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Review

Research Progress on the Applications of Electrospun Nanofibers in Catalysis

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Abstract: During the last two decades, electrospinning has become a very popular technique for the fabrication of nanofibers due to its low cost and simple handling. Nanofiber materials have found utilization in many areas such as medicine, sensors, batteries, etc. In catalysis, these materials also present important advantages, since they present a low resistance to internal diffusion and a high surface area to volume ratio. These advantages are mainly due to the diameter–length proportion. A bibliographic analysis on the applications of electrospun nanofibers in catalysis shows that there are two important groups of catalysts that are being investigated, based on TiO_2 and in carbon materials. The main applications found are in photo- and in electro-catalysis. The present study contributes by reviewing these catalytic applications of electrospun nanofibers and demonstrating that they are promising materials as catalysts, underlining some works to prove the advantages and possibilities that these materials have as catalysts. On one hand, the possibilities of synthesis are almost infinite, since with coaxial electrospinning quite complex nanofibers with different layers can be prepared. On the other hand, the diameter and other properties can be controlled by monitoring the applied voltage and other parameters during the synthesis, being quite reproducible procedures. The main advantages of these materials can be grouped in two: one related to their morphology, as has been commented, relative to their low resistance and internal diffusion, that is, their fluidynamic behavior in the reactor; the second group involves advantages related to the fact that the active phases can be nanoscaled and dispersed, improving the activity and selectivity in comparison with conventional catalytic materials with the same chemical composition.

Keywords: electrospinning; nanofibers; TiO_2; carbon fibers; electrocatalysis; photocatalysis

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1. Introduction

During the last decade, new synthesis methods have been developed for nanomaterials, i.e., those in which their shape and molecular composition (or both) at a nanometer scale can be controlled. In this manner, the availability of nanomaterials with a wide range of chemical and physical properties has increased exponentially during recent years. These materials, given their extraordinary properties, have great potential application in fields such as medicine, electronics, sensors and catalysis, among others. The terms nanotubes, nanowires and nanofibers are commonly used to refer to those materials that present a very high length to width ratio with respect to nanotubes and nanorods, especially in the case of nanowires [1,2]. The applications and synthesis methods for nanotubes and nanofibers are significantly different, and the present study will only focus on the applications of nanofibers in catalysis.

Nanofibers have several promising characteristics, such as a very large surface area to volume ratio, quite high mechanical performance and flexibility in surface functionalities and composition, in comparison with other materials [2–4] such as pellets, monolits or powers. Subsequently, they find new and novel applications in several fields, and several synthesis methods have been described, such as self-assembly, phase separation drawing processing, template-assisted synthesis or solvent casting [5–7]. Among all the described methods, the most simple and versatile is the electrospinning method, being subsequently

the most commonly used for a majority of applications [8–11]. In this technique, an electrostatic field is applied to a conducting fluid which is usually a polymer solution. When this electrostatic field is strong enough to overcome the surface tension of the fluid, the droplet at the tip of the spinneret becomes unstable and a tiny jet is ejected. The jet stream is collected, and by this way the fibers are obtained. A quick search in a database, such a Scopus in November 2021, shows that with the key words electrospinning and fibers in the title, keywords or abstract, almost 23,000 entries are found, published during the last two decades, demonstrating the high number of applications that are being developed for electrospun fibers, being around 4100 of those entries related with catalysts or catalysis. These data indicate that most of the applications of nanofibers are for nanomedicine, sensors and batteries, and catalysis is also a promising application for them. The software VOSViewer (Centre for Science and Technology Studies, Leiden University, The Netherlands) was used to generate a multi-dimensional map that groups bibliometric metadata into closely related clusters to analyze the most-cited entries (limited to 200) related to catalysis (Figure 1). One cluster (green), with 14 items, includes titanium oxide and photocatalysis and electrochemistry; another cluster (blue) with 11 items includes carbon nanofibers, lithium-ion batteries, electric batteries and secondary batteries; whereas the yellow cluster with 10 items includes nanocomposites, membranes and polyacrylonitrile. Then, there is one more cluster (red), with 13 items, including drug delivery, tissue engineering and biocompatibility, indicating that one of the main applications of electrospun fibers is in medicine, as has been already mentioned [1].

