Monoliths: A Review of the Basics, Preparation Methods and Their Relevance to Oxidation

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Abstract: Considerable research has been conducted on monolithic catalysts for various applications. Strategies toward coating monoliths are of equal interest and importance. In this paper, the preparation of monoliths and monolithic catalysts have been summarized. More specifically, a brief explanation for the manufacturing of ceramic and metallic monoliths has been provided. Also, different methods for coating \( \gamma \)-alumina, as a secondary support, are included. Techniques used to deposit metal-based species, zeolites and carbon onto monoliths are discussed. Furthermore, monoliths extruded with metal oxides, zeolites and carbon are described. The main foci are on the reasoning and understanding behind the preparation of monolithic catalysts. Ideas and concerns are also contributed to encourage better approaches when designing these catalysts. More importantly, the relevance of monolithic structures to reactions, such as the selective oxidation of alkanes, catalytic combustion for power generation and the preferential oxidation of carbon monoxide, has been described.

Keywords: monolith; coated monoliths; monolithic catalysts; homogeneous reactions; oxidative dehydrogenation; preferential oxidation

1. Introduction

In the past 30 years or so, there has been a gradual increase in the use of monoliths as catalyst supports. During this period, monoliths have mostly been used in environmental applications where high gas throughput and low pressure drop are required [1]. Some of the applications in which these benefits have proven useful include exhaust gas treatment [2,3], selective catalytic reduction (SCR) of NO\(_x\) [4], destruction of volatile organic compounds (VOCs) [5] and catalytic combustion [6]. More recently, there has been renewed interest in the use of monoliths for reactions where energy efficiency and cost reduction are required. In particular, these include catalytic combustion for power generation, the selective oxidation of alkanes and preferential oxidation (PrOx) of CO. In order for researchers to be able to improve on these reactions, an overall knowledge and understanding of the preparation of monolithic catalysts would be required.

There are several key reviews on the preparation of monoliths [1,7–9]. In addition, there are some informative reviews on coating monolith structures [10–12]. Also crucial to the preparation of monolithic catalysts can be transport phenomena [13]. However, a summary of the existing literature on the basics, reasoning and understanding behind the preparation techniques of monoliths and coating techniques may better prepare researchers for the application of monoliths, especially as applied to oxidation catalysis.

In this paper, we provide an overview of the literature, elaborating on the basic properties and relevance of monolithic structures. For the preparation of monoliths, we focus on ceramic and metallic structures, since these are most popular in the older and more recent literature. We then address
the coating of monoliths, more especially with alumina as a secondary support. Also, we discuss the coating of metals, zeolites and carbon onto monoliths. In some cases, common issues with the coating techniques are highlighted and solutions or alternatives are provided. Furthermore, extruded monoliths containing zeolites and carbon are discussed. Finally, we provide an outline of the use of monolithic catalysts in the selective oxidation of alkanes, catalytic combustion for power generation and preferential oxidation of CO (CO-PrOx).

2. Monoliths

2.1. Monolith Basics

Monolithic structures pose an attractive alternative to conventionally prepared catalyst pellets or powders due to a number of superior properties. Monoliths can offer better mass transfer, a low pressure drop, thermal stability and good mechanical strength over conventional catalyst pellets or powders [7,12,14]. Monoliths are essentially uniform blocks, consisting of parallel channels that can be extruded into different shapes and sizes. These structured supports are primarily sold in ceramic or metallic forms [14]. Monolithic structures can also be extruded from other materials, such as zeolites (Section 2.3.3) or carbon (Section 2.3.4). Major manufacturers of ceramic and metallic monoliths are Corning and Johnson Matthey, amongst others [14].

Monoliths can be manufactured into various shapes or sizes (see Figure 1). The shapes of monoliths can be circular, square, triangular or hexagonal, amongst others [7]. The geometry of the channels can influence the mass and heat transfer properties, and hence the catalytic performance [15]. For example, in catalytic combustors, circular and square channels are reported to have better mass and heat transfer characteristics, as well as light-off and gas heating rates, than triangular channels [16]. Herein, it was suggested by the authors that triangular channels show poorer characteristics due to their acute corners (without a washcoat). For a catalytic converter, hexagonal channels are preferred due to a better thermal mass efficiency than square channels [17]. In general, it has been suggested that there is no ideal geometry and, simply, it may just be problem/reaction dependent [7].

![Monoliths with different cell densities/sizes](image)

**Figure 1.** Monoliths with different cell densities/sizes: (a) side view; (b) top view.

The geometric model of a monolith can be represented by the following Equations (1)–(4) [18,19]. The physical dimensions of a monolith are usually expressed by cell density. The cell density (cpsi = cells per square inch) is determined by the width of the channels, as shown by Equation (1) [5,20]. Cell density can play a role in catalytic applications of monolith structures. Thus, in the selective hydrogenation of phenylacetylene, for example, it has been shown that a higher cell density can have a beneficial effect on the catalytic performance [21].

\[
\text{Cell density} = \frac{1}{l^2} \quad (1)
\]
Reactants passing through a single monolith channel and exiting as products. Monolith wall = lack, washcoat/active layer). The open frontal area, essentially the void fraction [19], can be calculated using

\[
\text{Open Frontal Area} = (l - t_w)^2 / l^2
\]

(2)

\[
\text{Geometric Surface Area} = 4(l - t_w) / l^2
\]

(3)

Hydraulic diameter = \(4(\text{Open Frontal Area}) / (\text{Geometric surface area})\) (4)

where \(l = \text{width/length of channel in inches and } t_w = \text{thickness of the wall in inches}\)

Also, geometric surface area, shown in Equation (3), can be an important factor for catalytic performance. Using a monolith with a higher geometric surface area can lead to a higher conversion, however, the trade-off would be a higher pressure drop [5]. The hydraulic diameter, Equation (4), can be used to determine the effect on the hydrodynamics from the size of channels [19]. In particular, the hydraulic diameter is dependent on the width of the channels and the thickness of the walls (including washcoat/active layer). The open frontal area, essentially the void fraction [19], can be calculated using Equation (4). Monolithic catalysts have a large open frontal area compared to catalyst pellets, therefore, there is little resistance to flow through the channels [5,20]. This allows for high space velocities to be reached. High space velocities can be used to fine tune the selectivities and yields to products, in a shorter time.

In general, the transport phenomena for monolithic systems is crucial to most applications. The literature on the influence of fluid dynamics [22–25], and mass and heat transfer [13,16,26–34], as summarized by some key papers, can be quite extensive. It is important to keep these contributions in perspective when designing monolithic catalysts.

