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Effect of the sol-gel conditions on the morphology and SCR performance of electrospun V-W-TiO$_2$ catalysts

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Abstract

V-W-TiO$_2$ catalysts are prepared as nanofibers for the removal of the NOx in exhausts via the NH$_3$ Selective Catalytic Reduction (SCR) method. By combining electrospinning and soft chemistry, materials are processed as nanofibers with the catalytic components (e.g. V$_2$O$_5$-WO$_3$) incorporated as dopants into the supporting anatase phase (e.g. TiO$_2$). The conditions for the chemical synthesis were investigated by varying the molar ratios between titanium alkoxide (tetraisopropoxide) and the chelating agent (acetic acid). Catalytic characterization clearly shows a impact of the starting precursor coordination on the final nanostructure, and thus on the catalytic performances. Superior NOx conversion are obtained for nanofibers formed by high coordination level, i.e. [Acetic acid]/[Ti cation] > 2, with high stability and control over the processing route.

KEYWORDS: Nanofibers; Electrospinning; Titania; SCR.
1 Introduction

Nitrogen oxides gaseous (NOx), emitted by high temperature combustion processes and road/marine transport systems, are regarded as a major environmental and human health concern [1, 2]. Their catalytic conversion into harmless products (nitrogen and water) via the selective catalytic reduction (SCR) method is the most efficient method in use [2-4]. In a typical system, the reducing agent used is either ammonia (NH$_3$) or urea, whereas the catalytic component consists in the active materials supported on an appropriate ceramic carrier (e.g. TiO$_2$ anatase) [2-4]. The state-of-the-art active material are either V$_2$O$_5$-WO$_3$ or V$_2$O$_5$-MoO$_3$ [2-4]. In this combination, the vanadium pentoxide (V$_2$O$_5$) is the active component [5, 6], whilst either tungsten or molybdenum trioxides (WO$_3$ or MoO$_3$) are exploited to support and enhance the V$_2$O$_5$ activity [7]. With respect to titania support, V$_2$O$_5$ is typically used at concentrations varying in the range of 0.5-3 wt%, while either WO$_3$ or MoO$_3$ amount are in the range of 8-10 wt% [5-7].

Despite the excellent performances, innovative methods and materials are being developed to meet the upcoming stringent regulations on NOx emission. In this context, nanostructured-based ceramic materials are considered ideal candidates for the development of cost and energy efficient innovative systems [8]. The confinement of either one or more dimensions into the nanoscale level confers to the material unique properties [8]. Significant enhancements have been obtained by using nanoparticles for developing catalyst endowed with high specific surface area (> 100 m$^2$/g) and high surface-to-volume ratio [8,9]. This approach enables for an overall increment of the active sites and of their exposure to the reactant species [8-10]. An alternative and particularly promising strategy is to use one-dimensional (1D) nanomaterials (e.g. nanotubes, nanofibers) [11, 12]. Despite their lower specific surface area compared with nanoparticles (< 100 m$^2$/g), 1D nanostructures own the merits of an even higher surface-to-volume ratio associated with a high aspect ratio [13].
These morphological traits ensure a wide area of exposure for the active sites that is expected to enhance the conversion activities [8, 11, 12]. With this respect, electrospun nanofibers offer the further advantage of a nanotextured and highly opened porous self-supported substrate [13] that enables a fluid dynamic regime favourable for enhanced catalytic activity [8, 11, 12]. In addition, the electrospinning allows an easy control over the morphological and composition features and an adequate dispersion of the catalyst on the supporting surface [13,14]. The electrospinning is indeed an inexpensive and easily up scalable processing technique that provides a wide range of possibilities to elaborate tailor-made novel advanced materials. A huge variety of ceramic nanofibers can be prepared by adjusting the electrospinning conditions and the chemistry of the starting solutions [13-15]. The spinning solutions are typically reactive sol-gel solutions that upon the hydrolysis/condensation reactions generate highly homogeneous macromolecular oxo-precursor network [16, 17]. It is an extremely flexible process due to the reactivity of the alkoxide precursors easily controlled by using nucleophilic ligands. The alkoxides are stabilized via coordination of the metallic centre that leads to more stable molecular precursors [18]. Among the most used chelating agents, acidic compounds are those generally used in the electrospinning as they promote a linear condensation of the reactants [19]. A number of studies have been conducted with the aim of explaining the effect of the concentration of the chelating agent on the sol-gel process and on the resulting morphology [19, 20]. However, to best of our knowledge, there is no investigation about the effect of the chelating agent concentration on the morphology of the nanofibers.

