Opportunities and Limitations of Metal Additive Manufacturing of Structured Catalytic Converters

Fatemeh Mehdipour[a,*], Tim Delrieux[b], Florian Maurer[b], Jan-Dierk Grunwaldt[b,d], Christoph Klahn[c], Roland Dittmeyer[a,d]

[a]*Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology (KIT), Germany*
[b]*Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Germany*
[c]*Institute for Mechanical Process Engineering and Mechanics (MVM), Karlsruhe Institute of Technology (KIT), Germany*
[d]*Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Germany*

Abstract

Utilising additive manufacturing (AM), reactors with composite structures, featuring locally tuned geometries and controlled porosity, can effectively be employed in chemical reactions. This innovation yields enhancements in flow and transport properties across both axial and transverse dimensions. Integrating structured catalysts with AM offers great potentials, albeit faces notable challenges. A significant challenge is scarce availability of suitable high-temperature materials for AM of catalytic converters. Furthermore, ensuring optimal adhesion and chemical interactions between catalyst systems and printed materials necessitates detailed investigations. This paper examines advantages and challenges associated with AM of structured catalytic converters, employing emission control systems as an illustration.

Keywords: Additive manufacturing, Structured catalysts, Locally tuned geometries, Optimal 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,

*fatemeh.mehdipour@kit.edu

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 was initiated by the implementation of emission standards (ESs). Over the past decade, environmental concerns have mandated many energy sectors to be upgraded and to utilise advanced catalytic converters. Consequently, there is a growing demand for enhancements in the manufacturing of catalytic converters [4]. ESs were legal requirements for specifying permissible limits of pollution from different instruments over a defined time frame. Initially, 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 [5, 6, 7].

It is important to notice that emissions can strongly vary depending on the source and/or process [8]. Future technologies, modern applications and upcoming processes potentially yield extra challenges for the manufacturing of catalytic converters. In this context, AM is of general interest due to its potential to enhance catalytic activity, control selectivity, and to optimise heat and mass transport properties in and for various reactions [9]. With upcoming focus on in-house air quality, emissions in restaurants, new applications in the chemical industry and biomass conversion, the removal of volatile organic compounds (VOCs) is coming into focus. They span from simple molecules like formaldehyde or methanol to alkenes, aldehydes, ketones to aromatics (e.g. xylene) [10].

Applications of AM in emission control offer innovative possibilities, which will play key roles in coping with challenging pollutants. Some captivating examples are selective oxidation of isoprene to citraconic anhydride or oxidative C-C coupling of methane reactions [11, 12, 13]. Another prime example for this condition is dealing with formaldehyde, 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. These limitations often lead to production of larger converters and the necessity to use greater quantities of catalyst materials [14, 15, 16].

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 the passengers. However, current versions/designs of catalytic converters encounter numerous operational challenges when applied for aviation purpose. These problems can be mentioned as large sizes, heavy weights and high pressure drops [17, 18].

A final example is given by non-road mobile-machinery (NRMM) such as chainsaws or power aggregates. Despite emitting the same type of pollutants as the traffic sector, these machines are still only regulated under the Euro V norm [7]. The intended catalytic converters for NRMM must be fitted in a very confined space with different geometries, while maintaining 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. Examples where additive manufacturing has allowed to design more sophisticated structures which cannot be achieved with classical approaches have been reported in several publications, including [19].

In this paper, we will be focused on emission control applications. The same conclusions can be derived for other (fast) gas phase reactions. Hence, we provide a concise introduction to heterogeneous catalysts utilised in emission control, the catalytic systems and the typical substrates. Subsequently, we discuss about applications of additive manufacturing in this domain, exploring both current and prospective use cases in the field of emission control by referring to the examples of VOC removal and ozone decomposition processes. We finalise by addressing some challenges, conclusions and outlooks for future developments.

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 due to high space velocities. 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 [20]. 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. 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 [21, 22, 23]. 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 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 [22, 24] and are commonly manufactured from the listed materials in Table 1.

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 [22, 24]. There are also organic polymer-based materials which are out of our focus.

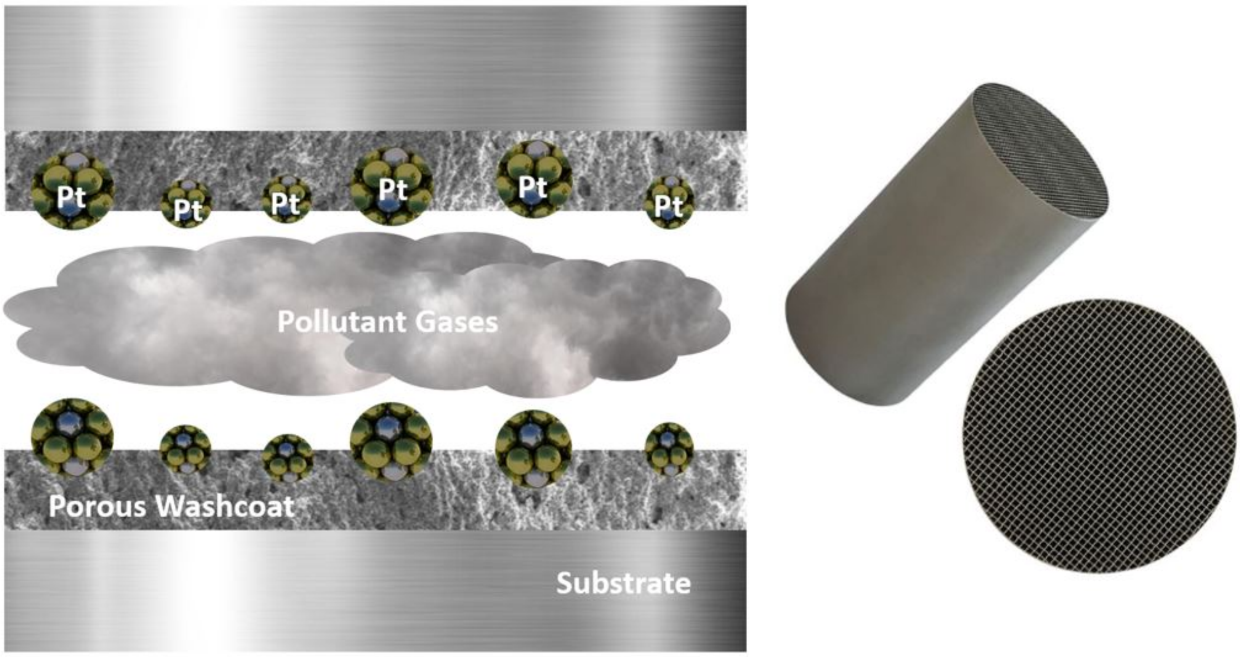

Figure 1: Schematic channel cross-section in a supported heterogeneous catalyst. Monolithic substrates are made of metals or ceramics. A porous ceramic layer called washcoat is coated on the top of this substrate to better accommodate the PGMs. Here, Pt nanoparticles in a solid phase are the active species.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

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 ($\alpha = 1 - 2 \times 10^{-6} {}^{\circ}C^{-1}$). 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 and thermal-expansion properties of cordierite with time [24, 25, 26, 27, 28]. 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 [24, 29].

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 [24, 30, 31].

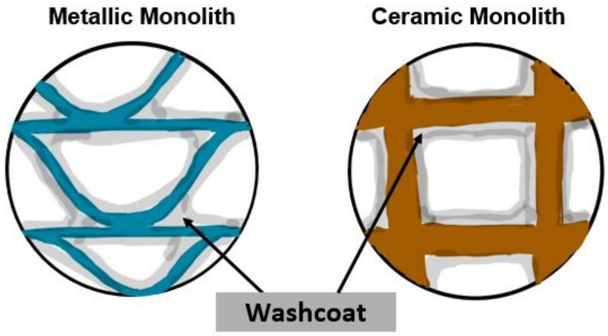

Figure 2: Washcoat accumulation at the corners known as fillet

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 [32, 33]. 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 [34, 35].