The preparation of a monolithic catalyst usually entails choosing the type of structural material (ceramic or metallic), applying a secondary support and finally coating the active phase/layer. Ceramic and metallic monoliths usually have low BET surface areas, therefore, a secondary support is required. The secondary support is typically coated onto the monolith prior to the active phase, to improve the dispersion and adherence of the active coating. The reactants pass through the parallel channels of the monolith, interact with the active phase that is itself on the secondary support, and exit as products (Figure 2). The exception to the washcoating technique is the preparation of an extruded monolithic catalyst, which consists of a high surface area material and active phase incorporated into the monolith structure.

\[\text{Monolith channel}\]

Reactants

Products

\[\text{Figure 2. Reactants passing through a single monolith channel and exiting as products. Monolith wall = lack, secondary support = grey, and catalyst layer = green.}\]

2.2. Preparation of Monoliths

Monoliths are commonly manufactured as ceramic or metallic structures. Ceramic and metallic monoliths differ greatly in physical and chemical properties, with respective advantages and disadvantages. Ceramic monoliths have advantages over metallic monoliths with properties such as better porosity, hence good coating adherence, and thermal stability, whilst metallic monoliths offer advantages with respect to better heat transfer, pressure drop, mechanical stability, wall thickness and overall volume [14]. Ceramic monoliths have good thermal stability due to a low thermal expansion coefficient, however, can still crack with significant changes in temperature [5,12,35]. Metallic monoliths, though, are becoming popular despite the difficulty of catalyst adherence. Ceramic and metallic structures are most popular in monolith research literature currently, therefore, the following sections discuss the preparation of these structures, along with their relevance to some applications.
2.2.1. Ceramic Monoliths

The industrial application of ceramic monoliths began in 1966 with the clean-up of nitric acid tail gases [7,36]. Soon after, ceramic monoliths were implemented for exhaust gas treatment in internal combustion engines [37] and later, as catalytic converters [38,39]. Ceramic monoliths are usually distinguished by two types, namely cordierite (honeycomb) and ceramic foams.

Ceramic cordierite monoliths are obtained via extrusion or corrugation with a variety of starting materials. The final result, for example, is a cordierite (2MgO·2Al₂O₃·5SiO₂) structure with a BET surface area of less than 1 m²/g [40]. The extrusion process is conducted with specially designed extruders and generally involves five steps [9,12,14,35]. The steps include, drying the solid oxides, adding the required plasticizers or other organic/inorganic additives, using the appropriate dies to extrude a particular shape needed, drying to obtain a uniform structure without cracking and finally firing the structure [1,9,41]. In some cases, firing can result in cracking of the structure, therefore, more controlled conditions would be required [42,43]. To solve this problem, the structure can be immersed in a surfactant solution prior to firing [42]. Alternatively, the ceramic can be fiber-reinforced [44,45]. The corrugation method for preparing ceramic monoliths involves adding inorganic oxides or salts to a mixture of starting materials, then the additives, binders and plasticizers, fibers for reinforcement, rolling and stacking and lastly calcining at the relevant temperature [7]. A more detailed explanation of the processes involved in extrudation and corrugation of ceramic monoliths has been reported by Avila et al. [1]. Additional preparative methods for ceramic monoliths are available in the patent literature [42,45-49], as well as in reviews on cordierite monolithic catalysts by De Luca and Campbell [50] and Lachman et al. [51-54]. Also, detailed rheological characterization of pastes for extruding ceramic monoliths have been reported by Forzatti et al. [9].

Ceramic foams were first used to filter molten metals [55] and hot gases [56]. They are preferred for reactions where a low pressure drop is required [57]. The porosity of the structure favours turbulent flow, which enhances mass transfer when compared to cordierite structures [58]. Also, convection of heat through the pores results in good radial mixing and hence improved heat transfer [59]. Ceramic foam monoliths can be prepared by immersing open cell organic foams made of, for example, polyurethane, in a slurry (alumina, silica, etc.), after which the excess slurry is removed and the cellular foam fired to remove undesired constituents [60,61]. Various shapes can be prepared due to the relatively easy preparation method. To improve the mechanical strength of ceramic foams, a fused crystallized glass coating can be used [62] or the viscosity of the slurry can be adjusted [63]. Figure 3 shows examples of ceramic foams.

Figure 3. Examples of ceramic foams [64].

2.2.2. Metallic Monoliths

Metallic monoliths were used initially for catalytic combustion, due a lower pressure drop and higher cell density compared to a ceramic structure [65,66]. Metallic monoliths are obtained through
corrugation, and usually contain iron, chromium, aluminium and rare metals [5,14,67]. The corrugated sheets can be prepared in several ways and are then cut to obtain the required shapes, for example parallel or spiral type structures [68]. A more detailed discussion of the preparation of metallic monoliths has been provided by Avila et al. [1].

Some of the material used to prepare metallic structures include nickel [69,70], FeCr Alloy containing aluminium [71], AISI (American Iron and Steel Institute) 304 Austenitic stainless steel [72–74] and aluminium foams [75,76]. Iron and aluminium are added to allow the monoliths to operate at relatively high temperatures, whilst other metals are included to aid in the adherence of the active catalyst layer onto the metallic monolith [7,77]. The addition of these metals to prepare metallic structures, though, can influence the catalytic performance. To prevent this, an enamel coating has been suggested, however, this seems to work only in some applications [78]. For example, in CO-PrOx, it has been shown to not work effectively, as iron and chromium still diffused through the enamel [79]. There were several types of layered metallic monoliths developed between 1968 and 1991, with the major innovator being EMITEC (Lohmar, Germany) [1,80–82]. Figure 4 shows examples of metallic monoliths.

![Figure 4. Examples of metallic monoliths [83].](image)

Preparation of ceramic and metallic monolith structures can be an intensive process and a skilled art, requiring specialized equipment. Most researchers therefore purchase these monolith structures, as opposed to designing them from the starting materials. The unavoidable task, however, is that of coating a secondary support and the active layer.

2.3. Preparation of Monolithic Catalysts

Preparing a monolithic catalyst usually requires that the active species be deposited onto a washcoated monolith, prior to catalytic testing. The washcoat is essentially a secondary support that can provide for better adherence and improved dispersion of the active species. The secondary support layer is usually a high surface area oxide, for example, γ-alumina. Due to issues with adherence, the methods to coat γ-alumina on metallic monoliths differ from those used for ceramic monoliths. Typical methods used for depositing γ-alumina onto ceramic structures are colloidal coating, sol-gel and slurry coating. For metallic structures, the coating techniques have to be modified to achieve good adherence. These methods will be discussed in the subsequent sections.