In a previous study, we demonstrated the superior catalytic efficiency of electrospun state-of-the-art catalyst (V_2O_5-WO_3/TiO_2) over the state-of-the-art nanoparticles catalyst [13]. The V-W molar ratio was fixed at 1, corresponding to a content of WO_3 and V_2O_5 of
5% and 3% in weight respectively. The content of the acetic acid was fixed at the value indicated in literature ([Ac]/[Ti]=10) [21].

Herein, the effect of the chelating agent amount on the morphologies and performances of (V_2O_5-WO_3/TiO_2) catalysts was investigated. Preliminary experiments on the catalytic activity were conducted only in dry conditions and in the absence of SO_2 to explore the intrinsic activity of the materials.

2 Experimental

2.1 Materials

All materials were reagent grade and used as received.

Titanium tetraisopropoxide (97% purity, Sigma Aldrich, Denmark), tungsten ethoxide (5% w/v in ethanol, Alfa Aesar, Denmark,) and vanadium acetylacetonate (99.98% purity, Sigma Aldrich, Denmark) were used as precursors. Polyvinylpyrrolidone (PVP, Mw ~1.3 M, Sigma Aldrich, Denmark) was used as carrier polymer, and glacial acetic acid (99.8%, Sigma Aldrich) served as a stabilizer to control the hydrolysis reaction of the alkoxides.

2.2 Preparation of spinning solution

The characteristics of the elements of interest are indicated in Table 1. Spinning solutions at different titanium tetraisopropoxide/acetic acid molar ratios (namely 2, 5, and 10) were prepared. In a typical procedure, titanium tetraisopropoxide was first mixed with acetic acid (e.g. molar ratio of TTIP:AcH =1:10) under magnetic stirring (20 °C) in a sealed container purged with inert gas (e.g. argon). The required amount of the other reagents was then added using adequate syringes. The concentration of PVP (~0.03 g/ml) is finally adjusted by adding an extra volume of pure ethanol. The solution was kept under magnetic stirring for 10 min, and finally loaded in a glass syringe equipped with a 21-gauge stainless steel needle. In Table 2 the compositions developed are indicated. The spinning solutions
were labelled as reported in Table 1, where V, W, and TiO$_2$ refers to vanadium, tungsten, and titania support, respectively. The numbers into the brackets, e.g. (10), refers to the [Ac]/[Ti] ratio.

### 2.3 Electrospinning of the solution and calcination of the green nanofibers

RT Advanced (Linari Engineering) electrospinning equipment was used. The syringe loaded with the precursor solution was first installed inside of the chamber of the RT Advanced with fixed humidity (22% RH) and temperature (20 °C). The grounded substrate drum was placed 8 cm away from the needle and covered by an aluminium foil to collect the nanofibers. The electrospinning process was conducted in air with a voltage supply of 36 kV and a feeding rate of 1 ml/h. The material, resulted in a flexible green mat, was thermally treated in an oven at 500 °C for 3 h (heating rate 1 K/min) to remove the organics and promote the formation of crystallographic phases.

