Opportunities and Limitations of Metal Additive Manufacturing of Structured Catalytic Converters

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Abstract

With the aid of unique features of additive manufacturing (AM), reactors with composite structures including locally tuned geometries and porosity can be used in chemical reactions. This leads to improvements in resulting flow and transport parameters throughout axial and transverse coordinates of reactors. A combination between structured heterogeneous catalysts and AM is promising, but simultaneously challenging. Limited high temperature materials are available for AM of catalytic converters. Moreover, adhesion and chemical interactions between catalyst system and printed materials require adequate investigations. This paper gives a critical review about advantages and challenges of utilising AM for manufacturing of structured catalytic converters.

Keywords: Additive manufacturing, Structured heterogeneous catalysts, Locally tuned geometries, Adhesion

1. Introduction

Additive manufacturing (AM) refers to a group of manufacturing technologies which build a 3D object by successive deposition of material layers. Along with precision, flexibility in design and manufacturing are key features of AM. These characteristics make AM to be seen as an optimal alternative method for traditional manufacturing techniques in many research and industrial fields. By putting emphasis on chemical industries and corresponding environmental issues, more accurate and competent tools and manufacturing methods are required. Chemical engineering sectors can greatly benefit from AM in the forms of improved efficiencies of existing chemical processing technologies, better process economics,

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reduction of wastes and emissions, and by localising the production lines (with the aid of AM technologies, parts can be manufactured on-site) [1, 2, 3].

Manufacturing of catalytic converters in chemical industry started by the approval of emission standards (ESs). Due to the increasing obligations of furnishing energy sectors with catalytic converters, improvements of this application are demanded. In fact, ESs are legal requirements for specifying permissible limits of pollution from different instruments over a defined time frame. Firstly, ESs restricted the amount of pollution caused by automobiles, motor-bikes and powered vehicles. Later, ESs expanded their regulations to limit emissions from power and incineration plants, industrial sectors, diesel generators, lawn mowers and every other equipment with air pollution risks [4, 5, 6].

It is important to notice that emissions can strongly vary depending on the source and/or process [7]. Future technologies, modern applications and upcoming processes potentially yield extra challenges for the manufacturing of catalytic converters; as new pollutants come into the focus of regulations. A prime example for this condition is about volatile organic compounds (VOCs) like formaldehyde [8], which is produced by paint shops, woodworking and even in the kitchens. While many of these substances can be converted at rather low temperatures, achieving high conversions is challenging. Due to the often laminar flow in conventional catalytic converters and the inherent diffusion properties of VOCs like formaldehyde, oxidation of the poisonous chemicals may suffers from transport limitations. Mostly these limitations result in larger converters and higher amounts of catalyst materials [9, 10].

A different field of application for emission control systems in which, size of the converter is of high importance, is the aviation sector. Aircrafts produce NO_x, which is a well-known pollutant. Besides that, ozone (O_3) circulation inside cabin causes harm to passengers. However, current catalytic converters face with multiple operational obstacles for this application. These problems can be mentioned as large sizes, heavy weights and high pressure drops [11, 12].

A last example is given by non-road mobile-machinery (NRMM) such as chainsaws or power aggregates. While these machinery emit the same type of pollutants as the traffic sector, they are still only regulated under Euro V norm [6]. Here, it is needed to fit the catalytic converter in a very confined space with different geometries, while showing high activity during the cold start. Furthermore, an overarching challenge is the need to increase the possibility for refurbishment and recycling of such systems.

In all the mentioned cases, additive manufacturing can offer unique possibilities to deal with emission issues by means of new designs of intense and light-weighted catalytic converters.

1.1. Heterogeneous Catalysis for Emission Control

The main type of catalytic converters applied in the field of emission control are based on heterogeneous catalysts. In heterogeneous catalysis, reactants and catalysts are present in two different states of matters/phases, here gas and solid. The system is designed from the nano to the macro scale [13]. For emission control purposes, the active catalyst phase often belongs to the platinum group of metals called PGMs. Noble metals such as platinum (Pt), palladium (Pd) or rhodium (Rh) can be used as few-atom clusters or as nanoparticles.

