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Nitrogen oxides (NO_x) are recognized as major air pollutants responsible for serious damages to the environment and human health. The most efficient and cost-effective technology available to convert NO_x into harmless products (nitrogen and water) is the selective catalytic reduction (SCR) method. Nanometric metal oxides electrospun as membranes hold a great potential for their use as enhanced catalyst due to their merits such as high surface-to-volume ratio, wide-open and interconnected porous network, and high porosity. However, the preparation of free standing electrospun ceramic membranes is critical because of their mechanical integrity. Herein, by integrating a co-electrospun polymeric component, we demonstrate highly porous WO₃-CeO₂/TiO₂ nanofibrous free standing membranes, enabling superior de-NO_x catalytic performances compared with nanofibers at same composition.

Highly porous Ce-W-TiO₂ free-standing electrospun catalytic membranes for efficient de-NO_x via ammonia selective catalytic reduction

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Abstract

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Highly porous Ce-W-TiO₂ free-standing nanofibrous membranes (FSM) are fabricated via electrospinning techniques to serve as NO_x-SCR catalysts. The precursor of the ceramic nanofibers (sol-gel solution) is co-electrospun with a poly(vinyl alcohol) (PVA) water solution. PVA integration into FSM is proven to avoid excessive bending of the nanofibers, and to prevent mechanical failure of the final ceramic nanofibrous structure. This is demonstrated to be associated with PVA higher thermal stability compared with the other organic additives. 3D tomography reconstruction indicates a resulting ceramic membrane with a great open and interconnected porosity of *ca.* 96%. The catalytic characterization, performed at the best working conditions (in absence of H₂O and SO₂), indicates the amorphous FSM as the best performing catalytic membrane. Superior catalytic performances for the developed FSM, over the nanofibers and the nanoparticles catalysts are proven, as a result of superior surface, morphological, and structural features. Long-term stability (120 h) and reproducibility (over 5 cycles) of the FSM are also demonstrated.

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Introduction

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Free-standing porous membranes are strongly required for a wide of practical applications that include biomedical engineering, water treatment, air purification, and catalysis [1-5]. Typically, free-standing membranes are fabricated starting from polymers that ensure an inherent flexible and mechanical stability [6,7]. However, when harsh conditions arise or operation at temperatures above 100-200°C are needed, ceramic membranes prevail offering wider spectrum of options and possibilities [6, 8]. For instance, this is the case of catalytic applications, where materials are usually subjected to extreme environmental conditions [6,8]. Ceramic porous membranes are typically prepared via colloidal processing that requires the dispersion of the ceramic powder into a solvent with the aid of an adequate dispersant, and the subsequent addition of a number of different additives to adjust the processability [9-12], and eventually to originate the porosity [13,14].

Beside the colloidal approach, in the recent years, electrospinning has emerged as a simple, inexpensive and versatile method of shaping materials into non-woven membranes composed of continuous nanofibers [15-20]. The resulting nanofibrous membranes possess a significantly high porosity (*e.g.* 80-90% [21]) that is associated with an arrangement of the nanofibers into a wide-open and well-interconnected porous network [21-25]. As a class of one-dimensional (1D) nanomaterials with cross-sectional diameters ranging from tens to hundreds of nanometres, nanofibers offer the further merit of an extremely high surface area-to-volume ratio. All these morphological features have been demonstrated to impart outstanding performances to the resulting nanofibrous ceramic membranes, especially in driven-pressure applications such as for instance filters for the abatement of air pollutants. This is associated with the dimensions of the nanofibers that match both the dimensions of the particles to be captured and of the molecular air flow parameters (*e.g.* λ , gas mean free path, for air at standard conditions is 68 nm) [24,26]. In addition, the electrospinning

approach offers the advantage of an easy control over the chemical compositions, allowing the preparation of a vast number of materials by simply adjusting the chemistry of the starting spinning solution [27].

