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## Current scenario and prospects in manufacture strategies for glass, quartz, polymers and metallic microreactors: A comprehensive review



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### ARTICLE INFO

#### Article history:

Received 29 July 2020

Received in revised form 23 April 2021

Accepted 3 May 2021

Available online 7 May 2021

#### Keywords:

Microreactors fabrication

Coating strategies

Quartz microreactors

Polymeric microreactors

Metallic microreactors

Additive manufacturing (AM)

### ABSTRACT

One of the most remarkable benefits of the microreactors is the achievement of more efficient processes by enhancing the heat and mass transfer phenomena, which is the key factor for processes intensification in chemical reactions, resulting in higher conversion, selectivity and yield towards desired products. Currently, the entire scenario of microreaction approach is an emergent technology and further advances are ongoing. Several strategies have been successfully applied for structuring processes that imply the fixation of the catalysts on the microreactors. However, there are features such as the physicochemical stability of the coatings under reaction conditions that must be improved, motivating the search for new protocols. This review provides a general overview of the most important methodologies applied for glass, quartz, polymers and metals microreactors manufacture and for their coating, analyzing the advantages and drawbacks of every procedure. Furthermore, an outline of the novel insights based on additive manufacturing techniques are described.

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### Contents

1. Introduction.....	14
2. Fabrication methods and materials used for designing microreactors.....	15
2.1. Conventional fabrication techniques for microreactors.....	15
2.1.1. Lithographie, Galvanoformung und abformung (LIGA).....	15
2.1.2. Etching process.....	16
2.1.3. Mechanical microcutting technology.....	16
2.1.4. Spacer method.....	16
2.2. Materials commonly used for fabrication of microreactors.....	17
2.3. Surface pretreatment of the microreactor.....	19
3. Coating methods for glass, quartz and polymeric microreactors.....	20
3.1. Sol-gel.....	20

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<https://doi.org/10.1016/j.cherd.2021.05.001>

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3.2.	Heat attachment.....	20
3.3.	Spray.....	20
3.4.	Hydrothermal.....	21
3.5.	Painting.....	21
3.6.	Other methods: dip coating, electrospinning and chemical vapor deposition (CVD).....	22
4.	Coating methods for metal microreactors.....	22
4.1.	Capillary force.....	23
4.2.	Spray coating, dip coating, spin coating and brush methods.....	23
4.3.	Sol-gel technology.....	23
4.4.	In situ combustion synthesis method.....	24
4.5.	Electrophoretic deposition (EPD) and electrostatic sol-spray deposition (ESSD).....	24
4.6.	Anodic oxidation and anodic spark deposition.....	24
4.7.	Electroplating and electroless plating.....	24
4.8.	Chemical vapor deposition (CVD): PACVD (plasma-assisted CVD), plasma spray deposition, plasma electrolytic oxidation (PEO).....	25
4.9.	Atomic layer deposition (ALD or ALE).....	25
4.10.	Flame-assisted vapor deposition (FAVD) and Flame spray deposition (FSD).....	25
4.11.	Physical vapor deposition (PVD): cathodic sputtering.....	25
4.12.	Electrospinning.....	26
4.13.	In situ catalytic growth.....	26
4.14.	Durability of the coatings under long-term operation conditions.....	26
5.	Novel manufacturing methods based on additive manufacturing (AM).....	27
5.1.	Inkjet printing.....	27
5.2.	Extrusion based methods: robocasting and fused deposition modelling (FDM).....	29
5.3.	Stereolithography (SLA).....	29
5.4.	Selective laser melting (SLM).....	29
6.	Summary and future prospects.....	30
	Declaration of interests.....	31
	Acknowledgments.....	31
	References.....	31

## 1. Introduction

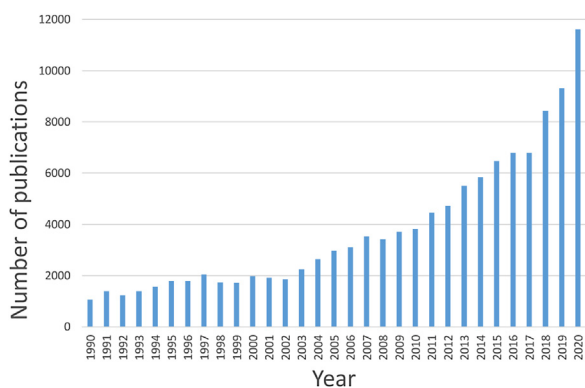
Microreactors technology represents an attractive replacement of the conventional heterogeneous catalytic reactors and evolves a crucial role in the improvement of process intensification (Venkik and Yang, 2017; Butcher and Wilhite, 2016). Microreactors, also known as microchannels or microstructured reactors, are microdevices for performing chemical reactions in which the reactants pass through channels with at least one dimension smaller than 1 mm (submillimeter range). Among the most relevant advantages associated to microreactors, it is worth stressing the following ones: (i) high gas throughput with low pressure-drop, (ii) high loading of catalyst per reactor volume unit, (iii) heat transfer management and (iv) control of the gas flow with efficient mass transfer (Jähnisch et al., 2004). Therefore, microreactors exhibit radically enhanced heat and mass transfer phenomena in combination with highly active, selective and stable heterogeneous catalysts. It is expected that these microdevices will influence notably in the future of the process industry (Kumar et al., 2011).

Microreaction technology is currently an area of emerging interest in diverse areas of application, most of them related with heterogeneous catalysis. A clear demonstration of its growing scientific-technical relevance is the exponential increment of the number of publications in this topic, particularly from the beginning of 21st century (Fig. 1).

The material selection for microreactor manufacture depends on its application, i.e. operating conditions of the reaction that will take place. Materials must have good functionality and durability, good thermal and electrical tolerance and chemical inertness to avoid undesired reactions (Microreactors in Organic Chemistry and Catalysis, 2008). Microreactors have been manufactured from silicon, quartz, metals, polymers, glass, ceramics or semiconductors among others (Microreactors in Organic Chemistry and Catalysis, 2008; Das and Srivastava, 2016; Watts and Wiles, 2007; Tanimu et al., 2017). For

instance, the microreactors used for photocatalysis applications should be transparent to radiation, namely made from glass (Ahsan et al., 2013), quartz (Matsushita et al., 2007), silicon (Lin et al., 2012) or different polymers (Ramos et al., 2014).

The inner geometric surface area of microreactors is typically undersized to accommodate the sufficient number of active centers. It is thus mandatory to get coatings with a large surface area on microstructured substrate materials for subsequent incorporation of the catalytically active phases (Munirathinam et al., 2015; Frost and Mutton, 2010). Depending on the physicochemical properties of the substrate and the catalyst to be coated, different methods can be used to deposit a catalyst layer on micro-structured reactors. Since the microreactors can be fabricated from a long variety of substrates, the choice of the coating method depends on the chemical compatibility and the thermal resistance of the substrate used. So far, these layer coatings can be deposited onto open microstructures (pre-coating) or into completely fabricated microdevices (post-coating). When pre-coating is used, the subsequent bonding steps must not affect the catalyst material (sintering or poisoning could occur). Additionally, the top surface of the reactor requires to be cleaned for subsequent sealing, so either the catalyst precursor must be injected precisely into the channel or the top surface has to be mechanically polished to remove the residues from spilled precursor before closing the microreactor. Otherwise post-coating should be applied. In that case, several of the coating methods could not be used, such as sputtering (Kestenbaum et al., 2002), spray coating (Deshlahra et al., 2011), spin-coating (Schimpf et al., 2002) or physical vapor deposition (PVD) techniques among others as they require a direct accessible surface (Meille, 2006). For reasons of production, it would be advantageous to have an integrated process in which the already manufactured components are coated later. For instance, the method typically used to deposit catalytic surface layers in manufactured ceramic and metal microreactors is the washcoating technique (Almeida et al., 2010; Peela et al., 2009; Cristiani et al., 2009; Xiaoding et al., 1995; Govender and Friedrich, 2017; Nijhuis et al., 2001;



**Fig. 1 – Number of scientific papers published per year related with microreactor and heterogeneous catalysis (Source: Sciedirect; Search items: microreactor AND heterogeneous catalysis OR heterogeneoys catalysts; Date of searching: 15th march 2021).**

Avila et al., 2005). This procedure allows obtaining post-coatings on most metallic and ceramic substrates with the required homogeneity, amount of catalyst loaded and high degree of adhesion.

Over the last decade, novel methods and approach for enhancing the fixation of the catalysts within the channels of the microdevices have been developed driven by the growing role of process intensification and the integration of microreactors technology on an industrial-scale (Stankiewicz and Moulijn, 2000). There are some strategies that have been applied up to now with considerable success. Nevertheless, there are some aspects such as the chemical and physical stability of the coatings under reaction conditions that can be clearly improved, and motivate the search for improvements in the current approaches as well as new protocols. On the other side, additive manufacturing (AM) or 3D printing has emerged in recent years as potential technique to make highly optimized microdevices and have opened new opportunities to design microreactors with complex geometries. The main purpose of this review is to show an overview of the most common strategies to incorporate the catalytic material into the channels of the glass, quartz, polymeric and metal microreactors as well as the new and innovative protocols for manufacturing and coating of microchannel reactors based on additive manufacturing (AM) techniques.

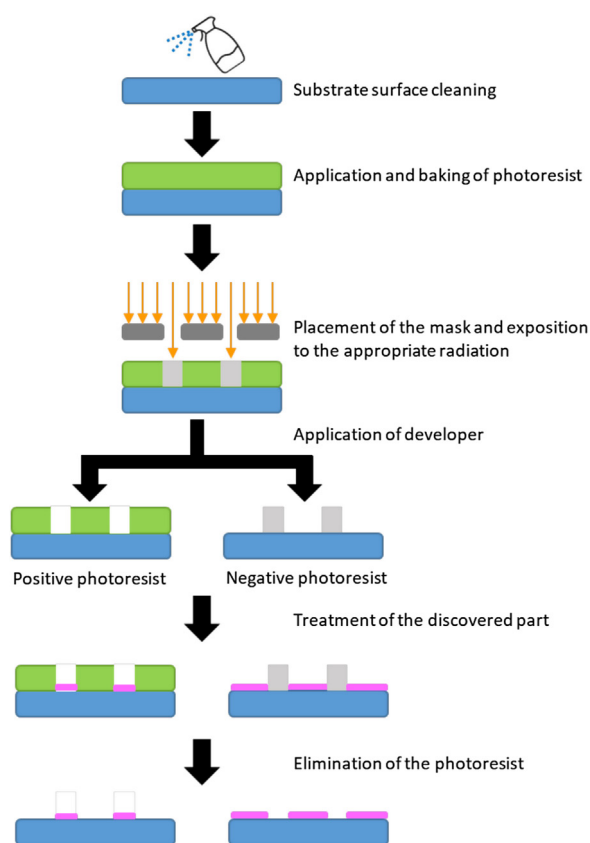
## 2. Fabrication methods and materials used for designing microreactors

In this section are discussed the most relevant techniques that has been developed to design the microstructured reactors and the materials typically used for manufacturing these microdevices. In addition, this part also includes the surface treatment required in some cases by the microreactor before the catalyst coating.

### 2.1. Conventional fabrication techniques for microreactors

Like all new technologies, microreactors applied in chemical processes have shown an important boom since their great potential to intensify processes became evident. This boom may have reached its peak between the last decade of the 20th century and the first decade of the 21st century. However, this boom generated that the application of these devices in more and more processes, led to detect their main limitations.

This situation was rightly highlighted by André de Vries of the Innosyn company at the Royal Society of Chemistry Symposium 2017 (de Vries, 2017), who showed that after the boom in microreactors, the need for these systems to provide better



**Fig. 2 – Steps of the manufacturing by means of LIGA.**

availability and flexibility is mandatory to ensure the transition to a new generation of microreactors with a wider and feasible scenario of applications.

These two concepts are closely related to the manufacturing processes for obtaining microreactors, because to achieve a much greater impact on the industry and exploit their performance to the maximum, microreactors must offer possibilities for more advanced designs, adapted for each process with high degrees of specificity. In addition, these advanced designs must be possible to manufacture through simple methodologies that allow a versatile and sustainable mass production.

According to this analysis, the microreactor manufacturing methods present certain limitations that may be due, mainly to the geometries that they allow to generate, especially inside these devices. For example, in microreactors with channels, these can have a relatively simple degree of interconnection, because it is not easy to machine parts on such a small scale with complex patterns while maintaining precision. Furthermore, the machined areas have geometry shapes also limited by the shape of the machining tools themselves.