### 2.4 Characterization

The occurring of the sol-gel process was followed by measuring the viscosity of solutions at different [Ac]/[Ti] ratios (2, 5, and 10). The viscosity was measured with a rotational rheometer (Anton Paar MCR302). A constant temperature of 21°C was maintained during the experiments using a temperature control unit. All the experiments were performed using a parallel plate of 50 mm in diameter (PP 50) at a gap distance of 0.6 mm. To prevent the evaporation of the solvent during the experiments, a proper solvent trap was used [22-26]. All rheological measurements were performed using a pre-shear at 0.1 s$^{-1}$ for 2 minutes followed by 2 minutes at rest (0 s$^{-1}$ shear rate), to remove any effects due to the sampling and loading of the slurries.

The TGA (NETSZCH, STA 409, CD) was conducted in air flux from room temperature to 700 °C with a heating rate of 2 °C /min.
BET (Brunauer-Emmett-Teller; Autosorb 1-MP, Quantachrome Instruments, Boynton Beach, Fl, USA) analysis was conducted to measure the specific surface area (SSA) of the fibrous materials developed. The results are indicated in Table 3.

X-ray diffraction (XRD, Bruker D8, Germany) patterns were recorded at room temperature (Cu Ka radiation) at scanning rate of 0.02 °/s in 2θ range from 20-90°. The crystallinity, the phase structure and crystal parameters were investigated by analysing the XRD pattern. The results are reported in Table 3.

The average size of the grain was determined using the Debye–Scherrer equation, whereas the spacing corresponding to the planes (101) and (200) of the anatase phase were determined by applying the Braggs’s equation.

The lattice parameters were estimated considering the tetragonal crystal structure for the TiO$_2$, with thus the lattice parameters following the conditions $a = b \neq c$ (and $\alpha = \beta = \gamma = 90^\circ$). The lattice parameters were calculated by applying the standard formula for the tetragonal system:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Equation 1

where $d$ is the interplanar spacing, $h, k, l$ represent the Miller indices of the planes and $a, b$ and $c$, are the lattice parameters.

The morphology of the nanofibers was analysed by using field emission scanning electron microscopy (FESEM, Supra, Carl Zeiss, Germany) and transmission electron microscopy (TEM, JEM3000F, Oxford Instruments, UK).

A home-made lab-scale experimental setup was used for the SCR characterization. The setup consists in a quartz reactor equipped with inlet- and outlet for feeding the reactants gases and measuring the resulting gases, respectively. It is equipped with sensors for NOx and CO$_2$, NO and NH$_3$ supply (equipped with mass flow controllers), gas analyzers (quadrupole mass spectrometer,
Omnistar GSD 301, Pfeiffer Vacuum, Denmark) and chemiluminescence detector (Model 42i High Level, Thermo Scientific, UK). The experiments were conducted on around 25 mg of titania-based nanofibers at gas concentrations such as [NO] = [NH\textsubscript{3}] = 1,000 ppm, [O\textsubscript{2}] = 8% vol., [CO\textsubscript{2}] = 5% vol., Ar balance (GHSV = 400,000 h\textsuperscript{−1}). Only the high range of temperatures (250-500 °C) was investigated.

The catalytic activity for the developed materials and for the nanoparticles material (V-W-TiO\textsubscript{2} catalyst, kindly provided by Haldor Topsøe A/S) was calculated from the NO conversion values by applying the formula of the first-order rate constant (cm\textsuperscript{3} g\textsuperscript{−1} s\textsuperscript{−1}):

\[ k = -\frac{F}{w} \ast ln(1 - x) \quad \text{Equation 2} \]

where F denotes the flow rate (cm\textsuperscript{3} s\textsuperscript{−1}), w the catalyst mass (g) and x the fractional conversion of NO.

The activation energies for the process were estimation by the Arrhenius fitting of the data using the following equation for the first-order rate constant (k):

\[ k = A \exp\left(\frac{E_a}{RT}\right) \quad \text{Equation 3} \]

where the pre-exponential factor A is associated with the number of the active sites and E\textsubscript{a} is the activation energy of the catalytic reaction.