Despite the great advantages, the preparation of free standing thick ceramic electrospun membranes still remains critical because of the mechanical fragility of the nanofibers when flexed above their critical strain. Typically, titania nanofibers from sol-gel chemistry exhibit a significant flexibility with tensile strength decreased and the Young's modulus increased for increasing calcination temperatures [28]. However, the transition from the as-spun material, containing both organic and inorganic precursors, to the final polycrystalline metal oxide is accompanied by the shrinkage of the materials, that can lead to strain easily above 50 % of the initial dimension [28]. This might cause an excessive bending of the single nanofibers, thus leading to the fracture of the membrane into small fragments. A number of investigations have been conducted to make possible the preparation of ceramic free-standing electrospun media [3, 4, 16, 27]. For instance, Wang *et al.* successfully prepared self-standing γ -alumina fibrous membranes by a careful optimization of the spinning parameters, and of the calcination conditions [4]. Yet, L. Shahreen *et al.* proposed to combine fragile catalytic nanofibers with more mechanically stable micron fibres of alumina into a fibrous catalytic media for the removal of NO and CO. The active nanofibers and the supporting microfibers, were separately electrospun and calcinated, then mixed to form a water-based slurry that was finally dried under vacuum into a mold to form a cylindrical filter [24].

Despite the promising performances obtained, the mentioned processing methods still suffer from limitations, the main one being the multi-steps approach. A simple manufacturing method is actually highly desirable to reduce the production costs and time.

We herein address the issue by proposing a single-step approach based on the integration into the nanofibrous structure of an additional co-electrospun polymeric component able to sustain the catalytic nanofibers during the removal of the organics. The structural supporting

effect is achieved by introducing a polymer with a higher thermal stability compared to the organic additives used in the electrospinning process. As supporting polymer, we propose poly(vinyl alcohol) (hereafter PVA) that is co-electrospun together with solutions precursors of Ce-W-TiO₂ into nanofibrous xerogel membranes. Upon the calcination process, highly porous free-standing electrospun membranes (FSMs) to serve as catalytic media for the abatement of NO_x via selective catalytic reduction (hereafter SCR) are achieved. The composition of the ceramic nanofibers is fixed based on the results we have recently reported on the de-NO_x efficiency of ceria-based catalysts [22]. To the best of our knowledge, this is the first report on the preparation of highly porous free-standing electrospun ceramic membranes using a supporting co-electrospun polymeric component to control the structural stability of ceramic nanofibers.

Experimental details

Materials

All materials were reagent grade and used as received. Precursors sensitive to the environmental humidity were stored in a desiccator. Titanium (IV) isopropoxide (97% purity, Sigma Aldrich, Denmark), tungsten (VI) ethoxide (5% w/v in ethanol, Alfa Aesar, Denmark), and cerium (III) nitrate hexahydrate (99.5% purity, Alfa Aesar, Denmark) were used as cationic precursors. Poly(methyl methacrylate) (PMMA; $M_w \sim 996,000$, Sigma-Aldrich, Denmark) and glacial acetic acid (99.8%, Sigma Aldrich) were used as carrier polymer and stabilizer for the hydrolysis reaction of the alkoxides, respectively. Ethanol (Anhydrous, 99.9%, Sigma Aldrich, Denmark) and acetone (99.8% purity, VWR International, Denmark) were used as solvent. Poly(vinyl alcohol) (PVA, 87-89% hydrolyzed; $M_w \sim 85,000$ -124,000, Sigma Aldrich, Denmark) and distilled water were used to prepare spinning solution of the supporting polymer.

Preparation of spinning solution

In an optimized procedure, the spinning solution for the ceramic nanofibers was prepared by firstly stabilizing titanium (IV) isopropoxide and tungsten (VI) ethoxide with the acetic acid (e.g. molar ratio of acetic acid per the alkoxides was kept at 15) under magnetic stirring (20 °C) in a sealed container purged with inert gas (e.g. argon) for 15 min. A salt solution of cerium (III) nitrate hexa-hydrate in anhydrous ethanol at the concentration of 39% w/w was added dropwise into the stabilized mixture under mild stirring until a transparent and homogeneous solution was obtained. The viscosity was then adjusted by adding a required amount of PMMA solution (7.5% w/w). The overall cationic concentration was kept at 0.4225 mol L⁻¹, while the ratio of PMMA to cations was fixed at 0.56 g g⁻¹. The molar ratio of titanium/cerium/tungsten was fixed at of 1.0/0.2/0.1. The PVA solution, at the concentration of 7.5% w/w, was prepared by dissolving PVA into distilled water. The two spinning solutions (*e.g.* the ceramic precursors and the polymer support solution) were finally loaded into two different glass syringes equipped with a 21-gauge stainless steel needles.

