



# Fibrous Material Structure Developments for Sustainable Heterogeneous Catalysis – An Overview

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Abstract: The continuous development of advanced catalysts to increase process yield and selectivity is crucial. A high specific surface area and a good active phase dispersion are generally essential to create catalytic materials with a large number of active sites. Notably, materials with a fibrous morphology are appealing because of their large surface-to-volume ratio and flexibility. This contribution highlights the morphology of different types of fibrous structures currently under investigation, all the way from the nanoscale to the macroscale and back, where the distinction lies in the length and diameter of the fibers, as well as in the connection between the structures. Fibers with at least one submicron to nanoscale characteristic result in a higher yield, but can display practical usability issues when unbound. Therefore, fibrous structure catalysts with a balance between the small diameter and handleability are important for industrial viability. By combining different morphologies, the best of both nanomaterials and macroscopic integer materials can be combined into advanced catalytic materials. This overview showcases the large potential of these materials but makes clear that further research is needed to keep expanding the use and effectiveness of fibrous structures in catalysis.

### 1. Introduction

In the search for optimal catalysts for today's environmental challenges, we generally aim for the use of heterogeneous catalysts. These solid catalysts are easy to recover from the reaction products, making them highly sustainable.<sup>[1,2]</sup> Moving toward porous structures with larger accessible specific surface area increases the available active sites and thus the catalytic performance by lowering the impact of diffusion limitations at the micro-scale at which concentrations can be defined.

Nanomaterials bring the highest specific surface area, and thus often an enhanced chemical reactivity.<sup>[3–7]</sup> Moreover, they often exhibit improved mechanical strength, hardness, and toughness

compared to their bulk counterparts because the small size generally allows for better control over the arrangement of atoms and thus the creation of stronger bonds.[8-10] Examples are (semi-)metal oxides, active carbon, porous polymers, zeolites, and metal-organic frameworks (MOFs).[11-20] These functional porous materials can act as both the catalytic structure itself or the support material for the catalyst, in this way enabling the specific creation of encapsulated nanoscale catalysts to avoid clustering of the active sites and thus loss in efficiency.<sup>[21-24]</sup> Generally, these nanomaterials are available in a powder-like form, with nm-to-µm characteristics. Moving away from these powdery materials, an essential step of catalyst development in the perspective of industrial applicability is "shaping". Nanoscale catalysts indeed have to be turned into macroscopic bodies (pellets, monoliths, extrudates, membranes, etc.) to improve their handleability, to allow easy recovery, and/or to be implemented in flow mode processes.<sup>[25-31]</sup> This is often overlooked in academic research, considering it as a matter of practical interest. However, shaping the catalyst significantly alters its application potential.[32-371

Interesting shapes are fiber-based structures due to their flexibility and mechanical integrity on the macro-scale, as well as the high available surface area and the presence of an orientation preference (**Figure 1**, top).<sup>[22,23]</sup> These include fibers and fiber bundles on the one-dimensional (1D) level; woven, knitted, braided, and nonwoven structures/fabrics on the 2D level; and intertwined fibers and/or fabrics with a macroscale thickness on the 3D level. Typical fibrous structures consist of fibers with a µmscale diameter and an extensive length. These can either consist of the catalytic active component or can be used as support material for a catalytically active phase. In the latter case, nanomaterials are often incorporated into/onto the fibrous support material, increasing the specific surface area, and thus the number of active sites. These can be incorporated in various dimensional options ranging from 0D nanocatalysts, with all

dimensions below 100 nm, over 1D nanofibers and 2D nanosheets to 3D (spherical) particles with all dimensions above 100 nm depending on the material design, see **Figure 1** bottom. [38-44]

To make use of the advantages of a fibrous structure, and even further increase the surface area, nanomaterials with a (partly) fibrous morphology are developed, ranging from particles with a radial fibrous structure, over nanowires to nanofibers. A prominent example that has gained interest as catalyst (support) materials is 1D nanofibers. These have a nanoscale diameter but a macroscale length, and thus form a bridge between the advantages of nanoscopic properties and the macroscopic handleability of common bulk materials.