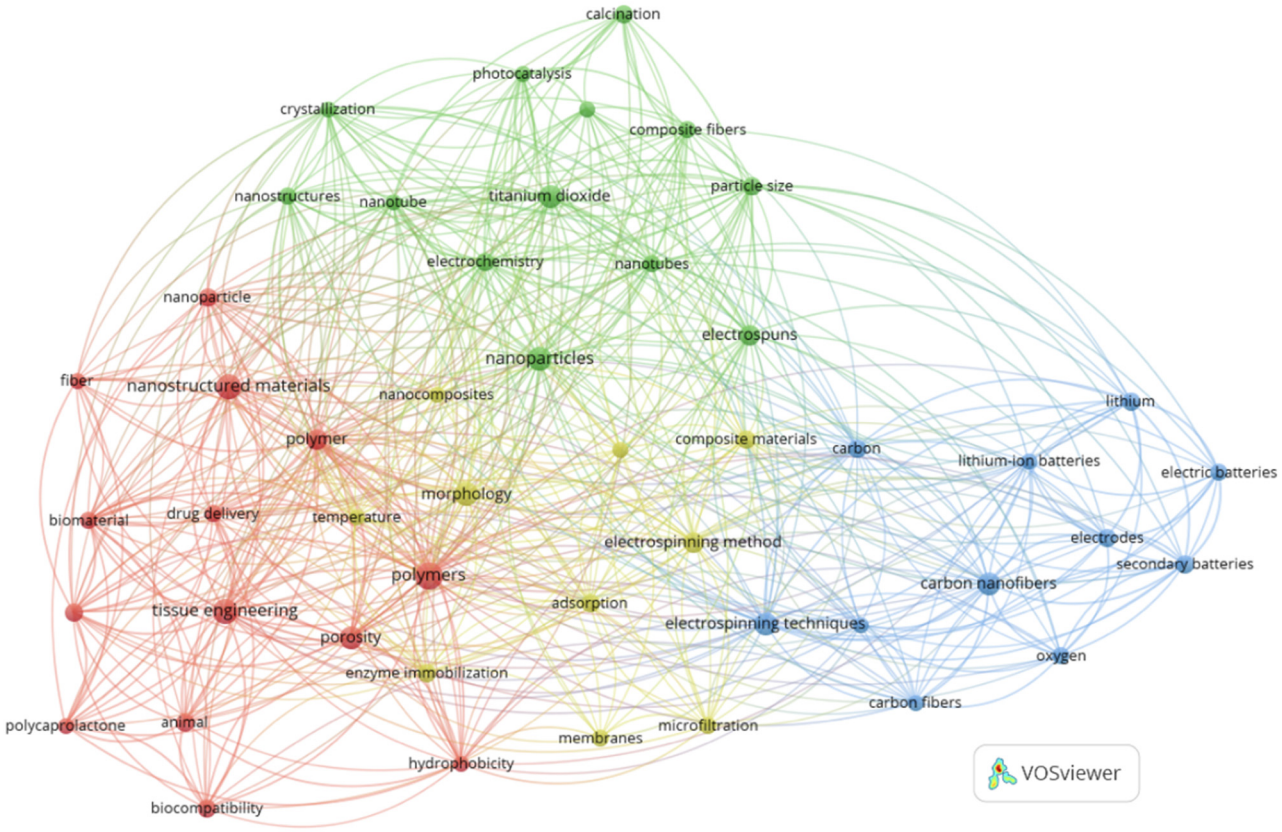


Figure 1. Bibliometric map of 48 keywords from the top 200 cited articles Scopus indexed for electrospinning, fibers and catalysis or catalysts. 4 clusters are identified. The size of the circle and font are proportional to the number of articles.

In catalysis, the fiber-based materials present several advantages with respect to other materials for several reactions and have been used as supports for many commercial catalytic processes. These materials present a low resistance to internal diffusion and quite

a high surface area to volume ratio, due to the diameter–length proportion. Some years ago, Reichelt et al. [12] reviewed the use of ceramic, metal and glass fiber materials as catalytic supports for several metal- and oxide-based active phases. They concluded that the fibers presented superior catalytic properties in terms of mass transfer and pressure drop, although this also depended on the reactor design. Although nanofibers and fibers may exhibit different properties due to the different diameter range considered, it is expected that nanofibers retain many of the advantages of conventional fibers and will present additional ones due to their nanostructure. As electrospinning equipment has become very popular in the last decade, many catalytic applications of electrospun nanofibers have been developed as shown by the bibliographic analysis results (Figure 1). Some review papers focus on the synthesis and characterization of nano- and microfibers [13,14] that can be used as catalysts themselves or as catalytic supports. The present study will try to provide a different perspective focusing on the catalytic applications of these materials, with the aim of describing the advantages and disadvantages that they present in different catalytic systems, as well as their perspective and future trends in catalysis. The bibliographic analysis (Figure 1) shows that there are two main applications in catalysis, centered in TiO_2 and carbon-based nanofibers, for photocatalysis and electrocatalysis.

2. Carbon Fiber Applications

Carbon materials have several advantages in catalysis, especially as catalytic supports, due to their availability, high surface area and mechanical stability, among other important properties [15–17]. Carbon, in addition, is an abundant element whose materials can be prepared from waste [18,19]. When used as catalytic supports, carbon materials present the advantage that, once the catalysts have lost their activity, the active phase can be easily recovered. On the other hand, carbon nanofibers prepared by electrospinning are relatively easy to prepare, since there are a high number of polymers that can be electrospun, giving rise to different types of carbon nano- and microfibers with different properties and sizes [20,21] after the corresponding carbonization step. These materials present intermediate diameters between conventional carbon fibers and carbon nanotubes, giving rise to a family of nano- and micromaterials very attractive as catalysts, as catalytic supports, and as a template for the preparation of other non-carbonaceous fibers. Apart from catalysis, these materials have found other applications, for example they are commonly used in electrochemical energy storage or for biosensing devices; however, these are outside the scope of present review-contribution.

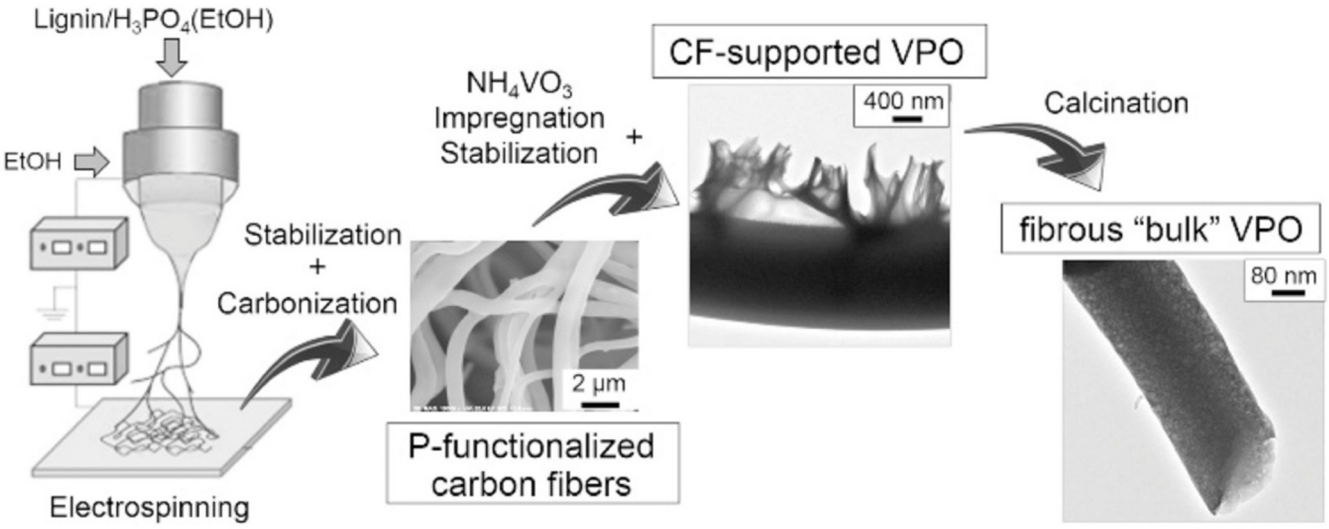
The use of carbon nanofibers (CNFs) in catalysis is more extensive, as catalytic support is required for electrocatalytic applications, that are necessary for the development of fuel cells, water-splitting systems and batteries [2]. For these applications, the electrodes made with fibrous materials present several advantages compared to those made from conventional catalyst powders, since they are binder-free and do not agglomerate. Recently, Wang et al. [22] published a review paper on the use of fibrous structures, including CNR, for oxygen electrocatalysis, underlining that the most investigated CNF material for this application are those fibers prepared by electrospinning mainly with PAN (polyacrylonitrile) and PVP (polyvinylpyrrolidone). Carbon nanofibers prepared by electrospinning have proved to be efficient catalytic supports for noble metals in electrocatalytic applications [2]. Alvi et al. [23] prepared Pd-Ce catalysts supported on carbon nanofibers prepared by electrospinning, and successfully detected the formation of Pd-Ce alloys on the surface of this support. This material was used to construct an anode for a direct methanol fuel cell (DMFC), presenting an excellent catalytic activity. Other groups have investigated the use of electrospun carbon fibers as support for Pt sites [24,25] also for DMFCs, optimizing the porosity of the support as a function of the polymer used and the electrospinning conditions. These examples demonstrated that the electrospinning procedure allows the modulation of the textural properties of the catalytic support, improving the stability and activity of these electrocatalysts compared to commercial Pt/C catalysts that uses Vulcan or E-TEK carbon materials. The properties of these Pt/CNFs can be modulated also with