For monolithic catalysts, coating the active layer is just as important as coating the secondary support. The techniques used for coating the active layer depend on the nature of the active species. In most industrial applications, metal oxides are supported on monoliths. Although this can be done simply by using a wet impregnation or precipitation technique, problems with homogeneity can arise. In addition to metal oxides supported on monoliths, there is also interest in supporting zeolites and carbon onto monoliths for environmental applications. The coating techniques for supporting zeolites
and carbon, respectively, onto monoliths are not as straightforward as those for a metal-based active layer. However, the strategy toward good adherence, homogeneity and dispersion of the coating is the same, independent of the nature of the active species. In the following sections, common methods and the respective issues when depositing metal oxides, zeolites and carbon onto monoliths will be discussed. Also, extruded zeolite and carbon monoliths will be briefly discussed.

2.3.1. Coating γ-Alumina as a Secondary Support

γ-Alumina is a widely used catalyst support, predominantly in the petrochemical and automobile industries, due to a combination of Lewis acidity and basicity, good porosity and high surface area [84–86]. γ-Alumina can be formed by the heat treatment of boehmite above 450 °C [86,87]. The formation of the γ-alumina phase from aluminium hydroxides or oxohydroxides can be strongly dependent on temperature. The typical temperature range is between 450 and 700 °C [86,87]. Paglia et al. have shown that a γ′-alumina phase forms at temperatures above 750 °C from boehmite [87].

γ-Alumina has a spinel structure similar to that of AB₂X₄ (MgAl₂O₄) [88], where in gamma-alumina magnesium is replaced by aluminium in the ideal MgAl₂O₄ structure [86,89]. The defect in the structure, due to the removal of a divalent cation and the presence of trivalent aluminium cations, results in the formation of a cubic close packing of the oxygen lattice, as well as octahedrally and tetrahedrally situated aluminium atoms in the spinel structure [86,89]. The macrostructure and acid/base properties of the surface of γ-alumina are discussed in detail by Trueba and Trasatti [86]. The properties exhibited by γ-alumina make it an attractive secondary support for monoliths. However, it is imperative that the effects of gamma-alumina coating in a particular catalytic system be studied prior to testing of the active catalyst.

Coating a secondary support, for example γ-alumina, onto monoliths usually involves repeated dipping of the monolith in a solution or slurry mixture, allowing it to soak for a few minutes, removing excess liquid from the channels with compressed air, followed by calcination. This allows for the formation of the required secondary support layer, upon each repetitive coating cycle. Adaptations to the coating method can be easily made according to preference, such as continued dipping, then drying and finally calcining or constant rotation of the monolith upon calcination. Repeated dipping, rotating, drying and final calcination may result in a more uniform coating across the channels [12]. The amount of coat layer on the monolith is usually expressed in weight percent and the loading can vary according to preference or application. Successful coating of monoliths with γ-alumina of up to 15 wt % has been reported [90], as has coating of up to 20 wt % using the sol-gel approach [91].

The open frontal area, geometric surface area and hydraulic diameter will be affected by the coating thickness. A thicker coating may result in a decrease in the open frontal area, which could prove limiting to higher space velocities or even diffusion of larger reactant molecules through the monolith channels. Indeed, there are several other important factors that need to be taken into consideration when applying a washcoat to a monolith structure. These factors may include pH, slurry concentration, appropriate calcination, drying or specific techniques for a required application. For example, adjusting the pH of the coating solution/slurry can affect the rheology [92] and hence coating homogeneity. The slurry concentration (viscosity, particle size, solid content) can also affect the coating adherence and homogeneity, as well as the reproducibility of the coating method [93–95]. In addition, the procedure of drying and calcining to coat the monolith should not be rushed, as this can affect the coat adherence and homogeneity [12].

Using different methods to washcoat ceramic monoliths can result in different adherence properties, as shown in Table 1. The common methods used to coat ceramic structures with γ-alumina are colloidal coating, sol-gel and slurry coating. Methods to deposit γ-alumina onto metallic structures are different due to the difference in the porosity of the surface. The subsequent sections summarize the methods used to deposit γ-alumina onto the surface of ceramic monoliths and metallic monoliths (See the Section of “Coating Alumina on a Metallic Surface”).
Table 1. Differences between pore filling and slurry coating [12,96].

<table>
<thead>
<tr>
<th>Pore Filling</th>
<th>Slurry Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>sol-gel/colloidal suspensions</td>
<td>slurry</td>
</tr>
<tr>
<td>little decrease in open frontal area</td>
<td>larger decrease in open frontal area</td>
</tr>
<tr>
<td>limitation of macropore volume</td>
<td>high loading of washcoat possible</td>
</tr>
<tr>
<td>better suited for highly active catalyst</td>
<td>suitable even for catalyst with low activity</td>
</tr>
</tbody>
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Colloidal Coating

Colloidal coating is a pore filling technique, using nanoparticles. These colloidal particles may be produced via different methods. Beauseigneur et al. report an average particle size between 1 and 100 nm in the colloidal coating of monoliths for exhaust gas treatment [97]. Larsson et al. used boehmite powder with hydrochloric acid to produce the required colloidal solution, followed by calcination producing the gamma-alumina coating onto the monolith [98]. Colloidal alumina can also be prepared from commercial boehmite peptized in acidic solution [99]. The gamma-alumina phase can be produced by calcination of the peptized boehmite between 500 and 700 °C [92]. Colloidal alumina is available commercially, and it can be dispersed in a solution containing water. For example, Özdemir et al. have used colloidal alumina dispersed in water to coat monoliths for carbon monoxide oxidation [100]. Barbero et al. have reported successful coating of their metallic monoliths with the use of colloidal alumina as a primer and a stabilizer [101]. Perhaps, for convenience, purchasing colloidal alumina may be the better option, unless researchers intend to investigate new methods of colloidal coating.

Sol-Gel

A sol refers to the dispersed form of a colloidal solution, and gelating occurs when an interlinked network is formed between colloidal particles, therefore, sol-gel is a dispersed form of the interlinked particles [102]. The sol-gel method used for coating monoliths involves preparing a sol, then coating the monolith and lastly calcining, which results in a γ-alumina layer. The outcome is better pore filling of the monolith as compared to conventional colloidal coating [12]. Sols can be prepared via a hydrolytic route or non-hydrolytic route as shown in Equations (5) and (6) [67].

\[
\begin{align*}
M(OR)_{n} + nH_{2}O & \rightarrow M(OH)_{n} + nROH \quad (5) \\
-M-OH + HO-M' & \rightarrow -M-O-M' + H_{2}O \quad (6)
\end{align*}
\]

where M = metal, for example aluminium.