Many strategies have been reported to prepare different types of 1D nanofibers, such as template-directed synthesis, melt-blown protocols, self-assembly methods, and electrospinning.[45-47] Electrospinning is the most versatile and widely used technique, regardless if the material is polymeric, inorganic, or hybrid.[47-52] Both melt and solvent electrospinning exist, but solvent electrospinning is used more frequently today because so far it allows for more morphology shaping of the fibers, and is more versatile. In addition, melt electrospinning still has quite some processability issues, such as polymer degradation and fiber stability.<sup>[53]</sup> By controlling the process parameters of the different electrospinning process, morphologies and microstructures can be made, e.g. hollow fibers, porous fibers, and core-shell fibers.<sup>[51]</sup> Generally, this results in a 2D macroscopic sheet consisting of 1D nanofibers (see example Figure 1). This makes them ideal candidates for application as catalyst and/or catalyst support. In the case of supported catalysts, the interactions between the support surface and the catalyst's active phase can strongly influence overall catalytic behavior.[54-<sup>57]</sup> For example, the redox properties and acid-base characteristics of transition metal oxide catalysts can result in such interactions, leading to different surfaces and electronic structures, and thus varying catalytic activity.[58]



Figure 1. Current state-of-the-art development of fibrous material structures as catalysts combines the advantage of fibers and fiber-based materials as a macroscopic integer shaping tool with the high specific surface area of nano-scale functionalities acting as catalytic active sites.

In this review, an overview of the most interesting fibrous catalytic structures as tools to combine a large specific surface area with good handleability is given. We highlight the development of fibrous structures for heterogeneous catalysis, building up from elementary nanoparticles with fibrous morphologies, over 1D nanofibers, and their assembly into 2D fibrous structures, all the way up to 3D catalytic materials, specifically targeting the morphology of the materials. In current state-of-the-art research, the incorporation of nanoscale catalysts in macroscale fibrous

structures combines the best of both worlds. As an important example for catalysis, special attention is placed on silica-based materials, but not exclusively. Combining nanoscale-designed materials with macroscopic handleability will result in the highly needed industrial promising catalysts.

Eva Loccufier graduated from the Faculty of Engineering and Architecture at Ghent University (Belgium) in 2017 with a Master of Science in Sustainable Materials Engineering with a major in Polymers and Fiber Structures. She obtained her Ph.D. in Materials Engineering in 2022. Her research focuses on the functionalization and processing of fiber materials for advanced engineering applications (e.g. catalysis and filtration).

Karen De Clerck studied textile materials engineering at Ghent University (Belgium, MSc and PhD) and textile technology at the University of Manchester University (UK). At present, she holds a position as a full professor at Ghent University and is heading the Centre for Textile Science and Engineering. Her research interests include fiber technology and textile chemistry, with a focus on the production and functionalization of nanofiber-based materials. Prof. De Clerck's group developed expertise in





several in-house designed electrospinning set-ups and spinning of many (functionalized) systems for a range of advanced applications, including catalysis.

### 2. Fibrous nanoparticles

Research in heterogeneous catalysis is nowadays more and more merging into the research of nanomaterials. Nanomaterials are considered for both the catalyst itself and the support material, where in the case of support material it is a porous substrate in which a small cluster of atoms/nanocatalyst is encapsulated (0D catalyst). Template examples are zeolites, microstructured silica (or other oxides), graphene derivatives, nanotubes, and MOFs.<sup>[59]</sup> These nanomaterials can also have a fibrous nature,<sup>[60]</sup> leading to more surface area, of which two examples are given in this section.

#### 2.1. Dendritic Fibrous Nanosilica

Dendritic fibrous nanosilica (DFNS) is a class of silica nanospheres with a fibrous pore morphology, first developed in 2010 by the research group of Prof. Polshettiwar. The microstructure of the nanospheres, also called KCC-1, is shown in **Figure 2**.<sup>[61]</sup> Today, further DFNS development has resulted in tunable properties, namely the (average) particle size (500 to 1200 nm), the surface area (500 to 1200 m<sup>2</sup> g<sup>-1</sup>), the pore volume with possible a more wide pore size distribution due to radially oriented pores (gaps between fibers), and the fiber density within individual DFNS spheres.<sup>[20,62,63]</sup>

DFNS possesses high thermal stability (up to 800°C), significantly better than other porous nanosilica due to the higher thickness of

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# **REVIEW**

the DFNS fibers of the fibrous sphere compared to the walls of typical porous nanosilicas (e.g. SBA-15 or MCM-41). They also have good mechanical stability (up to 130 MPa) because the silica fibers are covalently connected and, hence, not mechanically



disintegrated due to pressure or friction.

Figure 2. HRTEM images of dendritic fibrous silica nanospheres KCC-1 (Figure from Polshettiwar *et al.* 2010<sup>[61]</sup>).