the addition of another element as dopant that can be incorporated as nanoparticles during the synthesis procedure, such as Nb [26] or Fe [27].

CNFs are also an alternative as catalysts and as support to prepare electrocatalysts without noble metals. Liu et al. [28] prepared Fe-Co/CNF electrocatalysts, showing that with the electrospinning method it was possible to prepare mesoporous nanofibers with the active sites uniformly distributed; as a result, the material presented a high-power density, a low discharge-charge voltage gap and a high stability, being an excellent electrocatalyst. Other groups have developed a Ni-based electrocatalyst, such as Yang et al. [29], who prepared NiCo/CNFs electrocatalysts that showed a high-efficiency for both ORR and OER reactions, underlining the effect of the carbon fiber material that decreased the intrinsic and charge transfer resistance, conferring excellent electrocatalytic properties to the NiCo-based material. More works in the literature can be found [30–36] that show that Ni-based electrocatalysts supported by electrospun CNFs present excellent performances. This performance is attributed to the good dispersion and isolation of active phases on the surface of the carbon fiber, and to the high surface area values with abundant active sites, allowing the effective interaction between the electrolyte and the electrode during the electrochemical reaction [37]. These examples show that electrospun CNFs are an excellent support for various electrocatalytic applications, both for catalysts based on noble metals and for other alternatives, such as a Ni-based electrocatalyst.

In addition to electrocatalytic applications, there are some studies that demonstrate that electrospun CNFs are also a suitable catalytic support for thermal heterogeneous catalytic process. For example, Bai et al. investigated them as support for Pd nanoparticles (Pd/CNF catalysts) for Suzuki and Heck reactions [38]. As with the electrocatalysts, CNF proved to be an excellent material for a homogeneous distribution of the Pd nanoparticles, as the Pd/CNF materials demonstrated a stable and high efficiency in both reactions. The characterization results demonstrated that the Pd nanoparticles were as Pd (0), demonstrating that the CNF support prevented the oxidation of the active sites, and subsequently presented good activity results in both Suzuki and Heck reactions. Our group followed a similar approach for the preparation of VPO/CNF catalysts [39]. VPO (V-P-O) catalytic materials are well known as selective catalysts for partial oxidation reactions, being used commercially for the n-butane transformation into maleic anhidride. They are characterized by the interconversion, under reaction conditions, of several crystalline and amorphous vanadium phosphates, in which V can be at different oxidation states such as V^{3+}, V^{4+} or V^{5+}, being vanadyl pyrophosphate phase, $(VO)_2P_2O_7$, the active phase and main component in the industrial catalyst [40–43]. The procedure [39] that was developed consisted of the preparation of carbon fibers by electrospinning using lignin, a waste material, as the carbon source [44]. Then, the carbon fibers were activated with phosphoric acid in order to obtain a P-containing carbon material [44], that, after impregnation with vanadium precursor and thermal treatment, produced a VPO/CNF material (Scheme 1). Figure 2 shows the morphology of VPO/CNF samples thought SEM and TEM analysis. Another advantage of the P-containing carbon material [44] is that can be used under an oxidant atmosphere up to around 400 °C without being gasificated, since the phosphate groups on the surface prevent carbon oxidation. Further calcination of the VPO/CNF material gives rise to a bulk VPO fibrous material. The SEM and TEM analysis of this fibrous VPO material are shown in Figure 3. The chemical composition was analyzed by Raman and XRD [39], showing that the active phase ($(VO)_2P_2O_7$,) was formed and that it was quite dynamic, since the number of V^{4+} and V^{5+} species were changing under different environments, resulting in a very useful partial oxidation catalyst. This is due to the fact that these reactions occur through a Mars van Krevelen mechanism [45,46] that involves a redox cycle of the active phases that oxidizes and reduces under reaction conditions, facilitating the partial oxidation of the starting molecule. The synthesis procedures of VPO catalytic materials [40–43] is complex since the oxidation of vanadium sites and the disaggregation in V_2O_5 oxide have to be prevented. In this case, it seems that the carbon support prevented such oxidation, facilitating the formation of vanadyl pyrophosphate active phase, and the

subsequent redox cycles of V species during reaction, avoiding the disaggregation of VPO phases. These two papers show that CNFs are useful catalytic supports for thermal catalytic processes, since, in addition to the properties that the fibrous shape confer, the carbon is able to prevent active phases (Pd or VPO) oxidation and/or disaggregation.



Scheme 1. Synthesis procedure for VPO/CNFs and fibrous VPO catalytic materials. Reproduced with permission from the copyright owner (Elsevier 2016) from Ref. [39].