Electrospinning of the solution and heat treatment of the as-spun nanofibrous mats

The nanofibrous membranes were fabricated using RT Advanced (Linari Engineering, Italy). The two spinning solutions, loaded into two glass syringes, were connected to two separate syringe pumps and co-electrospun using the same spinning conditions of voltage (40 kV), tip-to-collector distance (12 cm), and solution-feeding rate (0.50 mL h⁻¹). The electrospinning process was conducted in air at a temperature of 20 ° C with relative humidity controlled at 23%. The nanofibers were collected in a form of flexible green membrane on aluminum foil wrapped on grounded drum rotating at 100 rpm. The total volume of both the cationic and the polymer solution was fixed at 10 mL for each fabricated membrane. The resulting green membranes were then thermal treated in air for 1.5 h at different temperatures (> 500 °C) with heat rate of 5°C min⁻¹, to promote the removal of the organic additives and favor the formation of the desired crystallographic phases.

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Material characterization

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The thermal properties of PVA, PMMA and of the as-spun nanofibrous membranes were investigated (TGA, NETSZCH, STA 409, CD) in air flux from room temperature to 700°C at a heating rate of 1 K min⁻¹. 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 materials. The pore volume and pore diameter of the fibrous developed membranes were evaluated using the Barrett-Joyner-Halenda (BJH) method (AUTOSROB software, AS1WIN). The X-ray diffraction (XRD, Bruker D8, Germany) patterns were recorded at room temperature (Cu Ka radiation) at a scanning rate of 0.01° s⁻¹ in the 2θ range from 10 to 90°. The morphology of the nanofibers was analyzed by using field emission scanning electron microscopy (FESEM, Supra, Carl Zeiss, Germany) and transmission electron microscopy (TEM, JEM3000F, Oxford Instruments, UK). The chemical composition of the samples was determined by energy-dispersive spectroscopy (EDS) coupled with FESEM.

The 3D structure of the membrane was evaluated by the FIB/SEM (Zeiss 1540 XB Crossbeam Scanning Electron Microscope, Carl Zeiss Microscopy GmbH, Germany). using a lateral E-T (Everhart-Thornley) detector and an In-lens detector. A gallium FIB slicing probe of 1 nA was used and the thickness of each slice was estimated to be 13 nm. The serial sectioning imaging was performed at 1 kV with a pixel size of 24×24 nm², giving a voxel size in the 3D-data set of 13×24×24 nm³. The nanofibrous membrane was prepared for FIB/SEM microscopy by vacuum infiltration with epoxy resin (from Struers) to enable high-quality grinding and polishing of the sample. Segmentation of the 3D FIB/SEM image data was performed with the program ImageJ (NIH). The uneven illumination observed in the 3D dataset does not allow to set a single threshold for the entire micrographs. The Sauvola algorithm [29,30] was thus used to perform local thresholds of the data. This algorithm works

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by dividing the input image into square windows ($n \times n$ pixel) and setting thresholds for each of them based on the mean and standard deviation of the pixel intensities. Visualization of the 3D reconstruction of the analyzed data was then performed with the program Avizo (FEI). The pore size distribution (PSD) was calculated according to the method described by Münch *et al.* [31]: the segmented 3D volume is filled with spheres of a given radius. By reducing the radius incrementally, more volumes will be filled. The PSD is then obtained by correlating the incrementally filled volume with corresponding radii. The fiber length distribution (FLD) was calculated based on the average path length method between two opposite vertices. However, from a thorough analysis of the 3D tomogram, some nodes are also observed. Here two or more adjacent fibers cross each other, leading to unavoidable uncertainties in the FLD calculation.

SCR tests

The catalytic experiments were conducted at dry conditions and in absence of SO₂, to characterize the intrinsic catalytic behaviour of the ceria-based catalysts. The setup for the SCR activity measurements is described in our previous work [21-23]. The different catalytic membranes were cut using pressing mold to fit their sizes to the quartz reactor tube (inner diameter 15 mm). To attain the desired GHSV values, in the reactor, a total gas flow rate was varied (3, 6, 9, 12 L h⁻¹). The inlet gases concentrations were fixed as follows: NO = 1000 ppm, NH₃ = 1000 ppm, O₂ = 8%, and CO₂ = 5%, with balancing argon gas. During the experiments, the temperature was increased stepwise from 100 to 500°C, whereas the NO concentration was continuously monitored by a mass spectrometer (Pfeiffer Vacuum, Omnistra™ GSD 301). The reaction system was maintained for 1 h at each reaction temperature to reach a steady state before performing the analysis of the catalytic performance.

