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A review on additive manufacturing and materials for catalytic applications: Milestones, key concepts, advances and perspectives

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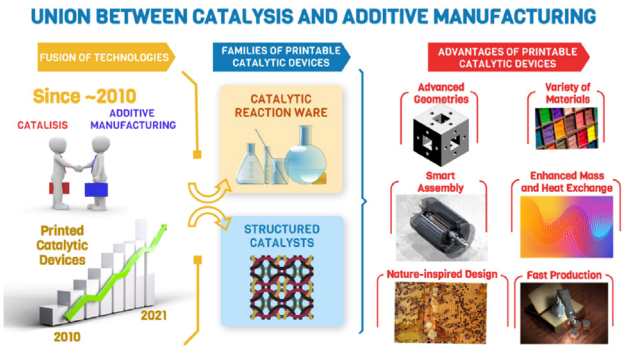
HIGHLIGHTS

- Process intensification: the link for merging catalysis and additive manufacturing.
- Since 2015 patents and scientific papers on this topic grows exponentially.
- Printed devices used in catalysis may be classified in two main families.
- Monoliths (wood-pile configuration) are the most studied printed catalytic devices.
- There is room for improvement in terms of the geometry efficiency of the prints.

GRAPHICAL ABSTRACT



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ABSTRACT

Catalysis, a driving force of the chemical industry is increasingly being influenced by additive manufacturing. The link between them is based on the need to intensify catalytic processes in order to make them more efficient and sustainable. Additive manufacturing can satisfy such a need, generating devices with an advanced design, easy production, and great adaptation, in addition to their catalytic functionality. The exponential growth of examples reported on the application of 3D-printing in catalysis has led to the need to compile and analyse these cases and thus establish, through this review, the most in-depth analysis done to date. The manuscript includes a brief background of the history of additive manufacturing and the classification of the different printing techniques. Subsequently, it identifies the intensification of processes, among other aspects, as the key for understanding the union of additive manufacturing and catalysis. Then, it explores in detail how such a combination occurs, establishing the most comprehensive classification to date between the two large groups of printable devices with catalytic properties. Finally, a series of perspectives are proposed in which the most probable courses of new advances in this field of research are identified.

Contents

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Nomenclature

Abbreviations

Acronym	Meaning
3DFD	3D fibber deposition
ABS	Acrylonitrile butadiene styrene
ASP	Acetoxy-silicone polymer
CDLP	Continuous direct light processing
CLIP	Continuous liquid interface production
CMC	Carboxymethylcellulose
CO-PROX	Preferential oxidation of CO in presence of H_2
D-ABS	Diamond - ABS
DED	Direct Energy Deposition
DIW	Direct ink writing
DLP	Direct light processing
DMLS	Direct metal laser sintering
DOD	Drop on demand
EBAM	Electron beam additive manufacturing
EBM	Electron beam melting
FDM	Fused deposition modeling
FFF	Fused filament fabrication
G-PLA	Graphene - PLA
HIPS	High impact polystyrene
HP	Hewlett-Packard
IPA	Isopropylalcohol
LENS	Laser Engineered Net Shape
MCS-30	MCS-30 activated carbon
MJF	MultiJet Fusion
MOF	Metal-organic framework
MS	Maraging Steel
NAPFFK	Acrylic hydrogelators (NAPFFK-acrylic acid)
NPJ	Nano particle jetting
ONPG	o-Nitrophenyl-beta-D-galactopyranoside
PA12	Polyamide 12
PAD	Prokaryotic phenacrylate decarboxylases
PBF	Powder Bed Fusion
PCL	Polycaprolactone
PDA	Polydiacetylene
PEG-DA	Poly(ethylene glycol) diacrylate
PLA	Polylactic acid
PMMA	Polymethilmetacrylate
PP	Polypropylene
SEBM	Selective electron beam melting
SLA	Stereolithography
SLM	Selective laser melting
SLS	Selective laser sintering
SS (316L)	Stainless steel (316L)
TAR	Transparent acrylic resin
TPGDA	Bisphenol A epoxy acrylate
TPU	Thermoplastic polyurethane

1. Introduction

Catalysis is one of the pillars of the chemical industry that has promoted its evolution since the 20th century, and today new trends are being observed that confirm its modernization. One of them is the application of additive manufacturing, one of the key elements of the new industrial revolution that is taking place today and is known as Industry 4.0. The appearance of additive manufacturing dates back to the 80 s, but its application in catalysis has only begun to be appreciated during the last decade. The growth of pieces of work that address this combination is exponential and this determines the birth of a special field of research, in which there are different strategies to obtain devices with catalytic properties.