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 efficiency [36, 37, 38].

In 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 [39, 40, 41, 42]. Newer versions of metal monoliths were optimised 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 [43]. However, developing more efficient catalytic reactors is still of high relevance in both research and 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 [44]. 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 [15, 45, 46].

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 [47, 48].

Last but not least, there are also major challenges 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 [49].

Enhancing functionality of the conventional reactors by increasing the mass transport and heat transfer is crucial for numerous emerging applications. Simultaneously, with the advent of additive manufacturing technologies, accurate design and rapid manufacturing of lightweight and architected catalytic converters have become feasible [50, 51].

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 possible. 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 [52, 11]. 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 [53]. 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 [54, 55].

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 [56, 57, 58, 59]. 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 [60, 61]. 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 [62, 63].

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 [64, 65].

2.1. Powder-based Additive Manufacturing of Metals

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 [66].

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 [67, 68, 69]. 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 [70, 71].
DLD	Ni-based alloys such as Inconel and Hastelloy, Co-based alloys such as stellite, carbides, stainless steels and titanium alloys [72]
BJ	Stainless steel, Ni-based alloys, tungsten carbide for low-cost parts and jewellery [73]

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 [67, 74, 75, 76].

- **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 parts by LB-PBF 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 [74, 78, 79].

- **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 [80, 81, 82].

[1] CO_2 lasers can be used in a continuous, pulsed, or super-pulsed modes [77].

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 [83, 84, 85, 86].

In many applications, surface finish of the 3D printed metal parts are considered as a weakness for AM. Quality of the surface finish and surface-texture parameters of 3D printed metal parts vary depending on the applied metal AM process, type of the used metal powder (material, size), post-processing techniques and part's design (surface type, print angle) [87, 88]. However, when it comes to catalytic coating, surface roughness of the metallic catalytic carriers can be advantageous.

To improve adhesion of the ceramic washcoats to conventionally manufactured metal substrates, it is essential to pretreat the metal substrates via chemical and thermal methods. These pretreatment processes aim to facilitate formation of oxide layers and to increase surface roughness of the metallic parts to enhance ceramic-metal adhesion bonding. This requirement leads to extended processing times, complex procedures, and increased manufacturing costs. In the case of sport and racing cars, where cost considerations take a backseat, metallic monoliths are preferred. In comparison to ceramic honeycombs, metallic monoliths exhibit a lower specific heat capacity and a greater thermal conductivity. Consequently, these properties result in rapid heating of the converter and enhanced responsiveness at elevated temperatures. Additionally, the metallic monoliths can be positioned in closer proximity to the engine for optimised performance. With more innovating preparation technologies, widespread application and adoption of cellular metallic monolith as standard substrate for environmentally-friendly catalysts is feasible [89, 90, 91, 92]. AM, as the primary physical pillar of the fourth industrial revolution, encompasses several distinct advantages, notably, design automation and ease of fabrication [93]. Surface roughness of metallic components produced via AM technologies is a subtle yet valuable factor for promoting cellular metallic monoliths.

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

Energy related fields such as process engineering are very conservative about applying new technologies. This conservatism is primarily driven by the sector's emphasis on safety, reliability, established practices and estimated costs. These parameters can make the industries cautious about embracing novel approaches. [94]. With this perspective, probably heat-exchangers and distillation systems are the most advertised applications of metal-AM for large-scale energy-related industrial sectors [95, 96].

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 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 [97]. For the sake of a better thermal management and to reach a higher heat flux; denser and simultaneously lighter structures are required [98]. Miniaturised heat exchangers with higher efficiencies compared to their conventional versions can be 3D printed via AM technologies [99]. 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 [100]. 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 [101, 102].

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 [103, 104, 105].

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

While it may be premature to consider mass production of catalytic converters using AM at this stage of time; recognising its potentials, understanding the involved obstacles and challenges, and exploring its interplay with other manufacturing techniques are crucial. This section delves into these aspects, illustrating them via selected examples.

2.3.1. Oxidation of VOCs

VOCs are detectable across a wide range of applications, typically at low concentrations. Notable environments where VOCs can be found include paint shops, woodworking workshops and domestic kitchens. However, the presence of VOCs is not without any concern. Most of VOCs are highly flammable, and some pose significant health and environmental risks even at low concentrations. Consequently, development of proper methods for catalytic removal of VOCs at low temperatures is increasingly gaining attention [106, 107]. Following this objective, many strategies using thermal or photo assisted catalysis were already proposed [108, 109].

On one hand, achieving low temperatures is a requirement of this type of catalytic oxidation reactions; while on the other hand, it confronts the challenge of high flows and gas space velocities. AM has been already applied for intensification of chemical engineering processing such as VOC oxidation [110, 111], but it just has recently gained increased attention for the generation of porous monolithic host sites for catalytic oxidation of toluene.

Especially in the case of zeolite and metal-organic framework (MOF) based catalysts, substantial efforts have been invested in optimising the interaction between the catalyst and the 3D printed structures [112, 113, 114].

While AM can be used to tune the catalytic/chemical properties, another important aspect is the 3D design of the reactor itself. Due to the mentioned high flows during VOC oxidation, it is crucial to minimise the back-pressure caused by the catalyst simultaneous with minimising mass transport limitations. In this regard, a study by Hajimirzaee et al. [115] on the examination of catalytic total oxidation of CH_4 on 3D printed cordierite monoliths can be mentioned. Where the influence of different layer rotation offsets of the 3D printed structures was correlated to pressure decrease depending on the gas velocity. This structural property (originating from design) of these hierarchical materials also influenced the overall catalytic activity of the samples, despite a constant amount of catalytic material was applied in the tests. Such behaviour could even be further translated to the design of packed bed reactors. In another study, the hydrodynamic performance of 3D printed "SpiroPak" structured packings was analysed, and topology optimisation was conducted aiming to enhance surface area while decreasing pressure drop values via a computational fluid dynamics (CFD) method [116].

While toluene and even more pronounced CH_4 oxidation suffer from low reaction rates due to the CH activation [117], 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 [15]. 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 [118]. 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. 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.

The excellent formability of materials in metal additive manufacturing positions these technologies as a strong contender for this application. Additionally, integration of design strategies with CFD simulations and knowledge-based engineering (KBE) approaches are advantageous. For instance, pressure drop can be preemptively simulated and thus mitigated [15, 119, 120].

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.

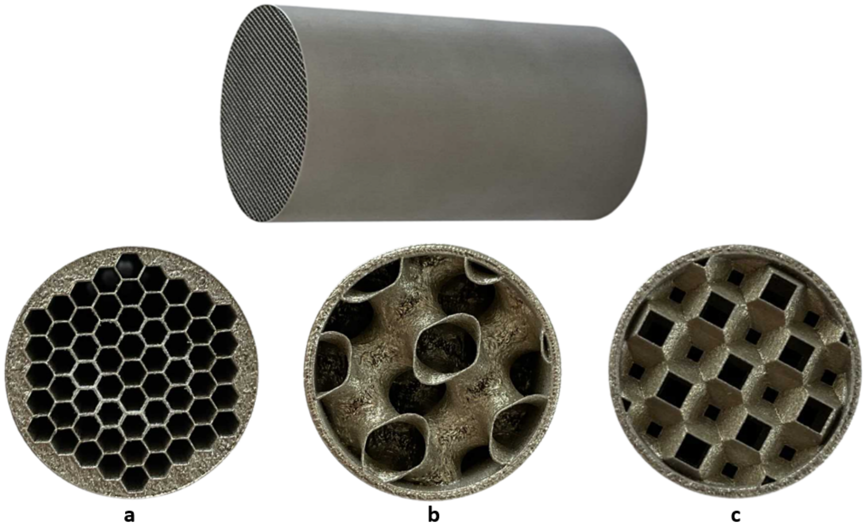

Figure 3: Cross-sectional view of the cores of catalytic converters which are additively manufactured via LB-PBF technology: a) Honeycomb-like structure with hexagon channels, b) TPMS structure generated from Gyroid cell with a rotation of 45°, c) Adapted from Schwarz-P cell of TPMS structures and adjusted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

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 [121, 122, 123]. 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 also for airplanes to carry catalytic converters [124, 49, 125]. 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 [126]. Thus, potentially light-weighted ozone converters or even catalytic converters can be 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" [127]. 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 [128, 129]. Additive manufacturing is one of those technologies, which opens new gateways towards utilising recycled materials [130, 128, 131]. 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.