Results and Discussion

Free-standing nanofibrous membranes (hereafter FSM) are fabricated by co-electrospinning the organic-precursor solutions of the Ce-W-TiO₂ with a water solution of PVA. The pure polymeric component (PVA) is herein selected to mechanically support the ceramic nanofibers during the calcination and avoid the fragmentation of the final ceramic membrane. The desired effect is achieved because of PVA higher thermal stability with respect to the other organic additives used in the electrospinning process. Figure 1a shows the thermogravimetric profiles together with the mass loss rate derivatives for the PVA (grey dash), nanofibers co-electrospun with PVA (FSM, grey line) and without (NF, black line). PVA is a semi-crystalline biocompatible and biodegradable polymer largely used for its excellent film forming, emulsifying, and adhesive characteristics [32,33]. The organic additives used in the process include the alkoxide of Titanium and Tungsten, whose thermal removal is in a range of 200-250 °C, and poly(methyl methacrylate (hereafter PMMA), used as spinning agent, that typically decomposes at temperatures lower than 500 °C (via depolymerization to monomers/monomers evaporation [34]). The TGA/DTG profiles of the NF sample indicate a complete removal of the organic additives (alkoxides and PMMA) at approximately 300 °C, whereas when nanofibers are co-electrospun with PVA (FSM) the complete decomposition is shifted to a temperature slightly lower than 500 °C. The observed shift in the decomposition temperature is likely ascribable to the PVA, whose complete thermal removal is identified at around 500 °C (Figure 1a). This experimental observation indicates that, when the decomposition of the organic additives is already occurring, PVA is not yet completely decomposed. PVA likely confers flexibility to the nanofibrous structure supporting the nanofibers during the thermal removal of the organic spinning additives, and avoiding their excessive bending. The subsequent complete removal of PVA has no effect on the mechanical integrity of the resulting organic-free catalytic nanofibers, because of the inherent mechanical stability of the titania nanofibers [28]. In the DTA profiles for NF and

FSM (Figure 1*b*), a light exothermic shoulder between 550-600 °C is observed and likely related to the formation of a crystallographic phase (e.g. anatase).

According to these results, the nanofibrous FSMs are calcinated at temperatures higher than 500 °C to ensure the removal of any residuals. As indicated by the TGA profile, during the calcination process the green FSM undergoes to the considerable weight loss of around 75%, that clearly corresponds to an equally significant shrinkage of the volume. The latter can be empirically evaluated by measuring the membrane dimensions before and after the calcination. Figures 2 *a-d* show the variation in lateral dimensions and thickness consequent on the calcination process at 500 °C. The ability of the co-electrospun PVA approach in ensuring the required structural stability is verified on a relatively large membrane, that represent the worst-case in terms of the internal mechanical stresses. The thermal induced conversion from the green to the pure ceramic nanofibrous FSM is indeed accompanied by a contraction of the volume of around 78%. It is worth noticing that despite the significant shrinkage, the nanofibrous membrane retains its shape, but above all its structural integrity. Yet, a long range (hundreds of microns) element analysis (EDX, inset Figure 2*c*) of the calcined nanofibers indicates a percentage of molar ratio for Ti/Ce/W (1.0000/0.1822/0.0723) that it is consistent with the molar ratio in the initial precursor solution, suggesting an adequate dispersion of the cations both in the initial spinning solution and in the electrospun membranes.

The effect of the different calcination temperature (all higher than 500 °C) on the crystallinity is then investigated. Figure 3 shows the diffraction patterns for the ceramic nanofibers calcinated at increasing temperature. No peaks associated with crystallographic phases are observed for materials calcinated at temperatures lower than 538 °C. For the sample calcinated at this temperature an initial formation of the anatase phase of the titanium oxide can be inferred. The peak corresponding to the diffraction plane (101) is identified. In contrast, at higher temperatures (e.g. 550 °C) the occurrence of the anatase of the titanium

oxide (diffraction plane (101)) and fluorite of the cerium oxide (diffraction plane (111)) phases is detected. An effect of cerium dopant in inhibiting the formation of anatase phase is observed and supported by literature [21-23,35]. This effect is likely ascribed to a large dimensional cations mismatch (Ce^{+4} (0.87 Å) vs Ti^{+4} (0.60 Å) in 6-fold coordination) that, at lower temperatures ($< 550\text{ }^{\circ}\text{C}$), causes reduced elemental diffusion of the cations. By contrast, at temperatures higher than $550\text{ }^{\circ}\text{C}$, the elemental diffusion is efficiently activated and the Ce-saturated TiO_2 anatase phase crystallizes [22].