For this reason, it is necessary to thoroughly evaluate as much as possible what has been studied to date in order to establish trends in this field, recognize their strengths, weaknesses and future prospects. Furthermore, it is important to identify and define concepts that allow an understanding of the strategies that are followed in order to incorporate additive manufacturing into

catalysis. This is why, the following review has been carried out, which aims to be an important reference to better understand the basis from which this field of research has been created. To achieve this, we start from important previous works [1,2] that have addressed this issue, but in this case, a greater volume of information accumulated after the publication of the aforementioned reviews it is provided, including a large number of patents not analysed until today, which allows to raise other types of perspectives to analyse this topic.

The review starts by a brief summary of the additive manufacturing background, showing in a general way the different types of printing technologies and highlighting which ones are used nowadays to produce devices with application in catalysis. This leads to the question of why catalysis needs additive manufacturing, which will be answered by exploring the key aspects that have motivated such a union.

In this exploration, it will be possible to establish that the main link between these two technologies is the need to incorporate the concept of process intensification into as many catalytic reactions as possible and to be able to take advantage of it at an industrial level. The intensification of processes is highly dependent on aspects such as shape or geometry, dimensions and the type of material from which the catalytic devices are made, and these concepts are addressed from the design. Therefore, if the intensification of processes creates the link between catalysis and manufacturing, design is the tool that consolidates this link because it starts from the needs of catalytic processes and allows the consolidation of solutions through additive manufacturing.

The large number of works cited in this review, including scientific papers and patents, allow to establish diagnoses on the materials and printing technologies most commonly used in the manufacture of devices for catalytic applications. Then, the classification of these types of devices is presented in detail, grouping them into two main families (catalytic reaction ware and printed structured catalysts), which in turn are subdivided depending on the printing strategy. In the case of printed structured catalysts, a classification is proposed that covers everything that has been published to date and can even be applied to future work.

Afterwards, a complementary section devoted to the perspectives on this topic is included. In this section, the innovative items that may positively affect in the near future the synergy between catalysis and additive manufacturing are identified and developed, and finally, a brief summary of the main aspects that can be extracted from the review is presented in the concluding remarks section.

2. General background of additive manufacturing

Additive manufacturing (AM) is a unique manufacturing approach that enables the flexible preparation of highly complex and precise 3D geometries that are difficult to realize using traditional fabrication methods such as casting and machining [3]. For this review, the term additive manufacturing will be used mainly, which is the most appropriate to refer to this manufacturing method according to ASTM (ISO/ASTM 52900:2015). However, it is important to consider that 3D printing or rapid prototyping expressions are often used in the same context, so it is possible that they appear sporadically throughout the document.

During a typical additive manufacturing process, layers of a material (polymer, metal, ceramic or composites) are built up to create a solid object. The structure of the final printed part is achieved by three main stages, which have also been defined in a previous review [1]:

a) The desired 3D geometry first is designed through computer-aided design (CAD)
b) The structure is converted to a G-code file via a slicing program
c) The printer is then prepared using the G-code and the specific material to get the final part [4].