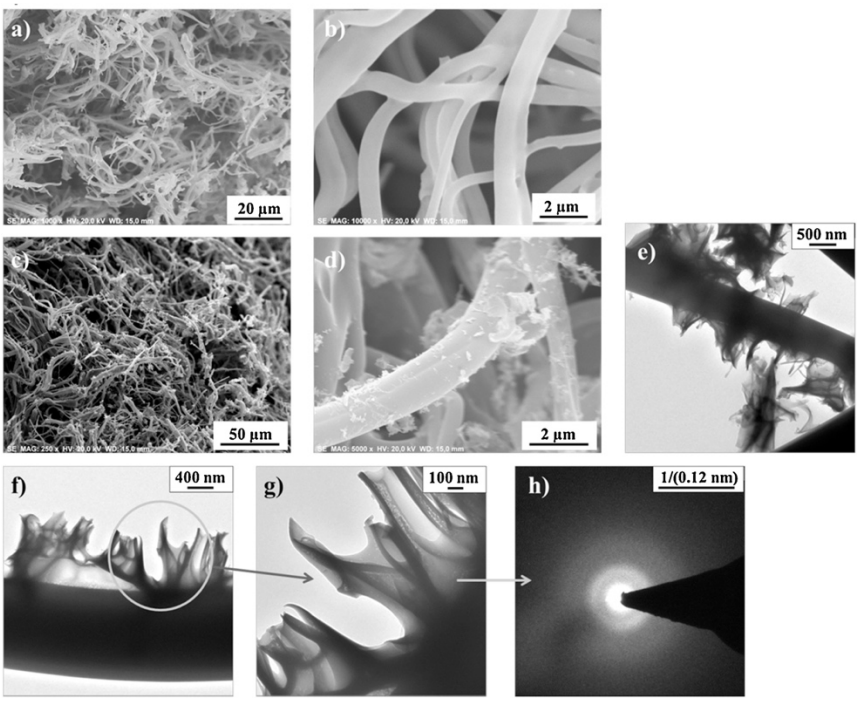


Figure 2. SEM (**a**–**d**) and TEM (**e**–**g**) images of carbon (**a**,**b**) and VPO/CNF (**c**–**h**) samples. Reproduced with permission from the copyright owner (Elsevier 2016) from Ref. [39].

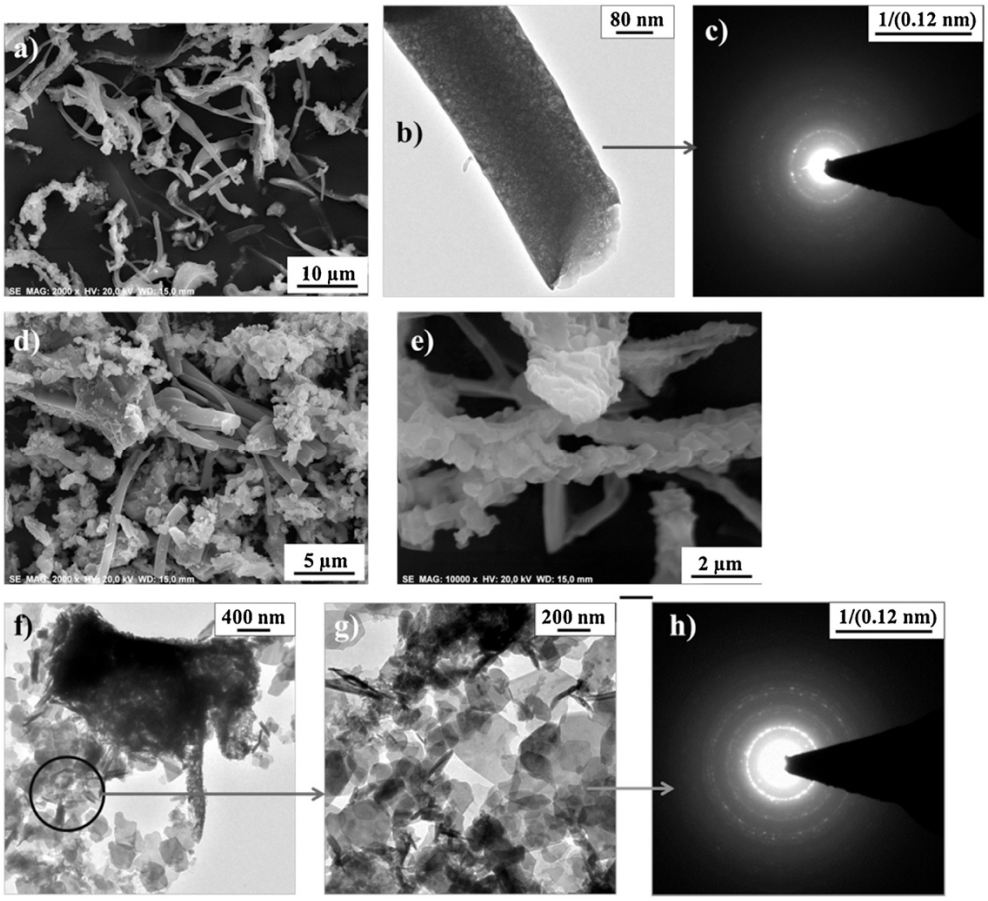


Figure 3. SEM and TEM (**a**,**b**,**d**–**g**) images of VPO fibrous catalysts at different magnifications and SAED analysis (**c**,**h**). Reproduced with permission from the copyright owner (Elsevier 2016) from Ref. [39].

The last example [39] shows that it is possible also to use the CNFs materials as template for the preparation of metallic or oxide fibers. The procedure would imply the impregnation of the CNF in a first step, and the further carbonization of the material by thermal treatment to eliminate the carbon material. Selecting the suitable parameters, it is possible to obtain the oxide material with fibrous shape, as it is shown in Scheme 1. These examples have demonstrated that CNFs are promising materials in both catalysis and electrocatalysis, and it is expected that many more applications in catalysis will be developed within the next few decades. Table 1 summarizes the main applications of advantages of CNFs in catalysis.

Table 1. Main advantages and applications of CNFs.