Equation (5) shows the hydrolysis reaction of the metal alkoxide using a suitable acid or base and water [67]. During the sol preparation with heat treatment and time, condensation occurs as shown in Equation (6) [103]. A more detailed description of the sol-gel process is provided by Schmidt [103]. Furthermore, Xiaoding et al. reported a study of sol-gel coating of monoliths via three types of aluminium sobs, namely pseudoboehmite with urea and nitric acid, hydrolysis of aluminium chloride and aluminium powder, and hydrolysis of tri-sec-butoxide aluminium [10]. It was concluded that sobs prepared via pseudoboehmite with urea and nitric acid and hydrolysis of tri-sec-butoxide are most suitable for sol-gel alumina coating of monoliths [10]. A typical sol-gel method of coating involves dipping the monolith in a sol from pseudoboehmite, urea and 0.3 M nitric acid in a weight ratio of 2:1:5, followed by emptying the channels, drying and finally calcination [104]. Sol-gel coating may be advantageous over conventional colloidal coating of monoliths, due to a strong adherence to the monolith, as the alumina layer forms on the surface of the channels.
Slurry Coating

For slurry coating, a monolith, an \( \gamma \)-alumina suspension is prepared with larger particles, preferably between 2 and 5 \( \mu \text{m} \), compared to the pore filling technique [96]. The general procedure involves the use of an acid to disperse alumina, after which the monolith is dipped in the slurry and excess liquid is removed by blowing compressed air through the channels, followed by drying and calcination or direct calcination [94,105]. Wet milling of the \( \gamma \)-alumina to attain a required particle size is very important, as factors such as pH and viscosity play a key role in adhesion to the monolith surface [105]. The particles inside a typical stirred mill are highly influenced by stress energy, number of stress events and specific energy [106]. Milling can be a tedious process to attain the required particle size; however, \( \gamma \)-alumina is available commercially with an average particle size less than 5 \( \mu \text{m} \). Nitric acid is suggested to be a most effective acid for slurry coating, as it helps to stabilize the slurry and allows for better alumina uptake [107]. The percentage of solids in the slurry also plays an important role in the efficacy and homogeneity of the coating [94]. Important to note is that with this technique, monoliths need to be coated in batches, since continued coating may result in an increase in the viscosity of the slurry mixture. This increase in viscosity may seriously impact the homogeneity and reproducibility of the coating. Also, upon repeated coating, the slurry will become more viscous than the initial concentration, until a point is reached where each coat adds excessive weight on the monolith, coherently affecting homogeneity. Capillary forces allow for water to be drawn into the pores of the monolith structure which creates competition for adherence of the slurry [108]. An intermediate pre-wetting step, discussed by Mogalicherla and Kunzru, allows for a high washcoat loading to be achieved [108]. Agrafiotis and Tsetsekou have reported an optimum slurry concentration of 45 wt % solids and viscosity between 50 and 150 mPa s [94]. In comparison, Villegas et al. reported homogeneous gamma-alumina coating with 25 wt % solids [90].

Dispersible powders of boehmite or aluminium hydroxide can be used to produce \( \gamma \)-alumina on the monolith surface after calcination [90,96]. It was reported, however, that an average particle size of alumina of 3 \( \mu \text{m} \) allowed for a higher loading of alumina and good adhesion properties, as compared to boehmite type powders [90]. Slurry coating may, therefore, be ideal for a high weight percent coating and the particle size of the alumina being coated may be controlled. Slurry coating can offer fewer coating repetitions and good adherence of \( \gamma \)-alumina. Considering advantages such as these, slurry coating may be more practical and less time consuming than the other coating approaches mentioned.

Characterization of the secondary support coating is usually performed by SEM, which may be used to show the coating inside the channels of the monolith as compared to a bare monolith. This characterization technique can further be used to assess the homogeneity of the coating and also aid in measuring the coating thickness. Figure 5 shows a sectioned ceramic monolith prior and after coating with 10 wt % \( \gamma \)-alumina, by the method of slurry coating. After coating of the secondary support, a layer is obtained within the monolith channels, which may provide for better interaction with the active layer as compared to the bare monolith.

Coating Alumina on a Metallic Surface

Metallic monoliths have a low BET surface area, hence a washcoat of secondary support is required. The main problem associated with coating alumina on metallic monoliths is the adhesion of the layer on the surface. Using a higher concentration of aluminium in the preparation of the metallic structure may allow for better adhesion [77,109], although controlling the adhesion quality through coating techniques is possible.
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Successes in coating methods, such as oxidation of bulk aluminium [110], slurry coating [111], chemical vapour deposition [112] and anodization of aluminium [113,114], have been reported. Slurry coating may be simpler and cost effective. A combination of sol-gel and slurry coating has also proven effective for coating alumina on metallic surfaces [111,115].

The preparation procedure for coating can significantly influence the activity of the catalysts as shown by Zwinkels et al., when preparing metallic monoliths for combustion catalysis [116]. Similarly, the preparation procedure, coating thickness and adhesion of the alumina layer play a significant role for monoliths.

2.3.2. Depositing Metals onto Monoliths

Monoliths coated with a metal oxide-based active layer are used for a number of reactions. More specifically for this review, they can be used for catalytic combustion, the oxidation of alkanes and preferential oxidation of CO. The general procedure for coating a metal oxide-based active layer

Figure 5. SEM images of channels of monolith: (a) uncoated; (b) coated with 10 wt % γ-alumina.
onto the secondary support involves dipping of the coated monolith in the solution or mixture, blowing out excess liquid from the channels, drying and calcining at the required temperature. The two common methods to employ this technique are wet impregnation and deposition-precipitation.

Coating monoliths by wet impregnation usually involves preparing a solution containing the metal which can be drawn up the channels through capillary forces. Impregnation seems to be popular for patented monolithic processes [117–120], possibly due to the ease of using the wet impregnation technique and that it can be used irrespective of the material make-up of the monolith. For example, Xiaodong et al. showed that an iron/copper active layer can be coated onto silica monoliths from mixed solutions of iron nitrate and copper nitrate [121]. Also, Thimmaraju et al. successfully coated molybdenum(VI) onto ceramic monoliths by impregnation [122]. Similarly, the active layer can be coated onto metallic surfaces [77].

However, impregnation has been suggested, in some instances, to result in a non-uniform distribution of the active metal on the surface [123]. Microwave heating or freeze drying has been suggested to resolve this issue [123]. Alternatively, optimizing the wetting and drying steps could lead to a more uniform distribution of the active layer [124].