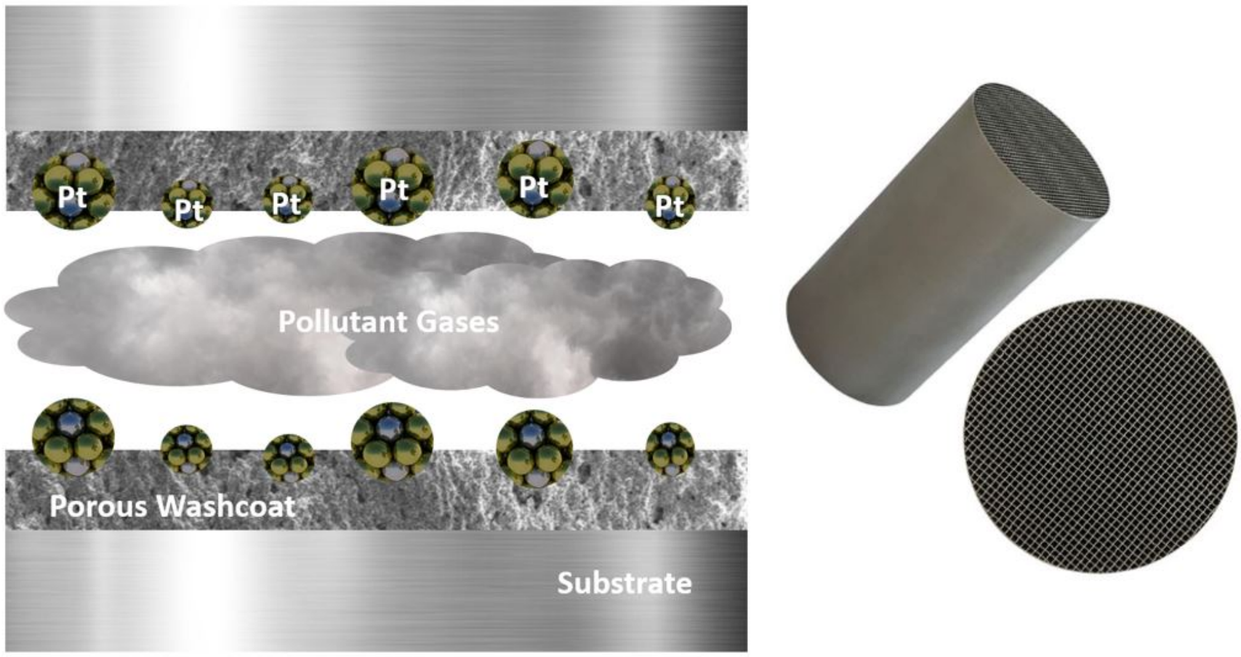

Figure 1: Schematic channel cross-section in a supported heterogeneous catalyst. Monolithic substrates are made of metals or ceramics. A porous ceramic layer called washcoat is coated on the top of this substrate to better accommodate the PGMs. Here, Pt nanoparticles in a solid phase are the active species. In this image the size of Pt is exaggerated.

Although PGMs were also used in bulk forms (unsupported), nowadays they are mainly deposited on porous support metal-oxides, e.g., alumina, titania or ceria for providing high and stable surface areas for noble metals. For emission control applications, the supported catalyst is then washcoated on metallic or ceramic monolithic substrates (carriers) with a cellular design [14, 15, 16]. Due to the multilayer design, this type of catalytic converters are regarded as structured catalytic converters. A graphical explanation of structured catalytic converters is provided in Figure 1. Such a design offers high mechanical stability, with a large surface area relative to the size of the catalytic converter while maintaining a low pressure drop.

1.2. Substrate Materials for the Manufacturing of the Cores

Monolithic catalyst cores (substrates) are designed to provide a higher surface area for the washcoat and active catalysts. These cores are dedicated to work at high temperatures [15, 17] and are commonly manufactured from the listed materials in Table 1.

Cordierite is a cost-effective synthetic ceramic, and cordierite substrates can be manufactured via extrusion and corrugation methods. Cordierite provides a good stability at harsh chemical and thermal conditions, although it has a low dielectric constant ($\varepsilon = 5-6$) and a very low thermal expansion coefficient ($\alpha = 1-2\times10^{-6}{}^{\circ}C^{-1}$). Besides that, the relatively low melting point of cordierite (1200-1435 °C) is very close to its optimum temperature range for sintering (1350-1400 °C). These facts unfortunately lead to degradation of the electrical

Material	Chemical Compounds
Cordierite	$2MgO.2Al_2O_3.5SiO_2$
Cordierite - Mullite	$2MgO.2Al_2O_3.5SiO_2 - 2Al_2O_3.2SiO_2$
Mullite	$3Al_2O_3.SiO_2$
Metallic Substrates	$Fe - Cr - Al - Y$

Table 1: Materials which are used in commercial manufacturing of monolithic carriers. Cordierite, mullite and zeolites are all inorganic materials based on aluminosilicates [15, 17]. There are also organic polymer-based materials which are out of our focus.

and thermal-expansion properties of cordierite with time [17, 18, 19, 20, 21]. Porosity and brittleness also impose negative influences on the thermal and mechanical durabilities of these ceramic monoliths. As a result, mechanical and thermal fractures happen frequently in ceramic cordierite monoliths. But still, cordierite monoliths meet the standard porosity and pore size distribution obligations for catalytic applications [17, 22].