3 Results and discussion

The active materials (V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}) were introduced as dopant elements into the anatase TiO\textsubscript{2} phase via sol-gel process. The reactivity of the titanium alkoxide was controlled by using the acetic acid as chelating agent. As reported in literature [18-20], the acetic acid plays dual actions. It acts as catalyst for the sol-gel reactions by increasing the lability of the alkoxides groups, and as chelate for the central Ti. The stability of the alkoxide at different content of acetic acid (expressed as [Ac]/[Ti]
ratio) was explored by measuring the viscosity. Extensive studies indicate for the acetate ions two different bidentate coordination modes, chelating and bridging [19]. The occurring of a mode over the other is influenced by the concentration of the acetic acid [19]. As long as the $[\text{Ac}]/[\text{Ti}] \leq 2$, the bidentate chelating mode has been observed, whereas beyond 2 mol. of acetic acid per titanium, the bidentate bridging mode is predominant [19]. Figure 1e shows the viscosity curves for the solutions at increasing amount of acetic acid. For all the solutions, a Newtonian behaviour is observed with a constant value of viscosity independent on the shear rate. The viscosity values were calculated from the slope of the flow curves [23-26]. Interestingly, the viscosity was observed to increase with the amount of the acetic acid. The highest viscosity value was observed for the solutions at $[\text{Ac}]/[\text{Ti}]=10$ and associated with the formation of poly-nuclear complexes via bridging mechanism of the acetate, as indicated in literature [19]. For this concentration of acetic acid, the precipitation of white oxo-acetate compound was also observed. This compound was found to be soluble in water. Indeed, the addition of water caused its dissolution. The solution turned to be transparent, indicating for the stabilized titanium-acetate bridges a tolerance toward water.

Viscosity of the spinning solution along with conductivity have been identified as the physical properties largely affecting the whipping and nanofibers formation step. Specifically, Thompson et al. have demonstrated that the process results from a balanced combination of the viscosity and the electrostatic forces, irrespective of their absolute magnitudes [27]. Specifically, the thinning of the jet and the following formation of the nanofibers, as a result of the solvent evaporation, only occurs if the viscosity is as low as to allow the electrostatic forces to exert a larger influence and efficiently counterbalance the viscosity. Typically, solutions for electrospinning polymeric nanofibers contains polymer in a concentration that originates a shear thinning behaviour, with low viscosity values at those shear conditions (high) that characterize the whipping of the jet. The decrease of the viscosity with the frequency allows the electrostatic forces to efficiently counterbalance the viscosity.
By contrast, solutions for electrospinning ceramic nanofibers contain the ceramic precursors and polymer carrier. When the precursors used is a metal alkoxide (as in the case of the current paper) low values of viscosity are required and a Newtonian behaviour is highly desired. Indeed, during the evaporation of the solvent (whipping step), the precursors condense forming a polymer-like structure into the shape of the fibers. In this case, an excessive high viscosity could be deleterious for the formation of the nanofibers as it could not be efficiently counterbalanced by the electrostatic forces likely resulting in inhomogeneous distribution of the diameters of the nanofibers.

The effect of the acetic acid content on the nanofiber morphology was then investigated. Figures 2 a-c show the morphology features for samples obtained at [Ac]/[Ti]=2, 5, and 10. Increasing values of [Ac]/[Ti] correspond to a marked increase in the homogeneity of the nanofibers diameters. The trend can be ascribed to the stabilizing effect of the acetic acid towards the hydrolysis/condensation process. The higher [Ac]/[Ti], the higher the control over the sol-gel process, thus the more homogeneous distribution of the nanofibers diameters is obtained.

For all the materials developed, regardless the homogeneity of the diameters, an extended nano-textured morphology with nanofibers having high aspect ratios is observed. The formation of any close porosity upon the electrospinning process is not observed. Wide open and highly interconnected porosity, associated with a large pore volume, characterized the nano-fibrous substrate [13]. Indeed, values in the range of 80-90 %vol have been obtained [13].