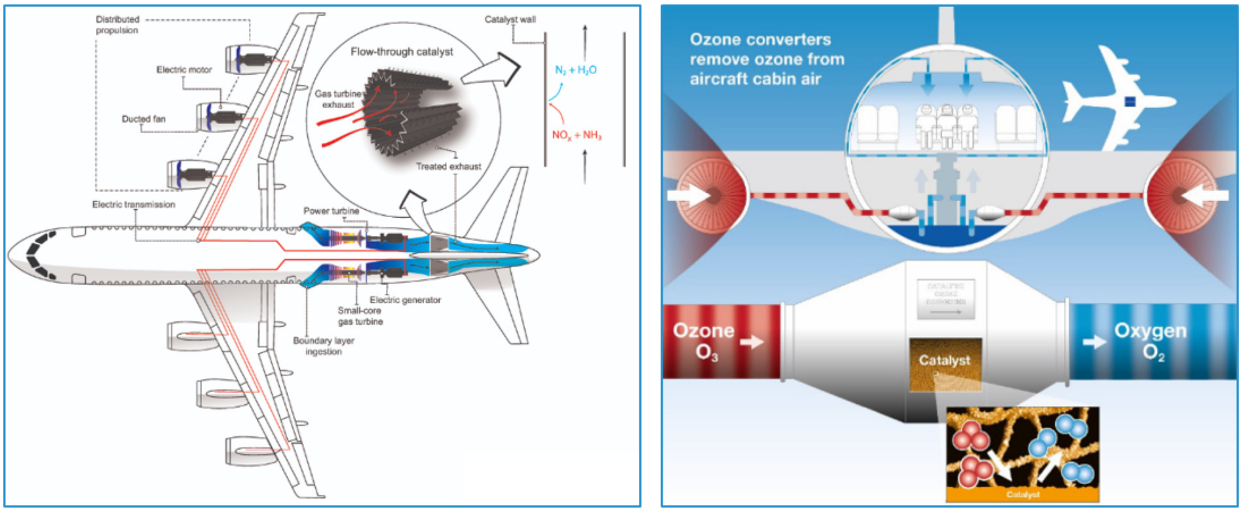

Figure 4: Left: Flow-through catalytic converter in hybrid-electric aircrafts (reproduced from Ref. [49] with permission from the Royal Society of Chemistry); Right: Ozone converter [124].

The recycled materials can be used for powder manufacturing in 3D printing. Hence, AM has considerable potentials for sustainable manufacturing [132, 133]. This means AM can quickly supply products by using the least amount of energy and natural resources while maximising financial and environmental profits [134]. In addition, small size industries and local manufacturing sectors also have the chance to provide their goods for their potential customers [135]. 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 [136, 137]. 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 [138, 139]. 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

The process of scaling a catalytic converter or chemical reactor from laboratory-scale to pilot-plant and then to production-scale necessitates a deep understanding of reactor physics, encompassing aspects like reaction kinetics, fluid flow, residence time, and heat and mass transfer limitations. Often, scaling a chemical reaction from lab to manufacturing scale often presents challenges. For example, scaling based on equal residence time might result in different yields. Other scaling issues may arise from industrial constraints such as operational time, control parameters, impurities in the raw materials and equipment reliability. Consequently, scaling size of a catalytic converter or chemical reactor is typically a lengthy, complex, costly, and labor-intensive procedure [140, 141].

In catalyst substrate manufacturing, AM has a major advantage of freedom of design over conventional shaping technologies like corrugation, welding and brazing. 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 predictable time frame [142, 143].

Along with scaling issues [144, 145], in the contemporary catalytic converter manufacturing, incorporating design novelty for creation of optimised monolithic structures is often viewed as a repetitive, manual, and laborious task. As a result, the most cost-effective designs are favored and have been accepted as standard shapes. These in particular include ceramic honeycombs featuring rectangular channels, which are advantageous for extrusion processes, and metallic monoliths with sinusoidal cells. The latter are formed while rolling and welding of metal sheets to each other. With increasing design complexity, predictability of associated scaling becomes more challenging [146, 144].

Nonetheless, with digital manufacturing methods such as AM technologies, design flexibility is a crucial aspect in achieving the ultimate objective of optimising topology and functionality of a catalytic converter [147]. Accordingly, using AM allows for easier and more feasible scaling of dimensions of a catalytic converter/reactor, whether enlarging or reducing its size. Various size adaptations of a design can be efficiently 3D printed using a single 3D printing machine, enabling them to be tested for a range of chemical reactions [148, 149].

2.3.5. Tuning Adhesion Properties for Washcoating

Concurrently with exploring the advantages of AM, it is imperative to adapt and finetune the process to meet specific demands of the washcoating procedure. As previously noted, applying catalytically active noble metals within a porous washcoat layer promotes a high dispersion of the active nanoparticles and enhances the interactions with the gas phase. With this implementation, the activity, durability and long-term stability of catalytic converters for emission control can be increased [150, 21].

Achieving a high-quality coating, in terms of adhesion stability and uniform thickness distribution, necessitates additional considerations [151, 152]. Generally, the adhesion of washcoats to monolithic substrates can be suboptimal, and the washcoat tends to be thicker on metal substrates. To ensure proper distribution of the washcoat over metal substrates, it is vital to stabilise catalyst suspensions with adequate rheological properties. These properties are influenced by factors such as solid content, pH, particle size, and chemical additives. Inadequate control over these factors can lead to sedimentation issues, resulting in uneven thickness of the washcoat layers [153, 154, 155, 92]. In some instances, substrate pretreatment using primers, etching, and oxidation methods is employed to achieve an adherent surface scale that is compatible with the coating, having appropriate surface roughness values [22, 152, 156, 157].

Currently, there are no specific standards for the design of monolithic substrates. However, it is observed that capillary forces acting during coating and slurry/suspension drying can lead to catalyst accumulation at the channel corners, as indicated in Figure 2. Therefore, avoiding sharp edges in channel designs is crucial [92]. By carefully managing AM process parameters, such as dimensional tolerances, pore formation, and surface roughness, one can effectively monitor and control these aspects which can be beneficial in improving washcoat adhesion and its stability on 3D printed monolithic support structures. The surface roughness and wettability of 3D printed metal monoliths with permeable thin-walled channels are key factors in ensuring acceptable adhesion to the washcoat. This comprehensive approach based on AM process optimisation is crucial for advancing functionality and performance of catalytic converters in modern applications [158, 159].