Main Properties of Carbon Materials as Catalytic Supports	Main Applications of CNFs	Advantages of CNFs in Electrocatalysis & Catalysis
Abundant source	Electrochemical energy storage	Do not agglomerate
High surface area	Biosensing devices	Blinder-free
Mechanical stability	Drug delivery	High stability
	Catalysis	Good Dispersion and isolation of active species
		Prevent active phase oxidation

3. TiO_2 Fibers Applications

It is well-known that titanium oxide is widely used as photocatalyst for many environmental and energy applications. TiO_2 oxide is also used in catalysis [47–49], for processes such as the selective reduction of nitrogen oxides [50] and has found other applications such as in white pigment, as a food additive and as a component of sensors and other devices. These important applications underline the interest in the development of TiO_2-based materials. It has been demonstrated that the performance is improved when primary TiO_2 particle sizes are at the nanoscale [47–49], but, unfortunately, these small sizes create several disadvantages, such as the presence of suspended nanoparticles when the photocatalyst is used in a liquid effluent; thus, several works can be found that describe the immobilization of TiO_2 nanoparticles for their use as photocatalyst. Subsequently, several synthesis methods for the preparation of TiO_2 nanomaterials have been developed, and electrospinning has proved to be one of the most useful due to its versatility. Kim and coworkers [51] prepared highly crystalline hollow TiO_2 fibers can be prepared by electrospinning, and with a uniform wall thickness. These authors first prepared polymer fibers by electrospinning and then used them as sacrificial template. By atomic layer deposition, a layer of TiOx was deposited on the polymeric fibers, then the polymeric material was removed by heat treatment, obtaining the crystalline hollow TiO_2 fibers with good crystallinity and controlled shape (diameter and wall thickness). A different approach for the preparation of TiO_2 fibers was followed by Nikfarjam [52] et al. They prepared a solution with a Ti precursor (titanium tetraisopropoxid), ethanol and acetic acid, that was mixed with the polymer PVP (polyvinyl alcohol). The mixture was electrospun with an aluminum foil as cathode. After calcination to decompose the polymer matrix, TiO_2 nanofibers were obtained. These fibers were used for gas-sensing applications. This approach of preparing fibers by the electrospining of Ti precursor-PVP solutions and subsequent heat treatment was used by other authors [53–57], demonstrating that this is a suitable technique. For some applications, such as for anode materials for Li-ion batteries, it is necessary to prepare mixed oxide fibers, such as $TiNb_2O_7$, and titanium niobium oxide nanofibers can be also prepared thought this procedure [58], involving the preparation of a precursor solution (titanium butoxide and niobium ethoxide) in ethanol/acetic acid that is mixed with a polymeric solution, electrospun, and then heated in air for polymeric matrix removal.

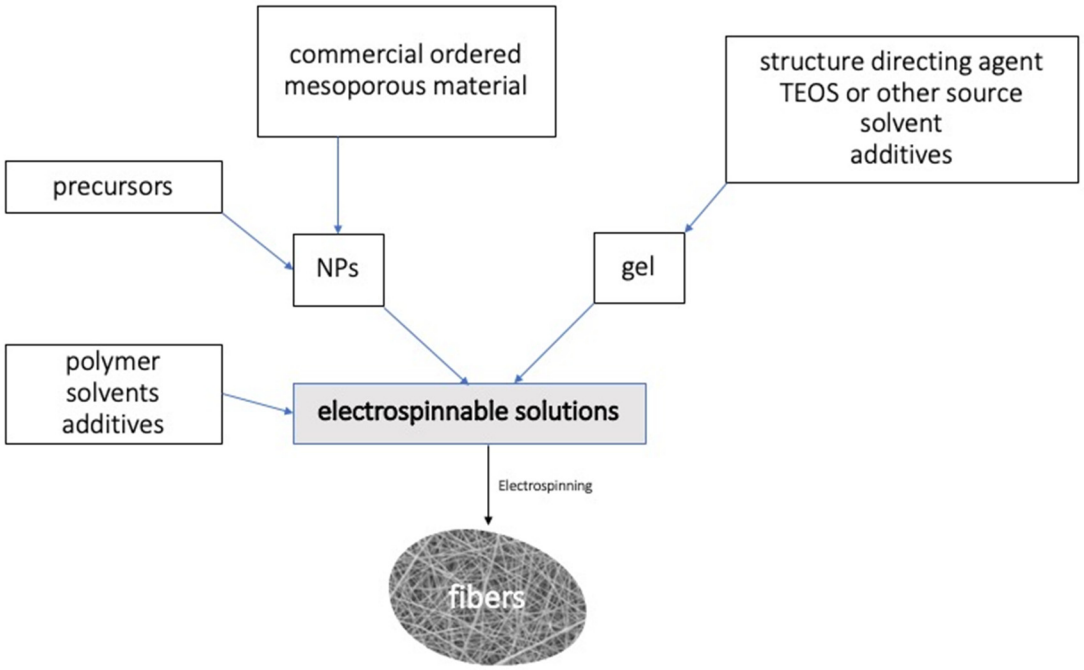
Thus, TiO_2 and mixed-Ti oxide fibers can be prepared by two methods: by deposition of the oxide layer on a CNF and subsequent calcination to remove the carbon material; or by the electrospinning of a suitable solution that contains the metal precursors and a polymer (usually PVP). In the same manner, the polymer can be removed by calcination in a following step. Most of these materials found applications for the preparation of batteries and gas sensing devices, although they also found some important uses as photocatalysts. For example, TiO_2-ZnS/fluoropolymer fiber composites can be prepared by electrospinning, as in [59,60]; they first prepared the fluoropolymer nanofibers by electrospinning and then immobilized TiO_2-ZnS composites on the surface of the electrospun fibers by hydrothermal synthesis. These materials have a low band gap and a quite good visible light response ability and demonstrated to be effective for methylene blue degradation reaction.