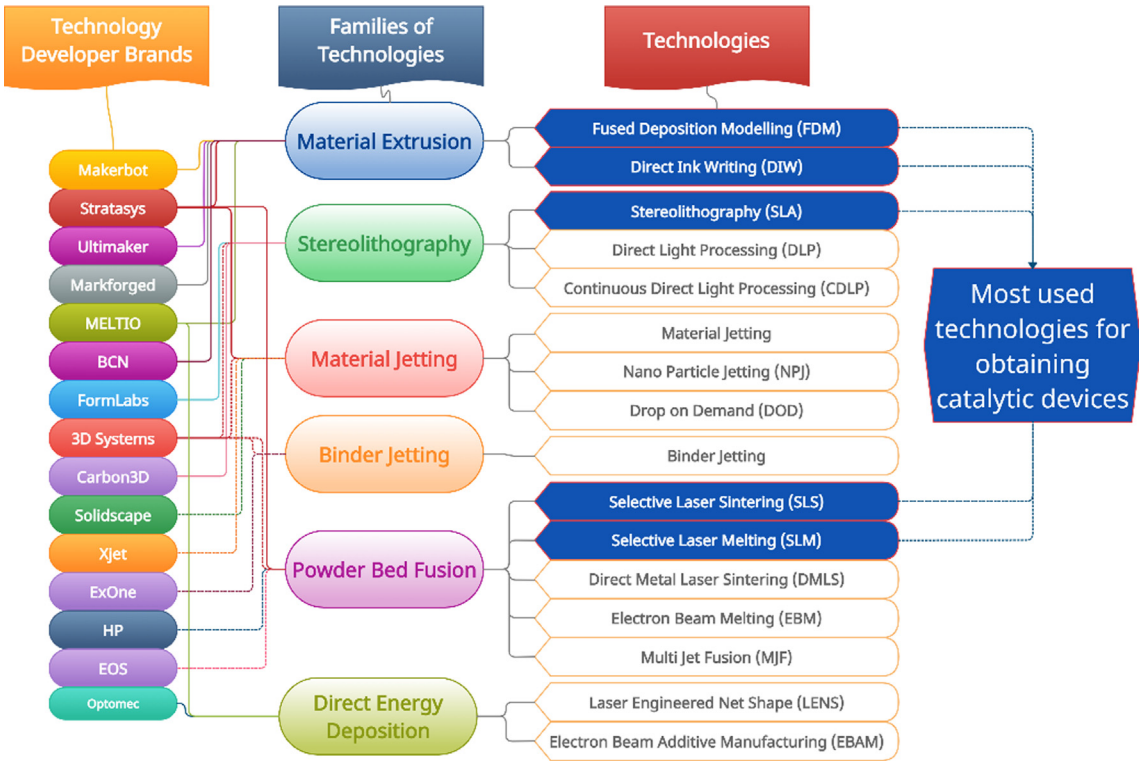

Fig. 1. Additive manufacturing technologies: classification and main technology developer brands.

Besides prototyping, the unique capability of transforming materials into functional devices with specific geometry using additive manufacturing technologies has stimulated a lot of interest in various fields to provide custom-made designs for tailored applications, such as product development, manufacturing aids, final parts amongst others [1]. For this, the main industrial sectors, such as aeronautical, automotive, medical, and also nowadays in the educational field [5,6] remain interested in this new manufacturing method.

Moreover, it should also be noted that the concept of additive manufacturing is framed within the new industrial movement known as Industry 4.0, and that this movement involves a significant transformation regarding the way products are produced thanks to the digitization [7].

The additive manufacturing concept was developed by Kodama in the early 1980's [8]. He was able to generate a complete 3D object from 2D cross sections, successively formed on top of one another, using photohardening polymers and UV light [8,9]. Later, in 1984, Charles Hull patented this technology called stereolithography (SLA) [10], and created 3D Systems®, one of the most recognized additive manufacturing companies worldwide. This technology is growing everyday due to its high accuracy and possibility of obtaining additively manufactured parts of all sizes with a high level of detail that generated interest within the industry and academic fields, since new materials were appearing.

Over the next years, Deckard and Crump patented two new manufacturing technologies based on layer by layer deposition: Selective Laser Sintering (SLS) that uses powders as printable materials [11], and Fused Deposition Modeling (FDM) [12] that uses polymer wire based printable materials.

From these first technologies, in the last 30 years different alternatives have been developed that allow today, to have a wide spectrum of additive manufacturing techniques, which can be classified into six main groups or families of printing techniques schematized in Fig. 1. This classification is based on aspects such as the presentation of the material (filaments, powder or in suspension), the methodology for the consolidation of the layers during printing, or the feeding of the printing material [13–17].