Combined with the large functionality potential of silica materials, this makes the DFNS family ideal for the development of catalysts with a very large specific surface area.<sup>[63–69]</sup> Recently, several examples where DFNS are functionalized for carbon dioxide (CO<sub>2</sub>) conversion reactions were reported.<sup>[70–73]</sup> For example, Saptal *et al.* reported the use of nitridated DFNS produced via ammonolysis as a heterogeneous catalyst in combination with tetrabutylammonium iodide (TBAI) for the synthesis of cyclic carbonates from CO<sub>2</sub> and epoxide, see **Figure 3**.<sup>[72]</sup>



**Figure 3.** (a) Schematic representation for the synthesis of nitridated dendritic fibrous nanosilica (N-DFNS) by ammonolysis at various temperatures. (b) Catalytic application of the N-DFNS to synthesize cyclic carbonates from epoxide and CO<sub>2</sub> (Figure from Saptal *et al.* 2021 <sup>[72]</sup>).

#### 2.2. Nanowires

When a nanomaterial has a length significantly longer than the width/diameter but both are still in the sub- to low-micron scale, we call them nanowires. Sometimes, the term nanorods or whiskers is used as well.<sup>[74]</sup> An example where the length is an order of magnitude larger than the width is given in **Figure 4**, namely silver nanowires produced via the polyol method by

Mattarozzi *et al*, with an average wire diameter of 61 ± 17 nm and an average length of 10 µm.<sup>[75]</sup> Also less extreme differences where the length-to-diameter ratio is less than 10 are studied extensively in literature as well.<sup>[76–79]</sup>



**Figure 4.** (a) Transmission electron micrographs of silver nanowires synthesized via the polyol method. (b) High magnification of two nanowires accompanied by the size distribution of the diameter of the as-synthesized silver nanowires (Figure adapted from Mattarozzi *et al.* 2023 <sup>[75]</sup>).

Nanowires have been widely considered in recent years due to their good mechanical flexibility and toughness, with remarkable tolerance against mechanical bending and exceptionally low flexural rigidities.<sup>[80–83]</sup> They showcase high surface functionalization possibilities and good optical transmittances. In addition, the fibrous structure results in anisotropic properties, making fibrous nanomaterials such as nanowires a good active (catalytic) material for many special fields such as flexible electronics, tissue engineering, oil/water separation, and energy storage.

Compared to typical spherical nanoparticles, the nm thickness and µm length of nanowires can overcome several drawbacks due to their high surface-to-volume ratio, the long segments of smooth crystal planes, and fewer surface defect sites.<sup>[84]</sup> The very high aspect ratio provides numerous catalytic sites for reaction and actively prevents dissolution and aggregation of the active sites.<sup>[85–87]</sup> An interesting example is the development of Pt-based ultrafine nanowires for applications in renewable energy-related devices. Pt-alloy electrocatalysts (such as Pt-Rh or Pt-Mo-Ni nanowires) can be used for the splitting of C-C bonds, making them ideal candidates for the development of direct methanol fuel cells (DMFCs).<sup>[76]</sup>

#### 3. Nanofiber Catalysts

An optimal balance between the advantages of nanoscopic properties and macroscopic handleability is achieved by developing long 1D nanofibers (see **Figure 1**). These have a nanoscale diameter and a macroscale length.<sup>[3]</sup> Accordingly, a large variety of nanofibers have been successfully developed by various methods, including template synthesis, molecular self-assembly, solution blow spinning, centrifugal jet spinning, hydrothermal methods, and electrospinning.<sup>[88,89]</sup> Among the various chemical and physical methods, electrospinning has been regarded as the most promising approach owing to the simple preparation process, suitability for upscaling, and excellent reproducibility and versatility.<sup>[11,48,50,90–92]</sup>

#### 3.1 Electrospun nanofibrous membranes

Electrospinning is a mechanical and electrical technique to produce continuous, ultrafine fibers in the submicron diameter range using high voltages. It is a technique by which a polymer solution is drawn into fibers in the presence of an electric field in the kV range. Typically, this results in the random deposition of continuous nanofibers due to the instability of the charged jet combined with the evaporation of the solvent, creating a standalone nanofibrous membrane with pores in the  $\mu$ m range. The macroscopic 2D membrane is thus composed of a random contribution of 1D nanofibers.