For all this, additive manufacturing or 3D printing of microreactors appears as the door to a new upswing in the use of the potential of microreactors. This will be addressed more fully in Section 5, but to understand the scope of this new manufacturing methodology, it is important to first understand the four most used traditional manufacturing methods (lithography, etching process, mechanical microcutting, and the spacer method) to produce microreactors so far.

#### 2.1.1. Lithographie, Galvanoformung und abformung (LIGA)

The main steps of LIGA method (Fig. 2), german acronym for Lithography, Electrodeposition and Molding, are (Kusakabe et al., 2001):

- i Substrate surface cleaning.
- ii Application of photoresist on the surface, generally by spin coating.
- iii Baking of the material to dehydrate photoresist, generating a solid film.
- iv Placement of a mask with the desired pattern.
- v Exposure of the film to the appropriate radiation.
- vi Treatment of the film with a chemical developer. If a positive photoresist has been used, the exposed film is removed. For negative ones, unexposed areas are eliminated. This process allows discovering only some areas of the substrate.
- vii Treatment of the discovered part of the substrate (attack of the material, implantation of ions or deposit of a new material).
- viii Elimination of the photoresist that protects the substrate with a chemical solution (eliminator).

Based on the nature of the source used to remove photoresist, different types of lithography can be considered: photolithography (sources of visible light, ultraviolet or extreme ultraviolet) and X-ray lithography (X-rays). The latter has the advantage that the diffraction of radiation is almost zero, which improves the quality of the manufactured device, however presents the limitation of higher cost, which restricts its use.

Another variant of the lithography is soft lithography (Xia and Whitesides, 1998), a low-cost, non-photolithographic strategy for obtaining micro- or nanostructures using self-assembly and replica molding processes. In this technique, patterned stamps made of elastomeric polymers are employed to produce structures with sizes between 30 nm and 100  $\mu\text{m}$ . The patterned stamp is obtained by cast molding. A prepolymer is deposited over a master with the adequate shape. Once cured, the elastomer is peeled off. For the fabrication of the master, different techniques have been proposed, e-beam writing, photolithography, micromachining, or from existing structures, such as TEM grids diffraction gratings, or structures etched in silicon or metals.

### 2.1.2. Etching process

Firstly, it has to be remarked that during etching, the partial removal of material from a substance called substrate occurs, and this may proceed *via* wet or dry approaches, as was recently stated by Bojang and Wu (2020). A photosensitive polymer is deposited onto the substrate to be etched, then it is exposed to a light source using a mask and then is developed. Depending on the type of polymer, the non-exposed parts or the exposed ones are not diluted by the solvent employed to eliminate the polymer that cover the zones to be etched. Therefore, the substrate is etched through the openings of an applied mask. Other methods can also be used to generate the etching mask, for example, direct laser mask writing (Microreactors in Organic Chemistry and Catalysis, 2008).

This technology offers the highest geometrical resolution and allows obtaining structures with accuracy less than 1 mm. As stated above, there are two types of etching approaches according to the physical state of the etched material: wet chemical etching, if the material is etched as a liquid phase and dry chemical etching, when it is eliminated as a gas. In turn, every type can be isotropic, when the etch rating is the same whatever the considered direction, or anisotropic, if etch rates reflect directions governed by the crystallographic orientation or a spatial direction (Microreactors in Organic

Chemistry and Catalysis, 2008; House and Li, 2008). Isotropic wet chemical etching (using buffered 10% hydrofluoric acid) or anisotropic dry etching (using inductively coupled plasma) could be used to achieve structures for glass microreactor fabrication, the last process presents the disadvantages of a small etching rate and the limitation in the maximum depth for glass (40–50  $\mu\text{m}$ ).

An example of a microreactor made by etched stainless steel microplates is that recently used by Behravesht et al. (2019) for the gas-phase partial oxidation of ethanol (Fig. 3), using a Au/Al<sub>2</sub>O<sub>3</sub> catalyst. In this example, the arrangement of the channels and their shape made it possible to generate a homogeneous catalytic layer that showed optimal performance in the aforementioned reaction.

### 2.1.3. Mechanical microcutting technology

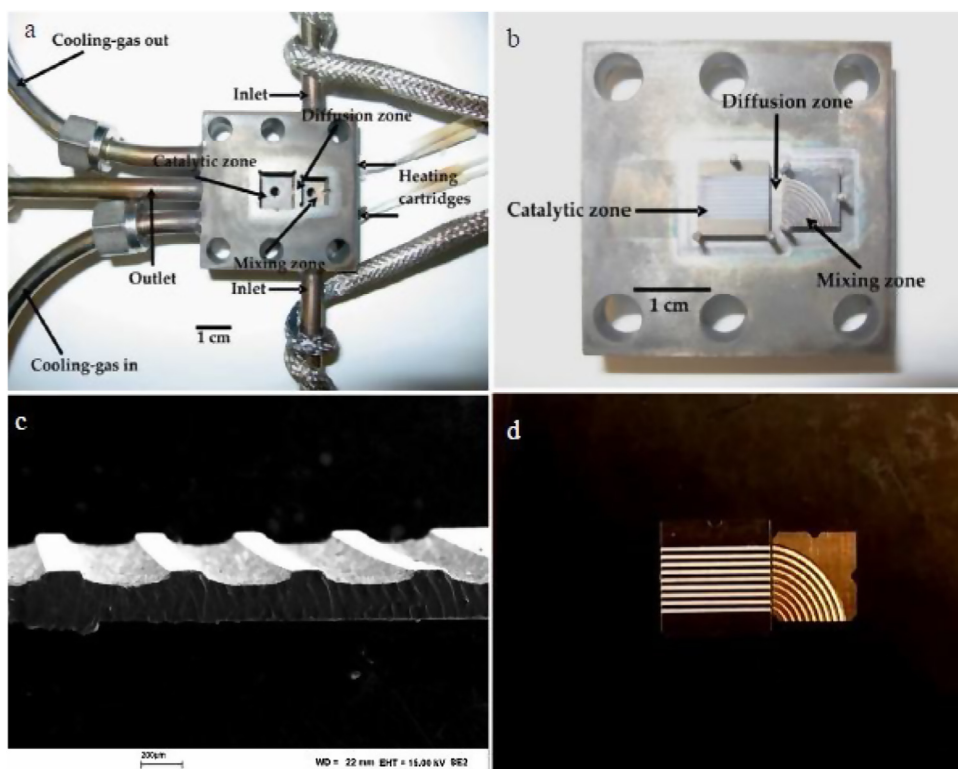
Microcutting is defined as the fabrication of microcomponents using geometrically defined cutter edges. In a similar way to conventional cutting processes, the desired surface of the workpiece is eliminated by mechanical methods. However, for microcutting smaller depths of cut are used, generally up to one micron. Among typical microcutting operations, micro-milling, micro-turning, microdrilling and micro-grinding could be found (Sun and Cheng, 2010). In Fig. 4, an example of a micro-milled stainless steel plate used for the manufacturing of a microchannel used in methanol steam reforming (Sanz et al., 2016) is presented.

When the size of the generated microchannel shrinks, issues such as the geometry of the cutting-edge tool or the grain size and orientation, with little impact at larger scales, became very important for the precision, integrity and quality of the machined element (Dornfeld et al., 2006).

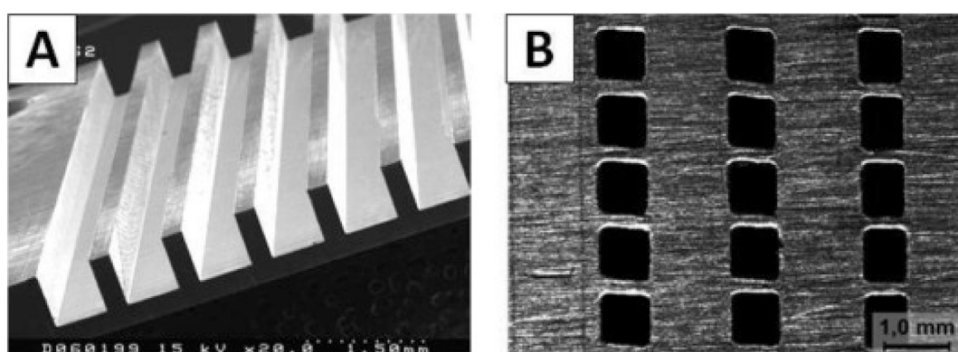
Microcutting presents some advantages over other micro-manufacturing technologies, due to the high level of machine precision. Therefore, pieces with excellent surface finishing and form accuracy can be obtained with very high machining speed. Contrasting lithographic techniques or micro-laser beam machining, this method does not involve a very expensive equipment, allowing the manufacturing of microdevices at moderate costs. It could be used on an extensive variety of materials, such as different metals, ceramics, glasses or polymers. In conventional cutting of brittle materials such as the glasses used in optical applications, large depths of cut generate sub-surface cracking. However, when the cut depth decreases, a transition from brittle to ductile in the material removal mechanism takes place as Shimada et al. (1995) observed. In their analysis of the phenomenon, the authors demonstrated that the low penetration of the cutting parts in micromachining generates a stress in the structure of the material to be cut, which is dissipated by the possible defects that said material has, inhibiting the formation of fractures. Consequently, the removal of material proceeds through a ductile way rather than a brittle one, achieving pieces with a good surface finish, free of cracks (Dornfeld et al., 2006).

### 2.1.4. Spacer method

This method allows to obtain microchannels in a monolithic substrate by embedding spacers with the adequate size and form before the consolidation of the substrate and eliminating the spacers after or during the substrate consolidation. This procedure has been described for the fabrication of metal microreactor, from the powder metal (Hakamada et al., 2007), or polymeric microreactors (Verma et al., 2006). The generated monolithic structures are not affected by problems of seal-



**Fig. 3 – Stainless steel microreactor made by means of chemical etching, used for the partial oxidation of ethanol: a) Microreactor body; b) mixing, diffusion and catalytic zone; c) cross section of a microplatelet ; d) a mixing and microplatelet. Reprinted from Ref. Behravesht et al. (2019).**



**Fig. 4 – Microchannel reactor for the methanol steam reforming: A) Single micro-milled platelet; B) welded micro-milled platelets. Reprinted from Ref. Sanz et al. (2016).**

ing, misalignment or bonding failures that can appear as it happens with other methods where 2D layer are stacked and bonded.

Fig. 5 shows the process used to generate straight microchannels in a polydimethylsiloxane (PDMS) monolith (Verma et al., 2006). Nylon threads are placed in a container of liquid elastomer prepolymer that is cured at 90 °C for 1 h. Then, the obtained polymeric block is swelled in chloroform and threads are withdrawn out obtaining the desired straight channels. Finally, the substrate shrinks back when drying.

## 2.2. Materials commonly used for fabrication of microreactors

Different materials including glass, quartz, ceramics, metal, metal alloys or polymers can be used for obtaining microreactors. However, taking into account that ceramic structures have been extensively studied so far, to the point that they have the most widespread application, which is that of the

three-way catalyst supported on cordierite monoliths for vehicles, this review will focus more on the other types of materials, which have advantages such as working temperature, workability, surface chemical properties and greater heat transfer abilities (Knitter et al., 2001). Table 1 summarises the main advantages and drawbacks of these materials and the preferred technology for their manufacture.

Firstly, glass is a useful material for technological applications in optics, chemistry, pharmacology or electronics. A great variety of special glasses with different chemical or physical properties are available. This material presents two main advantages to be used as raw material in microreactor fabrication, good chemical properties and high structural stability (Tiggelaar and Gardeniers, 2007). However, its propensity to fracture when brought under tension and poor resistance to temperature variations difficult the employment of the classic structuring methods. For example, chemical etching is only possible for the pieces with microchannels of low depth. Laser ablation is complicated by the glass low resistance to

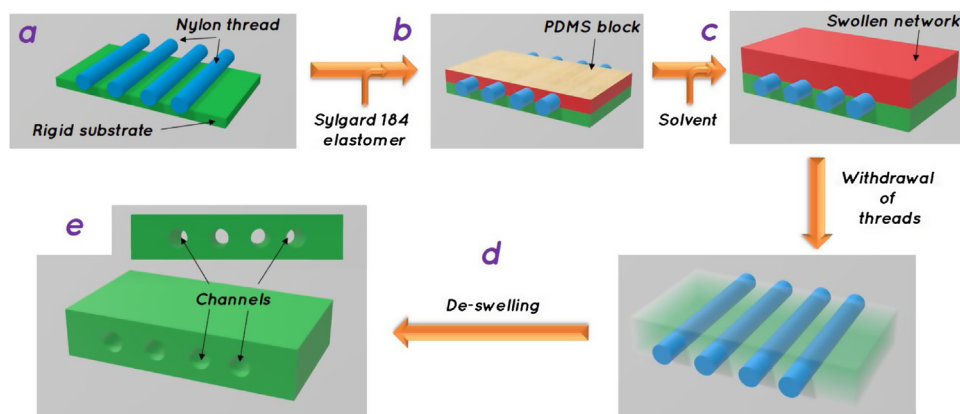


Fig. 5 – Generation of straight microchannels inside a PDMS block (Adapted from Ref. Verma et al. (2006)).