Electrospinning is also a suitable technique for the preparation of complex composite materials with TiO_2, that in some cases can be used as catalysts. For example, Li and coworkers [61] prepared Z-scheme TiO_2/g-C_3N_4/graphene oxide ternary heterojunction photocatalysts by direct electrospinning. They first prepared a solution with urea, graphene oxide, PVP and TBT (Titanium Butoxide) that was electrospun to obtain the fibers that then were calcined to obtain the final catalytic material. These ternary heterojunction photocatalysts show good activity as catalysts for the photodegradation of organic pollutants with sunlight, attributed to the high surface area, the formation of the Z-scheme heterojunction and the high separation migration efficiency of the photoexcited charge carriers. In another work, Chen et al. [62] prepared Ag silver nanoparticles filling in TiO_2 hollow nanofibers, by coaxial electrospinning of PVP/TBT and PVP/Si nanoparticles NPs precursor solutions. These materials exhibited a high photocatalytic activity during the degradation of

methylene blue. Another well-known catalytic materials dopant is Nb [63–65], due to its rich chemistry that facilitate Nb to combine with many elements. Upon such interaction form mixed phases such as alloys, Nb modulates redox properties and increases the acidity, rendering systems more catalytically efficient. These properties of Nb as a dopant are also extensive for the electrocatalytic applications, since, for example, $TiNb_2O_7$ has been reported as an attractive anode material for lithium-ion batteries due to its high capacity. Paik et al. [58]. Another composite TiO_2-based fiber has been synthesized by electrospinning, such as $SiOxTiO_2/C$ [66], TiO_2@Ag@Cu_2O [67], or Au@TiO_2 [68], among others. These examples demonstrate the potential of electrospinning technique to prepare TiO_2-based nanofibers that find applications mainly as materials for batteries or as photocatalysts.

4. Zeolite and Other Ordered Mesoporous Fibers Applications

Porous materials such as zeolite or MOFs have been extensively studied for many applications in catalysis, as adsorbents and for drug delivery [1,69,70], among other applications. As has been discussed for other materials, such as TiO_2 catalysts, zeolite nanoparticles have been found to have higher catalytic activity as compared to the correspondent micromaterial counterparts. In general, nanoscaled active phases catalysts [71,72] exhibit better mechanical properties, are more economical and present excellent activity and selectivity results, and these advantages also include nanoscaled ordered mesoporous materials. Despite these advantages, the use of nanomaterials in catalysis is limited due to their unavoidable agglomeration and, as has been discussed in the case of TiO_2 photocatalysts, when nanoparticles are used they can lynch to the liquid effluent. These disadvantages that nanoparticles present can be overcome with the use of nanofibers and, subsequently, several routes for the preparation of zeolite and other mesoporous materials fibers have been described, with electrospinning being one of the most extended procedures [73]. Hashaikeh et al. [73] have reviewed the applications and synthesis methods for zeolite and mesoporous inorganic nanofibers materials. The general procedure for synthetizing the mesoporous fibers would include [73–77] the preparation of a solution containing the organic structure directing agent in a solvent that, after heat treatment and stirring, gives rise to a gel that is mixed with polymer (PVA) and electrospun. The gel can be replaced by nanoparticles [77], which can be commercial ones. By using coaxial electrospinning [77], hollow fibers can be also obtained. With this procedure, two needles that contain two solutions form the core and the sheath, separately. A paraffin oil or a similar organic solvent can be used as an inner solution, then, it can be removed, forming the hollow fibers. Multilayer fibers with several needles and solutions can be subsequently produced with this procedure [78–80]; thus, the possible combinations are almost infinite. Scheme 2 summarized the general procedure for the synthesis of ordered mesoporous inorganic fibers by electrospinning. Following these procedures, the preparation of nanofibers such as those of silicates, ZSM-5, beta zeolite, SBA, faujasite and MOFs, ZIFs, among other inorganic ordered mesoporous materials, have been described [73,81,82]. Other methods include the growing of the mesoporous material on a carbon and polymeric electrospun fibers [83]. By the inverse procedure, electrospun mesoporous inorganic nanofibers, such as those of MOFs or ZIFs, can be used as template for preparing a mesoporous carbon material [84] by depositing the carbon material by CVD (carbon vapor deposition) and then the inorganic matrix can be removed by the use of the appropriate solvent, such as an acid; thus, carbon mesoporous ordered nanofibers can be obtained by this procedure.



Scheme 2. General procedure for the synthesis of ordered mesoporous inorganic fibers by electrospinning. NPs (NanoParticles). TEOS (TetraEtlyl OrthoSilicate).

Zeolites have quite strong acid sites along with redox and base, and the ordered structure allows site isolation and dispersion of the acid sites. Subsequently, commercial heterogeneous catalysts are in many important industries, such as the petroleumchemistry, and several catalytic applications of ordered mesoporous inorganic fibers and membranes have been described. Among the most studied of the applications of these materials is in gas phase separation [85–87], which is not the focus of present review paper, whose objective is to analyze the catalytic applications. By three-dimensional zeolite fiber deposition, different architectures can be manufactured. These 3D nanoarchitectured materials are very useful in catalysis since they avoid a trade-off between pressure drop and mass and heat transfer. In this sense, Noyen et al. [88] optimized a three-dimensional fiber deposition (3DFD) method for the coating of ZSM-5 fibers on different types of metallic or ceramic supports. They deposited the zeolite fibers on stainless steel structures by two different geometries, one with straight channels in the direction of the flow in combination with smaller radial channels in the two directions, and the other with zigzag channels in the flow direction and smaller straight channels in the two radial directions. These materials were shown to be useful and efficient catalysts for the conversion of methanol into dimethyl ether (DME) and olefins, showing that, by controlling the architecture, it can be modulated the residence times, and subsequently the yield to olefins.

Coaxial electrospinning was used by Zhao and coworkers [77] to prepare ZSM5 zeolite fibers. The coaxial method allowed the regulation of the feed rate of the inner fluid, the sizes of the macropores and subsequently the diameters of the hollow fibers, obtaining fibers with a variation of the average inner diameters from about 1.59 to 2.26 μm. They investigated these hollow fibers as catalysts for the cracking reaction of iso-butane to light olefins, demonstrating the higher performance of the hierarchical hollow fibers in comparison with conventional zeolite materials with the same chemical structure (ZSM5). Such excellent catalytic performance, in terms of high yield and good anti-cooking stability, is attributed to the combined effect of the suitable acidity, along with the ordered porosity, that promotes the diffusion and the accessibility to the active sites. Other authors [89,90] follow a similar approach to prepare zeolite fibers that presented a good performance as hydrocracking catalysts. In addition to hydrocracking, zeolite and ZIF fibers also presented a good performance as electrocatalysts for water oxidation [91–93].