Metallic monoliths provide high surface areas, but also have to withstand oxidising atmosphere at high temperatures. Austenitic steels (e.g. stainless steel 316L) and nickel-chromium (e.g. nichrome) alloys cannot fully withstand such conditions. However, aluminum containing ferritic steels are optimised for such operating conditions. In this case, a protective layer of aluminum oxide is shaped which guarantees functionality of the alloy up to 1500 K (equal to 1226.85 °C). Commercial metallic monoliths with high surface areas are made of Kanthal and Fecralloy. Foil sheets with a thickness of only 50 μm can be manufactured from these alloys. Hence, metal monoliths with very high cell densities can be manufactured [17, 23, 24].

High cell densities, stability of the washcoat systems, high conversion efficiency and low pressure drop are among the key indicators of a good catalytic converter [25, 26]. Due to the very thin walls, metallic monoliths have more cells per square inch compared to their ceramic counterparts. Metallic monoliths thus have a larger internal surface area which enables higher flows and a lower pressure drop. Another advantage of metallic monoliths is to reach the operating temperature of the PGMs faster than ceramic monoliths. Moreover, metallic monoliths are less prone towards mechanical damages [27, 28].

1.3. Manufacturing Challenges and Requirements for more-Efficient Designs

Historically, ceramic monoliths had straight channels, and therefore laminar flows and lower pressure drops. Due to lower pressure drop, fuel consumption was less and volumetric efficiency was higher. It is still common for ceramic monoliths to have square channels and to be referred to as honeycombs. Although, triangular, hexagonal, trapezoidal and round channel geometries are also possible, they are rarely considered for industrial applications. The first commercial metallic monoliths also had straight channels and the designs were based on sinusoidal channels. Figure 2 shows schematically the distribution of the washcoat layers (20-40 µm) on monolithic structures made of metal and cordierite ceramic. As it can be seen, the catalyst (washcoat and noble metals) are accumulated in the corners. This accumulation is mentioned as “fillets” and must be avoided to maintain a high catalyst

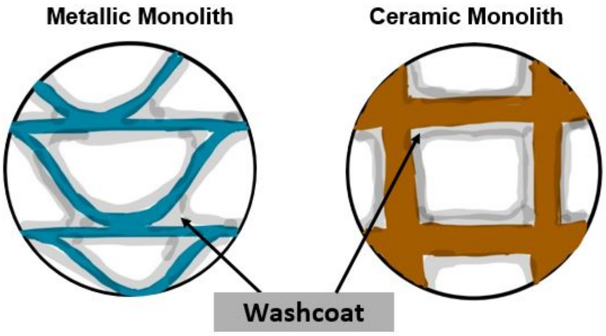

Figure 2: Washcoat accumulation at the corners known as fillet

efficiency [29, 30, 31].

As the next version of ceramic monoliths, channels were still straight but dual cell densities were introduced. The so-called flow adjustable design cell (FLAD) monoliths had a structure with a different cell cross-sectional area at the inner portion compared to that at the outer portion. In this design by enabling a more uniform gas flow within the catalytic converter, catalyst materials could be applied more efficiently. However, ceramic monoliths suffer from limitations coming from their low thermal conduction and the lack of radial mixing which yields to poor heat transfer to the walls [32, 33, 34, 35]. Newer versions of metal monoliths were optimized for increasing mass flow by means of Sherwood number. A fully turbulent flow leads to high pressure drops, therefore perforated foil (PE) and longitudinal structure (LS) designs with locally generated turbulence regions were developed [36]. However, developing more efficient catalytic reactors is still of high relevance also in industry.

As previously mentioned, tighter air quality legislation contributes in more frequent applications of catalytic converters. Statistics can sharply illustrate this uprising trend. With a compound annual growth rate (CAGR) of around 9.3%, the global catalytic converter market size started at USD 49.25 billion in 2021 and is expected to grow to USD 76.7 billion by 2030 [37]. However, like any other manufacturing industries, manufacturing of catalytic converters also has to deal with its own barriers.

For instance, one can consider emission control of formaldehyde. Although oxidation of formaldehyde has a very high intrinsic reaction rate, very low emissions are remarkably difficult to achieve. The reasons for such an issue are internal and external mass transport limitations which are occurring along the catalytic converter. In addition in the kitchens, high temperatures for oxidation are not easily reachable. A potential solution is to produce longer catalytic converters with higher concentrations of noble metals, but this proposal nevertheless leads to another failure. As the resources of noble metals are not enormous and whatever exists is rather expensive [9, 38, 39].