The analysis of the single nanofibers for all the samples provides similar observations. Therefore, for brevity, only the results on the material obtained at [Ac]/[Ti]=10 are herein reported. As indicated in Fig. 2d (TEM micrograph), the single nanofibers possess a polycrystalline structure, corresponding to the anatase phase arrangement (SAED, inset in Fig 2d). The observation is further supported by the HR-TEM image (Fig 2e) that shows a
well-defined organization of the atoms with a fringe spacing of 0.349 nm indexed to the (101) plane of the anatase.

The occurrence of anatase phase for all the co-doped samples is further confirmed by the long range XRD pattern (Fig. 3a). For sake of the completeness, the XRD pattern of the un-doped titania is also reported. For this last sample (prepared at [Ac]/[Ti]=10), both anatase and rutile phases can be observed. The co-occurrence of the two phases can be attributed to a size-dependent effect [28]. The addition of the dopants hinders the rutile phase formation likely because of the annihilation of the oxygen vacancies associated with the oxidation state of vanadium and tungsten (> 4) [29]. A further factor expected to inhibit the formation of the rutile phase is the expansion of the unit cell [30] as a consequence of the doping approach. To verify that, the crystal parameters were estimated considering anatase TiO$_2$ as a tetrahedral structure (a = b ≠ c and α = β = γ). Equation 1 (experimental section) was applied using the (101) and (200) crystal planes of the anatase. The doping of the hosting lattice causes the expansion of the unit cell as indicated by the increase of the lattice parameters compared to the un-doped TiO$_2$ (see Table 3). The expansion of the unit cell is consistent with a substitutional introduction of both V$^{5+}$ and W$^{6+}$ into the anatase unit cell. This confirms the formation a solid solution [31]. Interestingly, for the three different acetic acid concentrations, similar expansion of the unit cell is observed, excluding any effect of the [Ac]/[Ti] ratio on the crystallographic features.

The introduction of the two dopants also effects the grain sizes and the SSA with respect to the pure titania. The average grain sizes were estimated from XRD patterns using (101) plane of the anatase phase via the Debye–Scherrer equation. As indicated in Figure 3b, (and summarized in Table 3) from pure titania to V-W co-doped catalysts, while a slight decrease of the grain sizes is observed, the SSA values are observed to increase. This trend is likely
due to the solute drag effect that hinder the mass diffusion during the calcination (at 500 °C) [32, 33]. However, a slight discrepancy in the trends of the SSA and of the grain sizes is observed for the co-doped material prepared at [Ac]/[Ti]=10. Despite its average grain sizes value is similar to the values calculated for the other two nanofibrous catalysts, it is characterized by a lower SSA. An effect of the distribution of the grain sizes can be speculated. It is worth mentioning that the grain size obtained analysing the XRD patterns, are average values. Except for the material prepared at [Ac]/[Ti]=10, the other two samples are instead characterized by a wide distribution of the grain sizes, as indicated in Figure 3c (SEM magnification) for the nanofibers obtained at [Ac]/[Ti]=2. Grains with dimension ranging from 20 nm to 40 nm can be observed. Likely, the distribution of the grain sizes rather than their average values, impacts the SSA. Yet, a combined effect between the distribution of the grain sizes and nanofibers diameters can be identified as the factor determining the SSA. Specifically, the wider the distributions of both parameters, larger the SSA. Accordingly, the sample prepared at [Ac]/[Ti]=10 and characterized by the narrowest distribution of grain sizes and nanofibers diameters, possesses low SSA. By contrast, nanofibers prepared at [Ac]/[Ti]=2 exhibit a high SSA value. For the sample prepared at [Ac]/[Ti]=5, a SSA value similar to the value obtained for the [Ac]/[Ti]=2 nanofibers is obtained. This is likely due to a complex combination between the grain sizes and nanofibers diameters distributions.