Table 1 – Main advantages and drawbacks of materials used for microreactor production and preferred technology for their manufacture.

Materials	Most used	Main advantages	Main drawbacks	Most suitable shaping methods
Glass	Borosilicate Glasses fused silica Photoetchable special glasses	-Good chemical properties -High structural stability	-Fracture under tension -Poor resistance to temperature variations	-Grinding -Lapping -Sandblasting
Quartz		-Very shock resistant -High temperature and chemical resistance -Exceptional optical transmission	-High cost	-Sandblasting -Wet-chemical etching -LIGA
Polymers	Thermoplastics	-Production of complex structures with great precision -Unexpensive massive production	-Only for use at low-temperatures	
Metal alloys	PDMS Stainless steel Aluminium	-Highest heat and mass-transfer properties -Excellent candidates for catalyzed gas-phase reactions	-Poor dispersion of active species and cracks of the layer -High reactivity compromising integrity and interfering with performance of catalyst	-Mechanical microcutting

temperature changes, being only applicable to fused silica because of its lower thermal linear expansion coefficient. Last years, the emergence of new fields of application such as microsystems engineering have contributed to improve the shaping methods (Frank, 2008). Among them, only machining processes employing cutters operating with undefined geometry can be used for glass: grinding, lapping, and sandblasting on a miniature scale (Frank, 2008; Kim et al., 2004). For microreactors construction, the borosilicate glasses are the most frequently used, but also fused silica or photoetchable special glasses (lithium-aluminosilicate group) are reported (Frank, 2008). The former is characterized by its crystallization under UV-irradiation and after heating, being the crystallized parts easily dissolved in hydrofluoric acid. This property could be profited to obtain geometric microstructures by using a mask before UV exposition. Compared with glass microreactors, quartz ones have the advantages of their extremely low coefficient of expansion that make it very shock resistant, high temperature and chemical resistance and exceptional optical transmission, however their cost is higher (Maharrey and Miller, 2001).

Polymers are materials with a great potential for the manufacture of low-temperature micro-devices (up to 300 °C), since current technology allows obtaining complex structures at small scales with great precision (Brandner, 2012). Also their massive production is possible, which implies lower monetary cost. The used polymers are mainly thermoplastics because of their moldability. However, the use of elastomers as silicone is increasing (Lin et al., 2012). For example, (Castedo et al. 2016, 2017) describe the preparation of silicone devices by the polymerization of polydimethylsiloxane (PDMS) on a polylactid acid (PLA) mould obtained using an easy and unexpensive technology based on 3D printing. PDMS is a low-cost material with suitable features such as biocompatibility, flexibility, and transparency to ultraviolet-visible radiation. However, its use is restricted because of its incompatibility with certain solvents (dichloromethane, ethanol or toluene) due to the swelling of the polymer and its low resistance to high pressures or elevated temperatures (De Sá et al., 2016).

Other materials typically used to design micromonoliths are the metal and metal alloys. These are excellent candidates for catalyzed gas-phase reactions due to their high heat and

mass-transfer properties (Wiles and Watts, 2014). Besides this, they have a good mechanical strength and can be laminated, easing the machining procedure and allowing to fabricate micromonoliths with high cell density and low wall thickness, minimizing the heat and mass transfer phenomena (Sanz et al., 2013). Moreover, the high versatility in the composition, prize and properties of the metal alloy allows the selection of the adequate one for the long-term working under the reaction conditions (temperature, pressure, atmosphere etc.) of the considered application. Aluminium, different stainless steel alloys (FeCrAlloy, Inconel, AISI304), copper, iron, etc. have been successfully used. However, their application is limited since both the adherence of the catalytic material and the thermal expansion difference between the metal substrate and the catalytic layer remains as problems. This last can cause catalyst damage at high temperatures. Although impregnation method is preferred to deposit the catalyst the poor dispersion of active species on metal microchannels and cracks of the layer are the most popular problems (Munirathinam et al., 2015; Jensen, 2017). Moreover, adhesion, chemical compatibility, reactor size implication, migration effects, modular approaches and temperature/pressure requirement should be carefully studied before the selection of the method to achieve a homogeneous distribution of the catalytic material (Tanimu et al., 2017). A good selection of these parameters can prevent the cracking, the sintering and the loss of the catalysts. Moreover, the elected metal substrate cannot be always considered as a mere spectator in the catalytic reaction, even exerting a positive behavior due to migration of active metal species to the catalytic layer (Domínguez et al., 2014) or altering the dispersion and oxidation state of the active centers.

Despite the great versatility offered by the different types of materials described so far, used for the manufacture of microreactors, certain limitations can be seen. For example, polymeric materials offer considerable chemical stability and favorable workability, but have a relatively low operating temperature range, which makes it impossible to implement microreactors made with polymers in processes above 250 °C. On the other hand, in the case of metallic materials, including alloys, there is a window of operating temperatures and a higher heat transfer capacity. However, these materials have a high reactivity that compromises the integrity of the structures and can interfere with the performance of the catalyst.

This highlights the need to find new materials with advanced performance that better adjust to the requirements of catalytic reactions and an alternative may be the use of composites. Hybrid materials that combine properties of different types of materials can be a promising option when it comes to improving the performance of microreactors from the materials of manufacture. An interesting type of composite could be cermets, which combine properties of metals and ceramics. These materials are widely used for the manufacture of cutting tools thanks to their high mechanical and thermal resistance (Yuan et al., 2021). The main features of cermets are due to their chemical composition and their structural configuration so it would be possible that part of these properties are beneficial if cermets are applied to manufacture microreactors. As an example of this approach, Uvarov et al. (2014) successfully assembled a cermet membrane into a microreactor configuration for the recycling of byproducts generated during the Fischer Tropsch reaction, aiming to produce syngas and subsequently reinject it into the process. In this case,

the thermal properties and the chemical composition of the cermet based on the system Al-Ni-Co<sub>3</sub>O<sub>4</sub>, allowed obtaining a tailored porosity that enhanced the syngas production. Therefore, the combination of Fischer Tropsch and the recycling strategy resulted in the enhancement of the profitability of the entire process of fuels production.

### 2.3. Surface pretreatment of the microreactor

Before the incorporation of the catalytic material into microreactor a surface modification (or pretreatment) must be necessary to improve the adherence. The most used methods for substrate pretreatment include anodic oxidation (Javier Echave et al., 2010), thermal oxidation (Montebelli et al., 2014), UV radiation (Deverell et al., 2011), and grafting of reactive molecules to the substrate surface among others (Golshaei and Güven, 2017). For instance, FeCrAlloy microdevices grow an alumina layer of ca. 1 µm thickness on its surface at 900 °C–100 °C in an oxygen containing atmosphere which is ideal to improve the adherence (Kestenbaum et al., 2002; Ugues et al., 2004; Laguna et al., 2016a). In a similar way, metal oxide layers formed on top of the stainless steel at elevated temperatures have similar effects (Laguna et al., 2016a; Giornelli et al., 2006). The thermal treatments of austenitic stainless steels generate a highly rough and homogeneous oxide scale strongly attached to the alloy, which ensure the good adherence of the catalysts. The integrity, morphology and homogeneity of the oxide scale are mainly influenced by the time and temperature of treatment. Austenitic stainless steels develop, under oxidizing conditions at high temperatures, a protective chromia scale increasing the durability and corrosion resistance. The nature of the oxide scale may affect the catalytic properties of the microreactor, since the species of the alloy scale (manganese, iron and chromium oxides, among others) may present catalytic properties by themselves or in conjunction with the deposited catalytic layer. The interaction between the catalysts coating and the metal oxide scale could alter the chemical formulation and catalytic properties. The extension and nature of such modifications depend on the catalyst, the substrate and the reaction conditions.

By electrochemical etching using oxalic acid as electrolyte and 50 V at 12 °C the roughness of stainless steel microchannels can be increased modifying the smooth steel surface (Kestenbaum et al., 2002; Young et al., 2009). The deposition of a primer of boehmite slurry onto stainless steel microreactors also improves the adhesion of catalysts which is only a few µm thick (Peela et al., 2009). Often these intermediate layers are also used to adjust the chemical compatibility between the metal surface and the catalysts. However the use of colloidal binders is not recommended since they can cover the active sites and surface area of the support can be affected (Groppi et al., 2000). Even so, in some studies such approach has been successful. For instance, alumina boehmite was used as primer layer before the deposition of CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst on stainless steel microchannels without adherence problems (Park et al., 2004). Although the pretreatment or primer layers favor the adherence, clean and degrease the surface before the deposition of the active layer are mandatory. Oxidation by using oxidizers as piranha has been used to clean the metal microchannels increasing the adherence of the catalytic material (Conant et al., 2007). Sulphuric and nitric acids have been also used before to coat different materials into stainless steel microreactors (de la Iglesia et al., 2007).

### 3. Coating methods for glass, quartz and polymeric microreactors

#### 3.1. Sol-gel

Due to its structural control at a molecular level, sol-gel coating method is one of the most extended techniques to incorporate catalysts in microreactors. The application of this method has been extensively described for microreactors with different types of substrates (Das and Srivastava, 2016) such as inorganic polymers, glass (Matsushita et al., 2008), quartz or stainless steel (Eskandarloo et al., 2015). Among the main advantages of this method, it can be remarked the wide variety of possible compositions and the tunable porosity of the surface. In general, sol-gel method can be applied for producing porous bulk materials for catalysis and dense film coating with a low porosity on glasses (Haas-Santo et al., 2001).

Usually thickness of a few  $\mu\text{m}$  can be obtained by sol-gel method (Muraza et al., 2008a; Kolb et al., 2008). It favors uniform coatings on highly porous substrates. Among the coatings more frequently deposited using this method, alumina has been commonly used. In this case, pseudo-boehmite or aluminum alkoxide are normally used as precursors of the sol. This sol can be a binder for the metal particles on the coating. Moreover, urea is added as additive to favor the porosity (Tomašić and Jović, 2006).

Sol-gel coating methods has been applied for a large variety of engineering applications. Indeed, Eskandarloo et al. (2015) synthesized  $\text{TiO}_2$  nanoparticles in the microchannels of reactors made of steel and quartz by using the sol-gel method. The stainless steel substrate, with inscribed microchannels, is heated to  $70^\circ\text{C}$ . Then, deionized water and titanium butoxide dissolved in ethanol are introduced in counterflow into the microchannels with a dual-syringe pump. The hydrolysis takes place inside the channels when pumping the solutions, obtaining a colloidal suspension. Two hours later, the reac-

tion is complete and the microreactor is dried at  $100^\circ\text{C}$  for 5 h. To finish, the desired  $\text{Ag}/\text{TiO}_2$  catalyst is synthesized by means of the reduction of  $\text{Ag}^+$  to  $\text{Ag}^0$  assisted by UV-LEDs light on the surface of the titanium oxide. The efficiency of the microreactor in the elimination of terephthalic acid under UV-LEDs irradiation is nearly constant for all the tests carried out. Moreover, catalyst particles were not detected in the device outlet confirming the strong anchoring of  $\text{Ag}/\text{TiO}_2$  to the microchannels. In this way, the catalytic microreactor presents the necessary stability and reusability to be used in most photocatalytic applications. In another interesting example, Abrokwhah et al. (2019) also used successfully the sol-gel method for designing a silicon-microchannel microreactor achieving a uniform coating of Co, Fe or Ru supported titania catalysts for Fischer-Tropsch synthesis.

Similarly, Muraza et al. (2008b) deposited a film of mesoporous silica thin with hexagonal and cubic mesostructure by the evaporation induced self-assembly assisted sol-gel route on microchannels etched in a Pyrex<sup>®</sup>7740 borosilicate glass substrate. In order to enhance the adherence of the mesoporous films to the walls of the substrate, a film of  $\text{TiO}_2$  was firstly deposited on the substrate by atomic layer deposition from titanium tetrachloride and water as illustrated in Fig. 6. The authors demonstrated that this catalytic system is suitable to anchor efficiently metal nanoparticles and perform a number of fine chemicals synthesis reactions

#### 3.2. Heat attachment

In this technique, the immobilization of the catalyst in polymeric reactors occurs by thermal treatment at low temperature. The microchannels are filled with an aqueous suspension of catalyst and the microreactor is then subjected to a low temperature thermal treatment in order to eliminate the solvent and to allow the fixing of the catalyst particles on the surface. The non-fixed catalyst is eliminated by a flow of water. This procedure allows to control the catalytic coating mass, obtaining a uniform layer on the surface of the microchannel. Temperature and time of the treatment depend on the substrate nature, as illustrated in Table 2 for some polymers.