Deposition-precipitation is also frequently used to deposit the active layer. Applications of monoliths so prepared include biomass gasification [125], methane combustion [126], oxidation [127,128] and selective catalytic reduction [129]. The technique usually involves precipitation of a metal salt with a base [130]. The most common approach to deposition-precipitation coating involves the use of urea as the precipitating agent [127]. The metal salt and precipitating agent are in the liquid phase; the monolith can then be dipped into this solution and calcined. During calcination, the urea decomposes, allowing for an increase in pH and hence precipitation of the required active phase [12,127]. However, in comparison to impregnation, deposition-precipitation can present more difficulties in attaining a homogeneous layer. To resolve this issue, Barrio et al. propose using redox deposition-precipitation [128].

Other coating techniques include sol-gel coating [131] and solution-combustion [132]. In an example of the sol-gel technique, lanthanum nitrate and nickel nitrate solutions were added dropwise to a peptized boehmite sol, after which the pH was adjusted, and a binder and plasticizer added [131]. After the sol had formed, the monolith was dip-coated, dried and calcined to prepare the active layer. The concern with this coating technique is the possibility of losing some of the nickel/lanthanum to the pores within the structure, and also that the alumina/binder can form over the active metal phase. In solution-combustion, alumina can be grown onto the monolith by dip-coating (with rapid heating) using a solution containing aluminium nitrate and oxyldydihydrazide (ODH) [132]. Similarly, by dip-coating the monolith in a solution containing the active metal and ODH, the active layer can be formed over the surface/alumina.

2.3.3. Zeolite-Based Monoliths

Zeolites are commonly used in petroleum-based catalytic applications, for example, hydrocracking and isomerization [133]. Zeolite materials are advantageous due to their acidic nature and shape-selective behavior [134]. However, as fine powders or pellets in catalytic reactions, zeolites can be subjected to high pressure drops and also attrition in reactors [135]. Monoliths can serve as excellent supports for zeolites due to their lower pressure drop and better mechanical stability [136]. Zeolites can be extruded into a monolith structure or coated onto ceramic/metallic structures. Coating zeolites, as opposed to extruding, can be a simpler and less time consuming process. It is important to distinguish between extruding and coating zeolites onto monoliths to allow the choice of the most appropriate approach. The subsequent sections discuss the preparation of these structures.

Coating Zeolites onto Monoliths

Zeolites coated onto ceramic monoliths have mainly been used in environmental applications as an adsorbent [137,138] and for the selective catalytic reduction (SCR) of NOx [139,140]. Zeolites are
typically coated onto monolith surfaces via slurry coating or in situ synthesis [141]. Monoliths are most often slurry coated with zeolites due to the ease of applying a washcoat. In addition, coating a ready-made zeolite results in a shorter diffusional distance for the reactants, which can lead to a better catalytic performance [142]. Slurry coating involves dip-coating the monolith in a mixture of zeolite crystals together with a solvent, blowing out the excess liquid, drying and finally, calcining [143].

The most effective solvent for coating ZSM-5 onto cordierite structures is reported to be water [144]. The particle size of zeolites, as well as slurry concentration, can also influence the adherence [142,145]. To improve the adherence of the washcoat, a binder, for example silica, can be added [146,147]. Furthermore, the addition of silica as a binder can lead to improved activity and selectivity, when tested for NO\textsubscript{x} reduction [148]. On the other hand, it is suggested that adding a binder could result in a larger diffusional distance to the active site, thus decreasing the catalytic activity [135,149]. Also, a binder such as Al(NO\textsubscript{3})\textsubscript{3}, when used for a PtCo-ZSM-5 coating onto monolith, can interact with cobalt and form cobalt aluminate species that can decrease the catalytic activity [150]. In this instance, a binderless approach to coating zeolites may be better suited.

Buciuman and Kraushaar-Czarnetzki have demonstrated that it is possible to coat ceramic foams with a uniform layer of HZSM-5 without a binder [151]. Similarly, Landi et al. showed that it is possible to dip-coat La-doped Cu-ZSM-5 onto a cordierite structure without a binder [152]. Additionally, Zamaro and Miró have reported a washcoating-hydrothermal combination technique, which when used to coat a zeolite onto a cordierite monolith, results in an improved adherence and superior physicochemical properties [153].

The technique of growing zeolites onto monoliths was developed due to the need for a more robust zeolite layer [154]. In situ coating involves nucleation and growth of zeolites on the surface of monolith channels [155]. This results in a chemical interaction of the zeolite layer with the surface of the monolith, leading to a superior mechanical strength over slurry coating [156]. In situ coating, though, can be more complex than slurry coating. The in situ synthesis of zeolites can be performed on ceramic [157] and metallic structures [158–160]. In situ growth of zeolites onto monolith structures can be sub-divided into direct hydrothermal synthesis or direct synthesis with seeding (secondary growth) [161,162]. In the seeded growth method, colloidal zeolite seeds are prepared and dip-coated over a monolith surface [161,163]. Alternatively, the support can be pre-coated with silica or a template (tetrapropylammonium bromide) [164]. After seeding, the structures are hydrothermally treated in a precursor zeolite solution, rinsed, sonicated and dried [163,165]. In the unseeded method, crystallization of the zeolite occurs over the monolith surface during hydrothermal treatment. In a typical preparation, for example, the monolith is placed vertically in a mixture containing a silicon source, aluminium source and a base, and thereafter heat treated in an autoclave, rinsed, sonicated and dried [166].

In both the seeded and unseeded methods, the formation of the gel from the precursor zeolite solution is crucial to the coating. For example, the Si/Al ratio in the precursor gel can affect the morphology, crystallinity and orientation on the surface of the channels [136,163]. In addition, the water content in the precursor zeolite solution can affect the nucleation and morphology of the zeolite crystals [167]. Crystallization time and temperature can also affect zeolite growth and performance for cordierite monoliths [166].

**Extruding Zeolites into Monoliths**

Zeolites extruded into monolith structures were predominantly used for SCR of NO\textsubscript{x} [168,169]. The preparation of monoliths extruded with zeolites usually involves mixing the zeolite powder with a binder (inorganic/organic) and water, followed by extruding with dies, then drying and finally firing [170]. More details of this preparation process have been provided by Li et al. [170] and Aranzabal et al. [171]. In the preparation of these extruded monoliths, the added binder can be problematic, as it can block the pores of the zeolite [172–174]. Pulsed current processing has been
suggested to overcome this problem by making use of a high heating rate and compressive pressure, which can yield a porous structure with good mechanical strength (without a binder) [175–177].

Monoliths extruded with zeolites can be superior to structures coated with zeolites, due to their lesser susceptibility to abrasion [154]. Even so, there is limited literature on monoliths extruded with zeolites, although there has been renewed interest in the extrusion of monoliths with zeolites, particularly in the field of pressure-swing adsorption [178]. Pressure-swing adsorption offers an attractive alternative to the usual and expensive cryogenic separation of gases, for example, propane/propylene [179]. The conventional pressure-swing adsorption process, though, can be limited by particle attrition and large pressure drops; where in this case a monolith has proven a feasible alternative to the conventional process [180].

