-Ti, which was also evident from the exponential growth of TiO_2 crystallites for VW-Ti observed by XRD (Table 1). A further observation from the TEM data is that the addition of TMA-Si created regions of amorphous SiO_2 (Figure 6d). The formation of amorphous SiO_2 possibly reduced the contact between anatase particles, which is a possible explanation for the stabilizing effect of SiO_2 at elevated temperatures [50]. Since TMA-Si is not a molecular SiO_2 precursor [39, 51], it is likely that large SiO_2 agglomerates can be formed once supported on TiO_2 and that they serve as spacer between the TiO_2 particles thus preventing their coalescence.

The high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images and the corresponding elemental mappings from energy-dispersive X-ray (EDX) spectroscopy of 4SiVW-Ti after aging at 650°C are shown in Figure 7. The elemental mapping

revealed that the particles displayed in the HAADF image in Figure 7a mainly consist of Ti (Figure 7b), have uniformly distributed W (Figure 7c) but inhomogeneously dispersed Si (Figure 7d). Vanadium could not be detected due to its overall low concentration and because the main V peak overlaps with the second line of Ti in the EDX spectrum. The extended SiO₂ agglomerates cannot be solely responsible for the suppression of the TiO₂ sintering because of their limited dispersion. To that end, the fractional monolayer coverage of SiO₂ in SiVW-Ti catalyst with a loading up to 4 wt% SiO₂ was below 0.7, making it even more unlikely to suppress the contact between all TiO₂ particles. By close inspection of the elemental map in Figure 7d it is evident that beside large SiO₂ agglomerates, Si is dispersed over the whole region of TiO₂. Similar to W, Si covered all TiO₂ particles but with a higher degree of inhomogeneity. This suggests that finely dispersed Si units are also partly responsible for the delay in TiO₂ particle sintering at elevated aging temperatures. It may explain why already 1 – 2 wt% SiO₂ had a major effect on the inhibition of the TiO₂ particle growth after aging at 650°C (Table 1).

3.2.3 ²⁹Si- MAS-NMR

In order to investigate the nature of the silicate at a molecular level, ²⁹Si - magic angle spinning - nuclear magnetic resonance spectroscopy (²⁹Si MAS NMR) was applied to selected SiVW-Ti catalysts, namely 4SiVW-Ti and 10SiVW-Ti (Figure 8). The local structure of the tetrahedral SiO₂ units (Qⁿ, n is the number of Si-O-Si bonds) could be followed because the chemical shift is highly sensitive to the local environment [34].

Figure 8a shows the ²⁹Si MAS NMR of 10SiVW-Ti calcined at 450°C, 600°C and 650°C, respectively. In the fresh state, ca. 65% of SiO₂ was associated with the presence of three dimensional silicates (Q⁴), while layered/surface (Q³) and chain silicate (Q²) accounted for 25% and 10%, respectively. No isolated or dimeric silicates were found, which is reasonable because

the SiO_2 loading was responsible for ca. 80% of full monolayer coverage (Figure S4). Considering the structure of TMA-Si that consists of small polymeric clusters (i.e. cubic octamer nuclei, dependent on solvent and concentration [39, 40, 51]), monomeric and dimeric Si units are unlikely to be formed. An increase of the aging temperature to 600°C and 650°C resulted in increased Q^4 species and decreased Q^3 and Q^2 contributions. The increase of Q^4 species origins from the condensation of Si-OH groups to Si-O-Si bonds thus suggesting the formation of an extended network, which may coincide with the observation of the SiO_2 agglomerates in TEM.

The same behavior was observed for 4SiVW-Ti (Figure 8b) with increasing aging temperature but due to the overall lower SiO_2 concentration, the signal-to-noise ratio of the spectra was lower than in the 10SiVW-Ti sample. The deconvolution revealed that the Q^3 and Q^2 silicate fractions in the fresh state were slightly larger compared to 10Si-VWT, suggesting that the amorphous silicate particles were more dispersed, possibly due to their lower SiO_2 content [51]. It is plausible that Q^3 and Q^2 , accounting for ca. 30 – 40% of the SiO_2 units, play an important role in the stabilization of Si-VWT catalysts. The combination of STEM and ^{29}Si NMR results suggests that small and dispersed SiO_2 units play a role in hindering the TiO_2 particle sintering. We are aware that combination with other methods could improve the overall understanding of the Si stabilization effect and more work is needed to fully disentangle its impact.

Conclusions

A $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ catalyst synthesized via co-impregnation exhibited improved low temperature activity compared to an analogous catalyst obtained by impregnation of V on a commercial tungsta-titania support. Because the hydrothermal stability of the co-impregnated

sample was however poor, its stability was increased by co-impregnating TiO_2 with precursors of V, W and varying amounts of Si, a known stabilizing agent of SCR catalysts. With an accurate choice of the SiO_2 precursor, the co-impregnated catalyst resisted aging up to 650°C and remained highly active between 250°C and 500°C . This result is of particular importance because it demonstrates that the unfavorable trade-off between low temperature activity and high temperature stability of V-based SCR catalysts can be overcome. From the systematic study of the influence of SiO_2 loading, the addition of 2 – 4 wt % SiO_2 was sufficient to stabilize the catalyst, which is the concentration where a full theoretical surface coverage with SiO_2 was reached. However, due to the addition of SiO_2 , the WO_3 concentration started to exceed total surface coverage resulting in the agglomeration of WO_3 . Moreover, the silicates formed an amorphous phase that prevented most likely the TiO_2 particles from sintering, which is the main driving force for aging. SiO_2 was present as polymeric SiO_2 entities contributing to inhibit the inter-particle contact of the anatase TiO_2 crystallites by modification of the surface of the support in the form of localized agglomerates and of small well dispersed domains.