Regarding the applicability of the different additive manufacturing technologies, the field of catalytic processes is not usually included since this scenario is relatively new. However, there is increasing evidence that catalysts or catalytic materials, which are the essence of catalytic processes, may see their manufacture and performance improved by the incorporation of additive manufacturing in their production [2]. This is why it was sought to highlight in a special way in the classification of Fig. 1, what type of techniques are applied in the production of 3D objects applicable in catalysis nowadays.

From the broad classification presented in Fig. 1, it is observable that despite the great versatility that the different manufacturing techniques can offer only some of them seem to be capable of or at least are used in most of the cases for generating 3D objects applicable in catalysis, as will be analyzed in more detail in section 3. Therefore, it is essential to analyze why and how the fusion between catalysis and additive manufacturing occurs, to understand why certain techniques are applied so far and not others.

3. Why does catalysis needs additive manufacturing?

The outstanding evolution of the chemical industry during the 20th century was brought about by a series of relevant geopolitical and global events combined with the most prolific decades in terms of technological advances in the history of man. Consequently, without a doubt, the Heterogeneous Catalysis is a fundamental pillar in the rapid growth of large-scale energy, fuel, chemical and pharmaceutical industries [1]. The development of knowledge on Heterogeneous Catalysis began with a purely empirical approach, but a real understanding of the principles of the catalytic processes began only after the mid-twentieth century. This was thanks, amongst other things, to the discovery of characterization techniques with which to study phenomena on the surface of materials such as infrared spectroscopy or X-ray photoemission spectroscopy (XPS), which in fact motivated the field of study of surface science. At present, the gap between empirical results and their understanding from a theoretical point of view remains important, as was stated by Chorkendorff and Niemantsverdriet (see Fig. 2) [18]. However, the current scenario of a new industrial revolution (Industry 4.0) will surely contribute significantly to reducing this gap, since such a revolution is expected to change the paradigms within many of the traditional productive sectors. Additionally, the essence of this revolution, which is artificial intelligence, favours feedback between practice and theory [19].

Additive manufacturing is one of the pillars of industry 4.0 and its application in catalysis has aroused great interest over the last

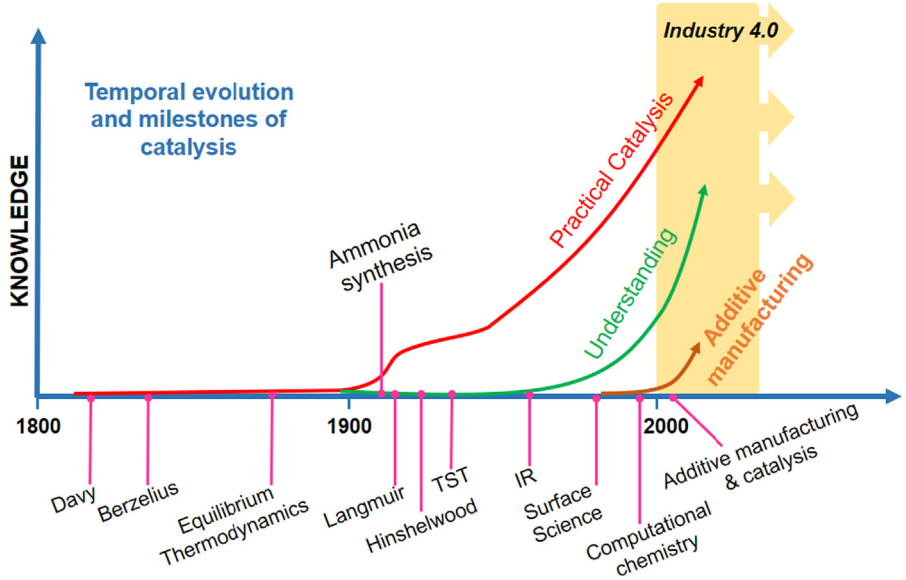

Fig. 2. Gap between knowledge in practical catalysis and theoretical understanding. Adapted from reference.

decade. Thanks to this, you can find very complete reviews [1,2,9,17] that give a detailed overview of a series of very promising applications of additive manufacturing in catalytic systems. However, the growth of this field is such that in 2019 there was a significant increase in work which focused on this theme, with new contributions that could not have been considered in these reviews, and this has opened new horizons in the integration of catalysis and additive manufacturing. This can be confirmed in Fig. 3, where the amount of already published scientific papers per year is presented, based on a bibliographic search using keywords such as *catalysis*, *printed catalysts*, *printed reactors*, *additive manufacturing*, *3D printing*, amongst others.