Based on XRD indication, further characterizations are only conducted on three selected samples: FSM@500, FSM@538, FSM@575. The three samples are selected because representative of an amorphous state, an initial stage of the phase formation, and crystallographic phase, respectively.

The effect of the calcination temperature on the morphology is then investigated by SEM and TEM (see Figure 4a-f) for three selected samples. The micrographs refer to membranes previously cut into discs with a diameter of around 15 mm after calcination (insets Figure 4b, 4d, and 4f). SEM images (Figures 4a, 4c, and 4e) indicate a defect-free nano-textured porous structure composed of nanofibers with high aspect ratios and a narrow diameter distribution. An open and interconnected porosity is also observed and associated with a large porosity volume. Yet, a slight contraction of the diameter of the nanofibers for increased calcination temperature is observed and explained as an effect of the temperature (Table 1). Figures 4b, 4d, and 4f show the corresponding TEM micrographs for the above discussed samples. In agreement with the discussion on XRD pattern, amorphous characteristics, consisting in a smooth surface, are observed for the nanofibers that form the membranes calcinated at $500\text{ }^{\circ}\text{C}$ (Figure 4b). In the corresponding diffraction pattern obtained using a selected-area-electron diffraction (SAED) technique (inset Figure 4b), no signals of an ordered disposition of atoms within a crystallographic unit cell is observed. The initial formation of crystallites on the surface of the nanofibers can be instead inferred for the membrane calcinated at 538

°C (Figure 4d). The incipient formation of a crystallographic phase is also supported by the corresponding SAED pattern (inset Figure 4d), where an early signal of crystallographic phase can be identified. Eventually, a rough surface and polycrystalline densely packed morphology characterize the nanofibers for the membranes calcinated at 575 °C (see Figure 4f), confirmed by the corresponding SAED (inset Figures 4f).

The surface properties of the nanofibers, of critical relevance for understanding the catalytic performances, are also investigated. Figure 5a shows the N₂ adsorption-desorption curves, while data of pore volume, pore diameter, and specific surface are (SSA) summarized in Table 1. The adsorption curves for the three membranes follow the typical profile of mesoporous materials (pore diameter 2-50 nm), with a V profile type and H2 hysteresis loop. Interestingly, while the value of the surface pore volume increases from sample calcinated at 500 °C to sample calcinated at 538 °C, it remains constant when the temperature is increased to 575 °C (Figure 5b, and Table 1). A continuous increment of the pore diameter values with the temperature is instead observed (Figure 5b, and Table 1), that corresponds to a decrease of the specific surface area (Table 1). The observed trends for the surface parameters are an effect of the temperature, expected to induce the growth of the TiO₂ crystallites [36].

Structural characteristics of the calcinated FSM are then investigated with the aim of achieving an insight into the porosity. Details on the membrane porous structure can be achieved via FIB/SEM analysis. Figure 6a shows the SEM image, after FIB slicing, recorded at higher magnification with the In-lens detector at 1 kV for the membrane calcinated at 500 °C. Inside the hole dug with the gallium probe, two phases are observed: the white structural texture, that corresponds to TiO₂ nanofibers, and the black bulk which is the epoxy resin used to infiltrate the pores. The 3D tomography reconstruction of a sub-volume of the fiber-based membranes (7×15×8 μm³) is shown in Figure 6b. The TiO₂ fibers are represented in white, while pores are shown as transparent. The high porosity of the developed membrane is undeniably evident from the 3D reconstruction image. The analysis of the image provides an

estimated value of around 96%. This is an extremely high value, larger than the value (ca. 80%) [21] reported in literature for the nanofibrous catalyst, and obtained by analyzing the SEM micrographs (via estimation of the mean intercept length) [37]. The high porosity obtained for the nanofibrous FSM is likely ascribable to PVA, that exerts its action not only by avoiding the excessive bending of the single nanofibers, but also by limiting the shrinkage of the porous membrane structure during the thermal removal of the alkoxides and PMMA. Some further relevant details both on the structural porous network and on the nanofibers are shown in Figure 7a and 7b, respectively. Figure 7a suggests an average pore diameter value of around 650 nm, whereas Figure 7b indicates an average fiber length value of around 12.3 μm . It is worth mentioning that this latter estimated value is influenced by the dimension of the volume analyzed, and its value is likely expected to be higher when the entire volume of the membrane is considered.