Innovative design concepts for modern catalytic converters based on 3D printing, and subsequently attractive numerical methods for virtual analysis (simulations) and evaluations have been initiated [160, 161]. Nevertheless, additive manufacturing of catalytic converters is still an emerging field of research with industrial outlooks, which demands for detailed investigations. Therefore, there is a notable scarcity of practical, experimental studies focused on the implementation of additively manufactured structured catalytic converters. The existing body of research which briefly addresses washcoating of 3D printed metal and ceramic substrates is limited, and predominantly focuses on membrane reactor configurations [162, 163]. In the current state of literature, little focus is put on specific challenges and techniques involved in coating the internal channels of densely packed cellular monoliths, an area that warrants further explorations and studies. To our knowledge, currently there is one paper available on 3D printing of metallic monolithic converters with experimental evaluations for a similar application (dry reforming of methane), which already shows high potentials of metal additive manufacturing for this field [164].

3. Conclusions and Outlook

Metal additive manufacturing is gaining attention in the realm of chemical processes, especially for the design and manufacturing of chemical reactors. Key developments, such as design automation and localisation of versatile manufacturing steps are driving this technology forward and presenting intriguing possibilities to revolutionise life-cycle management 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. Additionally, there exists the potential to employ a broader spectrum of metal substrates, encompassing those that were previously deemed incompatible or impractical in traditional manufacturing methods which typically rely on brazing of thin metal foils. 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 utilising 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, additive manufacturing 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. Production of ferritic steel alloy (FeCrAl alloy) powders, specifically tailored with an optimised particle size, plays a crucial role due to the inherent compatibility of these alloys with washcoating processes. Simultaneously, refinements and advancements in coating methodologies must be harmonised with additive manufacturing technologies to more effectively equip modernisation of catalytic converters. In the future research studies, it is important to investigate strategies for creating adherent porous washcoats on 3D printed metal monoliths.

Acknowledgements

The financial support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) via SFB 1441, Project-ID 426888090 is acknowledged. Moreover, Dr. Maria Casapu is highly appreciated for her valuable inputs and discussions regarding this paper and its scientific relevance.

References

[1] D. Godec, A. Pilipović, T. Breški, J. Ureña, O. Jordá, M. Martínez, J. Gonzalez-Gutierrez, S. Schuschnigg, J. R. Blasco, L. Portolés, Introduction to additive manufacturing, in: A Guide to Additive Manufacturing, Springer International Publishing Cham, 2022, pp. 1–44.

[2] A. Adel, Future of industry 5.0 in society: Human-centric solutions, challenges and prospective research areas, Journal of Cloud Computing 11 (1) (2022) 1–15.

[3] M. Brandt, S. K. Bhargava, An introduction to the world of additive manufacturing, in: Additive Manufacturing for Chemical Sciences and Engineering, Springer, 2022, pp. 1–18.

[4] M. Van der Hoeven, Y. Kobayashi, R. Diercks, Technology roadmap: Energy and ghg reductions in the chemical industry via catalytic processes, International Energy Agency: Paris 56 (2013).

[5] n. S. u. V. Bundesministerium für Umwelt, Naturschutz, First general administrative regulation pertaining the federal immission control act, accessed: 2023-03-14.
URL `https://www.bmu.bund.de/fileadmin/Daten_BMU/Download_PDF/Luft/taluft_engl.pdf`

[6] C. Kellermann, H. Schweinberger, B. Auler, Innovative solutions for the use of catalytic converters in hand-held engine-powered equipment under severe conditions, Tech. rep., SAE Technical Paper (2006).

[7] EU, Consolidated text: Directive 97/68/ec of the european parliament and of the council of 16 december 1997 on the approximation of the laws of the member states relating to measures against the emission of gaseous and particulate pollutants from internal combustion engines to be installed in non-road mobile machinery, accessed: 2023-07-14.
URL `https://eur-lex.europa.eu/eli/dir/1997/68/2017-01-01`

[8] O. Deutschmann, J.-D. Grunwaldt, Exhaust gas aftertreatment in mobile systems: status, challenges, and perspectives, Chemie Ingenieur Technik 85 (5) (2013) 595–617.

[9] S. Mehla, R. D. Gudi, D. Mandaliya, T. Hisatomi, K. Domen, S. K. Bhargava, Additive manufacturing as the future of green chemical engineering, in: Additive Manufacturing for Chemical Sciences and Engineering, Springer, 2022, pp. 239–307.
[10] P. Losch, Synthesis and characterisation of zeolites, their application in catalysis and subsequent rationalisation: methanol-to-olefins (mto) process with designed zsm-5 zeolites, Ph.D. thesis, Université de Strasbourg (2016).
[11] C. Parra-Cabrera, C. Achille, S. Kuhn, R. Ameloot, 3d printing in chemical engineering and catalytic technology: structured catalysts, mixers and reactors, Chemical Society Reviews 47 (1) (2018) 209–230.
[12] R. Knitter, M. A. Liauw, Ceramic microreactors for heterogeneously catalysed gas-phase reactions, Lab on a Chip 4 (4) (2004) 378–383.
[13] J. Wortman, V. O. Igenegbai, R. Almallahi, A. H. Motagamwala, S. Linic, Optimizing hierarchical membrane/catalyst systems for oxidative coupling of methane using additive manufacturing, Nature Materials (2023) 1–8.
[14] ec.europa.eu, 7-1_formaldehyde_cas 50-00-0, accessed: 2023-03-14.
URL `https://ec.europa.eu/docsroom/documents/30861/attachments/39/translations/en/renditions/native`
[15] B. Torkashvand, L. Maier, M. Hettel, T. Schedlbauer, J.-D. Grunwaldt, O. Deutschmann, On the challenges and constrains of ultra-low emission limits: Formaldehyde oxidation in catalytic sinusoidal-shaped channels, Chemical Engineering Science 195 (2019) 841–850.
[16] R. Zhao, H. Wang, D. Zhao, R. Liu, S. Liu, J. Fu, Y. Zhang, H. Ding, Review on catalytic oxidation of vocs at ambient temperature, International Journal of Molecular Sciences 23 (22) (2022) 13739.
[17] J. Spengler, S. Ludwig, R. Weker, Ozone exposures during trans-continental and trans-pacific flights, Indoor Air 14 (2004) 67–73.
[18] E. Terrenoire, D. A. Hauglustaine, Y. Cohen, A. Cozic, R. Valorso, F. Lefèvre, S. Matthes, Impact of present and future aircraft no x and aerosol emissions on atmospheric composition and associated direct radiative forcing of climate, Atmospheric Chemistry and Physics 22 (18) (2022) 11987–12023.
[19] C. Y. Chaparro-Garnica, P. Jorda-Faus, E. Bailon-Garcia, R. Ocampo-Perez, C. G. Aguilar-Madera, A. Davo-Quinonero, D. Lozano-Castello, A. Bueno-Lopez, Customizable heterogeneous catalysts: non-channeled advanced monolithic supports manufactured by 3d-printing for improved active phase coating performance, ACS Applied Materials & Interfaces 12 (49) (2020) 54573–54584.
[20] J.-D. Grunwaldt, J. B. Wagner, R. E. Dunin-Borkowski, Imaging catalysts at work: a hierarchical approach from the macro-to the meso-and nano-scale, ChemCatChem 5 (1) (2013) 62–80.
[21] S. Govender, H. B. Friedrich, Monoliths: a review of the basics, preparation methods and their relevance to oxidation, Catalysts 7 (2) (2017) 62.
[22] P. Avila, M. Montes, E. E. Miró, Monolithic reactors for environmental applications: A review on preparation technologies, Chemical Engineering Journal 109 (1-3) (2005) 11–36.
[23] G. Hofmann, A. Rochet, E. Ogel, M. Casapu, S. Ritter, M. Ogurreck, J.-D. Grunwaldt, Aging of a pt/al 2 o 3 exhaust gas catalyst monitored by quasi in situ x-ray micro computed tomography, RSC Advances 5 (9) (2015) 6893–6905.
[24] S. Irandoust, B. Andersson, Monolithic catalysts for nonautomobile applications, Catalysis Reviews Science and Engineering 30 (3) (1988) 341–392.
[25] M. Camerucci, G. Urretavizcaya, M. Castro, A. Cavalieri, Electrical properties and thermal expansion of cordierite and cordierite-mullite materials, Journal of the European Ceramic Society 21 (16) (2001) 2917–2923.
[26] M. Awano, H. Takagi, Y. Kuwahara, Grinding effects on the synthesis and sintering of cordierite, Journal of the American Ceramic Society 75 (9) (1992) 2535–2540.
[27] L. Li, Preparation and properties of cordierite ceramics obtained via a pouring-sintering method, Integrated Ferroelectrics 215 (1) (2021) 103–115.
[28] M. R. SHAHBAAZ, Belgaum, karnataka-590018, Ph.D. thesis, Visvesvaraya Technological University (2018).