The search was filtered to include pieces of work that effectively combined additive manufacturing and catalysis, and, even though additive manufacturing emerged in the 1980 s, an exponential growth is clearly observed in the last decade of research in this field as presented in Fig. 3. Therefore, the question arises as to why catalysis needs additive manufacturing. To answer this question, the global context cited above has to be considered again, since the technological revolution scenario (Industry 4.0) that has been highlighted, demands the modernization of industry that must be transformed and adapted to enhance the use of renewable energy sources and find viable and profitable alternatives to oil. This is not only because it is a finite resource, but also because its use as the main source of energy has a considerably negative effect on the environment. Consequently, it has been defined as a priority for the next 30 years to reduce greenhouse gas emissions and thus to begin to slow down the effects of climate change [20,21].

The problem of alternative energy sources is that their efficiency is still low, compared to that of traditional sources, which affects their profitability and thus slows their incorporation into the market. One of the main challenges of industry today, therefore, is to achieve highly energy efficient processes, minimizing the demand for fuel (regardless of its origin) and reducing losses due to dissipation, that is, promoting adiabatic processes in those that maximize the reuse of energy. The concept of reusing energy is in accordance with one of the strategies that has been proposed today to adapt industry to a less polluting scenario. This is to transform the linear productive model into a circular one that maximizes the efficiency with which all resources (not just energy) are used to reduce generation of waste. In this strategy, known as the Circular Economy, the recycling of raw materials is greatly enhanced to reduce the exploitation of resources [22].

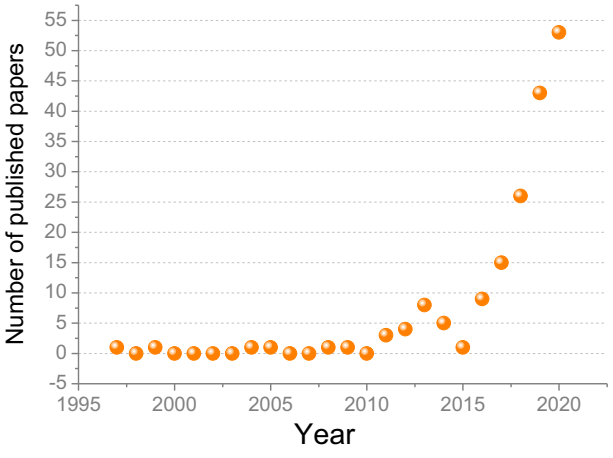

Fig. 3. Search for articles published in the last 25 years where additive manufacturing and catalysis are combined (sources: Web of Science and Scopus / Updated to December 2020).

From the point of view of chemical processes, what is then sought is to produce renewable fuels and value-added products, through sustainable processes, with maximum productivity, thanks to a minimum energy and economic investment, and minimal CO_2 footprint. This is what is known as *process intensification*. In this concept, miniaturization is also one of the main pillars because the smaller the site where the process occurs, the greater the control that can be done on its efficiency and this does not have to assume a reduction in production volume [23]. One of the clearest examples of process intensification is the used of microchannel reactors to carry out processes, both on a laboratory scale [24,25] and on an industrial scale[26]. Microchannel reactors promote both heat and mass transport phenomena thanks to the submillimeter dimensions of their channels, making reactions occur faster, more selectively and with greater energy efficiency, in a very small volume. However, the widespread application of microchannel reactors technology is hampered by the complex design of the reactor, the high fabrication cost, and the low volume of catalyst per unit volume of reactor as was recently highlighted by Konarova et al. [23] The same authors point out, however, that such obstacles could be overcome with the incorporation of additive manufacturing.