Both melt electrospinning (in which a polymer melt is used as the spinning solution) and solvent electrospinning, (in which a polymer is dissolved in a solvent (mixture)) exist, but solvent electrospinning is used more frequently today due to simplicity and versatility. The electrospun nanofibrous membranes have a very high specific surface area and porosity, resulting in their use in a large range of advanced engineering applications in the fields of catalysis, energy storage and generation, healthcare, and biomedical engineering, as well as water treatment and environmental remediation.<sup>[89]</sup>

Tuning of the electrospinning procedure resulted in the development of various fibers (porous, hollow, multichannel, coreshell, triaxial, helical) and veil structures (random, aligned), further opening up the application potential by increasing the specific surface area or creating composite structures.<sup>[93-96]</sup> This results in the use of electrospun nanofibrous structures as catalysts and/or catalyst support materials.

Both metal and metal oxide catalysts are commonly used in heterogeneous catalysis.<sup>[97-99]</sup> Initially, electrospinning was only used for organic polymers, because the spinning solution needs to have a large enough macromolecular structure to allow for the entanglement of the molecules to keep the filament together during the severe stretching of the electrospinning process. However, by combining the use of for example sol-gel technology with electrospinning, possibly assisted by a sacrificial organic polymer, extension towards electrospun nanofibers in all material classes is possible today.<sup>[100-105]</sup> Prominent examples of catalytic fibers are MOF and zeolite-like nanofibers, while carbon and silica nanofibers are often used as catalytic support materials for another nanoscale catalyst (examples in Section 3.2).[39,106-111] Despite the large number of reports and review papers on the successful use of electrospun nanofibers in various applications, the relatively new technology still needs improvement related to scale-up, especially for the more complex structures of interest for heterogeneous catalysis.<sup>[112]</sup> Even though continuous electrospinning equipment is commercially available, and their product yield is in line with those of advanced coating lines, this is focused on generic nonwoven structures.[113-115] To tackle this issue, more systematic research (both experimental data and

theoretical modeling) is necessary to fundamentally understand the effects of fiber dimension, morphology, surface roughness, and fibrous structure on catalytic performance.<sup>[3,51,52,116,117]</sup> In addition, there is still room for optimization of the mechanical stability of the 2D nanofibrous sheets. Generally, there is a relatively low connection between the individual 1D nanofibers (sliding over each other upon loading), making them fragile. Further research to better understand the mechanical properties and improvement and tuning strategies are thus paramount. Furthermore, the electrospinning process requires the use of high voltages, which is not well applicable to some electrical charge sensitive materials, especially biomolecules.<sup>[112]</sup> On the contrary, solvent electrospinning avoids the need for high temperatures in the material synthesis, which could be even more problematic in several cases.

#### 3.2. Multi-level nanoscale nanofibers

Combining multiple nanoscale materials into one catalyst has emerged very recently as a promising technique to increase the surface area and amount of active sites on a more easy-to-handle catalytic structure by avoiding clustering of the active sides.<sup>[51,110,118,119]</sup> Therefore, encapsulation or incorporation of nanocatalysts in another particle is very promising. By then combining this nanomaterial with a macroscopic integer material, easy-to-handle, reusable catalysts with high industrial potential can be designed, as schematically illustrated for fibrous structures in **Figure 1**.<sup>[22]</sup>

One group of promising support materials is electrospun nanofibrous membranes. Most commonly, nanoparticles are added to the solution before electrospinning, often referred to as inline functionalization, creating doped nanofibrous membranes. Surface modification after electrospinning is also an option resulting in nanoparticles on top of the fibers. They can be applied via for example dip-coating, chemical vapor deposition, atomic layer deposition, or direct synthesis of the nanoparticles in the presence of the electrospun nanofibers.<sup>[120]</sup> Upon designing the synthesis, well-defined catalysts with a homogeneous distribution of the nanoparticles along the fiber length and thickness can be created.<sup>[121]</sup> By combining this with one of the many morphological structures producible with electrospinning, the exposure of active sites can be maximized even further.<sup>[116]</sup>



**Figure 5.** SEM images of a-Al<sub>2</sub>O<sub>3</sub> sphere (a) and the reduced Ni/Al<sub>2</sub>O<sub>3</sub> catalysts with different NiO contents and morphologies: (b) 25 wt%, and (c) 35 wt%. SEM images of fibrous catalysts with different NiO contents: (d) 25 wt%, (e) 35 wt%, (f) 45 wt%. Effect of gas flow rate on reaction rate (g) over the different Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. The reaction rate is defined as the amount of methane converted per gram of nickel catalyst and minute (Figure adapted from Ma *et al.* <sup>[122]</sup>).