2.3.4. Carbon-Based Monoliths

Carbon is typically used as a support in heterogeneous catalysis, due to its high surface area and stability in acidic or basic media [181]. Porous carbon materials such as activated carbon and carbon nanofibers have become even more popular [182]. These materials have often been used as adsorbents, but recently also as gas storage media [183–185].

In general, carbon materials are supported on or extruded into monolithic structures to improve their adsorption capacity and reduce the pressure drop in the reaction [186]. Although carbon coated structures can have better mechanical strength, extruded monoliths with good mechanical strength can be prepared. The following sections, therefore, outline the relevance of these carbon materials coated onto monoliths and briefly summarize possible preparation methods.

Coating Carbon Materials onto Monoliths

Carbon coated monoliths are typically used in environmental applications, for example, selective catalytic reduction systems [187,188], hydrocarbon adsorption [189] and catalytic combustion [190,191]. The common technique used to coat carbon onto monoliths is dip-coating [11]. This can be achieved by dipping a monolith into a liquid polymer that has been crosslinked and carbonized, followed by curing to the required temperature [192]. Detailed studies on coating carbon onto monoliths have been published [192–196].

Carbon nanofibers can offer a reasonable alternative to common support materials, due to their high surface area and high macro-porosity [197]. However, in slurry phase operation, carbon nanofibers in the powder form can agglomerate and be difficult to filter [198]. Also, in a fixed-bed reactor, carbon nanofibers can be exposed to a high pressure drop [198]. To resolve these issues, carbon nanofibers are supported onto monoliths. They can be grown onto monoliths by heating methane or ethylene together with hydrogen, in a quartz reactor, over a nickel coated monolith structure [199,200]. From these studies, it is important to note that methane was determined to be the preferred carbon source, since ethylene accelerated nanofiber growth, resulting in damage to the monolith structure. Also, a larger nickel particle size resulted in nanofiber growth outside of the monolith. To enable a better growth rate and uniform distribution of nanofibers, García-Bordeje’ et al. have suggested using a thin γ-alumina washcoating of approximately 0.1 µm [104,201].

Extruding Carbon into Monoliths

Monoliths extruded with carbon have gained interest due to their potential as gas storage media. A carbon monolith can be prepared by mixing a carbon precursor together with a binder and plasticizer, followed by extrusion, drying and finally carbonization [193,202]. However, preparing the carbon monolith, as such, may not be the best approach to obtaining the best possible porosity. It is possible, though, to control the pore structure of carbon, whilst extruding the monolith [203]. The extruded carbon monolith can thus have a meso- and macro-porous structure [204]. This pore structure would allow for the reaction/adsorption of molecules, with better mass transfer and a low pressure drop [205]. To prepare this structure, a porous silica monolith template is impregnated with a
carbon polymer precursor, then carbonized [206–208]. Thereafter, the silica template can be removed with acid treatment, leaving behind a negative carbon monolith (walls of silica become the pores of the carbon structure) [183]. Other proposed templates include polymeric foams [205,209]. In some instances, these templated structures can crack during preparation. To solve this problem, a carbon source that acts as a self-binding agent can be used, for example, sucrose [210–212] or polyfurfuryl alcohol [213].

2.4. Monolithic Catalysts in Oxidation Catalysis

The industrial application of monolithic catalysts began in 1966 with the clean-up of nitric acid tail gases, using a palladium-coated ceramic structure [7,36]. Monolithic catalysts were later used in car exhausts as three way catalysts for emission control [7]. Since the notable success of monoliths in this regard, monolithic structures have become the standard catalyst support for catalytic converters. Just as popular has been the use of monoliths for environmental applications and catalytic gas-phase reactions. For example, in environmental applications, monolithic structures are mainly used for DeNOx catalysis [214] and catalytic combustion [6]. Catalytic combustion, particularly, has been of greater interest due to its potential to produce energy [215]. In catalytic gas-phase experiments, monolithic catalysts were found to give olefins with good selectivities from the oxidation of alkanes, however, further research showed that this was due to homogeneous-gas phase reactions.

More recently, in oxidation catalysis, monoliths have shown promise in the preferential oxidation of CO. The sections that follow discuss the relevance of monoliths to combustion, oxidation of alkanes and the preferential oxidation of carbon monoxide.

2.4.1. The Oxidation of Alkanes

The conversion of alkanes to more valuable products, such as olefins or synthesis gas, is very relevant to the petrochemical industry. Industrially, olefins are produced via steam cracking of hydrocarbons [216]. The technology used for this process can be energy intensive and expensive to operate [217]. As an alternative, alkanes can be oxidatively-dehydrogenated, typically over transition metal oxides, to yield olefins and oxygenates [218–220]. Interesting has been the potential of monolithic catalysts in this regard.

To produce syngas, methane is converted via steam reforming (endothermic) over a nickel-based catalyst [221]. This process, however, can require a separation unit or a water-gas shift step to adjust the H2/CO ratio for the downstream process [222]. To resolve this, alkanes can be partially oxidized (exothermic) to carbon monoxide and hydrogen over supported catalysts [222]. Importantly, the partial oxidation reaction over monoliths can offer shorter contact times and higher throughput. Thus, there has been significant work carried out on the oxidation of alkanes over monoliths and there seems to now be clarity on the contribution of homogeneous gas-phase reactions, and the heterogeneous catalytic mechanism to these aforementioned reactions. This section summarizes the available literature to highlight the differences.

Initially, Huff and Schmidt showed that ethane can be converted to ethylene, with a 70% selectivity, on ceramic foam monoliths [223]. Coating the monolith with platinum showed the greatest activity (>80%) and selectivity (70%) towards ethylene formation, whilst rhodium facilitated the production of mainly synthesis gas, and palladium induced carbon formation. A similar behavior was reported for the oxidation of propane, butane and iso-butane over platinum coated monoliths [224,225]. The formation of ethylene was suggested to occur via H-abstraction by adsorbed oxygen, forming the alkyl which then finally undergoes β-H-elimination [226]. Alternatively, formation of ethylene can occur through homogeneous gas phase reactions.