The catalytic performances were then explored. Aiming at characterizing the intrinsic activity of the developed materials, experiments were conducted only in dry conditions and in the absence of SO$_2$. In addition, the experiments were intentionally conducted on a small amount of materials (20 mg) [13]. The catalytic performances of the nanofibrous catalysts prepared at different content of acetic acid were compared with the catalytic performance of
the-state-of-the-art Ti-V-W catalyst obtained by Haldor Topsøe in the form of nanoparticles. For clarity, the reference material is hereafter indicated as HT.

Figures 4 a-c show catalysis performances of the nano-fibrous materials. The profile of the HT catalyst is also shown. The catalytic activity, shown in Figure 4a as function of the reaction temperature, is expressed as the first-order rate constant (cm$^3$ g$^{-1}$ s$^{-1}$) and it is obtained by applying Equation 2 (Experimental section). Indeed, the NH$_3$-SCR reaction on V$_2$O$_5$-WO$_3$-TiO$_2$ is known to be first order with respect to NO under stoichiometric NH$_3$ conditions [7, 34, 35]. Steady increase in activity is observed for all the catalysts with the temperature, though significant differences are also obtained. For all the nanofibrous catalysts, a plateau corresponding to the maximum in the activity is reached at temperature higher than 400 °C. The materials possessing the superior activity are the nanofibers prepared at [Ac]/[Ti]=5 and 10, for which a wider regime plateau is obtained. The results then indicate the HT material as the catalyst with the poorest catalytic activity. For this material, a maximum in the activity is achieved at 350 °C, while at higher temperatures, its activity rapidly decreases.

The catalytic behaviour of the materials was further investigated by studying the kinetic of the process. The estimation of the activation energy ($E_a$) was obtained by applying the Equation 3 (experimental section). In figures 4b the Arrhenius plot for the nano-fibrous and the nanoparticles catalysts are shown. For all of the samples two regions associated with two mechanisms of reaction are observed depending on the temperatures. In the region at lower temperatures reaction is dependent on the temperature, whereas at higher temperatures no dependence is observed with activation energy values ($E_a$) close to zero. This represents the regime region, where the reaction is likely controlled by transport phenomena of reagents. Interestingly, the transition from the first region to the second one occurred at different
temperatures for the investigated materials. The observed trend of the transition temperatures ($T_a$) is: the HT nanoparticles catalyst < nano-fibrous catalyst at $[\text{Ac}]/[\text{Ti}]=5$ and 10 < nano-fibrous catalyst at $[\text{Ac}]/[\text{Ti}]=2$ (see Fig. 4c). The $E_a$ values for the first region together with the $T_a$ are reported in Table 4. The HT material possesses the lowest $T_a$ and $E_a$ with respect to the three nano-fibrous materials. Despite that, it is the catalyst with the poorest activity, while the nanofibers prepared at $[\text{Ac}]/[\text{Ti}]=5$ and 10 as the best performing catalyst. Indeed, the two materials are characterized by the largest regime plateau, whereas both the nanofibers prepared at $[\text{Ac}]/[\text{Ti}]=2$ and the HT catalysts exhibit narrow regime plateau. Yet, as already pointed out, the performances of HT rapidly decrease starting from 400 °C. It is worth mentioning that the nano-fibrous material prepared at $[\text{Ac}]/[\text{Ti}]=5$, despite its inhomogeneous distribution of the nanofibers diameters, show remarkably high performances that are comparable with the performances observed for the material characterized by highly homogeneous distribution of the nanofibers diameters ($[\text{Ac}]/[\text{Ti}]=10$). This can be ascribed to the unique morphologies characterizing the nano-fibrous catalysts. Indeed, the well-connected and open porosity structure are the discriminating features that might ensure the favourable fluid-dynamic regime and an efficient exposure of the reactive materials.