One of these examples is reported by Ma et al., where fibrous Ni/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by one-step electrospinning, and their catalytic activity compared to conventional spherical monolithic Ni/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by impregnation for catalytic methane partial oxidation (**Figure 5**).<sup>[122]</sup> The fibrous catalysts exhibited smaller and more uniform Ni particles, indicated in **Figure 5b,c**, and **f** with red circles, resulting in a stronger catalyst/support interaction and higher catalyst loadings compared to the spherical catalysts. In addition, the fibrous catalysts demonstrated faster mass transfer and higher resistance to carbon deposition during methane partial oxidation, resulting in higher syngas yield (**Figure 5g**).<sup>[122]</sup>

Another example is reported by Loccufier *et al.*, where they encapsulated a metallic 0D ruthenium (Ru) nanocatalyst into 3D MIL-101 MOF nanoparticles to avoid clustering of the Ru catalyst, which were then deposited onto 2D macroscopic silica membranes consisting of 1D nanofibers to increase the handleability of the MOF nanoparticles.<sup>[119]</sup> This fibrous composite showcased good potential as a catalyst for the CO<sub>2</sub> methanation reaction. Note that 0D nanoparticles is a terminology used in catalysis for particles with a nanometer size in all directions to indicate a significantly smaller size than catalyst pellets, but are never fully zero-dimensional.

### 4. Microfiber Catalyst

To avoid the difficulties associated with the use of nanomaterials, immobilization on textile fibers has been considered. These fibers readily solve the issue of catalyst "shaping" as they have a micrometer range diameter and are therefore easy to handle or can even be arranged to form macroscopic 3D self-standing objects such as membrane modules (see schematic in **Figure 1**). Microfibers are also generally quite inexpensive. Several approaches to prepare heterogeneous microfiber catalysts have been used, e.g. covalent linking, immersing, spraying, or dispersing the fibers into a liquid containing the active species precursors, and chemical vapor deposition.<sup>[25,123]</sup>

Depending on the application, either natural or synthetic fibers are used as support material. Synthetic fibers are generally more tunable with more diverse functionalization possibilities but they also tend to have poor biodegradability, which can lead to environmental and sustainability issues.<sup>[123]</sup>

The use of oriented fiber structures (e.g. aligned fiber bundles, yarns) has the potential advantage of using this orientation to facilitate for instance the liquid flow along the fiber direction, controlling the flow behavior in catalytic reactors.<sup>[124–126]</sup> One specific class of such fibers is hollow fiber catalytic membranes.

Hollow fiber membranes have a hollow core with a (layered) porous wall with an external fiber diameter in the micrometer range. By pushing fluid through the inner channel, a crossflow mode operating unit can be designed in which the permeate has passed through the pores of the fiber.<sup>[127,128]</sup> This is exemplified in **Figure 6** using several morphology options accompanied by microscopy images of the cross-section of some of these fibers.<sup>[129]</sup>

Hollow fiber membranes play a vital role in the industrial application of membranes due to their distinct advantages for incorporation in membrane modules such as high surface-to-volume ratio, good flexibility, scalability, and self-supporting characteristics.<sup>[129,130]</sup> In the case of flat sheet membrane modules,

generally more complex and additional hardware (e.g. porous supports or spacers) are required, so that the self-supporting properties and good flexibility of hollow fiber membranes help to reduce the complexity of the hardware fabrication during the module assembly and operation. In addition, these modules also have a high packing density.<sup>[129,131]</sup> For example, a 20 cm diameter and 1 m long hollow fiber module filled with fibers of 100 µm diameter results in ~300 m<sup>2</sup> membrane area, while for a spiral-wound module with equivalent dimensions the membrane area is only 20-40 m<sup>2,[129,132]</sup>

This membrane separation process is driven by a concentration gradient. This gradient can be increased by using a sweep gas, applying a vacuum in the permeate side of the membrane, or using a chemical reaction to maintain the large potential difference across the membrane.[133] These hollow fibrous structures are thus very interesting as a tool to combine a membrane separation with a chemical modification. Therefore, making these fibers from catalytic active materials, or adding a catalytic component to the fibers has attracted significant research interest.<sup>[129,131,134-137]</sup> Metallic or metal oxide fibers are widely studied and easy to make via e.g. fiber drawing and extrusion.[134,138] Metallic nickel hollow fiber membranes consisting of a dense skin layer integrated on a porous nickel substrate produced by Wang et al. can be directly applied for hydrogen production from methane steam reforming (MSR), see Figure 7.<sup>[134]</sup> The porous internal surface functions as a catalyst bed for the MSR reactions, while the external dense skin layer serves as the membrane for hydrogen extraction from the reaction products. It was showcased that the reaction operation temperature should be above 800°C and the H<sub>2</sub>O/CH<sub>4</sub> ratio controlled around 3 to achieve both high methane conversion and high H<sub>2</sub> production rate.