For PFA microreactor, the temperature is fixed at the lower limit of the polymer melting point range (Ramos et al., 2014). At that temperature, the catalyst anchoring occurs on the thermally expanded surface of the microchannels. Some relevant conclusions can be extracted from this study:

- The homogeneity of the catalyst layer rises with the number of coatings or increasing the catalyst suspension concentration.
- The thickness of the catalytic layer is determined by the suspension concentration.
- The thickness of the catalytic layer not influences the reaction rate of phenol decomposition, indicating that the larger limitations in the transfer of matter/load due to the greater thickness compensate the benefits of a higher homogeneity of the catalytic layer.
- Reaction rate in phenol degradation using sol-gel prepared microreactors is higher by one order of magnitude than attained when slurry reactors are used.

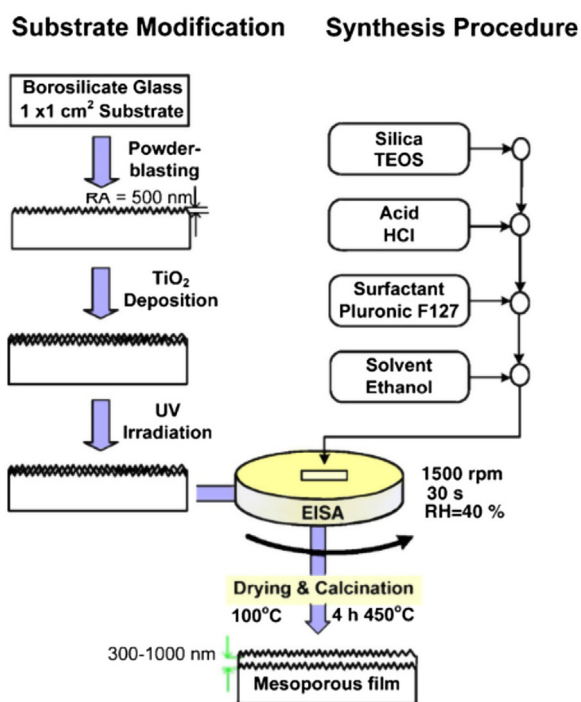


Fig. 6 – Method for preparation of mesoporous catalytic films on a pyrex substrat modified with titania. Reprinted from Ref. Muraza et al. (2008b).



**Table 2 – Temperature, time and number of coatings for some polymers and epoxy resin.**

Polymer	Catalyst	Temperature (°C)	Time (min)	Number of coatings	Reference
Perfluoroalkoxide (PFA)	TiO <sub>2</sub>	285	5 min	1	Ramos et al. (2014)
Polymethyl methacrylate	TiO <sub>2</sub>	100	–	3	Eskandarloo and Badiei (2015)
Epoxy resin	TiO <sub>2</sub>	50	60	20	Charles et al. (2011)

### 3.3. Spray

In this method, a stable colloidal suspension of the catalyst was directly sprayed on the substrate uniformly using a spray gun and the coated substrate is heated in order to eliminate the solvent. The use of this method to deposit the catalyst on various types of substrates has been described: UV transparent cellulose acetate (Marinho et al., 2017), silicon-photoresist (Li et al., 2014) or carbon paper (Cheng et al., 2016; Chen et al., 2017a).

Marinho et al. (2017) used this method to immobilize the catalyst on an pioneering micro-meso structured reactor applied to Cr(VI) photocatalytic reduction. The reactor comprises multiple stacking slabs of different nature: a back channelled acrylic one, a frontal UV transparent borosilicate slab and, between them, an UV transparent slab made of cellulose acetate (CA) uniformly covered with TiO<sub>2</sub>-P25. The 2 wt.% titanium oxide suspension is sprayed on the CA slab and dried at 50 °C for 20 min, after cooling at room temperature the slab is weighed. This process is reiterated until the desired quantity of TiO<sub>2</sub> is reached. According to these authors, the obtained device offers an effective exposure of TiO<sub>2</sub>-P25 CA sheets to light and its laminar flow allows a high degree of mixing, maximizing Cr(VI) reduction reactions. These type of systems are suitable for Cr(VI) reduction in a continuous mode, without observed loss of efficiency during three successive photocatalytic cycles. The reaction rate increases with the amount of TiO<sub>2</sub> up to a certain optimum value above which the particles block the UV light penetration (Fig. 7).

### 3.4. Hydrothermal

This process has been employed to grow nanorods or nanowires of different catalyst (ZnO, TiO<sub>2</sub>) on the surface of different substrates: glass slides, silicon, Si/SiO<sub>2</sub>, fluorine-doped tin oxide (FTO) or indium tin oxide (ITO) (Han et al., 2013; Cheng et al., 2017; Kumar et al., 2010). In a typical process, the substrate is ultrasonically cleaned and dried or baked before its introduction in a hydrothermal reactor containing precursor solution. This method has the advantage to obtain coatings of micropore materials using mild conditions.

Han et al. (2013) described the hydrothermal procedure for the ZnO nanowires (NWs) growth on a glass substrate. The glass was previously cleaned in an ultrasonic bath using different solvents (acetone, isopropyl alcohol and DI water), heated 10 min at 200 °C and treated in plasma for 3 min. Next, zinc oxide seeds are deposited by spin-coating at 3000 rpm for 30 s of an aqueous solution containing PVA and zinc acetate dehydrate and subsequent annealing at 500 °C for 3 h. These ZnO nanoparticles serve as nucleation sites for the hydrothermal growth of ZnO NWs. First, a reaction area is defined on the ZnO coat by a conventional photolithography process. Later, the patterned piece was introduced in a sealed flask containing the reaction medium (zinc nitrate hexahydrate, hexamethylenetetramine (HMTA), polyethyleneimine (PEI) and ammonia) and the growth take place at 95 °C for 12 h. The piece was suspended upside down into the solution

**Table 3 – Summary of materials for which each of the techniques described in this section have been applied.**

Method	Materials
Sol-gel	Inorganic polymers Glass Quartz Silicon
Heat attachment Spray	Polymers Cellulose acetate Silicon Carbon paper
Hydrothermal	Glass Silicon Oxides (SiO <sub>2</sub> , ITO, FTO)
Painting	Glass
Dip-coating	Glass
Electrospinning	Glass
CVD	Pyrex glass

to avoid undesired precipitation of ZnO NWs homogeneously grown on the substrate. After reaction, the coated glass was cooled down, cleaned with acetone to remove the remaining photoresist, rinsed in DI water and dried by blowing dry N<sub>2</sub>. Lastly, zinc oxide seeds covered by the resist were eliminated before the reactive ion etching (RIE), applied to enable the irreversible bond of the glass and a PDMS layer obtained by soft lithography. The assembly of the two layers leads to the final microfluidic device, which has revealed improved photodegradation efficiency under continuous flow conditions compared to the conventional method using dispersed ZnO NW. The proposed preparation method is robust, economical and high performance, being applicable to different photocatalytic systems.

Truter et al. (2016) also applied this method to incorporate a zeolite-based catalyst into borosilicate glass chip microreactors. In this work, the microreactor was initially pretreated with a NH<sub>4</sub>F solution in hydrothermal conditions at 150 °C for 48 h to improve the roughness and wettability of the glass surface. Afterwards, *in situ* hydrothermal synthesis of the zeolite was also successfully performed into the microchannels starting from the precursor suspension. This microreaction system showed an optimal operability and durability at relatively high temperatures and pressure for fine chemical and pharmaceutical synthesis reactions.

### 3.5. Painting

This method was employed by Lei et al. (2010) to create a porous TiO<sub>2</sub> film on the glassy surface of a resin-glass microfluidic photocatalytic reactor. In a first step, a stable TiO<sub>2</sub> colloid containing water, acetylacetone, Triton X-100 and polyethylene glycol is prepared. In a second step, four edges of the glass slide were covered using adhesive tape to control the thickness of the resulting TiO<sub>2</sub> film and preserve the uncoated zones. Then, the colloid was spread on the uncovered region. After drying in air at 80 °C, adhesive tapes were detached and the glassy piece submitted to a calcination step for 2 h at 500

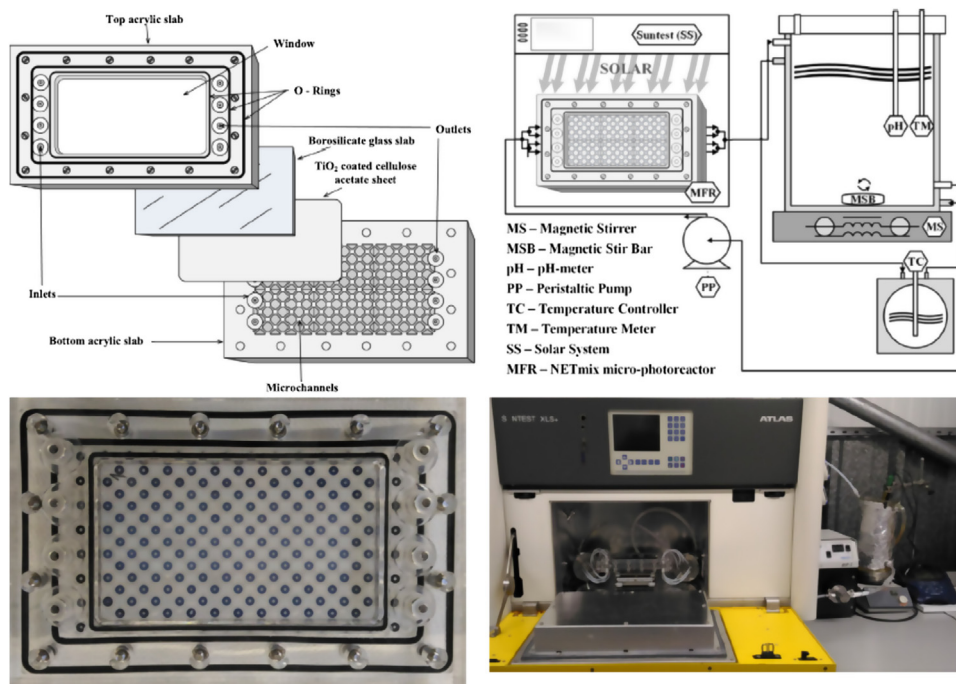


Fig. 7 – Scheme and images of the micro-meso-structured photoreactor. Reprinted from Ref. [Marinho et al. \(2017\)](#).

°C in air. The catalytic device is built by stacking two TiO<sub>2</sub>/glass slides separated by a thin layer of a microstructured resin. The whole fabrication method is quick, low cost and improves the catalytic efficiency with respect to a bulk reactor using the same porous TiO<sub>2</sub> film.

Same authors make a comparison of three different methods to prepare TiO<sub>2</sub> coats for microfluidic based devices ([Wang et al., 2011](#)). Two of them obtained colloids of titania P25 using ethanol or water as solvent. The third one produced titanium oxide from tetrabutyl titanate (TBT). The obtained results permit to conclude that the aqueous P25 colloid method is the best one for preparing microfluidic reactors, being TBT method the one that generates less active catalytic systems due to the compactness of the TiO<sub>2</sub> film.

### 3.6. Other methods: dip coating, electrospinning and chemical vapor deposition (CVD)

[Hakki et al. \(2018\)](#) described a dip coating process to deposit TiO<sub>2</sub> on glass plates. TiO<sub>2</sub> was previously synthesized by the sol-gel method using tetraisopropoxide, isopropanol, diethanolamine and distilled water in a mole ratio of 1:25:1:1, respectively. The glass slides were cleaned with soap and water to remove the pollutants, rinsed in a HCl solution and finally in distilled water. Then, they were dried at 60 °C before coating. TiO<sub>2</sub> sol was deposited on glass plates by 5 vertically dip-coatings, between them, glass slides were dried at 100 °C for 2 h. The coatings were calcined for 3 h at different temperatures (between 400 and 700 °C), testing its effect on the photocatalytic activity of TiO<sub>2</sub> coatings in the methylene blue degradation reaction under UV-A irradiations in a batch reactor. The highest methylene blue degradation was achieved by the coating calcined at 500 °C, where only small and highly dispersed anatase TiO<sub>2</sub> crystallites were obtained.