[29] S. T. Gulati, R. D. Sweet, Strength and deformation behavior of cordierite substrates from 70 to 2550 f, SAE transactions (1990) 102–107.
[30] R. Prasad, L. a. kennedy, and e. ruckenstein, Catal. Rev. Sci. Eng 26 (1) (1984) 1.
[31] J. Cairns, R. Nelson, G. Acres, The evolution of fecralloy® steel-based catalysts, International Journal of Materials in Engineering Applications 1 (3) (1979) 162–166.
[32] J. Schmidt, A. Waltner, G. Loose, A. Hirschmann, A. Wirth, W. Mueller, J. Van den Tillaart, L. Mussmann, D. Lindner, J. Gieshoff, et al., The impact of high cell density ceramic substrates and washcoat properties on the catalytic activity of three way catalysts, SAE transactions (1999) 179–189.
[33] E. Kritsanaviparkporn, F. M. Baena-Moreno, T. Reina, Catalytic converters for vehicle exhaust: Fundamental aspects and technology overview for newcomers to the field, Chemistry 3 (2) (2021) 630–646.
[34] R. M. Heck, R. J. Farrauto, Automobile exhaust catalysts, Applied Catalysis A: General 221 (1-2) (2001) 443–457.
[35] A. Fornalczyk, J. Cebulski, M. Saternus, J. Willner, Possibilities of platinum recovery from metal supported spent auto catalysts, Metalurgija 53 (4) (2014) 609–612.
[36] R. Hayes, B. Liu, R. Moxom, M. Votsmeier, The effect of washcoat geometry on mass transfer in monolith reactors, Chemical Engineering Science 59 (15) (2004) 3169–3181.
[37] R. Pesic, A. Davinić, S. Petković, D. Taranovic, D. Miloradović, Aspects of volumetric efficiency measurement for reciprocating engines (2013).
[38] W. A. Majewski, Cellular monolith substrates, accessed: 2023-07-19 (2023).
URL `https://dieselnet.com/tech/cat_substrate.php`
[39] I. Cornejo, G. Garreton, R. E. Hayes, On the use of dual cell density monoliths, Catalysts 11 (9) (2021) 1075.
[40] C. Reinao, I. Cornejo, A model for the flow distribution in dual cell density monoliths, Processes 11 (3) (2023) 827.
[41] DiselNet, Toyota, denso introduce catalyst substrate with dual cell density, accessed: 2023-07-19 (2023).
URL `https://dieselnet.com/news/2017/02toyota.php`
[42] F. C. Patcas, G. I. Garrido, B. Kraushaar-Czarnetzki, Co oxidation over structured carriers: A comparison of ceramic foams, honeycombs and beads, Chemical Engineering Science 62 (15) (2007) 3984–3990.
[43] M. Presti, L. Pace, W. Müller, O. Witte-Merl, Vehicle mass lightening by design of light-weight structured substrates for catalytic converters, Tech. rep., SAE Technical Paper (2011).
[44] Z. M. Research, Global catalytic converter market to grow to around usd 76.7 billion by 2030, accessed: 2023-01-12 (2023).
URL `https://www.zionmarketresearch.com/news/global-catalytic-converter-market`
[45] G. Bozzano, F. Manenti, Efficient methanol synthesis: Perspectives, technologies and optimization strategies, Progress in Energy and Combustion Science 56 (2016) 71–105.
[46] A. Zupanc, J. Install, M. Jereb, T. Repo, Sustainable and selective modern methods of noble metal recycling, Angewandte Chemie International Edition 62 (5) (2023) e202214453.
[47] F. Lettner, H. Timmerer, P. Haselbacher, Deliverable 8: Biomass gasification–state of the art description, Guideline for safe and eco-friendly biomass gasificafion (2007).
[48] T. Murtonen, N. Nylund, Fuel effects on emissions from non-road engines (2003).
[49] P. Prashanth, R. L. Speth, S. D. Eastham, J. S. Sabnis, S. R. Barrett, Post-combustion emissions control in aero-gas turbine engines, Energy & Environmental Science 14 (2) (2021) 916–930.
[50] T. D. Ngo, A. Kashani, G. Imbalzano, K. T. Nguyen, D. Hui, Additive manufacturing (3d printing): A review of materials, methods, applications and challenges, Composites Part B: Engineering 143 (2018) 172–196.
[51] S. Kim, D. H. Kim, W. Kim, Y. T. Cho, N. X. Fang, Additive manufacturing of functional microarchitected reactors for energy, environmental, and biological applications, International Journal of Precision Engineering and Manufacturing-Green Technology 8 (2021) 303–326.