The performance of a hollow fiber membrane module depends on both intrinsic membrane transport properties and fluid hydrodynamics within the module. Therefore, further research in the design to promote a uniform shell flow, enhance mixing, and incorporate internal sweep within the module is needed to inspire novel designs for next-generation hollow fiber modules. This process involves different disciplines and requires a thorough understanding of the intended application, as no design serves by default all demands.<sup>[132]</sup>

The combination of multiple microfibers or oriented yarns into microfiber-based supports produced in the form of cloths or fabrics is another very promising use of fibers in heterogeneous catalysis and will be discussed in the next section.

### 5. Fabric Catalyst Supports

A very promising method for the development of novel and effective catalytic processes is the design of processes based on catalysts with a new geometric shape that decreases the diffusion limitations and results in higher efficiency of the heat and mass transfer, thus providing the maximum use of the catalysts' active components.<sup>[139–141]</sup>

Structured 2D fibrous supports, typically consisting of microfibers, are a relevant example and are different from traditional catalysts due to their specific geometric structure, flexibility, and handleability on the macroscopic scale.<sup>[142–144]</sup> The fabrics can be produced via well-known (conventional) textile production techniques at high production rates (e.g. weaving), making them

generally cheap support materials. In addition, combining such 2D structures can result in the development of 3D macroscopic integer catalytic structures.<sup>[145]</sup>

The high potential of fabrics as technical textiles, with catalyst development as an example, has resulted in a vast amount of research into the surface modifications of fabrics to alter their physico-chemical properties.<sup>[92,107,146–152]</sup> Examples of 2D and 3D macroscopic fiber-based catalysts are given in this section, focusing on both woven and nonwoven fiber structures made from polymer, glass, mineral, ceramic, carbon, or other microfibers.

#### 5.1. Nonwoven Microfiber Fabrics

Nonwoven fabrics are textiles that have been created through a process of bonding fibers together, either by some kind of chemical adhesion, mechanical or heat treatment, or a combination of those. There is no weaving or manual construction involved, which makes nonwoven fabrics often even more cost-effective and more quickly to manufacture than oriented fibrous structures. They are however usually less strong than woven fabrics because of how they are manufactured, but can be strengthened by bonding multiple layers.<sup>[153]</sup> Depending on the thickness of the structure, 2D fibrous sheets (**Figure 8**) or 3D sponge-like structures (**Figure 9**) are created, allowing for a diverse range of applications.

Most commonly, polypropylene (PP) nonwovens are used,<sup>[154–157]</sup> but other materials such as cotton<sup>[158]</sup> or polyethylene terephthalate<sup>[159]</sup> (PET) are also under research. PP nonwovens are lightweight, water-repellent and breathable, non-toxic and non-irritating, antibacterial, have good air permeability and particle retention rate, and are chemically passive substances. This makes them ideally suited as catalyst support material for amongst others air filtration,<sup>[154]</sup> reusable (water) purification and filtration systems,<sup>[160–162]</sup> as well as protective clothing and masks<sup>[163,164]</sup>. An interesting example is the combination of a PP nonwoven with MOFs<sup>[163,164]</sup>, as exemplified in **Figure 8**, where Lee *et al.* created a fibrous composite by functionalizing a PP nonwoven with Zr-based MOFs. In this case, the MOF fraction on the fabric and defect density in the MOF structures was controlled by an in situ seeded growth, where the PP fiber surfaces are

pretreated with titanium dioxide (TiO<sub>2</sub>) by atomic layer deposition (ALD). The resulting MOF-fiber composite shows a rapid catalytic hydrolysis rate for the chemical warfare agent simulant *p*-nitrophenyl phosphate with a half-life of less than 5 min and a significant permeation restriction of a real chemical warfare agent vapor through the composite. In addition, the composite fabric has a notably superior moisture vapor transport rate (15,000 g m<sup>2</sup> day<sup>-1</sup>) compared to other commercially available chemical-protective fabrics, overcoming the breathability/detoxification trade-off currently present in chemical-protective fabrics on the market.<sup>[164]</sup>