Manufacturing of catalytic converters for decentralised combustion engines and local emissions are also demanding. Considering the particular case of hand-held power equipment like chainsaws, maintaining a high performance via compact and light-weighted structures is a key challenge. Unlike other incinerators, these systems are therefore subject to Euro V standard. [40, 41].

Last but not least, there are also major challenge in the aviation sector. An airplane is driven via a jet engine holding a gas turbine, which powers the propeller. This configuration has made it almost impossible to use catalytic converters, as they would hinder the thrust by the engines. Additionally, an airplane has to be as light as possible to meet with the maximum engine performance. Based on those manufacturing points and priorities, airplanes are currently mainly exempt for emission regulations [42].

Enhancing functionality of the conventional reactors by increase mass transport and heat transfer is important for many other emerging applications. Now, light-weighted architected catalytic converters can be accurately designed and 3D printed in a short time by using additive manufacturing technologies [43, 44].

2. Additive Manufacturing of Structured Catalytic Converters

The concept of process intensification is a key trend in the field of process engineering. Yet mass, momentum and energy transfers impose limitations on the efficient usage of heterogeneous catalysts. With the help of AM methods, fabrication of geometrically optimised converters and reactors is feasible. Specifically, continuous flow reactions can become more intense with the employment of AM technologies. Application of AM technologies in the manufacturing of non-isothermal catalytic converters and reactors which are dealing with multi-phase flows is more challenging, thus classified as high-technology product developments [45, 46]. A taxonomy is required to fully realise the integration of additive manufacturing in catalysis research and industry. Following this path, it is possible to define which additively manufactured objects can be useful for a selected catalytic process. A classification consisting of two main groups was proposed by Laguna et al.(2021) in reference [47]. The first group is mentioned as "catalytic reaction ware". Although these devices can aid the catalytic process, they do not necessarily undergo a catalytic coating. However, the second group called "structured catalysts", convey a catalytic coating. This catalyst might be included within the printing materials or it can be afterwards integrated with the device through a chemical/physical coating method [48, 49].

Initially, researchers have been mostly using plastic additive manufacturing methods such as fused deposition modeling (FDM) for printing of a mold-like structure. This plastic mold is filled via a ceramic suspension which is resembling the washcoat. Finally, this plastic mold is removed through a heat treatment step. The remaining object is a hard and porous ceramic core with a honeycomb-like structure. Some interesting examples on this strategy have been described in references [50, 51, 52, 53]. Although with this strategy independent manufacturing of honeycombs in the laboratory scale is possible, but it is very similar to the traditional manufacturing of monoliths and therefore AM is not considered as a standalone manufacturing technique. Furthermore, protecting structures from contamination during mold removal step is risky.

There is a second strategy which is using metal-ink 3D printing for manufacturing of catalytic converters. For example, Tubio et al.(2016) and Quintanilla et al.(2018) used copper-based and Fe-Doped silicon carbide inks and tested their performance in an Ullmann reaction and in a wet peroxide oxidation process, respectively [54, 55]. However, this strategy is a rather expensive method which makes it more suitable for manufacturing of complex micro-scale electronic and biomedical devices than for large-scale catalytic converters [56, 57].

The third strategy fully trusts the abilities of AM for rapid production of cores of structured catalytic converters. In this strategy, monolithic substrates are directly produced by AM. Different sorts of designs with varies cpsi (cells per square inch) can be included in this fabrication strategy and dimensions are not limited. However, this strategy has to be adapted according to operating temperature. At elevated temperatures, polymers cannot be used. Only metals, ceramics and metallic-ceramic composites can be seen as suitable materials [58, 59].

2.1. Additive Manufacturing of Metal Powders

There are multiple technologies for additive manufacturing of metals with the most known ones as: laser-beam powder-bed fusion of metals (LB-PBF), direct laser deposition (DLD) and binder jetting (BJ). Each of these technologies can be suitable manufacturing methods depending on the selected priorities, such as: price, speed, size of the parts and surface quality [60].

According to ASTM F42 and ISO/TC 261 standards, LB-PBF is a powder bed fusion technology which is suitable for functional prototyping and production of near net-shape parts with relative density of about 99.9%. DLD is a direct energy deposition technique for prototyping and repairing of metallic parts and fixtures. BJ can be utilised in prototyping and investment casting [61, 62, 63]. Processable available materials for each of these technologies are summarised in Table 2.