Liebmann and Schmidt later suggested that a combination of heterogeneous-homogeneous gas phase reactions are possible for higher alkane to oxygen feed ratios, especially for the partial oxidation of iso-butane over Pt coated monoliths [227]. However, Beretta et al. showed that the oxidation of propane over Pt/γ-Al2O3 on a ceramic support, at temperatures above 500 °C, was probably due
to homogeneous gas phase reactions [228]. The experiments showed that high olefin selectivities are possible for propane/oxygen mixtures above 500 °C using an annular reactor, in the presence and absence of the catalyst, respectively. In an adiabatic reactor, a similar behavior was observed for propane oxidation over a metallic monolith coated with Pt/γ-Al2O3 [229]. Interestingly, the formation of olefins was enhanced in the adiabatic reactor with a Pt/γ-Al2O3 coated monolith, leading the authors to deduce that the Pt-catalyst merely served to ignite gas phase reactions over the surface of the support [229,230]. In addition, the heat generated from the exothermic gas phase reactions is suggested to facilitate the production of olefins [231,232]. Similar to propane oxidation experiments, ethylene can be formed from ethane with high selectivities, via homogeneous gas phase reactions [233–235]. For the oxidation of longer chain alkanes over monolithic catalysts, oxygenates can form along with olefins and dienes [236]. For example, in the oxidation of n-hexane over monoliths, the reaction proceeds by means of a radical type mechanism to predominantly form cyclo-oxygenates, with olefins and dienes in minor quantities [237].

Although olefins are suggested to form over monoliths by a homogeneous gas phase mechanism, synthesis gas on the other hand may form via a catalytic mechanism. Hickman and Schmidt initially proposed that synthesis gas can be formed from methane, over monoliths coated with noble metals, via pyrolysis [238]. To confirm the proposed mechanism, the authors modeled high-temperature reactor simulations of methane oxidation, which showed that CO and H2 are formed as a result of pyrolysis [239]. Furthermore, Fathi et al. and Silberova et al. showed that synthesis gas formed from the oxidation of ethane and propane over Rh/Pt-coated monoliths, however, it did not form during the empty reactor test [240,241]. This led the authors to suggest that syngas could form via a catalytic mechanism in the presence of a monolith coated with a noble metal catalyst.

For the direct oxidation of methane to synthesis gas, Rh-coated monoliths are superior to Pt-coated monoliths [242]. The better performance of the Rh-coated monoliths is attributed to a higher energy barrier for OH formation, ultimately allowing hydrogen gas to desorb more easily from the surface of rhodium as compared to platinum [242,243]. Further work showed that rhodium is more active and robust toward syngas formation compared to other noble metals and transition metals [244]. In addition, Rh-coated monoliths are reported to convert longer hydrocarbons to synthesis gas in high yields (>90%) [245–247].

2.4.2. Catalytic Combustion

Catalytic combustion offers an alternative means for the production of energy (power generation) compared to the previously established gas-phase combustion process, which needs to be operated within flammability limits and can produce undesired NOx gases [215]. In the catalytic combustion approach, methane or natural gas can be converted over a noble metal-based catalyst to drive a gas-turbine for power generation [248–250]. Alternatively, syngas can be converted to power in a more portable/smaller scale. This can be achieved by catalytically stabilized thermal combustion, which is currently being investigated by e.g., the Combustion Research Group at the Paul Scherrer Institute (Villigen, Switzerland) [251–259]. In these studies, the researchers focus on converting fuel/syngas mixtures, via a combination of heterogeneous-homogeneous reactions, over platinum-based catalysts coated onto micro-channels.

Noble metal-based catalysts, though, can be expensive. In methane combustion, noble metal-based catalysts can also be susceptible to poisoning or thermal stress [260]. Even when supported on monolithic structures, noble metal-based catalysts are expensive and would still be exposed to sintering at the high temperatures employed [261].

Perovskite-based catalysts offer a much cheaper alternative to noble metal-based catalysts [262]. It has been shown that perovskite-based catalysts can be deposited onto cordierite monoliths via deposition-precipitation [263]. In addition, it has been reported that LaMnO3 supported on La-γ-Al2O3 coated cordierite is more active and thermally stable, in the catalytic combustion of methane, than the catalyst in powder form [126,264].
Recently, it has been shown that the addition of hydrogen to the methane feed can reduce the ignition temperature of the catalytic combustion [265]. Owing to this, there is now interest in the catalytic combustion of fuel mixtures. In the assisted combustion of methane, Cimino et al. showed that nearly complete conversion of methane occurred over LaMnO$_3$ supported on monoliths, when CO/CH$_4$ mixtures were used [266]. For mixtures consisting of H$_2$/CH$_4$ and C$_3$H$_8$/CH$_4$, the reaction was suggested to proceed via a homogeneous gas-phase mechanism.

The Combustion Research Institute (Naples, Italy) showed, by using simulation experiments performed at high pressures, that the homogeneous gas-phase reactions over the LaMnO$_3$-based monoliths allow for the reaction to overcome mass transport limitations [267]. These researchers also showed, using experimental and mostly numerical studies, that the channels of the monolith coated with LaMnO$_3$ initiate methane activation, then through radial heat transfer, the non-coated channels propagate the homogeneous conversion of methane [268,269]. Furthermore, a kinetic study performed on the catalytic combustion of CH$_4$, H$_2$ and CO over a LaMnO$_3$-coated plate-like structure revealed that the Mars-van Krevelen mechanism could be ascribed to the oxidation of CH$_4$ and CO [270]. In a more recent simulation study, a monolith coated partially with LaMnO$_3$ showed a higher methane conversion than a fully coated material [271]. Finally, in the latest study performed by these researchers, an experimental validation has been described [272]. This work showed that coating the external channels of the monolith, whilst keeping the internal channels uncoated, can activate a homogeneous reaction.

2.4.3. Preferential Oxidation of Carbon Monoxide

In a PEM (proton exchange membrane) fuel cell, carbon monoxide can poison the platinum-based catalyst [273]. To solve this, the CO PrOx reaction is performed to minimize the carbon monoxide content in a typical hydrogen feed that is sent to a PEM fuel cell [274]. Monoliths can offer several benefits to conventionally prepared catalysts for the preferential oxidation of CO. For example, coating the active metal on monoliths for the CO PrOx reaction can result in an enhanced catalytic performance, compared to the catalyst in powder form [275]. In this recent study, the authors showed that supporting Pt and Pd nanoparticles on silica-monoliths led to an improved activity and selectivity for the reaction, possibly due to better mass and heat transfer properties. In addition, monoliths are attractive supports for PrOx reactions due to their low pressure drop, high geometric surface area, large open frontal area and mechanical strength [276].