The catalytic activity of the developed membranes is then explored, and the set of obtained information are used to better understand the performances. Aim of the study is the characterization of the intrinsic catalytic activity of the highly porous FSM. Accordingly, the experiments are conducted only in dry conditions and in the absence of SO_2 . FSMs in the shape of discs with the diameter of 15 mm (after the calcination) and the thickness of approximately 100 μm are tested. Each catalytic disc corresponds to the extremely low weight of material (CeWTiO_2) of around 8 mg.

Figure 8a shows the NO_x conversion as a function of the reaction temperature for three membranes: FSM@500, FSM@538, and FSM@575. Three regions in the catalytic activity of the materials can be identified: low, intermediate, and high temperatures. In the first region, the NO_x conversion values are low and almost constant, whereas steady increase is observed in the intermediate range of temperature, until a plateau, corresponding to the maximum in the NO_x conversion is reached at temperature around 300 $^\circ\text{C}$. This represents the *regime* region, where the reaction is only controlled by the transport phenomena of the reagents.

Interestingly, for all the three investigated catalysts, NO_x conversion declines at temperature as high as 500 °C, likely due to increased rate of ammonia oxidation at these temperatures [38]. In the intermediate temperature region, differences in the NO_x conversion trend for the three samples are observed, with the amorphous FSM (FSM@500) resulting the best performing material, being characterized by conversion values of around 60 % and 90% at 200 °C and 250 °C, respectively. Details on the reaction mechanism are obtained by exploring the kinetic of the process [39]. Estimation of the activation energy (E_a) and of the number of the active sites, associated with the pre-exponential factor (A), can be obtained by the Arrhenius fitting of the experimental data. Figure 8*b* shows the Arrhenius plot for the three catalytic membranes, while the corresponding fitting parameters together with the T_a are reported in Table 2. In the region at the lowest temperatures, the Arrhenius analysis is not conducted because of the insufficient number of experimental data (only two). At the intermediate range, the plot indicates a reaction dependent on the temperatures, whereas at the high temperature region no dependence is observed with an activation energy values (E_a) close to zero. The transition from intermediate to the regime region is observed to be shifted at higher values with the increased calcination temperature of the catalytic membranes (see the inset in Figure 8*b*). The observed trend follows the order: FSM@500 < FSM@538 < FSM@575. The amorphous catalyst is the material with the lowest activation temperature (259 °C), thereby characterized by the widest regime region. Interestingly, regardless the calcination temperature and the crystallographic phase, similar E_a values are observed, suggesting a similar reaction mechanism for the three catalytic FSMs. In contrast, a significant difference in the pre-exponential factor (A) is obtained. Specifically, similar number of active sites (within the experimental errors) are observed for FSM@500 and FSM@538, whereas the lowest number of active sites is associated with the FSM@575, likely as an effect of the highest calcination temperature. Overall, superior catalytic performances for FSM@500 is obtained, possible ascribable to the amorphous phase and its

corresponding larger specific surface area (Table 1). Indeed, the amorphous phase is generally regarded as promising substrate for the catalysis as it is considered chemically homogeneous with respect to the related surface properties [22,40,41].