AM Technology	**Applicable Metals**
LB-PBF	Alloys based on Ni, Cu, Al, Fe, CoCr, Ti and W. Since tungsten has a high melting point and a high ductile-brittle transition temperature, manufacturing of Tungsten parts via LB-PBF is in particular very promising [64, 65].
DLD	Ni-based alloys such as Inconel and Hastelloy, Co-based alloys such as stellite, carbides, stainless steels and titanium alloys [66]
BJ	Stainless steel, Ni-based alloys, tungsten carbide for low-cost parts and jewellery [67]

Table 2: Metals which are printable with LB-PBF, DLD and BJ technologies

- **Laser-beam powder-bed fusion of metals (LB-PBF)**: It is the most popular AM process for metal 3D printing. It is also mentioned as selective laser melting (SLM). In this AM technology, high-power laser beams are used to fully melt and fuse metallic powders. Coordinates for powder melting are specified via a CAD file. After melting the powders at high temperatures (up to 1250 °C), a liquid pool is shaped. Consolidated materials inside this pool quickly cool down, solidify and form one layer of the final product. A recoater provides new powders and this process is repeated until when the CAD file is fully 3D-constructed. To protect LB-PBF manufacturing against oxidation of the metals, the construction chamber is filled with an inert gas like argon or nitrogen [61, 68, 69, 70].

- **Direct laser deposition (DLD)**: It is also called laser metal deposition (LMD). In this technology, a CAD design can be printed with a coaxial powder feeding laser. Although LB-PBF is using very fine powders, DLD can use both metal wires and powders. Thus, finished SLM parts have finer surface qualities than parts which are manufactured via DLD process. Besides, continuous-wave diode lasers in DLD have much higher powers compared to the CO_2 lasers[1] in LB-PBF additive manufacturing. Consequently, printed layers by DLD are thicker than layers made by LB-PBF [68, 72, 73].

- **Binder jetting (BJ)**: BJ is typically faster than LB-PBF for AM of metals. Similar to LB-PBF, BJ also uses metal powders as its raw materials. However, LB-PBF and BJ manufacturing processes are completely different. LB-PBF uses a laser-beam for layer-wise fusion of the powders, however; in BJ no melting of powder particles is accomplished. Instead, BJ process happens in multiple steps, including: deposition, de-binding, curing, sintering and hipping. These steps are completed outside the 3D printer itself. For example, 3D printed green-parts by BJ must be transferred to an external furnace/oven for sintering/curing. Since these green-parts are not yet stiffed, they are fragile and susceptible towards damage during this transportation step [74, 75, 76].

3D printing of alumina, zirconia, aluminum nitride, silicon carbide and silicon nitride with similar AM technologies are possible. In particular, binder jetting has been also used for the manufacturing of metal-ceramic composites. However, unlike thermoplastics and metals, fusion of ceramic powders is not easy. This is a result of their high melting points. Besides that, low ductility, low toughness, and cracks in 3D printed ceramics are not avoidable. Furthermore, to form a smooth part, extra post-processing for removing the floating ash from the surface is still necessary [77, 78, 79, 80].

2.2. Initial Industrial Applications of Metal Additive Manufacturing in Process Engineering

Generally, energy related fields such as process engineering are very conservative about applying new technologies. With this perspective, probably heat-exchangers and distillation systems are the most advertised applications of metal-AM for large-scale energy-related industrial sectors [81, 82].

In the conventional manufacturing of metallic heat-exchangers, individual plates or fins are bonded with each other via brazing or welding. This is a laborious manufacturing

[1] CO_2 lasers can be used in a continuous, pulsed, or super-pulsed modes [71].

process with a high risk of failure between brazed (or welded) joints. However via metal-AM, a single-unit heat-exchanger with lower operational failure risk can be quickly captured. Besides that, there would not be a need for extra processing steps such as welding, brazing or forming [83]. For the sake of a better thermal management and to reach a higher heat flux; denser and simultaneously lighter structures are required [84]. Miniaturised heat exchangers with higher efficiencies compared to their conventional versions can be 3D printed via AM technologies [85]. The freedom of design concept which is provided by AM technologies, makes it possible to produce lightweight monolithic heat exchangers with extraordinary designs. Abstract algebra patterns like lattice structures or triply periodic minimal surfaces (TPMS) can be included while 3D designing of a heat exchanger's core. Such designs provide larger surface area with improved heat transfer [86]. There are already two famous industrial prototypes on these, including a heat-exchanger and a radiator for a CubeSat which are printed by GE researchers and NASA's Jet Propulsion Laboratory, respectively [87, 88] .