4 Conclusions

V-W doped-titania nanofibers were prepared to serve as de-NOx catalysts in NH$_3$-SCR process. The active materials were introduced as dopants element into the supporting titania. The chemistry of the sol-gel spinning solutions was adjusted with the aim of exploring its effect on the morphology of the nanofibers and on the final performances. Specifically, the control over the alkoxides precursors was optimized by varying the amount of the chelating...
agent (acetic acid). Contents of chelating agent larger than the stoichiometric molar ratio ([Ac]/[Ti]=2) led to best performing catalysts. The well-connected and open porosity characterizing the nano-fibrous substrate were indicated as the main factors impacting the NOx efficiency conversion and conferring superior catalytic performances.

Acknowledgements

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Haldor Topsøe A/S is also gratefully acknowledged for providing the nanoparticles state-of-the-art catalyst.

5 References


Tables Captions

**Table 1**- Characteristics of the elements used.

**Table 2**- Compositions of the materials developed.

**Table 3**- Structural parameters for the complete series of samples prepared.

**Table 4**- Arrhenius fitting parameters for the investigated materials.
### Table 1

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ionic Radii (nm)</th>
<th>Electronegativity (Pauli scale)</th>
<th>Standard Reduction Potentials (V)</th>
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<tr>
<td>Titanium ($\text{Ti}^{4+}$)</td>
<td>0.0605</td>
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<td>Tungsten ($\text{W}^{6+}$)</td>
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<td>Vanadium ($\text{V}^{5+}$)</td>
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<td>1.63</td>
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Table 2

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<td>V-W-TiO₂-(10)</td>
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<td>V-W-TiO₂-(2)</td>
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Table 3

<table>
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<th>Sample</th>
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<td></td>
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<td>c (Å)</td>
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<td>TiO₂</td>
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<td>W-TiO₂-(5)</td>
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<td>3.794 ± 0.002</td>
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<td>V-W-TiO₂-(2)</td>
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<td>3.792 ± 0.003</td>
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Table 4

<table>
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<th>Sample</th>
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<th>Pre-exponential Factor, $A$</th>
<th>Activation Temperature, $T_a$ (°C)</th>
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<td>V-W-TiO$_2$-(10)</td>
<td>33 ± 4</td>
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<tr>
<td>V-W-TiO$_2$-(5)</td>
<td>31 ± 4</td>
<td>$90<em>10^3 \pm 2</em>10^3$</td>
<td>350</td>
</tr>
<tr>
<td>V-W-TiO$_2$-(2)</td>
<td>33 ± 4</td>
<td>$91<em>10^3 \pm 2</em>10^3$</td>
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<tr>
<td>State-of-the-art</td>
<td>24 ± 3</td>
<td>$18<em>10^3 \pm 1</em>10^3$</td>
<td>300</td>
</tr>
</tbody>
</table>
**Figures Captions**

**Figure 1.** Chemical structure of (a) titanium alkoxide, (b) acetic acid, (c) bidentate chelating structure, (d) bidentate bridging structure, and (e) viscosity curve for the samples prepared at increasing content of acetic acid.

**Figure 2.** (a), (b), and (c) SEM pictures of nanofibers prepared at increasing amount of acetic acid; (d) TEM micrograph for the V-W-TiO$_2$ sample ([Ac]/[Ti]=10) with the SAED as inset; (e) HT-TEM micrograph for the V-W-TiO$_2$ sample ([Ac]/[Ti]=10) with the fringe spacing attributed to (101) plane of anatase.

**Figure 3.** (a) XRD pattern (the rutile phase is indicated with the star) and (b) average grain sizes and SSA for the nano-fibrous samples prepared at increasing content of acetic acid; (c) SEM micrograph for the nanofibers prepared at [Ac]/[Ti]=2.

**Figure 4.** (a) SCR activity, (b) the Arrhenius plot for the nano-fibrous samples prepared at increasing content of acetic acid, (c) transition temperature ($T_a$).
Highlights

- V-W-doped titania nanofibers were synthesized via electrospinning.
- Spinning solutions were prepared starting from alkoxides precursors.
- The effect of the chelating agent content on morphology and performances was explored.
- Optimized nanofibers exhibited remarkable high performances.