The catalytic performances of FSM@500 are then further explored. In Figure 9a the NO_x conversion values at different values of gas hourly space velocity (GHSV) are plotted as function of temperature. As expected, high conversion (~98%) is obtained at the lowest values of GHSV (163 000 h⁻¹ and 326 000 h⁻¹) within a relative wide range of temperature (300-450 °C). Notably, at GHSV 653 000 h⁻¹, the catalyst still retains a NO_x conversion value around 90%. Figure 9b shows the comparison with the NO_x conversion of CeWTiO₂ nanofibers, and with the-state-of-the-art V-W-TiO₂ in the form of nanofibers and nanoparticles (kindly provided by Haldor Topsøe, Denmark). For clarity, the reference materials are hereafter indicated as CeWTiO₂-NF, V-W-TiO₂-NF, and V-W-TiO₂-PWD HD, respectively. The nanofibrous FSM exhibits undoubtedly the highest conversion values in the entire range of investigated temperature and at different GHSV experimental conditions. This can be ascribed to the extended and highly porous network that characterized the nanofibrous FSM and that enables a favourable fluid-dynamic regime through the membrane. In such a structure, any single nanofiber can be considered as a nanoreactor arranged with the other nanofibers into a highly porous and lightweight SCR unit. In Table 3 a comparison between the NO_x conversions of the nanofibrous FSM developed in the current study, and literature data from both nanofibers and nanoparticles ceria-based mixed oxide [22,42-44] is indicated. The comparison is only reported at temperatures lower than 300 °C (150 and 200 °C), before the catalysts reach the *regime* region. Superior catalytic behavior of the nanofibrous FSMs is observed both over the nanofibers and nanoparticles. Indeed, conversion values of around 30% and 73% are obtained at 150 °C and 200 °C respectively for the FSM at GHSV of 163000 h⁻¹. At the same temperatures the data from literature indicate conversion values of

around 15% and 40-60% respectively at any GHSV values (e.g. 25 000, 200 000, and 250 000 h⁻¹) [22,42-44].

The long-term stability of the FSM@500 sample is also investigated over a time frame of 120 h, at 300 °C, and at 326 000 h⁻¹ (Figure 10a). Remarkably, the material exhibits stable and high de-NO_x conversion value over the entire range of time frame investigated. Yet, no deactivation of the activity is observed for the catalysts after the continuous long-term stability test (inset), compared to the fresh materials. The stability of the material upon 5 working cycles is also verified (Figure 10b). The reproducible conversion profiles observed further confirm the high stability of the developed FSM at the working conditions. Notably, FSM@500 disc after 5 SCR testing cycles still retains its integrity (Figure 10c).

Conclusions

Free-standing Ce-W-TiO_{2-δ} nanofibrous membranes (FSM) are successfully electrospun to serve as catalysts for the removal of NO_x in selective catalytic reduction (SCR) process. The structural stability is achieved by integrating into the nanofibrous membrane a co-electrospun polymeric component able to sustain the catalytic nanofibers during the removal of the organic additives at around 300 °C. The supporting polymer used is PVA, whose complete thermal decomposition occurs at around 500 °C. In such a combination, PVA is able to hold the structural stress deriving from the removal of the additives and from the corresponding shrinkage. PVA is also proven to exert its role by limiting the volumetric contraction of the whole membrane. This results in an extremely high porosity value of *ca.* 96%.

The surface and morphological features of the nanofibers along with the structural and porous characteristics of the resulting FSM are definitely the main factors responsible for the exceptional catalytic performances. Indeed, these characteristics are expected to favor a fluid-dynamic regime that enables an efficient exposure of the active sites towards the reactant gases, thereby enabling high NO_x conversion levels: values as high as 95% at GHSV of 326

000 h⁻¹ are observed in a wide range of temperatures. Yet, high conversion values (ca. 90%) are maintained even at high gas speed (653 000 h⁻¹). Notably, the comparison with the same composition nanofibers (NFs), indicates superior performances for the nanofibrous FSM. Besides, highly long-term stability and over multiple working cycles are also demonstrated.

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Conflicts of interest

There are no conflicts to declare.

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Tables Captions

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Table1- Characteristics of nanofibers (phase, diameter, specific surface area, pore diameter, pore volume) calcinated at 500, 538, and 575 °C.

Table 2- Arrhenius fitting parameters for the investigated materials (intermediate range of temperature).

Table 3- Literature data for Ceria-Tungsten-based mixed oxide catalysts. The compositions are reported indicating the Ce/W molar ratio and considering equal to the unit (1) the molar content of Ti. For each reference, only the data of the best performing catalysts are listed.