Currently, more efficient catalytic converters are also sorely being demanded for the environmental protection. State-of-the-art versions of catalytic converters are required to be upgraded in hybrid and electric vehicles. This efficiency is not only the matter of higher chemical conversions, but also easier manufacturing of smaller light-weight catalytic converters is significantly important [89, 90, 91].

Despite of having such important perspective, additive manufacturing of structured catalytic converters for high temperature applications is still in its early research stages. In the next sections, we try to draw attention towards the importance of this research field and the need for its development towards industrial applications. At the end, it is also mentioned why this type of manufacturing is more challenging than other applications in the growing AM market in chemical engineering.

2.3. Potential Benefits of Additively Manufactured Structured Catalytic Converters

Although it is probably still early to aim for mass production of catalytic converters via AM, it is important to be aware of the potentials, challenges and relations with the other manufacturing techniques. Theses are discussed with a few examples in this section.

2.3.1. Oxidation of VOCs: Formaldehyde as an Example

Formaldehyde oxidation has a very high intrinsic reaction rate, but it is restricted by internal and external mass transport limitations which are occurring along the catalytic converters [9]. Accordingly, it is very demanding to achieve ultra-low emissions. To obtain such ultra-low emissions a possibility is to use longer catalytic converters, or to use more catalyst mass. But, this is not a feasible solution in many cases. In this case, the possibility of incorporate design complexity of additive manufacturing can help with providing a better solution and can give new possibilities in the broad classical field of product design [92]. Flows in standard monolithic converters are often in the laminar regime, which entails slow diffusion from the gas phase to the washcoated walls. Turbulent flows contain swirls and so called eddies, which help to transport the gas from the middle of the channel to the catalytic layer. One possibility to overcome these limitations is by changing to a turbulent flow field.

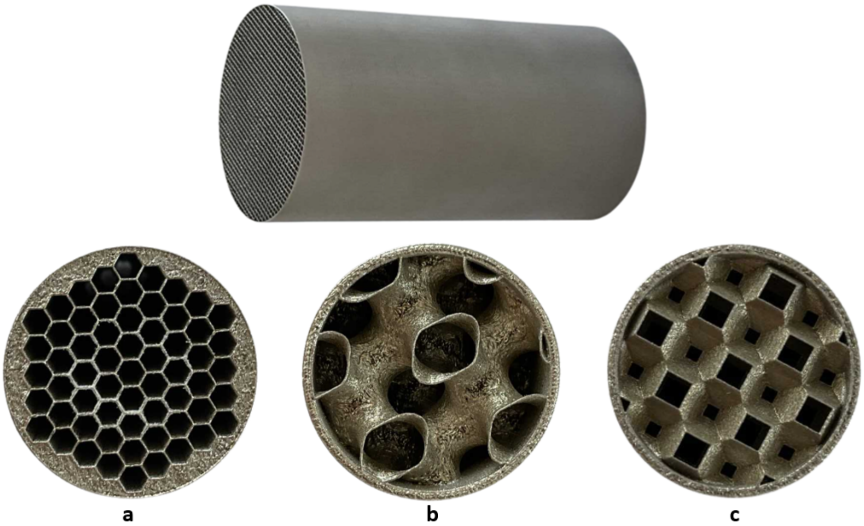

Figure 3: Cross-sectional view of the cores of catalytic converters which are additively manufactured via LB-PBF technology: a) Honeycomb-like structure with hexagon channels, b) TPMS structure generated from Gyroid cell with a rotation of 45°, c) Adapted from Schwarz-P cell of TPMS structures and adjusted to the the conditions of a Realizer SLM 125 machine

As size of the converter is limited, introducing flow breakers or changing the channel size along the catalyst bed may be a powerful solution. Creative irregular designs (some examples are shown in Figure 3) are highly demanded for the manufacturing of catalytic oxidation systems for the removal of VOCs and other pollutants. Good material formability makes metal additive manufacturing a promising candidate for this use case. Furthermore, the connection between design strategies with CFD simulations is also attractive. For instance, the pressure drop can be simulated in advance and therefore be avoided [9, 93].