[52] T. Van Gerven, A. Stankiewicz, Structure, energy, synergy, time - the fundamentals of process intensification, Industrial & engineering chemistry research 48 (5) (2009) 2465–2474.
[53] O. Laguna, P. Lietor, F. I. Godino, F. Corpas-Iglesias, A review on additive manufacturing and materials for catalytic applications: Milestones, key concepts, advances and perspectives, Materials & Design 208 (2021) 109927.
[54] A. Rogolino, G. Savio, Trends in additively manufactured microfluidics, microreactors and catalytic materials, Materials Advances 2 (3) (2021) 845–855.
[55] M. Bracconi, Intensification of catalytic reactors: A synergic effort of multiscale modeling, machine learning and additive manufacturing, Chemical Engineering and Processing-Process Intensification 181 (2022) 109148.
[56] M. Kramer, M. McKelvie, M. Watson, Additive manufacturing of catalyst substrates for steam–methane reforming, Journal of Materials Engineering and Performance 27 (2018) 21–31.
[57] G. J. Lim, Y. Wu, B. B. Shah, J. J. Koh, C. K. Liu, D. Zhao, A. K. Cheetham, J. Wang, J. Ding, 3d-printing of pure metal–organic framework monoliths, ACS Materials Letters 1 (1) (2019) 147–153.
[58] O. A. Alimi, C. A. Akinnawo, R. Meijboom, Monolith catalyst design via 3d printing: a reusable support for modern palladium-catalyzed cross-coupling reactions, New Journal of Chemistry 44 (43) (2020) 18867–18878.
[59] N. Kovacev, S. Li, S. Zeraati-Rezaei, H. Hemida, A. Tsolakis, K. Essa, Effects of the internal structures of monolith ceramic substrates on thermal and hydraulic properties: additive manufacturing, numerical modelling and experimental testing, The International Journal of Advanced Manufacturing Technology 112 (2021) 1115–1132.
[60] C. R. Tubío, J. Azuaje, L. Escalante, A. Coelho, F. Guitián, E. Sotelo, A. Gil, 3d printing of a heterogeneous copper-based catalyst, Journal of catalysis 334 (2016) 110–115.
[61] A. Quintanilla, J. A. Casas, P. Miranzo, M. I. Osendi, M. Belmonte, 3d-printed fe-doped silicon carbide monolithic catalysts for wet peroxide oxidation processes, Applied Catalysis B: Environmental 235 (2018) 246–255.
[62] C. Zhu, Z. Qi, V. A. Beck, M. Luneau, J. Lattimer, W. Chen, M. A. Worsley, J. Ye, E. B. Duoss, C. M. Spadaccini, et al., Toward digitally controlled catalyst architectures: Hierarchical nanoporous gold via 3d printing, Science advances 4 (8) (2018) eaas9459.
[63] D. P. Parekh, C. Ladd, L. Panich, K. Moussa, M. D. Dickey, 3d printing of liquid metals as fugitive inks for fabrication of 3d microfluidic channels, Lab on a Chip 16 (10) (2016) 1812–1820.
[64] J.-P. Poirier, Creep of crystals: high-temperature deformation processes in metals, ceramics and minerals, Cambridge University Press, 1985.
[65] A. Katz-Demyanetz, V. V. Popov, A. Kovalevsky, D. Safranchik, A. Koptyug, Powder-bed additive manufacturing for aerospace application: Techniques, metallic and metal/ceramic composite materials and trends, Manufacturing review 6 (2019) 5.
[66] A. Järvenpää, D. B. Kim, K. Mäntyjärvi, Metal additive manufacturing, in: Welding of Metallic Materials, Elsevier, 2023, pp. 493–536.
[67] Y. Zhang, L. Wu, X. Guo, S. Kane, Y. Deng, Y.-G. Jung, J.-H. Lee, J. Zhang, Additive manufacturing of metallic materials: a review, Journal of Materials Engineering and Performance 27 (2018) 1–13.
[68] ISO, Iso/astm 52900:2021(en), accessed: 2023-03-14.
URL `https://www.iso.org/obp/ui/#iso:std:iso-astm:52900:ed-2:v1:en`
[69] K. Munir, A. Biesiekierski, C. Wen, Y. Li, Selective laser melting in biomedical manufacturing, Metallic biomaterials processing and medical device manufacturing (2020) 235–269.
[70] C. Tan, K. Zhou, W. Ma, B. Attard, P. Zhang, T. Kuang, Selective laser melting of high-performance pure tungsten: parameter design, densification behavior and mechanical properties, Science and Technology of advanced MaTerialS 19 (1) (2018) 370–380.
[71] S. Solutions, Slm metal powder & material parameters, accessed: 2023-03-14.
URL `https://www.slm-solutions.com/products-and-solutions/powders/`
[72] N. Shamsaei, A. Yadollahi, L. Bian, S. M. Thompson, An overview of direct laser deposition for additive manufacturing; part ii: Mechanical behavior, process parameter optimization and control,

Additive manufacturing 8 (2015) 12–35.
[73] A. Mostafaei, A. M. Elliott, J. E. Barnes, F. Li, W. Tan, C. L. Cramer, P. Nandwana, M. Chmielus, Binder jet 3d printing—process parameters, materials, properties, modeling, and challenges, Progress in Materials Science 119 (2021) 100707.
[74] D. Herzog, V. Seyda, E. Wycisk, C. Emmelmann, Additive manufacturing of metals, Acta Materialia 117 (2016) 371–392.
[75] C. Y. Yap, C. K. Chua, Z. L. Dong, Z. H. Liu, D. Q. Zhang, L. E. Loh, S. L. Sing, Review of selective laser melting: Materials and applications, Applied physics reviews 2 (4) (2015) 041101.
[76] W. M. Tucho, P. Cuvillier, A. Sjolyst-Kverneland, V. Hansen, Microstructure and hardness studies of inconel 718 manufactured by selective laser melting before and after solution heat treatment, Materials Science and Engineering: A 689 (2017) 220–232.
[77] A. Patel, Anesthesia for laser airway surgery, in: Benumof and Hagberg's Airway Management, Elsevier, 2013, pp. 824–858.
[78] J. Bedmar, A. Riquelme, P. Rodrigo, B. Torres, J. Rams, Comparison of different additive manufacturing methods for 316l stainless steel, Materials 14 (21) (2021) 6504.
[79] C. Bernauer, T. Merk, A. Zapata, M. F. Zaeh, Laser metal deposition with coaxial wire feeding for the automated and reliable build-up of solid metal parts, in: Key Engineering Materials, Vol. 926, Trans Tech Publ, 2022, pp. 65–79.
[80] M. Ziaee, N. B. Crane, Binder jetting: A review of process, materials, and methods, Additive Manufacturing 28 (2019) 781–801.
[81] M. Li, W. Du, A. Elwany, Z. Pei, C. Ma, Metal binder jetting additive manufacturing: a literature review, Journal of Manufacturing Science and Engineering 142 (9) (2020).
[82] P. K. Gokuldoss, S. Kolla, J. Eckert, Additive manufacturing processes: Selective laser melting, electron beam melting and binder jetting—selection guidelines, materials 10 (6) (2017) 672.
[83] A. Zocca, P. Colombo, C. M. Gomes, J. Günster, Additive manufacturing of ceramics: issues, potentialities, and opportunities, Journal of the American Ceramic Society 98 (7) (2015) 1983–2001.
[84] L. Yang, H. Miyanaji, Ceramic additive manufacturing: a review of current status and challenges, in: 2017 International Solid Freeform Fabrication Symposium, University of Texas at Austin, 2017.
[85] D. A. Snelling, C. B. Williams, C. T. Suchicital, A. P. Druschitz, Binder jetting advanced ceramics for metal-ceramic composite structures, The International Journal of Advanced Manufacturing Technology 92 (2017) 531–545.
[86] B. Zhao, Research on the application of ceramic 3d printing technology, in: Journal of Physics: Conference Series, Vol. 1827, IOP Publishing, 2021, p. 012057.
[87] A. W. Hashmi, H. S. Mali, A. Meena, Improving the surface characteristics of additively manufactured parts: A review, Materials Today: Proceedings (2021).
[88] A. Charles, A. Elkaseer, U. Paggi, L. Thijs, V. Hagenmeyer, S. Scholz, Down-facing surfaces in laser powder bed fusion of ti6al4v: Effect of dross formation on dimensional accuracy and surface texture, Additive Manufacturing 46 (2021) 102148.
[89] W. Wang, S. Zhao, X. Tang, C. Chen, H. Yi, Stainless steel catalyst for air pollution control: structure, properties, and activity, Environmental Science and Pollution Research 29 (37) (2022) 55367–55399.
[90] L. Xolo, P. Moleko-Boyce, H. Makelane, N. Faleni, Z. R. Tshentu, Status of recovery of strategic metals from spent secondary products, Minerals 11 (7) (2021) 673.
[91] L. NiWire Industries Co., Metallic vs ceramic catalytic converters, accessed: 2024-01-20 (2024). URL `https://www.niwire.com/metallic-vs-ceramic-catalytic-converters/`
[92] L. Almeida, F. Echave, O. Sanz, M. Centeno, J. Odriozola, M. Montes, Washcoating of metallic monoliths and microchannel reactors, in: Studies in surface science and catalysis, Vol. 175, Elsevier, 2010, pp. 25–33.
[93] J. Butt, Exploring the interrelationship between additive manufacturing and industry 4.0, Designs 4 (2) (2020) 13.
[94] G. Towler, R. Sinnott, Chemical engineering design: principles, practice and economics of plant and process design, Butterworth-Heinemann, 2021.