The use of electrospinning has been reported to prepared microfluidic reactors with a photocatalyst based on TiO<sub>2</sub> nanofibers instead of TiO<sub>2</sub> film ([Meng et al., 2013](#)). The fabrica-

tion procedure included three main steps: (i) electrospinning of the TiO<sub>2</sub> precursor; (ii) change of the TiO<sub>2</sub> precursor into TiO<sub>2</sub> nanofiber by means of a calcination treatment, (iii) obtaining of the final microreactor by sealing the nanofibrous TiO<sub>2</sub> between a PDMS substrate (obtained by soft lithography) and a glassy cover. In order to compare, a TiO<sub>2</sub> film microreactor was also prepared and both of them tested in methylene blue photodegradation. The TiO<sub>2</sub> nanofiber microreactor exhibits higher catalytic activity than the TiO<sub>2</sub> film one, thanks to its higher surface to volume ratio.

[Castellana et al. \(2006\)](#) integrated TiO<sub>2</sub> into PDMS-pyrex flow reactors systems by chemical vapor deposition. Pyrex 7740 wafers were submitted to a thorough cleaning process: treatment in a vigorous oxidant H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> solution, washing with purified water, drying and thermal treatment at 500 °C for 5 h. Then, wafers were immersed in concentrated H<sub>2</sub>SO<sub>4</sub>, successively rinsed with water and methanol, and subsequently dried with nitrogen. After cleaning, wafers were exposed for 2 h to titanium (IV) isopropoxide vapor at room temperature. The reaction was stopped by washing out with water and acetone. To finish, covered slides were treated once more at 500 °C for 5 h to obtain the TiO<sub>2</sub> film. This method allows obtaining homogeneous layers of TiO<sub>2</sub> with a thickness of 6 nm.

[Table 3](#) summarises the materials for which the use of each of the above techniques has been described. Among the methods described, heat attachment, spray, painting and dip-coating are the simplest, but also the most restricted in terms of the variety of materials for which they can be used. CVD and electrospinning have the disadvantage of requiring more sophisticated equipment for their application.

Hydrothermal and, especially, sol-gel methods seem to be the most advantageous, as they are more universal in terms of the materials to which they can be applied and do not require particularly complex equipment. In fact, according to the available literature, the sol-gel method is the most widely used of all those mentioned.

## 4. Coating methods for metal microreactors

There are several available techniques for the deposition of catalyst on metal microreactors (Tanimu et al., 2017; Meille, 2006; Kundu et al., 2007). Among them the flow coating methods, either in the liquid or gas phase, are the most employed (Tanimu et al., 2017). Plasma spraying and chemical vapor deposition (CVD) are used from gas-phase (Meille, 2006), whereas from liquid-phase dip-coating, sol-gel (Schimpf et al., 2002; Haas-Santo et al., 2001), micro pipetting (Wan et al., 2001), electrochemical deposition and electroless plating (Jensen, 2017) are commonly used. The deposition of previously prepared powder catalyst is mandatory being the liquid-phase methods the preferred. In this case the successful deposition of catalytic layers of controlled thickness is rapidly obtained with a good reproducibility (Jensen, 2017). However, both the viscosities of suspensions and precursor loading, as well as the removal of excess solid and drying of deposited material must be carefully controlled since thin layers or blocking can be obtained.

In next sections the most used methods from liquid or gas precursors to deposit catalytic materials onto metal microreactors are shown:

### 4.1. Capillary force

In this case, the microchannels are filled with a viscous fluid by using the capillarity forces and cleared by forcing the gas through it to remove the excess. This procedure can be applied before or after the microfabrication (Chen et al., 2005). The viscosity of the suspension must be higher than dip-coating method to obtain good thickness. The evaporation of the solvent in the catalyst precursor should be very slow to preserve the uniformity of the deposited layer. Zapf et al. (2003) showed a manual coating procedure for stainless-steel microchannels. The procedure started with the filled of the channels with an excess of the catalyst slurry following by blowing of air to eliminate the excess, dried and calcination without contamination issues. Although this method is easy, low cost and efficient, some issues should be improved, for instance, a homogeneous distribution of the active phase in both lateral and horizontal directions of the channels.

### 4.2. Spray coating, dip coating, spin coating and brush methods

In the spray coating, a spray of the suspended catalysts can be applied on specific areas of the microreactors using masks. This procedure can only be applied before the structured foils are assembled as complete reactor. The uniformity of the coating thickness, the adherence and the distribution of the inlet stream across the various channels may be critical variables (Pfeifer et al., 2004).

The dip coating method, also known as washcoating, is a versatile method for coating catalytic solid on different metal substrates. This technique consists of dipping the microstructured substrate into a colloidal suspension or slurry of the catalyst and subsequent withdrawing under controlled speed. Then, the excess of suspension is removed and the devices is thermally treated. This process is repeated until to obtain the desired catalyst loading on the metal support.

Zhao et al. (2003) compared both plasma spray and dip coating methods to deposit catalysts on FeCrAlloy microchannels.

The precursors were alumina, polyvinyl alcohol and water for plasma-spray, and alumina and boehmite for dip-coating. The same thickness was obtained with both methods but the adherence was favored by spray coating.

Spin-coating can be also used for metal microchannels (Schimpf et al., 2002). This method allows to obtain a uniform catalytic layer onto a substrate by using centrifugal force. Indeed, spin-coating was used to incorporate alumina, silica, zirconia and titania onto a substrate previously coated with a pseudo-boehmite primer. It can be remarked that exists a correlation between the film thickness, viscosity and the spin speed. This procedure is usually applied on opened structures, being restrictive for coating on preformed reactor, since the elimination of the catalysts excess by spin speed would not be successful.

The utilization of a brush to deposit a thin layer has been also proposed. For example, Walter et al. (2005) used this method to coat a suspension of  $V_{75}Ti_{25}O_x$ -catalyst onto the open walls of microchannels. Despite the simplicity of this method, low reproducibility, inhomogeneity and contamination problems limit their application.

### 4.3. Sol-gel technology

The aim of this technology is to deposit thin porous oxide layers on inner walls of metal microreactors. Sol-gel techniques allow to prepare stable and well stucked porous thin coatings of metal oxides like alumina, silica and titania. Sometimes, both sol-gel and washcoating methods are simultaneously used to increase the thickness of the catalytic layer (Haas-Santo et al., 2001). The drawback is the deposition of the catalytic material in desired areas. Herein, the use of masks is mandatory. However, this increases costs since the manual handling of each plate is required. Alumina layers have been coated on stainless steel microreactors by using aluminium-butylate and aluminium-triisopropylate as starting materials (Meille, 2006). In this case, the microstructured reactors were coated in a vertical position to favor the wetting of all channels by the dip coating method. In this case, the deposition of a wet liquid film by immersion of the substrate into a solution containing the alumina precursors and its withdrawal at constant speed into an atmosphere controlled is required. Afterwards, air flow is used to eliminate the excess from the channels and subsequently, a thermal treatment is normally necessary to generate the final oxide. This is a low-cost, reliable and reproducible method. A large variety of catalytic films and thicknesses can be deposited by controlling several factors: immersion time, withdrawal speed, number of dipping cycles, catalytic gel composition, concentration and temperature, and environment humidity, among others. The optimum control of these parameters achieves uniform and high-quality catalytic films in short time.

Chen et al. (2005) demonstrated that the direct injection of the sol into each individual microchannel is difficult to be applied for industrial procedures due to the high consumption of time. In this case, the catalyst was deposited onto the inner surface of microchannel reactors by closed-channel, open-channel and surface-selective infiltration methods. The thickness of the catalyst layer can be controlled by the infiltration method and the number of cycles carried out. In comparison to the closed-channel method, the open-channel infiltration technique forms thicker catalyst layers per infiltration and drying cycle; however, the contamination of the top surface results in a poor sealing of the microreactors. For this

reason, the selective infiltration method is commonly used for coating inner microchannels. In this method, the catalyst precursor is selectively infiltrated without surface contamination. Both the infiltration volume and the catalyst weight loading determine the number of injection cycles.

Haas-Santo et al. (2001) have reported the deposition of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  from alkoxides on metal FeCrAlloy microreactors, using acetylacetonate as stabilizer, nitric acid as catalyst and ethanol as solvent. The type of alkoxide used, the solvent and the thermal treatment affect the properties of metal oxide coatings (adhesion and surface area). The best results were obtained using ethanol as solvent, and aluminum-sec-butylate and tetraethyl-ortho-silane as layer precursors. Additionally, it was demonstrated that the adhesion was influenced by the viscosity, which depends on the pH value and the aging time of the sol. In a similar way Jackson et al. (2004) deposited silica on aluminum microreactor using sulfuric acid and  $\text{Na}_2\text{SiO}_3$  dissolution. The gel was transformed into  $\text{SiO}_2$  after thermal treatment and successfully used as carrier for different catalysts.

#### 4.4. In situ combustion synthesis method

This method has been used to incorporate alumina into metal microchannels. In this case,  $\text{Al}(\text{NO}_3)_3$  was simultaneously deposited with active species by precursors solution spraying followed by *in situ* Solution Combustion Synthesis (SCS) method on metal plates previously coated with  $\text{Al}_2\text{O}_3$  by plasma spray with two different layer thickness (Specchia et al., 2010; Galletti et al., 2009). The main advantage of this method is the quick obtaining of the desired oxide on the structured catalysts with a high specific surface area.

#### 4.5. Electrophoretic deposition (EPD) and electrostatic sol-spray deposition (ESSD)

An interesting possibility for the deposition of nanoparticles from colloidal solutions in metal microchannels is Electrophoretic Deposition (EPD) (Nedyalkova et al., 2009; Yang et al., 2003; Nedyalkova et al., 2010). This method is based on the movement of charged particles in suspension between two electrodes (electrophoresis), and the deposition of the particles on one of them (electrocoagulation). The deposition occurs on the anode (positive electrode) if the negatively charged particles are deposit (anodic electrophoretic deposition) on the contrary if the particles are charged positively (cathodic electrophoretic deposition) the deposition is in the cathode (Nedyalkova et al., 2009). Two requirements are necessary for EPD, firstly colloidal particles that can carry a charge and secondly that can form stable suspensions. The final properties of the layer should be related with the composition, pH, voltage density and deposition procedure duration (Yang et al., 2003). Alumina nanoparticles are usually used for electrophoretic deposition using glycerol, oxalic acid or aluminum oxide gel as solvents (Wunsch et al., 2002). It was found that the adhesion decreases when oxalic acid is used; however, it increases in presence of glycerol and aluminum oxide. In a similar way, the direct deposition of oxide nanoparticles of ZnO, CuO and  $\text{Al}_2\text{O}_3$  on micro-structured metal microreactors has been also done by EPD (Haas-Santo et al., 2002; Holgado et al., 2001). EPD layer can also serve as support to adhere the catalysts by dip-coating afterwards (Vorob'eva et al., 2000). In some cases, polymer binders like poly (ethylenimine) (PEI), poly (diallyl dimethyl ammonium chloride) (PDDA), and poly

(allylamine hydrochloride) (PAH) are required to stabilize the suspension of catalyst particles decreasing the viscosity. Additionally they can favor the adhesion of the deposit avoiding the cracking phenomena (Zhitomirsky and Petric, 2000a, b).

Electrostatic sol-spray deposition (ESSD) has been used to spray a sol of titanium tetrahydropropoxide on stainless steel microchannels (Nomura et al., 2003). A high control of the morphology of the deposited layer was obtained after combining the heating of the substrate to coat and the generation of a charged aerosol. The reaction conditions such as substrate supply rate, temperature and composition of the solution can be independently fixed.

#### 4.6. Anodic oxidation and anodic spark deposition

A porous alumina layer can be generated on microchannels containing aluminum by anodic oxidation (Sanz et al., 2009; Gorges, 2002). This method can be used as pretreatment before another coating method or can be directly used to incorporate an active metal. A direct current (or direct voltage) in an appropriate electrolyte in contact with the aluminum microchannel is necessary. Parameters like time, temperature, electrolyte concentration, voltage and current must be controlled to obtain the desired aluminum oxide layer. Wunsch et al. (2002) used AlMg microreactors. In this case the anodic oxidation of the microstructure was achieved at constant voltage 50 V, 12 °C and 1.5 % of oxalic acid as electrolyte passing through the microchannels. After 6 h the anodized layer was 7  $\mu\text{m}$  thick. However some studies have been demonstrated that the anodic oxidation is unfeasible in the fine microchannel because penetration of electrolyte into the depth of the structure is very difficult (Meille, 2006). A modification of anodic oxidation could be the anodic spark deposition. It favors the growth of ceramic oxide layers on passivating zirconium titanium or aluminum (Gorges, 2002).