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Figures

Figure 1 NO_x reduction efficiency of V-WTi (impregnation of V on WTi) and VW-Ti (co-impregnation of V and W on Ti) after calcination at (a) 450°C for 10 h and after hydrothermal aging at (b) 600°C and (c) 650°C for 16 h.

Figure 2. NO_x reduction efficiency of co-impregnated SiVW-Ti catalysts with different SiO₂ loadings using a TMA – silicate as precursor at (a) 250°C, (b) 350°C and (c) 550°C in the fresh state (calcination at 450°C) and after consecutive hydrothermal aging at 600°C, 650°C and 700°C. All catalysts comprise 2 wt% V₂O₅ and 10 wt% WO₃.

Figure 3. (a) NO_x reduction efficiency of co-impregnated Si stabilized catalyst with each 4 wt% SiO₂ after hydrothermal aging at 650°C for 16 h. (b) Performance comparison of the optimized 4SiVW-Ti (SiO₂ from TMA-Si) catalyst with the V-SiWTi (commercial Si-stabilized tungsta-titania support) in the fresh state and after hydrothermal aging at 650°C. All catalysts comprise 2 wt% V₂O₅ and 10 wt% WO₃.

Figure 4. XRD patterns of TiO_2 , VW-Ti and SiVW-Ti after aging at 650°C .

Figure 5. XRD patterns of the 2θ region between 22.5° and 24.6° of TiO_2 , VW-Ti and SiVW-Ti catalysts after aging at (a) 450°C , (b) 600°C , (c) 650°C and (d) 700°C . The full XRD patterns of a-d are shown in Figure 4 and Figure S6. The correlation between WO_3 peak intensity, SiO_2 loading and aging temperature is shown in Figure S7.

Figure 6. TEM images of VW-Ti (no SiO₂) calcined at (a) 600°C and (b) 650°C and 4SiVW-Ti (4 wt% SiO₂) calcined at (c) 600°C and (d) 650°C. The red colored area next to the arrows in (d) indicates the presence of amorphous SiO₂ particles.

Figure 7. (a) HAADF-STEM image of 4SiVW-Ti calcined at 650°C and the corresponding elemental mapping of (b) Ti, (c) W and (d) Si.

Figure 8. ^{29}Si MAS NMR of (a) 10SiVW-Ti and (b) 4 SiVW-Ti calcined at 450°C, 600°C and 650°C, respectively.

Table 1. BET surface area, TiO₂ XRD crystallite size, reaction rate constant k_{mass} , calculated fractional V surface coverage ($f_{\text{m,o}}$) of Si-stabilized VWT catalysts with different SiO₂ loadings and precursors after aging at 650°C. All catalysts comprise 2 wt% V₂O₅ and 10 wt% WO₃.

Name	Si-precursor ^(a)	After aging at 650°C				
		SiO ₂ [wt%]	BET [m ² g ⁻¹]	XRD [nm]	k_{mass} @ 250°C [cm ³ g ⁻¹ s ⁻¹]	$f_{\text{m,o}}$ ^(b)
VW-Ti	-	0	19	44.6	54	0.88
1SiVW-Ti	TMA-Si	1	37	28.9	104	0.45
2SiVW-Ti	TMA-Si	2	52	24.3	111	0.32
3SiVW-Ti	TMA-Si	3	52	24.8	126	0.32
4SiVW-Ti	TMA-Si	4	55	23.6	143	0.30
5SiVW-Ti	TMA-Si	5	59	24.0	126	0.28
7SiVW-Ti	TMA-Si	7	68	22.5	109	0.25
10SiVW-Ti	TMA-Si	10	66	21.3	83	0.25
4Si-TEOS-VWT	TEOS	4	37	30.5	115	0.45
4Si-col-VWT	Colloidal silica	4	33	34.8	102	0.51
4Si-fumed-VWT	Fumed silica	4	50	26.9	84	0.34
10Si-fumed-VWT	Fumed silica	10	65	25.0	75	0.26
V-WTi ^(c)	-	0	35	32.8	118	0.48
VW-SiTi ^(d)	-	10	78	15.3	84	0.21
V-SiWTi ^(e)	-	10	90	14.5	82	0.19
Support TiO ₂	-	-	-	30.0	-	-
Support W-Ti	-	-	-	24.8	-	-

^(a)TMA-Si (tetramethyl ammonium silicate, 17 wt% SiO₂, Sigma Aldrich), TEOS (Tetraethyl ortho silicate, Sigma Aldrich), colloidal silica (Ludox AS30, Sigma Aldrich), fumed SiO₂ (silica, 7 nm, Sigma Aldrich). ^(b)calculated according to eq. S1. ^(c)Commercial support 10 wt% WO₃-TiO₂ (DT-52, Cristal Global), ^(d)commercial support 10 wt% SiO₂ -TiO₂ (DT-S10, Cristal Global) and co-impregnation of 2 wt% V₂O₅ and 10 wt% WO₃, ^(e)commercial support 10 wt% SiO₂ - 9 wt% WO₃-TiO₂ (DT-58, Cristal Global)