[95] F. Grinschek, A. Charles, A. Elkaseer, C. Klahn, S. G. Scholz, R. Dittmeyer, Gas-tight means zero defects-design considerations for thin-walled fluidic devices with overhangs by laser powder bed fusion, Materials & Design 223 (2022) 111174.
[96] B. Blakey-Milner, P. Gradl, G. Snedden, M. Brooks, J. Pitot, E. Lopez, M. Leary, F. Berto, A. du Plessis, Metal additive manufacturing in aerospace: A review, Materials & Design 209 (2021) 110008.
[97] S. A. Niknam, M. Mortazavi, D. Li, Additively manufactured heat exchangers: a review on opportunities and challenges, The International Journal of Advanced Manufacturing Technology 112 (3) (2021) 601–618.
[98] J. Miao, Q. Zhong, Q. Zhao, X. Zhao, Spacecraft thermal control technologies, Springer, 2021.
[99] I. Kaur, P. Singh, State-of-the-art in heat exchanger additive manufacturing, International Journal of Heat and Mass Transfer 178 (2021) 121600.
[100] A. du Plessis, S. M. J. Razavi, M. Benedetti, S. Murchio, M. Leary, M. Watson, D. Bhate, F. Berto, Properties and applications of additively manufactured metallic cellular materials: A review, Progress in Materials Science (2021) 100918.
[101] D. Schuhmann, G. Pinto, M. Merkel, D. K. Harrison, A study on additive manufacturing of metal components for mobility in the area of after-sales with spare and performance parts, Vehicles 4 (4) (2022) 957–977.
[102] A. L. Evans, Design and testing of the cubesat form factor thermal control louvers, in: SmallSat Conference, no. GSFC-E-DAA-TN69063, 2019.
[103] S. Bagheri, Y. Huang, P. Walker, J. Zhou, N. Surawski, Strategies for improving the emission performance of hybrid electric vehicles, Science of The Total Environment 771 (2021) 144901.
[104] A. Pridemore, K. Hampshire, R. German, J. Fons, A. Unterstaller, A. Reichel, A. Lukewille, E. Peris, M. Jozwicka, M. Adams, et al., Electric vehicles from life cycle and circular economy perspectives, European Environment Agency: Copenhagen, Denmark (2018).
[105] energy5, The latest catalytic converter technology for electric cars: Overview, accessed: 2023-07-08 (2023).
URL https://energy5.com/the-latest-catalytic-converter-technology-for-electric-cars-overview
[106] T. Adamová, J. Hradeckỳ, M. Pánek, Volatile organic compounds (vocs) from wood and wood-based panels: Methods for evaluation, potential health risks, and mitigation, Polymers 12 (10) (2020) 2289.
[107] W. Liu, S. Wang, R. Cui, Z. Song, X. Zhang, Enhancement of catalytic combustion of toluene over cumnox hollow spheres prepared by oxidation method, Microporous and Mesoporous Materials 326 (2021) 111370.
[108] H.-S. Kim, H.-J. Kim, J.-H. Kim, J.-H. Kim, S.-H. Kang, J.-H. Ryu, N.-K. Park, D.-S. Yun, J.-W. Bae, Noble-metal-based catalytic oxidation technology trends for volatile organic compound (voc) removal, Catalysts 12 (1) (2022) 63.
[109] B. I. Stefanov, D. Lebrun, A. Mattsson, C. G. Granqvist, L. Osterlund, Demonstrating online monitoring of air pollutant photodegradation in a 3d printed gas-phase photocatalysis reactor, Journal of Chemical Education 92 (4) (2015) 678–682.
[110] S. Lawson, X. Li, H. Thakkar, A. A. Rownaghi, F. Rezaei, Recent advances in 3d printing of structured materials for adsorption and catalysis applications, Chemical Reviews 121 (10) (2021) 6246–6291.
[111] S. Haase, P. Tolvanen, V. Russo, Process intensification in chemical reaction engineering, Processes 10 (1) (2022) 99.
[112] J. Lefevere, S. Mullens, V. Meynen, The impact of formulation and 3d-printing on the catalytic properties of zsm-5 zeolite, Chemical Engineering Journal 349 (2018) 260–268.
[113] J. Yao, F. Dong, X. Xu, M. Wen, Z. Ji, H. Feng, X. Wang, Z. Tang, Rational design and construction of monolithic ordered mesoporous co3o4@ sio2 catalyst by a novel 3d printed technology for catalytic oxidation of toluene, ACS Applied Materials & Interfaces 14 (19) (2022) 22170–22185.
[114] Y. Xi, F. Dong, Z. Ji, Z. Tang, J. Zhang, Design order macro-meso porous structure monolithic co3o4/sio2 catalyst via a novel 3d printing for the highly efficient catalytic combustion of toluene, Journal of Cleaner Production 379 (2022) 134694.

[115] S. Hajimirzaee, A. M. Doyle, 3d printed catalytic converters with enhanced activity for low-temperature methane oxidation in dual-fuel engines, Fuel 274 (2020) 117848.

[116] B. Sun, T. Bhatelia, R. P. Utikar, G. M. Evans, V. K. Pareek, Hydrodynamics of a novel 3d printed structured packing–spiropak, Chemical Engineering and Processing-Process Intensification 167 (2021) 108533.

[117] K.-i. Fujimoto, F. H. Ribeiro, M. Avalos-Borja, E. Iglesia, Structure and reactivity of pdox/zro2catalysts for methane oxidation at low temperatures, Journal of Catalysis 179 (2) (1998) 431–442.

[118] C. Klahn, M. Meboldt, F. Fontana, B. Leutenecker-Twelsiek, J. Jansen, et al., Entwicklung und konstruktion für die additive fertigung, Grundlagen und Methoden für den Einsatz in industriellen Endkundenprodukten 1 (2018).

[119] M. L. Rodriguez, L. E. Cadus, Mass transfer limitations in a monolithic reactor for the catalytic oxidation of ethanol, Chemical Engineering Science 143 (2016) 305–313.

[120] Y. Xiong, A. G. Dharmawan, Y. Tang, S. Foong, G. S. Soh, D. W. Rosen, A knowledge-based process planning framework for wire arc additive manufacturing, Advanced Engineering Informatics 45 (2020) 101135.

[121] J. N. Armor, Environmental catalysis, Applied Catalysis B: Environmental 1 (4) (1992) 221–256.

[122] W. Schlenker, W. R. Walker, Airports, air pollution, and contemporaneous health, The Review of Economic Studies 83 (2) (2016) 768–809.

[123] L. E. Teoh, H. L. Khoo, Green air transport system: An overview of issues, strategies and challenges, KSCE Journal of Civil Engineering 20 (3) (2016) 1040–1052.

[124] BASF, Deoxo™ ozone and ozone/voc converters, accessed: 2023-09-18.
URL `https://zenodo.org/record/4464556/files/ACA2019_Leung.pdf`

[125] F. Mayer, R. Fox, D. Space, A. Bezold, P. Wargocki, Iaq in commercial air transportation, in: Handbook of Indoor Air Quality, Springer, 2022, pp. 1–38.

[126] S. C. Joshi, A. A. Sheikh, 3d printing in aerospace and its long-term sustainability, Virtual and Physical Prototyping 10 (4) (2015) 175–185.

[127] P. Patel, F. Defersha, S. Yang, Resilience analysis of additive manufacturing-enabled supply chains: an exploratory study, Frontiers in Manufacturing Technology 6.

[128] S. Massari, M. Ruberti, Rare earth elements as critical raw materials: Focus on international markets and future strategies, Resources Policy 38 (1) (2013) 36–43.

[129] S. Schmidheiny, F. J. Zorraquin, Financing change: the financial community, eco-efficiency, and sustainable development, MIT press, 1998.

[130] V. Shanmugam, O. Das, R. E. Neisiany, K. Babu, S. Singh, M. S. Hedenqvist, F. Berto, S. Ramakrishna, Polymer recycling in additive manufacturing: an opportunity for the circular economy, Materials Circular Economy 2 (1) (2020) 1–11.