#### 4.7. Electroplating and electroless plating

Electroplating can be also used to produce metal coatings on metal microchannels by an electric field action (electrodeposition) (Stefanov et al., 2000; Löwe and Ehrfeld, 1999). The cathode is the microchannel to be plated and the metal to be plated is the anode. Both components are immersed in an electrolyte composed by dissolved metal salts or ions through which the flow of electricity is conducted. A power supply oxidizes the metal atoms of the anode and allowing them to dissolve in the solution. These ions "plate out" onto the cathode. The rate at which the cathode is plated is equal to the rate at which the anode is dissolved. This method has been used to deposit layers of  $\text{ZrO}_2$  using a  $\text{ZrCl}_4$  alcoholic solution (Stefanov et al., 2000) and silver films (Löwe and Ehrfeld, 1999) on stainless steel microreactors.

Other method that uses ionic solutions is Electroless Plating. In this case, the catalysts deposition in the microchannels is carried out after the oxidation of a reducing agent present in the solution itself without electric current (Li et al., 2017; Sudagar et al., 2013). Different catalysts can be coated in metal microstructures, as for instance, Pt on FeCrAl (Sudagar et al., 2013) or copper-based catalyst on aluminium microchannels (Fukuhara et al., 2004, 2005). In the first case, a platinum plating bath ( $\text{H}_2\text{PtCl}_6$ , EDTA, ethylenediamine, NaOH and  $\text{NaBH}_4$ ) were used to deposit the platinum metal on the metal surface by chemical reduction. Sodium borohydride was used as a reducing agent.

For copper catalyst, the samples were firstly immersed in a zinc oxide plating bath and then in a copper plating bath with  $\text{Cu}(\text{NO}_3)_2$  using a formaldehyde solution as reducing agent. Results demonstrated the effectiveness of the electroless plating for the preparation of structured reactor system. It was concluded that both the composition of the bath and plating conditions favor the catalytic performances. Herein, a uniform deposition of catalyst components and *in situ* catalyst regeneration were achieved in short time, making electroless plating an advantageous method for the preparation of catalysts for wall type metal reactors.

#### 4.8. Chemical vapor deposition (CVD): PACVD (plasma-assisted CVD), plasma spray deposition, plasma electrolytic oxidation (PEO)

Chemical Vapor Deposition (CVD) is normally used as a post-coating method (Tanimu et al., 2017). Only the microreactor and the volatile catalysts precursor must be present in the deposition chamber. The deposition rate and the adherence determine the homogeneity of the catalytic layer deposited. They are affected by the temperature, the flow velocity and the microchannel diameter. A good example of this technique to deposit catalysts was developed by Janicke et al. (2000). In this case, aluminium oxide coating on stainless steel micromonoliths was obtained by using the CVD technique. The precursor (aluminium isopropoxide) was deposited at 300 °C and oxygen was added to avoid the build-up of carbon. After 1 h the direction of the gas was reversed to increase the homogeneity of the layer. To enhance the deposition rate PACVD (plasma-assisted CVD) can be used at lower temperatures (Tanimu et al., 2017). However, the layer deposited by PACVD normally presents low porosity with respect to obtained by impregnation methods. Plasma spray deposition has been also studied to obtain well-adherent coatings on microchannel with large surface areas. It offers both higher thermal stability and mechanical strength of the coated layer (Pranevicius et al., 2000a). Additionally Plasma electrolytic oxidation (PEO) has been used to deposit thick oxide ceramic layers with good structural and textural characteristics (Nie et al., 1999).

#### 4.9. Atomic layer deposition (ALD or ALE)

ALD is a subclass of the conventional CVD technique (O'Neill et al., 2015; Gu et al., 2017). It is a thin-film deposition method based on alternate pulses of the catalysts precursors that are separated by inert gas purging. The number of cycles determines the thickness of the layer. It permits a control of the homogeneity and composition of the films (O'Neill et al., 2015). Moreover, smaller catalyst particles can be obtained with narrower size distribution (Gu et al., 2017). This technique is less explored in microdevices systems since the growth is better controlled in open surfaces. However, some studies have revealed that highly activity and selectivity microreactors can be prepared with ALD (Mies et al., 2005). Chen et al. (2017b) prepared Cu microchannels using a ALD by passing firstly  $\text{I}_2$  (g) and then a vapor of  $\text{ZrO}_2$  using  $\text{Zr}[\text{N}(\text{C}_2\text{H}_5)(\text{CH}_3)]_4$  and  $\text{H}_2\text{O}$  as precursors. The authors reported that ALD requires the gas phase reactions at low or medium vacuum conditions. This can be coupled directly to an ultrahigh vacuum (UHV) analysis chamber for an *in situ* surface characterization of the catalytic layer growing. This approach favors the quick detection of undesirable reactions such as surface oxidation, reactions with adsorbed species and contamination presence, making

the ALD deposition a versatile method to deposit catalyst. Nevertheless, the control of the chemical anchoring during the ALD process may be a problem, since the precursor can be decomposed during the deposition. Thus, a strict control of the deposition variables (pressure, temperature, precursor, time, among others) is mandatory to achieve the desired ALD layer.

#### 4.10. Flame-assisted vapor deposition (FAVD) and Flame spray deposition (FSD)

FAVD, also called flame pyrolysis, is an interesting alternative to deposit catalysts on microreactors. It is performed in an open atmosphere without vacuum systems, being the atomized chemical precursor of the catalysts burned in a flame (Johannessen et al., 2004). It is used to deposit oxides (i.e.  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CeO}_2$  or  $\text{Cr}_2\text{O}_3$ ) (Jones, 1997). In comparison with sol-gel techniques, the problems associated to the crack of the thick layers persist and carbon or other unwanted species can be formed on the layer.

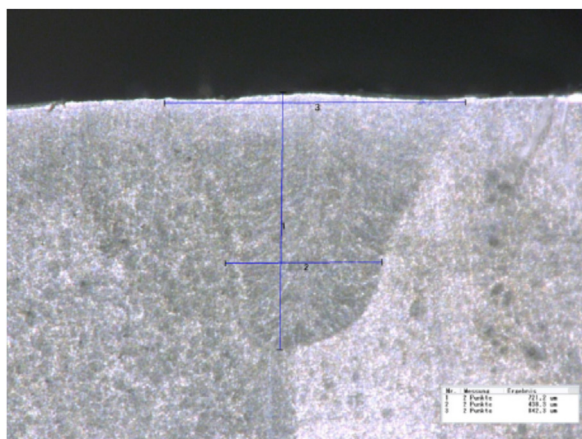
Flame spray deposition (FSD), also called Reactive Plasma Spraying Deposition (RPSD), is a modification of the FAVD in which the precursors are sprayed in a flame at high temperature whereas the metal substrate is maintained at lower temperature. FSD is different to conventional spraying since the oxide powder is directly deposited, opposite to deposition from a suspension. Ismagilov et al. (2001, 1999) developed the FSD method to coating powder in titanium and nickel microstructures using an arc-plasma spray gun at atmospheric pressure in argon/air mixture. The reaction between oxygen and reactive metal species lead to highly stoichiometric oxides. In general, plasma spray gun, operating at atmospheric pressure in air, forms well adherent coatings on steel microchannels.

Similarly, Pranevicius et al. (2000a, b) deposited Al- $\text{Al}_2\text{O}_3$  coatings on steel microstructures by using a plasma gun. Aluminium particles were oxidized in air assisted by plasma and the  $\text{Al}(\text{OH})_3$  was mixed with aluminium powder. Finally, a catalytic layer of 50  $\mu\text{m}$  constituted of 70%  $\text{Al}_2\text{O}_3$  with a specific surface area of 100  $\text{m}^2 \text{g}^{-1}$  was obtained.

#### 4.11. Physical vapor deposition (PVD): cathodic sputtering

Catalysts can be also deposited over metal open microchannel by using Physical Vapor Deposition (PVD) techniques. In this method, the use of shadow masks favors the sputtered of the catalyst onto the metal walls in a uniform coat or in defined areas. By Cathodic Sputtering, a plasma is generated between the target made of the catalytic material to be deposited and the microchannels to coat. The coating material is the cathode and the structured surface is the anode. This method has been employed to sputter Ag on oxidized FeCrAl microchannels with excellent structural characteristics (Kestenbaum et al., 2002). However, the textural properties are not well optimized.

Müller et al. (2003) used a wet chemical procedure from a suspension and sputtering to prepare supported catalyst in metal microreactor. This method controls the deposition area, but the catalyst films are smooth and low surface areas are obtained with low porosity. For this reason, PVD (and also CVD) is usually discarded to deposit catalysts since the textural properties are limited. Additionally, sometimes their application in microreactors is very difficult. By contrast, they avoid



**Fig. 8 – Microsection of a welding seam of the reformer reactor after operation for 1060 h. Reprinted from Ref. Wichert et al. (2011).**

the problem associated with the non-uniform solvent removal presented in dip-coating or sol-gel methods.

#### 4.12. Electrospinning

The electrospinning is an ideal method for fabrication of one-dimensional nanomaterials on metal substrates due to its low cost and easy setup. By means of this technique, nanofibers of the catalysts can be electrodeposited on metal microchannels using large and complex polymeric molecules at lower temperatures with appropriate viscosity (Yeom et al., 2015; da Silva et al., 2017). The nanofiber performances can be modified by electroless metal deposition or by direct incorporation of particles into the precursor polymeric solution.

Yeom et al. (2015) reported the Ni nanofibers deposition from nickel nitrate salt and poly(vinyl)pyrrolidone on nickel metal microdevices using electrospinning. The authors studied several parameters such as applied voltage, tip-collector-distance and humidity in order to coat uniformly the surface of metal foams by electrospinning. Both morphology and thinner were optimized increasing the voltage at humidity below 30%. Under these conditions, the balance of the surface tension forces favored the homogeneity of the nanofibers.

On the other hand, the production of nanofibers inside microchannel could be difficult due to the intense electric fields formed close the acute angles that favors the growing of nanofibers outside the channels. It is known that the production of nanofibers inside microchannels requires a time-consuming method, expensive reactants and complex equipment. To force the electrospinning inside the channels, electrodynamic focusing process is employed, in which the fibers grow in the electric field direction through orifices of metal masks, depositing nanofibres in selected areas of the substrate.

da Silva et al. (2017) prepared fixed bed microreactors and packed microcolumns by electrospun of fibers inside microchannels by electrodynamic focusing method. In this case different polymeric nanofibers containing metal particles were successfully deposited on metal microchannels.

#### 4.13. In situ catalytic growth

Catalysts can be also *in situ* growth in the metal microreactor. In this case, zeolites, carbon nanotubes and molecular organic frameworks (MOFs) can be directly obtained on the

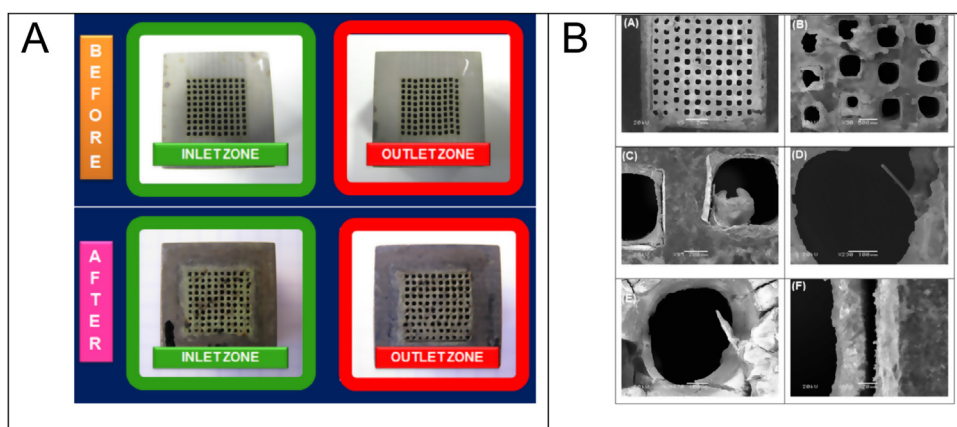
metal microchannel (Zhang et al., 2015; Pérez et al., 2013; Papurello et al., 2017; Ishigami et al., 2007). For instance, multichannel stainless steel plate was *in situ* covered by ZIF-8/NaA (Zhang et al., 2015). NaA zeolite membrane was first growth. Subsequently, the catalytic layer of ZIF-8 membrane was growth by using ZnO-induced synthesis method. Similarly, ZIF-8 films were also growth by solvothermal synthesis on copper microchannels (Papurello et al., 2017). In this case well-anchored crystals was obtained covering the microchannels. After that the impregnation with silver solutions for CO oxidation was achieved. High dispersion of silver particles avoiding their sintering and keeping the MOF structure were observed during the catalytic reaction. The layer of MOFs showed excellent textural properties. This favored the functionalization of their porous walls.