Other ordered mesoporous materials that are becoming very popular, especially for biomedical applications [1], are MOFs (Metal Organic Frameworks). These materials have metal ions coordinated to organic ligands, forming on, two- or three-dimensional structures. By carbonization of electrospun MOFs nanofibers, Zhang et al. [94] obtained Co/N-doped porous carbon fibers that had a quite high electrochemical performance, in comparison with non-electrospun samples. This good performance was attributed to the promoted mass transfer and exposure of active sites that present the electrospun structure. This superior performance of metal–organic framework-based materials as electrocatalysts was also corroborated by other authors [95,96] with core-shell and hollow fibers with different compositions.

5. Other Materials

Bibliographic analysis (Figure 1) showed that the main applications in catalysis of electrospun fibers are related to polymeric and carbon or TiO_2-based materials, as has been exposed. Other applications have been explored; for example, metal and oxide based-fibers that can be obtained by electrospinning, directly by the electrospun of a solution containing a precursor of the metal or the oxide, or by the impregnation of a carbon or polymeric fiber with the metal precursor, and subsequent calcination to remove the carbonaceus material.

Our group prepared VOx/ZrO_2, $V\text{-}Mo\text{-}O/ZrO_2$, and $V\text{-}Nb\text{-}O/ZrO_2$ electrospun fibers [97,98] thought a polymer solution containing the corresponding metallic precursors. Figure 3 shows the schematic procedure of the synthesis process, including the electrospinning procedure (Figure 4). These materials are particularly useful for partial oxidation reactions [99,100], since V-based materials are well-known catalysts for such processes. The STEM images from some of the prepared fibbers, with several V concentrations, are shown in Figure 4, along with the EDX elemental mappings. These date show vanadium species are dispersed in the V-containing fibers F-PZr-V5.0 and F-PZr-V13.3 (Figure 5f,i). For comparative purpose, a V/ZrO_2 fiber was prepared by V impregnation (FI-PZr-V5.0 (Figure 5j–l). In this case most vanadium species are not located in the fiber structure, and a good VOx dispersion is not obtained. Thus, the described procedure was adequate to prepare mixed-oxide fibers in only one step, with adequate dispersion and isolation of the active phases. The reported activity results [97,98] during propane oxide-hydrogenation reaction were quite promising in comparison with those reported for non-fibrous materials.

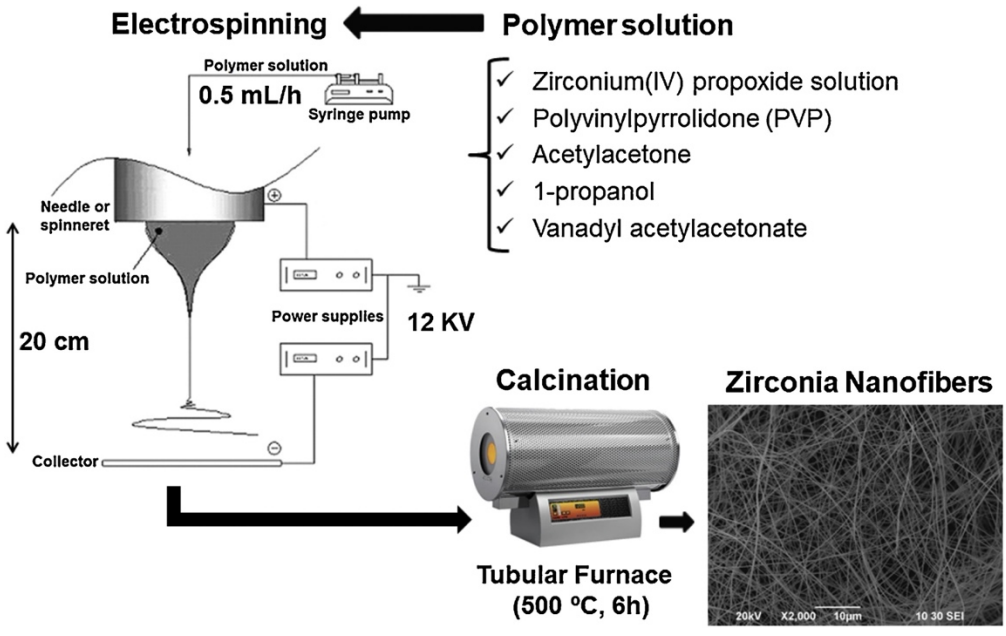


Figure 4. Schematic procedure followed for the preparation of vanadium-containing Zirconia submicron-fibers. Reproduced from [98] with permission from the copyright owner (Elsevier 2019).