2.3.2. Ozone Converters and Catalytic Converters for Airplanes

Power stations, road vehicles and trucks are all equipped with some kind of a catalytic converter. But so far, the aviation sector based on admissible reasons has been an exception. Therefore, although airplanes emissions make a great contribution in air pollution and climate changes; there has not been any catalytic converter in their engines or exhaust paths. Catalytic converters in such a scale would be extremely heavy and might put safety of the air-travelers at risk [94, 95, 96]. In the meanwhile, there are two open topics of ozone converters and flow-through catalytic converters which are recently developed by BASF and MIT, respectively (Figure 4). Some airplanes carry the so called ozone converter, which follows a similar operating principle as any catalytic converters. Ozone converters are used to improve the inside-cabin air quality by converting ozone into oxygen. Furthermore, the proposed concept of hybrid-electric or "turbo-electric" design from MIT researchers makes it possible for also airplanes to carry catalytic converters [97, 42, 98]. Powders of light-weighted metals including: aluminum, titanium and Inconel are already available in the market for metal additive manufacturing and can be employed for serving the aerospace industry [99]. Thus, potentially light-weighted ozone converters or even catalytic converters can be also

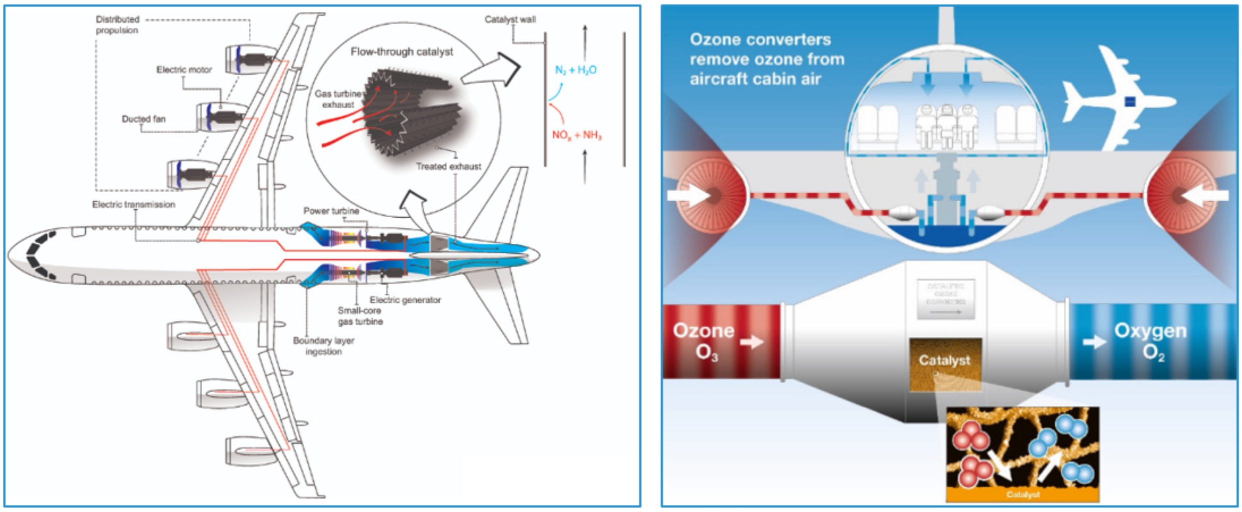

Figure 4: Left: Flow-through catalytic converter in hybrid-electric aircrafts (reproduced from Ref. [42] with permission from the Royal Society of Chemistry); Right: Ozone converter [97].

3D printed in a short course of time.

2.3.3. Sustainability and Supply Chain Resilience

"Unparalleled level of globalisation and fierce competition have made supply chains exceedingly complex and fragile as ever before" [100]. Similar to the other goods, countries often rely on distant overseas for the manufacturing of catalytic converters. Although these types of transactions are sometimes unavoidable, employing judiciously planned recycling strategies will significantly reduce dependencies of the respective countries [101, 102]. Additive manufacturing is one of those technologies, which opens new gateways towards utilising recycled materials [103, 101, 104]. Not only the main catalyst (PGMs), but also the metal cores (made via AM) can be recycled and used again as the raw materials for 3D printing. The recycled materials can be used for powder manufacturing in 3D printing. Hence, AM has considerable potentials for sustainable manufacturing [105, 106]. This means AM can quickly supply products by using the least amount of energy and natural resources while maximising financial and environmental profits [107]. In addition, small size industries and local manufacturing sectors also have the chance to provide their goods for their potential customers [108]. In parallel with the transportation issue, COVID-19, wars, unsustainable consumption and production practices are obvious reasons to show the importance of expanding domestic and recycling-based markets [109, 110]. Recycling is aimed for financial and environmental reasons. Catalytic converters are expensive devices and should not be an exception. In the case of current monolithic catalytic converters, recycling is done to give the remaining precious metals a second life. Good overviews about available methods for the recovery of noble metals from catalytic converters in petrochemical processes are provided by [111, 112]. Nonetheless, recycling of a monolithic substrate itself (ceramic or metal) is also a step forward towards a wiser and more environmentally friendly uages of the material resources.