#### 4.14. Durability of the coatings under long-term operation conditions

The catalytic converter of cars is the most common example of a structured system, submitted to prolonged use under extreme operation conditions including large temperature gradients, variable atmospheres and mechanical stress, which allows understanding the use of ceramic substrates for supporting the three-way-catalysts, whose are very stable, looking for high thermal and chemical durability. Consequently, the deactivation of the entire convert is principally associated to mechanical, thermal or chemical effects over the three-way-catalyst during the operation, rather than possible alterations of the ceramic substrate. Maybe, the only scenario where damages of the catalytic layer has been related to the substrate is in the case where the differences in the coefficient of thermal expansion of both components results in fractures under extreme thermal gradients, but more for a physical rather than a chemical principle (Gulati, 2006).

The invariability of the substrate seems have been assumed for other configurations of structured reactors designed for other processes, where metals, polymers or carbon instead of ceramic materials have been applied for the coating of catalysts. Consequently, the analysis of the chemical evolution of substrates in structured reactors, including microreactors or studies that correlate the stability of the structured system to alterations in the substrate have been rarely reported.

One of the few studies that takes into account different aspects of the durability of microreactors is precisely that carried out over a fuel cell/fuel processor system VeGA<sup>®</sup>, which was developed by the company TRUMA Gerätetechnik GmbH & Co. KG and the Institut für Mikrotechnik Mainz GmbH (IMM) (Wichert et al., 2011). VeGA<sup>®</sup> is a miniaturized fuel processor for Liquefied Petroleum Gas (LPG) operated as a compact hydrogen supply system for low power applications such as recreational vehicles. This consists of integrated micro-structured stages of evaporation, reforming and water-gas-shift reaction, including burners and heat exchangers, and after a continuous running during 1060 h with including repeated start-up and shut-down cycles, the general conclusion was that device is highly durable and reliable. Concerning the integrity of the material of the reactor, the authors categorically stated that the stainless steel was not affected by the operating temperature above 700 °C. As prove of this, the authors provided a microsection of a welding seam (Fig. 8) where no damages can be detected after disassembly of the reactor were observed. In addition, they confirmed that the mechanical integrity of the catalyst coatings was preserved.



**Fig. 9 – A) Images before and after the operation of the microchannel reactor for the PROX reaction; B) SEM micrographs from different zones of the outlet zone of the microreactor. Reprinted from Ref. Laguna et al. (2016b).**

Nevertheless, in a recent study led by J.A. Odriozola, evidences of a clear degradation of a microchannel reactor were presented through the analysis of a deactivated microchannel reactor coated with a  $\text{CuO}_x/\text{CeO}_2$  catalyst that was submitted to different temperature ranges and feed-streams for carrying out the preferential oxidation of CO in presence of  $\text{H}_2$  (PROX) during 360 h (Laguna et al., 2016b). In this case, the deactivation of the device was forced and its postmortem study evidenced important damages of the catalytic layer such as cracks and detachments, including displacement of the coating to the mouth of the channels in the direction of the reaction flow (Fig. 9). Nevertheless, not only the catalytic layer was affected. The metal substrate also demonstrated alterations during the operation, such as migration of some elements such as Fe, Cr and Y to the surface, which resulted in the enhancement of the detachment of the catalytic layer.

Considering the evidences of the alteration of the microreactor in this study, beyond the establishment of a controversy about the stability of the metal substrates, it is important to remark that further considerations should be taken into account during the design and preparation of microchannel reactors. For instance, the fact that probably there are some reactions that affect the stability of the metal substrates. In this sense, some strategies have to be implemented in order to protect not only the catalytic layer but also the substrates, because in atmospheres with carbon activities above unity, the typical stainless steel alloys used for manufacturing microreactors may suffer metal dusting promoting carburization.

Prior to the coating of the microchannel reactor presented in Fig. 9, a protective layer of alumina had been generated through a thermal treatment of the metal block. However, this alumina layer seemed to be not enough to protect the interface between the catalyst and the walls of the channels. In this sense, Serres et al. (2012) have recently proposed an alternative to avoid the metal dusting and to inhibit the modification of the catalyst in metal microreactors based in the creation of an enamel barrier between the substrate and the catalyst. These devices were used for the methane oxidative coupling, adapting Sr/La perovskites catalysts and different protective layers were tested (commercial enamel frits with different compositions), and the results demonstrated that in the density is a key factor that control the migration of cations from the metal substrate to the catalytic layer. In addition, the chemical composition of the enamel also must be optimized.

In agreement with this, Domínguez et al. (2014) also studied the enameling of metal micromonoliths (FeCrAlloy) using

a commercial enamel supplied by Ferro Spain. The catalytic layer was principally composed by the  $\text{CuO}_x/\text{CeO}_2$  catalyst, and the micromonoliths were tested in the PROX reaction. However, evidences not only of migration of cations from the metal substrate towards the catalytic layer were observed, but also of some cations of the enamel, thus at least in the PROX reaction, the metal substrates and other additives such as the enamels are not mere spectators.

## 5. Novel manufacturing methods based on additive manufacturing (AM)

During the last decade, the application of additive manufacturing (AM) technologies has emerged with force (Löb, 2020). Additive manufacturing (AM), also referred as 3D-printing, is a “bottom-up” technique for assembling materials layer by layer to generate 3D objects (Parra-Cabrera et al., 2018). The procedure is assisted by a 3D model designed through computer-aided manufacturing software. The application of AM technologies to heterogeneous catalysis facilitates greater design complexity, rapid prototyping, control over reactant stoichiometry and unique catalyst immobilization routes (Hurt et al., 2017; Konarova et al., 2017). According to the data reported in the literature, two strategies are typically used for fixation catalysts in AM structures: (i) ‘Integration’, in which chemically active 3D-printed structures are obtained by dispersion of catalyst species into printable matrices prior to the printing process, and (ii) ‘Functionalization’, in which the catalyst is coated on the 3D-printed material in a post-treatment step (Manzano et al., 2017). Currently, there are a great variety of AM techniques available. In this review, only the most relevant methods will be described: inkjet printing, robocasting, fused deposition modelling (FDM), stereolithography (SLA) and selective laser melting (SLM). Table 4 includes the main characteristics of these AM techniques.

### 5.1. Inkjet printing

Inkjet printing is a technique for coating complex open microstructures. This method presents the advantage of being highly reproducible and automatable. Inkjet printing is based on the digitally controlled addition of small droplets of functional ink from a print head onto a substrate. The ink is added in a precise quantity which can be ejected as either continuous mode (CIJ) or drop-on-demand (DOD) (Pan et al., 2015). Continuous mode (CIJ) pumps ink through a nozzle to form

**Table 4 – Comparison of AM techniques more relevant in catalysis (adapted from Refs. Parra-Cabrera et al. 2018 and Hurt et al., 2017).**

AM technique	Layer thickness	Typical materials	Comments
Inkjet printing	1–50 $\mu\text{m}$	Metal oxides, metals, polymers, ceramic, glasses	Direct inkjet printing of ceramic and metal substrates is possible using inks containing ceramic precursors or nanoparticles followed by sintering
Robocasting	30–500 $\mu\text{m}$	Mixed metal oxides, metal alloys, polymers, supported metals	Concentrated suspensions of a wide range of materials can be formulated as a viscous paste that preserves its shape after extrusion. The printed object is often fired to remove additives.
FDM	50–300 $\mu\text{m}$	Polymers	Chemical and thermal stability depends on the used polymer. Hybrid polymers can improve the poor properties of polymers, e.g. composites with metal oxides or graphene
SLA	1–50 $\mu\text{m}$	Photopolymers	Acrylate or epoxy-based resins are typically used. Stereolithography resins with suspended ceramic or glass particles enable the fabrication of green parts. Burning out the cross-linked polymer binder and sintering the ceramics enables the formation of high-quality ceramic substrates
SLM	20–150 $\mu\text{m}$	Metals and metal alloys	Typical materials for SLM are stainless steel, titanium, aluminum, etc. The metals are stable to high temperatures and resistant to a range of chemical solutions

a liquid jet and droplets are controlled through periodic perturbations of the jet that overcome the liquid surface tension. Drop on demand (DOD) printing is less rigid for ink requirements and acoustic pulses thermally or piezo-electrically eject ink droplets from a reservoir through the nozzle (Hurt et al., 2017). The DOD printing mode is preferred for the deposition of functional inks acting as catalyst materials since provides a picolitre precision that enhances the control of the deposition of material onto the substrate surface and very thin coatings can be obtained with a scalable thickness lower than 5  $\mu\text{m}$ .

The following aspects must be considered to achieve optimal printing results: (i) the generation of stable and printable inks, (ii) suitable substrate selection and pretreatment, (iii) droplet generation, (iv) the printing algorithm, and (v) the drying steps (Siebert et al., 2017). The physico-chemical properties of inks are the most important parameters in inkjet printing, which have an enormous influence on the generation of ink droplets, the interaction between ink droplets and substrate, and drying of ink droplets to form coatings (Pan et al., 2015; Liu et al., 2015). Liu et al. (2015) reported that the properties usually required for inks used in inkjet printing depend on the action mode (Table 5). The viscosity and the surface tension affect strongly the dynamic fluid of the droplets and consequently these properties must be carefully adjusted.

During the last decade, the inkjet printing technology has emerged in catalysis research as a promising and valuable method for depositing a thin layer with catalytic properties. The critical features for fabrication of an optimum catalyst layer are the composition and structure of the materials used. Additionally, by using screen printing, three-dimensional geometric metal microchannels can be selectively coated without leaving excess of coating (Wolf et al., 2015). Nevertheless, this method requires the utilization of high boiling point solvent and colloidal suspension of catalyst with high viscosity. In general, the viscosity of catalyst slurries prepared for spray coating or dip coating methods is much lower (in the range < 50 mPa s) than that required for inkjet printing (>200 mPa s) (Xie et al., 2008). Wolf et al. (2015) used additives like poly(vinylpyridine) and acidic ion exchange polymers like Nafion<sup>®</sup> with a water/1-propanol mixture as solvent for preparing the slurry. Meanwhile, Hwang et al. (2011) applied a

mixture of isopropanol and water. It is worth mentioning that both solvent mixtures might create problems during the inkjet printing procedure owing to drying of the slurry on the metal microchannel.

Siebert et al. (2017) used drop-on-demand inkjet printing to deposit a catalyst based on nanoparticles of GaPd<sub>2</sub> as thin and uniform layer coatings on steel microchannels reactors. They performed the inkjet printing in three manners: (i) Direct printing of GaPd<sub>2</sub> nanoparticles into the wall microchannels, (ii) Printing of an  $\alpha\text{-Al}_2\text{O}_3$  layer first and subsequent printing of GaPd<sub>2</sub>, and (iii) Pre-immobilization of GaPd<sub>2</sub> nanoparticles on  $\alpha\text{-Al}_2\text{O}_3$  support and subsequent printing of the GaPd<sub>2</sub>/ $\alpha\text{-Al}_2\text{O}_3$  material. They found the third methodology of printed showed the most optimal catalytic results for the selective hydrogenation of acetylene reaction. In another example, Lee et al. (2013) applied the inkjet printing technique for the precise deposition of alumina nanoparticles in microchannels as a catalyst support achieving thin and uniform layers, where the thickness of the layer could be adjusted by repeated printing. Afterwards, they impregnated rhodium phase into this layer and the formed catalyst layer was tested in the methane steam reforming reaction. The catalytic results obtained showed a maximum of CH<sub>4</sub> conversion equal to 98.9 % at 973 K, which was stable for more than 60 h.

Furthermore, inkjet printing has been successfully tested as an efficient method for applications in photocatalysis and polymer electrolyte fuel cell (PEMFC). For the manufacture of devices with photocatalytic applications, extrusion or powder-based tools (if the starting material is a polymer) and inkjet printing or stereolithography-based methods (if the starting material is a photoresin) can be used. For example, this last technique has been used by different authors to obtain catalytic devices fabricated with epoxy resins and application in the degradation of salicylic acid (Charles et al., 2011; Corbel et al., 2012). Arin et al. (2011) prepared a transparent thin film of TiO<sub>2</sub> with a thickness of 85 nm over a glass substrate by inkjet printing and proved its photocatalytic performance. Taylor et al. (2007) reported a method based on inkjet printing to fix catalysts materials onto gas diffusion layers (GDL) that are made into membrane assemblies (MEAs) for polymer electrolyte fuel cell PEMFC.