[131] M. Javaid, A. Haleem, R. P. Singh, R. Suman, S. Rab, Role of additive manufacturing applications towards environmental sustainability, Advanced Industrial and Engineering Polymer Research 4 (4) (2021) 312–322.

[132] M. K. Niaki, S. A. Torabi, F. Nonino, Why manufacturers adopt additive manufacturing technologies: The role of sustainability, Journal of cleaner production 222 (2019) 381–392.

[133] N. E. Gorji, R. O'Connor, A. Mussatto, M. Snelgrove, P. M. González, D. Brabazon, Recyclability of stainless steel (316 l) powder within the additive manufacturing process, Materialia 8 (2019) 100489.

[134] M. Kumar, M. Mani, Sustainability assessment in manufacturing: perspectives, challenges, and solutions, in: Sustainable Manufacturing, Elsevier, 2021, pp. 287–311.

[135] N. Gupta, C. Weber, S. Newsome, Additive manufacturing: status and opportunities, Science and Technology Policy Institute, Washington (2012).

[136] S. Fox, Third wave do-it-yourself (diy): Potential for prosumption, innovation, and entrepreneurship by local populations in regions without industrial manufacturing infrastructure, Technology in Society 39 (2014) 18–30.

[137] J. Sarkis, M. J. Cohen, P. Dewick, P. Schröder, A brave new world: Lessons from the covid-19 pandemic

for transitioning to sustainable supply and production, Resources, Conservation and Recycling 159 (2020) 104894.
[138] M. Faisal, Y. Atsuta, H. Daimon, K. Fujie, Recovery of precious metals from spent automobile catalytic converters using supercritical carbon dioxide, Asia-Pacific Journal of Chemical Engineering 3 (4) (2008) 364–367.
[139] A. Fornalczyk, Industrial catalysts as a source of valuable metals, Journal of Achievements in Materials and Manufacturing Engineering 55 (2) (2012) 864–869.
[140] S. D. Zondag, D. Mazzarella, T. Noël, Scale-up of photochemical reactions: Transitioning from lab scale to industrial production, Annual Review of Chemical and Biomolecular Engineering 14 (2023) 283–300.
[141] A. Coker, C. Kayode, Chapter thirteen—scale-up in reactor design, Modeling of chemical kinetics and reactor design. Gulf Professional Publishing, Woburn (2001) 1034–1081.
[142] A. Charles, M. Salem, M. Moshiri, A. Elkaseer, S. G. Scholz, In-process digital monitoring of additive manufacturing: Proposed machine learning approach and potential implications on sustainability, in: Sustainable Design and Manufacturing 2020: Proceedings of the 7th International Conference on Sustainable Design and Manufacturing (KES-SDM 2020), Springer, 2020, pp. 297–306.
[143] L. R. Rosseau, V. Middelkoop, H. A. Willemsen, I. Roghair, M. van Sint Annaland, Review on additive manufacturing of catalysts and sorbents and the potential for process intensification, Frontiers in Chemical Engineering 4 (2022) 834547.
[144] G. Donati, R. Paludetto, Scale up of chemical reactors, Catalysis today 34 (3) (1997) 483–534.
[145] A. K. Coker, Modeling of chemical kinetics and reactor design, Gulf Professional Publishing, 2001.
[146] T. Haakana, E. Kolehmainen, I. Turunen, J.-P. Mikkola, T. Salmi, The development of monolith reactors: general strategy with a case study, Chemical engineering science 59 (22-23) (2004) 5629–5635.
[147] C. A. Grande, T. Didriksen, Production of customized reactors by 3d printing for corrosive and exothermic reactions, Industrial & Engineering Chemistry Research 60 (46) (2021) 16720–16727.
[148] P. J. Kitson, R. J. Marshall, D. Long, R. S. Forgan, L. Cronin, 3d printed high-throughput hydrothermal reactionware for discovery, optimization, and scale-up, Angewandte Chemie 126 (47) (2014) 12937–12942.
[149] D. S. D. C. R. Engineering, Roadmap chemical reaction engineering, accessed: 2024-01-25 (2023). URL `https://dechema.de/dechema_media/Downloads/Positionspapiere/2023+Roadmap+\%E2\%80\%9EChemical+Reaction+Engineering_+engl_-p-20009528.pdf`
[150] W. A. Majewski, Catalytic coating & materials, accessed: 2022-02-15 (2022). URL `https://dieselnet.com/tech/cat_mat.php`
[151] E. Shim, Joining textiles (2013).
[152] M. I. Domínguez, M. A. Centeno, M. Martínez, L. F. Bobadilla, Ó. H. Laguna, J. A. Odriozola, Current scenario and prospects in manufacture strategies for glass, quartz, polymers and metallic microreactors: A comprehensive review, Chemical Engineering Research and Design 171 (2021) 13–35.
[153] M. Nonnenmann, Metal supports for exhaust gas catalysts, SAE transactions (1985) 814–821.
[154] L. He, Y. Fan, L. Luo, J. Bellettre, J. Yue, Preparation of pt/γ-al2o3 catalyst coating in microreactors for catalytic methane combustion, Chemical Engineering Journal 380 (2020) 122424.
[155] R. Balzarotti, C. Cristiani, S. Latorrata, A. Migliavacca, Washcoating of low surface area cerium oxide on complex geometry substrates, Particulate Science and Technology 34 (2) (2016) 184–193.
[156] Q. Zhang, D. Wu, Mechanical stability of monolithic catalysts: The influence mechanism of primer on the washcoat adhesion to the metallic substrates, ChemistrySelect 4 (11) (2019) 3214–3221.
[157] J. Yang, M. Odén, M. P. Johansson-Jõesaar, L. Llanes, Influence of substrate microstructure and surface finish on cracking and delamination response of tin-coated cemented carbides, Wear 352 (2016) 102–111.
[158] A. H. Maamoun, Y. F. Xue, M. A. Elbestawi, S. C. Veldhuis, Effect of selective laser melting process parameters on the quality of al alloy parts: Powder characterization, density, surface roughness, and

dimensional accuracy, Materials 11 (12) (2018) 2343.

[159] J. Žigon, M. Kariž, M. Pavlič, Surface finishing of 3d-printed polymers with selected coatings, Polymers 12 (12) (2020) 2797.

[160] R. K. A. Al-Rub, O. G. AL-KETAN, Catalytic converter substrates comprising triply periodic minimal surfaces, uS Patent 11,286,831 (Mar. 29 2022).

[161] G. H. Jeong, S. Kim, Y. T. Cho, Numerical study of the thermal and fluid behavior of three-dimensional microstructures for efficient catalytic converters, Energies 15 (12) (2022) 4200.

[162] L. L. Trinkies, M. Crone, M. Türk, M. Kraut, R. Dittmeyer, Supercritical deposition of mono-and bimetallic pd and pt on tio2 coated additively manufactured substrates for the application in the direct synthesis of hydrogen peroxide, Chemical Engineering and Processing-Process Intensification 195 (2024) 109618.

[163] L. L. Trinkies, D. Ng, Z. Xie, C. H. Hornung, M. Kraut, R. Dittmeyer, Direct synthesis of hydrogen peroxide at additively manufactured fluid guiding elements as structured catalysts, Chemical Engineering and Processing-Process Intensification 188 (2023) 109353.

[164] F. Agueniou, H. Vidal, J. de Dios López, J. C. Hernández-Garrido, M. A. Cauqui, F. J. Botana, J. J. Calvino, V. V. Galvita, J. M. Gatica, 3d-printing of metallic honeycomb monoliths as a doorway to a new generation of catalytic devices: the ni-based catalysts in methane dry reforming showcase, Catalysis Communications 148 (2021) 106181.