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Sample	Crystallographic Phase	Average nanofiber diameter (nm)	Specific Surface Area (m²/g)	Pore volume (cm³/g)	Pore diameter (nm)
CeWTiO ₂ @500	Amorphous	229 ± 42	59.89	0.08	3.5
CeWTiO ₂ @538	Anatase/Fluorite	219 ± 53	43.48	0.13	7.3
CeWTiO ₂ @575	Anatase/Fluorite	212 ± 59	38.88	0.13	9.1

Table 2

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Sample	Activation Energy, E _a (kJ/mol)	Pre-exponential factor, A	Activation Temperature, T _a (°C)
CeWTiO ₂ @500	40.10 ± 3.60	6.16*10 ⁶ ± 0.15*10 ⁶	259
CeWTiO ₂ @538	41.74 ± 2.15	7.34*10 ⁶ ± 0.23*10 ⁶	274
CeWTiO ₂ @575	40.38 ± 2.28	2.87*10 ⁶ ± 0.11*10 ⁶	300

Table 3View Article Online
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Catalyst	[NH3] [NO] (ppm)	GHSV (h ⁻¹)	NO _x Conv. (%) @150°C	NO _x Conv. (%) @200°C	Reference
Ce ₁ W ₁ TiO _x powder	500	250 000	10	50	38
Ce ₁ W ₁ TiO _x powder	500	25 000	15	60	39
Ce ₃ W ₁ TiO _x powder	1000	200 000	< 10	40	40
Ce _{2.6} W ₁ TiO _x Nanofibers	1000	200 000	19	56	22
Ce _{2.6} W ₁ TiO _x Nanofibers	1000	400 000	16	51	22
Ce _{2.6} W ₁ TiO _x Nanofibrous Membranes (FSM@538)	1000	163 000	30	73	Current study
Ce _{2.6} W ₁ TiO _x Nanofibrous Membranes (FSM@538)	1000	326 000	24	64	Current study

Figure Captions

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Figure 1- (a) TG/DTG and (b) DTA profiles of PVA (grey dash), FSM (grey line), and NF (black line).

Figure 2- (a) Digital photo of as produced FSM and (b) its SEM cross-sectional view; (c) digital photo of FSM calcinated at 500 °C and (d) its SEM cross-sectional views. The inset in (c) is the EDX analysis for the calcinated FMS.

Figure 3- XRD patterns of Ce-W-TiO₂ FSM calcinated at different temperatures. The fluorite phase of cerium oxide is indicated with a star.

Figure 4- Top-view SEM micrographs of Ce-W-TiO_{2-δ} FSM calcinated at (a) 500 °C, (c) 538 °C, and (e) 575 °C; TEM images of Ce-W-TiO_{2-δ} FSM calcined at different temperatures: (b) 500 °C, (d) 538 °C, and (f) 575°C; the lower-inset in (b), (d), and (f) are the corresponding selective area electron diffraction (SAED) patterns and the upper-inset are the digital photos of Ce-W-TiO₂ FSM discs.

Figure 5- (a) N₂ adsorption–desorption isotherms of Ce-W-TiO_{2-δ} FSM calcinated at 500 °C, 538 °C, and 575 °C; (b) pore size distribution of the different FSM catalysts. The insert in (b) shows their corresponding pore diameters and pore volumes.

Figure 6- (a) SEM micrograph of FSM calcinated at 500 °C after FIB slicing, and (b) the corresponding 3D FIB tomography reconstruction of a sub-volume (7×15×8 μm³).

Figure 7- (a) The pore size distribution, and (b) the fiber length distribution corresponding to FSM calcinated at 500 °C.

Figure 8- (a) SCR activity of Ce-W-TiO_{2-δ} FSM calcinated at 500 °C, 538 °C, and 575°C, and (b) the corresponding Arrhenius plot.

Figure 9- (a) NO_x conversions at different GHSVs of Ce-W-TiO_{2-δ} FSM calcinated temperature at 500°C, and (b) comparison in NO_x conversion with same composition nanofibers and with the-state-of-the-art material (V-W-TiO₂) in the form of nanofibers and nanoparticles. The latter catalyst is kindly provided by Haldor Tpsøe A/S.

Figure 10- (a) Long-term stability test (120 h) at 300°C of the FSM@500; (b) and its reproducibility test over 5 working cycles. Both tests are performed at GHSV of 326 000 h⁻¹; (c) digital photos of fresh FSM@500 and after 5 SCR testing cycles.

Figure 1

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Figure 2

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Figure 9

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Figure 10

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Highly porous free-standing ceramic membranes to serve as SCR catalysts are achieved by controlling the structural stability of the nanofibers via integration of a co-electrospun supporting polymeric component.