On top of nonwovens from natural and organic polymer fibers, inorganic and metal-based microfiber nonwovens are used as catalyst support material. They are often even more promising for a diverse range of applications because they generally can withstand more extreme conditions. In addition, these materials can be used as carrier material and have a catalytic function as such.[165-171] Two examples of such structures on both the macroand microscopic scale are given in Figure 9.[168,169] Zhao et al. developed a thin-felt Pd-MgO-Al<sub>2</sub>O<sub>3</sub>/Al-fiber catalyst for high by throughput catalytic methane (CH<sub>4</sub>) combustion hydrothermally growing Mg-AI mixed oxide precursors on AI-fiber surfaces followed by placing 0.5 wt% on the as-obtained substrates by impregnation, see SEM images in Figure 9a. This catalyst is less prone to water poisoning than most alternatives, opening up their use in compressed natural gas vehicles to reduce the impact of residual CH<sub>4</sub> in the exhaust gas.<sup>[168]</sup> In another study, Zhou et al. reported the use of a porous Cu-Al fiber sintered felt (Figure 9b) as catalyst support for hydrogen production from methanol steam reforming. By combining Cu and Al fibers, much higher methanol conversion and H<sub>2</sub> flow rate could be achieved compared to Cu or Al fibers on their own.<sup>[169]</sup>

Compared to PP, which has a melting point of around 160 °C, tests at significantly higher temperatures could be performed when using metal or metal oxide felts. These are thus very promising packing materials for catalytic reactors, however, their specific surface area is significantly lower than nanomaterials before the shaping into e.g. macroscopic pellets.

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Figure 6. Schematic of (a) single-layer, (b) dual-layer, and (c) thin film composite (TFC) hollow fibers accompanied by cross-section morphologies of each hollow fiber membrane under different magnifications (d-f) (Figure from Shen Lau *et al.* <sup>[129]</sup>).



**Figure 7.** (a) SEM images of the nickel asymmetric hollow fiber membranes: A-cross section; B-hollow fiber wall; C-inner surface; D-outer surface.(b) Stability test of these Ni hollow fiber membranes for MSR and H<sub>2</sub> production (Pure CH<sub>4</sub> feed rate =  $2.6 \ 10^{-5} \ mol \ s^{-1}$ ; H<sub>2</sub>O/CH<sub>4</sub> = 3, Sweeping flow rate =  $4.46 \ 10^{-5} \ mol \ s^{-1}$ ) (Figure adapted from Wang *et al.* <sup>[134]</sup>).



Figure 8. Optical photograph of UiO-66-NH<sub>2</sub> MOF-textile composite swatch ( $\approx$ 12 cm x 20 cm) prepared by a scale-up synthesis process, associated by SEM images of non-modulated UiO-66-NH<sub>2</sub> MOF coated fibrous mats: (a) MOF growth with no seeds on PP@TiO<sub>2</sub>, (b) subsequent MOF growth to (a), and (c) succeeding MOF growth to (b). (d–f) Enlarged SEM images in the dotted square area of (a–c), respectively (Figure adapted from Lee *et al.* 2022 <sup>[164]</sup>).



Figure 9. Two examples of non-polymeric microfiber nonwovens as catalysts: (a) Optical photograph and SEM images of MgAI-LDHs/AI-fiber chips developed for the catalytic combustion of methane (Figure from Zhao *et al.*<sup>[168]</sup>), (b) porous Cu-AI fiber sintered felts as catalyst support in a cylindrical methanol steam reforming microreactor for hydrogen production (Figure adapted from Zhou *et al.*<sup>[169]</sup>).

#### 5.2. Glass Fiber Fabric Catalysts

Catalysts based on glass fiber fabrics possess the typical advantages of a fibrous structure but are also known for their high mechanical strength, and excellent thermal and chemical resistance, opening up possibilities for the creation of new types of reactor systems (e.g. various shaped structured beds) with reduced pressure drop and improved heat and mass transfer.<sup>[172]</sup> Compared to PP nonwovens, glass fiber catalysts can thus be used under more harsh conditions.

Glass fiber catalysts (GFCs) are a relatively new type of catalytic system, where the support consists of glass fibers structured in the form of threads in a woven or knitted fabric.<sup>[142]</sup> An intensively studied material route is illustrated by Zagoruiko *et al.*, highlighting the production of mechanically self-sustaining catalytic 3D cartridges with a tunable shape and internal geometry, avoiding the need for additional structuring and support elements.<sup>[143,172-176]</sup> Such GFC cartridges are characterized by a quite high mass transfer efficiency and a low pressure drop. Various geometries are used to tune the structure of the packing (**Figure 10**). The most intuitive packing design is a layer-wise pile to form a multi-layered GFC stack. In this case, the reaction fluid flows through

the different fabric layers (**Figure 10a-b**). Such stacks have insufficient efficiency, due to a non-optimal structure of the internal reaction mixture flow and also have an unreasonably high pressure drop. One can change the stacking of the fabrics and the dimensionalization inside the cartridge (**Figure 10c**) by allowing axial flow of the reaction mixture and/or changing the geometry of the fabric itself (**Figure 10d-e**) to improve the catalytic performance of the GFC cartridge. This resulted in the promising use of these catalysts in various reactions such as the deep oxidation of hydrocarbons, organic and halogen-organic compounds, the oxidation of SO<sub>2</sub> and H<sub>2</sub>S, and the selective hydrogenation of acetylenes.<sup>[143,172–174,176,177]</sup>