Different types of catalysts are used for the selective oxidation of CO, the most popular of which include supported noble metals, supported gold and copper-ceria [277]. Noble metals supported on monoliths have shown considerable promise and can even be scaled for relatively small power generation units [278–281]. To minimize poisoning of the anode in a proton exchange membrane fuel cell, PrOx catalysts should selectively oxidize carbon monoxide, exiting from reforming, to a concentration less than 10 ppm [278,279]. Maeda et al. showed that it is possible to selectivity oxidize CO in a synthetic (model) feed to less than 10 ppm using monolithic catalysts [282]. Specifically, the authors showed that a 4 wt % Pt-0.5 wt % Fe/mordenite supported on a ceramic monolith can reduce the concentration of CO to less than 10 ppm at low O$_2$/CO ratios. They also reported a good long-term stability with no significant change to the CO concentration over 500 h. For a realistic stream containing H$_2$O and CO$_2$, Yu et al. obtained CO concentrations between 1 and 10 ppm for a Pt-Co/\(\gamma\)-alumina-monolith catalyst at 140–170 °C [283]. Furthermore, the authors reported catalyst stability even after 100 h on stream. Similarly, a ceramic monolith coated with Pt-CuFe can achieve low CO concentrations (<10 ppm) for a variety of feed compositions, inlet temperatures and turn down ratios [280].

Supported gold catalysts are typically used for their good catalytic performance at lower temperatures, for the oxidation of CO [284]. Similar to powder catalysts, Au/CeO$_2$ supported on a ceramic monolith showed a better catalytic performance than a monolith coated with Au/Al$_2$O$_3$ [285]. Martinez-Tejada et al. showed that this behavior can similarly be seen on metallic monoliths [72].
Although the enhanced performance can be attributed to the redox properties of ceria [286], Martinez-Tejada et al. suggest that the leaching of metals from the support may also improve the activity of gold supported on metallic monoliths [72,287]. Furthermore, the authors showed, using glow charge display optical emission spectroscopy (GD-OES), that there are higher levels of metals from the metallic structure after CO oxidation [288,289]. Interesting to note from this work is that GD-OES revealed metals from the metallic structure present prior to catalytic testing. This indicates that the active coating was probably not homogeneous, thereby leaving some exposed metallic surface/s. The authors also reported that the non-coated metallic monolith showed some activity toward CO oxidation [287]. In a later paper the authors showed, using SEM images, that cracks could be seen between the active layer after catalytic testing [290]. One can therefore not rule out the possibility of exposed metallic sites, from a non-homogeneous coat or cracks, which could contribute to the activity.

It has been shown that CuO-CeO$_2$ catalysts can prove more active and selective at comparable temperatures to supported gold and noble metals on a support [277,284]. Due to their good catalytic performance for CO oxidation, they are also being incorporated onto monolith surfaces. Thus, Snytnikov et al. showed that Cu/CeO$_{2-x}$ coated on 26 microchannel reactors can be used for a 100 W (electrical) fuel cell system [291]. In the study, the catalyst was reported to reduce the CO in reformate gas to below 10 ppm, at 230–240 °C.

The CuO-CeO$_2$ can be supported onto a cordierite surface using wet impregnation followed by washcoating, but in the presence of a feed containing H$_2$O/CO$_2$, the catalyst deactivates rapidly [274]. On the other hand, a modified dip-coating procedure for copper-ceria on a cordierite monolith can lead to a better adhesion and catalytic performance than the powder catalyst [292]. Modification of the authors’ previous method for coating [293] led to a larger fraction of smaller ceria particles, which probably improved the washcoat adherence. The catalytic performance in this work, however, was assessed in the absence of H$_2$O/CO$_2$. In comparison, sol-pyrolysis of CuO-CeO$_2$/Al$_2$O$_3$ on a metallic monolith resulted in a good catalyst adherence, as well as a complete conversion of CO at 165 °C in the presence of H$_2$O and CO$_2$ [294]. In addition, coating monoliths by solution-combustion synthesis has given materials with good catalytic performance for the PrOx reaction in the presence of H$_2$O and CO$_2$ [295,296]. Other properties that should be optimized to enhance the performance of copper/ceria monolithic catalysts include the coating thickness [297] and cell density of the structure [293].

3. Conclusions and Perspective

A considerable amount of information on the preparation of monolithic catalysts has been summarized. Applying a secondary support, for example γ-alumina, is an important pre-requisite for an improved catalyst adherence. The simplest technique to achieve strong adherence of γ-alumina on ceramic monoliths is slurry coating, however, a combination of coating techniques may be required for a strong adherence of alumina on metallic surfaces. The loading of γ-alumina coated onto monoliths can vary between 10 and 15 wt %, although loadings can be varied according to preference. The preferred method of depositing metals onto monoliths is via wet impregnation. The main challenge when using wet impregnation is the coating uniformity, which can be improved with a correct choice of drying technique. For coating metallic monoliths, it must be emphasized that it is possible for metals from the monolith structure to diffuse outward to the surface. This clearly must be considered when using metallic structures for some applications. Solution-combustion synthesis provides an interesting alternative to typical alumina/active layer coating, since the layer can be grown onto the support. Zeolites grown onto monoliths also can lead to a better adhesion to the monolith surface compared to slurry coating. Indeed, growing an active layer seems to be the more attractive option over conventional dip-coating techniques. This can be quite complex at times, but should certainly be considered for some applications.

On the application side, monoliths extruded with zeolites seem to have a promising future in pressure-swing adsorption. In the case for carbon, it has become popular to support carbon nanofibers onto monoliths, and more so now to extrude carbon monoliths with meso- and macro-porosity.
Monolithic catalysts show a promising future in oxidation catalysis. Noteworthy is the dearth of literature on the application of monolith catalysts in the partial oxidation of medium chain length linear alkanes, which have low value, yet high abundance. The vast majority of reports have focused on methane to propane. In the oxidation of alkanes, two mechanisms dominate. Homogeneous gas phase reactions can be attributed to the formation of oxygenates, olefins and dienes, whilst synthesis gas is formed catalytically. Similarly, in the catalytic combustion for power generation, a heterogeneous-homogeneous mechanism exists. Replacing noble metals as the active layer for monoliths will be difficult, though, monoliths coated with a perovskite-based catalyst can be an effective replacement for expensive noble metal-based catalysts. Furthermore, monolithic catalysts have been shown to be beneficial to the PrOx reaction and can be employed to reduce the concentration of CO from a reforming mixture to less than 10 ppm. Noble metals and copper-ceria supported on monoliths are reported to perform better for CO oxidation than gold coated on monoliths. Copper/ceria, thus, seems a promising alternative to using noble metals as the active layer on monoliths.

Due to their success in catalytic combustion, it may be reasonable to expect that microchannel reactors will become even more popular in oxidation catalysis in the near future. Also, quite promising in the near future, particularly to oxidation reactions, will be the preparation of conductive monoliths, where heat transfer is maximized by conduction [15,298–301].

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