2.3.4. Digitisation and Size Scaling

Scaling size of a catalytic converter/chemical reactor from laboratory-scale to pilot-plant to production-scale requires a careful understanding of the reactor physics, including reaction kinetics, fluid flow, residence time, heat and mass transfer. However, scaling a chemical reaction from laboratory to manufacturing orders is often difficult. For instance, it is possible that after scaling based on equal residence time, reactors produce different yields. Other scale-up problems can come from industrial constraints such as operation time, control parameters, impurities in the raw materials and reliability of the equipment [113, 114]. Thus, scaling size of a catalytic converter/chemical reactor can be a long, challenging, expensive and laborious procedure.

For the manufacturing of catalysts substrates, AM has a major advantage of freedom of design over conventional shaping technologies (corrugation, welding, brazing, etc). AM is an automated manufacturing method and by digital monitoring of AM in-process parameters, reduction of lead-time and waste are possible. These privileges enable AM technologies to produce customised catalytic converters with an economic approach within a plannable time frame [115, 116]. In the current manufacturing of catalytic converters, designing a shape in computer is considered as a repetitive, manual and tedious operation. However, in digital manufacturing methods like AM, design is a flexible and fundamental step for the final goal of optimising topology of a catalytic converter [117]. Therefore, with AM, scaling the dimensions of a catalytic converter/reactor up-or-down is more feasible. Different size variations of a design can be 3D printed within only one 3D-printing machine and be tested under different chemical reactions.

2.3.5. Washcoat Adhesion

Simultaneous with learning about benefits of AM, it is important to adapt/adjust with the requirements of washcoating procedure. As already mentioned, washcoating is an essential process for increasing the catalytic activity, durability and stability. This is done by providing a higher surface area (compared to that of monolithic substrates) needed for the dispersion and activity of the noble metals [118, 14]. Obtaining a good coating in the terms of its adhesion stability and uniformity of its thickness distribution requires extra considerations [119, 120]. In general, washcoat adhesion to monolithic substrates is not always optimal and the washcoat is relatively thicker on metal substrates. To reach a proper washcoat distribution over metal substrates, stabilising catalyst suspensions with sufficient rheological properties controlled by the solid content, pH, particle size and additives is very important. Sedimentation issues will result in an uneven thickness distribution of the washcoat layer [121, 122, 123, 124]. In some cases, pre-treatment of the substrates by using primers, etching and oxidation methods is additionally conducted for obtaining an adherent surface scale compatible with the coating with appropriate surface roughness values [15, 120, 125, 126]. At present, there are no specific standards for designing of the monolithic substrates. Yet, as was shown in Figure 2, capillary forces which are acting during coating and drying steps create a certain accumulation of the catalyst at the channel corners. Therefore, sharp edges must be avoided in the channel designs [124]. By taking control over AM process parameters, dimensional tolerances, pore formation and surface roughness parameters can be monitored.

Surface roughness and wettability of 3D printed metal monoliths with permeable thin-walled channels provide an acceptable adhesion to the washcoat [127, 128].

3. Conclusions and Outlook

Metal additive manufacturing is gaining attention in the realm of chemical processes, especially for the design of chemical reactors. Key developments, such as design automation and localisation of versatile manufacturing are driving this technology forward and presenting intriguing possibilities to revolutionize the life-cycle of catalytic converters. In particular, when it comes to catalytic reduction and the removal of emissions, which heavily rely on scarce and expensive noble metals, new manufacturing technologies for fabricating catalytic systems are vital to address emerging pollutants and increasingly stringent emission limits. Adapting to these evolving requirements, the manufacturing of catalytic devices, specifically structured catalytic converters, must continuously improve to ensure optimal device performance. With the aid of additive manufacturing, more intricate shapes with favorable flow properties can be introduced to mitigate mass transport limitations. There is also a possibility for using new materials. Depending on the thermal properties of the metal powders employed in metal-AM, the developed structured catalytic converters can operate within a wide temperature range, a critical factor for effective emission control. Additionally, the heat transfer within the substrate can be tailored, opening up new possibilities for cold-start applications. Another significant advantage of metal AM is its ability to customise catalysts to fit even the smallest devices and reduce weight for mobile applications. By utilizing these parameters to tailor catalytic properties, AM not only improves catalytic performance but also enhances sustainability aspects of the converter. Based on these factors, it is undeniable that additive manufacturing will play a significant role in the development of modern catalytic converters. However, AM of creative support structures for catalytic applications is still on its early stages and it has to provide with a convincing adhesion to the washcoat layers in order to be used in practice. Hybrid and new coating methods can also influence and accelerate this progress.

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