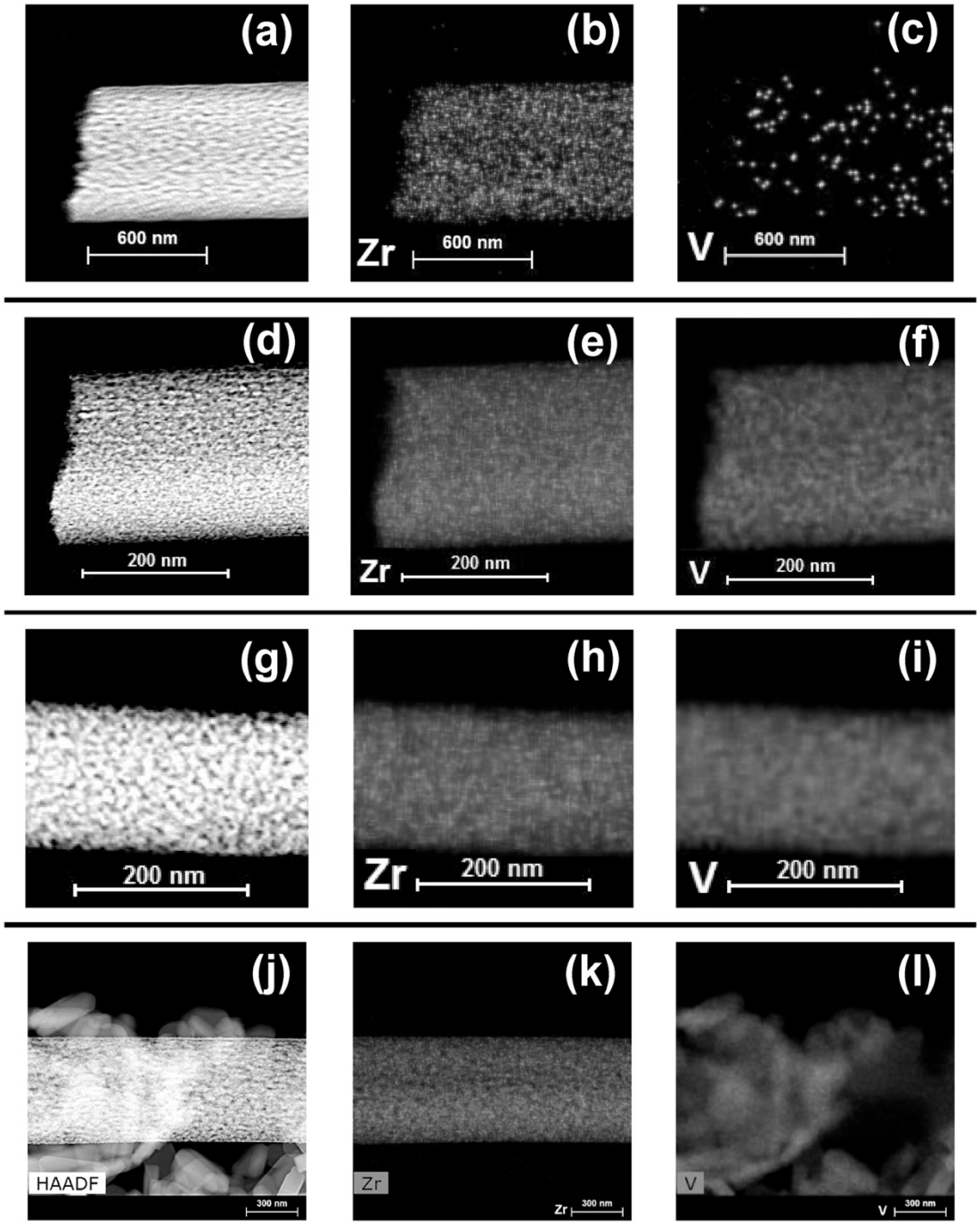


Figure 5. HAADF-STEM images and EDXA elemental mappings of Zr and V for the electrospun fibers with different V compositions. F-PZr (**a**–**c**), F-PZr-V5.0 (**d**–**f**), F-PZr-V13.3 (**g**–**i**), and FI-PZr-V5.0 (**j**–**l**). Note that the scale of each figure has been adapted to the size of the sample. Reproduced from [97] with permission from the copyright owner (Elsevier 2019) [97].

Several authors claimed to control important parameters in the preparation of metallic oxide fibers by electrospinning, such as the shape and diameter or the oxidation state [101–105] with reproducibility by simply tuning the electric field strength during electrospinning and controlling the heat treatment parameters after the electrospinning step. These synthesis possibilities, in addition to the advantages that fibrous heterogeneous catalysts have in terms of pressure drop and mass transfer, makes these materials attractive catalysts for many of the processes that are catalyzed by metallic or oxide active sites. In this sense, Milt el at. [106] prepared Ce_3O_4/CeO_2 electrospun nanofibers that probed to

be active for soot and CO oxidation, which are reactions with environmental application, for the removal of two well-known pollutants. Chen et al. [107] prepared similar catalytic materials by coaxial electrospinning, in this case, the fibers had a Co_3O_4 shell with a CeO_2 core. With this configuration, the exposed Co_3O_4 active sites can rapidly react with the reactant molecule (they tested these materials for the total oxidation of propane), while CeO_2 in the core has a high oxygen storage capacity, enhancing the oxidation rate. In addition, the continuous grain boundary provides a fast mass transfer channel for lattice oxygen, favoring the mobility of active oxygen species.

Figen [108] reported the synthesis by electrospinning of Ni and Cu metal oxide materials that were active for the NH_3BH_3 methanolysis at room temperature. The electrospun materials presented a very high pore volume–area ratio, much higher than those of catalytic materials of the same composition but prepared by sol-gel and without the fibrous configuration. Such properties made the electrospun materials attractive catalysts for the methanolysis at room temperature, with important application for on-board hydrogen production.

These quite recent examples show the possibilities of mixed oxide electrospun fibrous materials, given that the fiber configuration endows the catalyst with excellent properties as catalysts. The applications of oxide fibers in catalysis are hardly explored, and given these adventages, and the different configurations that allow the coaxial procedure, it is expected that they will be highly explored and developed within the next decade.

6. Conclusions

It has been performed a bibliographic analysis that showed how there are two important groups of electrospun-fiber-catalysts that are being investigated, based on TiO_2 and in carbon materials, being the main applications in photo- and in electro-catalysis. Along other materials such as mixed oxides can be prepared by electrospinning and are also useful catalysts, as have been reviewed. The reviewed studies results have shown that the possibilities of electrospun fibers are quite advantageous due to several factors:

- As fibers, they present a low resistance to internal diffusion and a high surface area to volume ratio, due to their diameter–length proportion;
- As nanomaterials, the activity and selectivity of isolated nanoscaled catalytically active phases is higher, as has been demostrated for many catalytic systems;
- The possibilities that allow the electrospinning procedure are almost infinite since this equipment has become very popular, due to its low cost and simple handling. In addition, there is the possibility to prepare multilayered fibers with modulated properties. It has been also discussed how, with the control of the electrospinning parameters, such as voltage, being applied, the materials' properties such as the diameter of the fibers can be modulated and the synthesis methods are quite reproducible.

Althought most of the applications that have been explored to date for these materials are focused in medicine and for the manufacture of sensors and batteries, the superior properties of these materials indicate that they can be considered a new class of catalysts that are going to be more important for the improvement of several catalytic processes and for the development of new ones.

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