**Table 5 – Fluid properties requirements for inks (adapted from Liu et al. (2015)).**

		Particle size $\mu\text{m}$	Viscosity Cp	Surface tension $\text{dynes cm}^{-1}$	Density $\text{g cm}^{-3}$
Continuous mode (CIJ)		<1	1–10	25–70	~1
Drop-on-demand mode (DOD)	Thermal	<1	5–30	35–70	~1
	Piezoelectric	<1	1–20	35–70	~1

### 5.2. Extrusion based methods: robocasting and fused deposition modelling (FDM)

A moving extrusion xyz print-head controlled by computer model is used to fabricate the slices and selectively deposit the material. The extrusion can be performed in continuous or discontinuous mode, in which the latter mode affords more flexibility to the process. Robocasting is a direct implementation of this approach, which was firstly illustrated for the rapid prototyping of ceramics by extruding particle-based pastes (Chen et al., 2019). Recent advances have enabled also the application for metals, polymers, and composites (Parra-Cabrera et al., 2018). Robocasting dispenses concentrated colloidal suspensions called ‘inks’ through a nozzle or syringe that are self-supporting during assembly due to rapid setting mechanisms. Robocasting has relatively larger layer thickness, especially compared to stereolithography (Hurt et al., 2017).

The design of immobilized catalysts by robocasting requires inks with the appropriate viscosity and the complexity of the process can vary in function of the material. Tubío et al. (2016) prepared a Cu/Al<sub>2</sub>O<sub>3</sub> catalyst with a wood-pile porous structure by robocasting and then sintered at high temperature generating a Cu-supported robust structure with controlled porosity, high mechanical strength, and a high surface-to-volume ratio. The ink consisted of Al<sub>2</sub>O<sub>3</sub> powder suspended in an aqueous solution of Cu(II) nitrate hemi(pentahydrate), and the viscosity modifier used was hydroxypropyl methylcellulose (HPMC). The application of robocasting leads to Cu catalytic species that are fixed in the Al<sub>2</sub>O<sub>3</sub> matrix avoiding the Cu leaching into the reaction medium. In another example, Symes et al. (2012) studied the possibility of printing catalysts into the structure of an elastomer batch reactor by robocasting. To this end, they used an acetoxysilicone ink containing a Pd/C catalyst. The slices printed using this functionalized ink catalysed efficiently the transfer hydrogenation of styrene to ethylbenzene reaction and no leaching of Pd phases into the solution was observed.

Another extrusion based technique is the so-called fused deposition modelling (FDM) which designs three-dimensional objects using thermoplastic materials. The fused deposition modelling produces 3D objects by depositing layer-by-layer thermoplastic materials that were previously heated to their semi-molten state before extrusion at the dispenser nozzle. Once deposited, the material cools and solidifies creating a uniform hard layer which stacks on top of the previous layer according to the sliced model design. Thermoplastic materials such as polylactic acid (PLA), acrylonitrile, butadiene styrene (ABS), polycarbonate (PC), polyamide (PA) are commonly used (Ambrosi and Pumera, 2016). Apart from room temperature printing, the feedstock material is the critical distinction between the robocasting method and fused deposition modelling (FDM). In this sense, robocasting is more versatile since an almost infinite number of materials can be deposited, ranging from ceramic, plastics, metals, composites, etc.

FDM is the most available AM technology since it is not very expensive. Among the different uses of FDM in catalysis, a very interesting example of application in photocatalysis was reported by the group of Llorca and co-workers (Castedo et al., 2016, 2017). They designed a silicone microreactor in which the microchannels were coated with Au/TiO<sub>2</sub> photocatalyst. As shown in Fig. 10, the silicone microreactors were fabricated by casting poly-dimethylsiloxane (PDMS) prepolymer over a polylactic acid (PLA) mould manufactured with a 3D printer. The Au/TiO<sub>2</sub> photocatalyst was deposited on the walls of the silicone microchannels from a sonicated ethanol suspension containing the photocatalyst particles and to attain an optimal immobilization, a corona discharge plasma treatment was previously applied over the microchannels to generate a silanol-terminated surface.

### 5.3. Stereolithography (SLA)

Stereolithography (SLA) is an AM technique that uses UV light for the selective solidification of photopolymer resins. This method uses a digital microarray device (DMD) to create dynamic photomasks that can be assembled into a 3D complex structure through layer-by-layer photopolymerization of materials (Gou et al., 2014). The photopolymers are commonly formed by a mixture of epoxides and acrylates doped with the appropriate photoinitiators (Parra-Cabrera et al., 2018). One of the fundamental advantages of stereolithography over other 3D-printing technologies are the small layer thickness attained (about 25  $\mu\text{m}$ ).

Manzano et al. (2017) designed architectures with catalytically active sites by photopolymerizing bifunctional molecules using the SLA technique. Functionalities in the monomers included a polymerizable vinyl group to assemble the 3D structures and a secondary group to provide the accessible carboxylic acid, amine, and copper carboxylate functionalities catalytically active for the Mannich, aldol, and Huisgen cycloaddition reactions, respectively. The functional groups in the 3D-printed structures were also amenable to postprinting chemical modification. This approach involves covalent anchoring of active sites on the printed structures preventing catalyst leaching and consequent loss of activity.

Snowden et al. (2010) demonstrated one of the first applications of SLA for electrocatalysis. These authors designed a versatile flow cell able to accommodate different types of electrodes for specific electrochemical experiments. The results showed that the use of SLA technique improved upon current channel electrode flow cell production techniques by enabling the batch production of cells, which are easy and rapid to assemble and can support very high volume flow rates without leaking.

### 5.4. Selective laser melting (SLM)

Selective Laser Melting (SLM) is an Additive Manufacturing (AM) method designed to use high power-density laser to melt and fuse metal powders (Yap et al., 2015). A set of successive

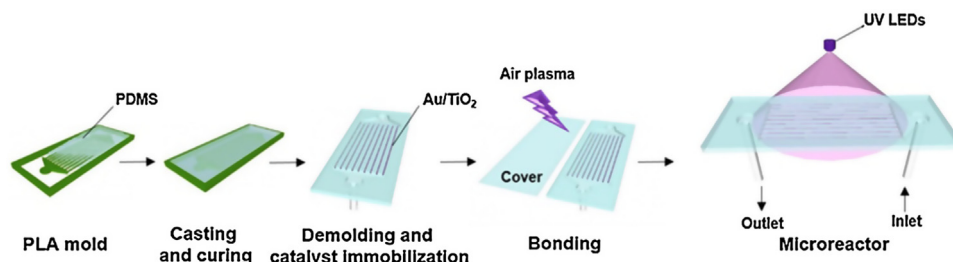


Fig. 10 – Scheme of the fabrication steps of the silicone microreactors. Reprinted from Ref. Castedo et al. (2016).

layers of metal powders are overlapped by applying a high energy density laser to melt and fuse each layer according to the computerized data. This is repeated up to build a 3D object. The effective fabrication of materials using selective laser melting depends strongly on the process parameters and require to be carefully controlled to generate pieces without defects such as porosity, cracks, or different chemical composition by selective vaporization (Prashanth et al., 2017). The materials mostly used are metal alloys such as Ti, Al, CoCrMo, steels and refractory metals (Hurt et al., 2017). The high temperature required for this process make unbuildable many materials like polymers.

This method is more expensive than other AM techniques and for this reason it is less commonly available. One of their most interesting applications was reported by Ambrosi et al. (2016), that proved the use of selective laser melting (SLM) technique to design bespoke electrodes to be used as platform for different electrochemical devices such as pseudo-capacitor, catalytic system for electrogeneration of oxygen, and pH sensor. The 3D printed stainless steel electrodes were functionalized with IrO<sub>2</sub> and presented excellent capacitive and catalytic activity in alkaline solutions as well as a Nernstian behaviour as potentiometric pH sensor.

## 6. Summary and future prospects

In latest years, the interest and uses of microreactors in heterogeneous catalytic applications has exponentially increased. Among the great advantages of microreactors, it is highlighted their reduced volume, which increase the safety of the chemical processes and reactions, allowing the working at high pressures. In addition, the high surface area-to-volume ratio of the microchannel is advantageous for the control of highly exothermic or endothermic reactions and those with heat and/or mass transfer limitations. In terms of productivity, microchannels reactors are excellent candidates to produce significant amounts (up to kg per day or more) of desired products with marked selectivity and decreasing the waste generation. Moreover, microreactors avoid production scaling problems allowing the concept of numbering up and easing the adaptability of the production to the marked, minimizing costs. It is generally accepted that the use of catalytic microreactors is the key point to successfully achieve the process intensification in chemical reaction engineering. Intensifying processes by using microreactors is the challenge strategy that can take multiple catalytic reactions to a higher level where resources are most efficiently leveraged. This is particularly crucial, for example, in the use of renewable energy sources or the development of biorefinery strategies, which require versatile and decentralized infrastructures. Today, however, it can be said that there is considerable room for improvement for

microreactor technology, especially from the point of view of design, manufacturing and the materials used.

In this review, an overview of the new insights about the protocols for manufacturing of microchannel reactors proposed in the literature is comprehensively discussed. Besides the more traditional methods, Computer Aided Design (CAD) tools are more and more used to design microreactor geometries, with almost no limits in terms of complexity. The challenge is to develop manufacturing methods able to produce the designed 3D reactor in a high degree of detail at the micro-scale. Additive manufacturing with 3D printers arises as the near and promising future. This strategy will allow to produce microreactors with optimized geometries for the desired application. However, efficient devices for printing 3D objects with materials usually used as microreactor substrates (ceramics, carbon, metal) are currently under development and some barriers must be still overcome as for instance increasing the control of surface roughness of microreactor walls or reducing the printing costs. In any case, the development of prototyping microreactors using additive manufacture methods is increased notably in the last years, but it still requires intense research effort to make large-scale 3D-printing process economically viable. In any case, the high level of versatility and adaptability makes additive manufacturing a dynamizing complement to microreactor technology and will must drive to sustainable and a cost-effective mass production.

As for the manufacturing materials, they must fulfill the requirement of the demanding operating conditions in terms of temperature, pressure, optical properties and harsh chemical environments. For real applications, the economic impact of the materials in the final price of the microreactor must be also evaluated. In any case, a large variety of materials can be used as substrate for microreactor fabrication. In this review, only glass, quartz, polymeric and metallic materials are visited. Other very interesting and used substrates, as ceramics and carbons, are out of the scope of this paper. Evidently, the optimal fabrication strategies, coating methods and applications are different from one material to another. For instance, for catalytic applications related to the energy, CO<sub>2</sub> capture and utilization sector or biorefinery, ceramics or metals, and possible composites that combine the characteristics of different families of materials become the more interesting substrates. For photocatalytic applications, transparent materials, as glass and quartz must be the elected substrate.

At this point, researchers have a wide open window in which to fabricate novel microreactors that combine novel substrates and demanding applications. For instance, a challenge is to generate bio-active microreactors in which it is integrate the consistent matrix with a controlled geometry

and the integrity of the bio-active agents under heterogeneous conditions.

One of the most common problems with heterogeneous catalysts in microreactors is how to immobilize the catalyst in the flow microchannels. In the present review, particular attention has been paid to coating methods, analyzing the chemical compatibility of the catalysts with the substrate and the durability of the coatings under long-term operation conditions. This review presents a comprehensive overview of the most important coating strategies applied for glass, quartz, polymers and metals microchannel reactor, analyzing the advantages and drawbacks of every procedure. If a low-cost and massive production of coated microreactors is desired, post-coating methods (such as wash-coating, sol-gel or capillary force ones) will be preferred faced to other methods less economics, as sputtering, PVD or spray coating.

### Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Declaration of Competing Interest

The authors report no declarations of interest.

### Acknowledgments

Financial support for this work has been obtained from the Spanish Ministerio de Ciencia, Innovación y Universidades co-financed by FEDER funds from the European Union (RTI2018-096294-B-C33 and ENE2017-82451-C3-3-R).

O.H. Laguna thanks the financial support provided by the University of Jaén through the “Acción 6 del Plan de Apoyo a la Investigación de la Universidad de Jaén (2017-2019)”.

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