Despite that these catalysts have a high industrial potential, there are still various optimizations that need to be investigated concerning amongst others diffusion limitations by improving the mass transfer, both experimentally and with modern advanced modeling methods (e.g. computational fluid dynamics (CFD)). <sup>[143]</sup> To model these complex systems, simplifications are required, such as reducing the channel geometry from 3D to 2D or using a stationary model instead of a non-stationary one. These lead to a loss in the quality of the simulation, and thus significant errors in the catalyst performance predictions.<sup>[143,173]</sup>



Figure 10. Example of an experimental GFC cartridge: external view of blocks with crossflow stacking of GFC layers (a), cartridges with a longitudinal flow with a volumetric mesh (b), and a corrugated and flat metal mesh (c). The type of weaving influences the mass transfer, and hence the apparent activity of the samples. Different weavings can be studied, e.g. an openwork (d) or a sating weave (e) (Figure adapted from Golyashova *et al.* 2022 <sup>[176]</sup>).

# 6. (Dis)advantages, Overall Challenges, and Outlook

Recent advances in materials science, material synthesis, and nanotechnology have led to the availability of a variety of approaches to prepare and design catalysts in a controlled manner. In this review, we have discussed key examples of fibrous structures that have been developed for catalysis applications over the recent years. The review was organized to follow the morphological possibilities in fibrous structure from the nanoscale to the macroscale and combined.

Specifically, functional fibrous materials are very promising materials for catalysis, as they are highly porous, have a large surface-to-volume ratio, are flexible, and can be designed via various routes depending on the desired dimension and functionalities of the material.

Nanomaterials have a very high specific surface area, allowing for the largest relative amount of active catalytic sites. Nanomaterials

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# REVIEW

with a fibrous morphology, e.g. dendritic fibrous nanosilica, have been developed to overcome problems with deactivation, metal sintering, and coke deposition associated with conventional spherical nanoparticles. Furthermore, this fibrous morphology improves the physicochemical characteristics. However, these nanomaterials have a difficult, labor-intensive, and expensive synthesis process. In addition, nanoparticles can generally not straightforwardly be implemented in industrial reactor setups, due to issues with their powder-like nature, e.g. dust formation, tendency to agglomerate, and clogging.

Combining 1D nanomaterials into macroscopic integer structures, with nanofibers produced via (solvent) electrospinning being the most promising one, can overcome these problems. They possess the advantages of large-scale fabrication, moderate production conditions, and convenience of handling and recycling. Previous reviews have shown the virtually unlimited structural and geometrical possibilities of electrospun nanofibrous structures, allowing the development of a 2D macroscopic material consisting of 1D nanofibers. Even extensions towards the development of 3D structures using electrospinning are under research today (creating sponge-like fibrous materials), showing very promising characteristics for further opening up the application field of these materials.

Nonetheless, a large number of demonstrated applications of electrospun nanofiber-based structures are still confined within academic and research environments, especially the advanced heterogenous catalysts proposed today. Even though nanofibrous membranes are already used in industry today for particle-size-based filtration processes, extensive research to apply them in catalysis is still required.

A currently more economically viable use of fiber catalysts is the use of continuous 1D filaments and yarns, or 2D fabrics. These fabrics can be used as flat sheets but their geometry can be modified, creating stand-alone and self-sustaining 3D catalytic structures. These have a significantly lower specific surface area than nanomaterials but are still interesting due to their high surface area-to-volume ratio. They possess a high porosity compared to typical packed bed reactors, reducing the pressure drop, allowing for the development of less energy-intensive processes, and having both economic and ecological importance. To implement the significant advantages of nanotechnology in catalysts for today's environmental challenges, research and development in the synthesis and testing of multidimensional, multifunctional catalysts in academia and industry are of utmost importance over the coming years. Especially combining macroscopic fibrous structures such as yarns and fabrics with nanomaterials is very promising.

**Keywords:** Fiber-based catalysts • Nanofibers • Porosity • Surface-to-volume ratio

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