The link between catalysis and additive manufacturing as an alternative to the search for process intensification was also established by Parra-Cabrera et al. [2] in their comprehensive review about additive manufacturing technologies applied to chemical engineering and catalysis. They proposed that the foremost opportunities for integrating process intensification and additive manufacturing primarily lie in continuous flow reactions that use heterogeneous catalysts and/or present transport limitations. Then, more complex scenarios of non-isothermal reactions and multi-phase environments would determine the advances in this field [2].

In the case of Hurt et al. [1], who also presented a very complete review, they propose that there is a driving force to implement additive manufacturing in heterogeneous catalysis (although it could well be extrapolated to catalysis in general) based on two fundamental motivations: i) to scale down the reactors as a sustainable approach to producing chemicals on demand on-site. This is based on the fact that miniaturization does not have to mean a decrease in conversion, as demonstrated by Tubío et al. [27] with their printed monoliths with Cu-based catalyst tested in different Ullmann reactions; And ii) secondly, it is necessary to adapt the large scale chemical manufacturing units to a mode of operation that minimizes the environmental impact while maximizing energy efficiency. Despite this being very difficult challenge and one which is considerably expensive, the great versatility that additive manufacturing offers may allow the achievement of the gradual change that large industries require, without this entailing designing and building their facilities from scratch. As can be inferred, these two motivations are in full agreement with the principles of process intensification. Therefore, the idea that additive manufacturing can bring multiple benefits to the chemical industry through its integration with catalysis is clear.

4. How can catalysis and additive manufacturing be integrated?

There is no defined strategy for the integration of catalysis and additive manufacturing. In fact, this depends on several aspects such as the principles of the printing method, the nature of the printing materials, the conditions in which the printed device will be evaluated, the design of the catalytic solution, amongst others. For this, it is reasonable that one of the first reviews on the subject classified the types of catalytic applications according to the additive manufacturing method used [17]. Nevertheless, Parra et al.[2]

introduced two criteria to the classification of the already published works that allowed identification of which of them had focused on the manufacture of reactors and / or mixers and which on obtaining heterogeneous structured catalysts. Hurt et al. [1], presented a first attempt to address the classification of the work depending on the strategy used for the catalysis / additive manufacturing integration, and this classification was made possible by identifying the advantages and challenges of integration. The advantages are mainly those of traditional structured systems (low pressure drops, ease of removal from the reaction medium), maximized by the possibility of designs with advanced shapes. Although, perhaps most interesting is the technological challenges they pointed out. One such challenge is a limited materials palette, since the number of materials that can be used for additive manufacturing as "printable materials" is low compared with the huge number of catalytic processes and this makes it difficult to cater to the specific needs of temperature or solvent compatibilities of different chemical processes [1]. Such limited availability of materials is also exacerbated by the strategy of most of the additive manufacturing providers. This strategy is one of locking their users into using only their own-brand products, making the process more expensive and slowing down the advances on new printable materials. On the other hand, taking into account that the catalytic properties of the printable materials, by themselves, are limited, it is necessary to combine them with real catalysts and the interaction between these two systems (before, during or after printing) can be inefficient or even adversely effect the performance of the catalyst [1].

Moreover, the printing processes often results in solids being made through a layer-by-layer procedure, with this generating solids whose properties tend to be anisotropic since the setting processes to solidify through the union of layers depend on direction[1]. This can be a drawback when the parts are subjected to mechanical stress in an unfavorable direction during consolidation, such as in pressurized reactions. Finally, they pointed out the cases in which the combination of the catalyst with the printable material may have generated a part that is not yet in thermodynamic equilibrium [1]. Therefore, additional treatments are required, generally thermal and / or chemical that do not affect the catalyst and this is somewhat difficult to achieve.

Taking into account the validity of the criteria of the reviews presented up to now to classify the works that combine catalysis and additive manufacturing [1,2,17,28,29], merging them to obtain a more comprehensive diagnosis of the advances in this field it is proposed, including the incorporation of more up-to-date reports. To begin with, the updated statistics in Fig. 4 on the printing methods and materials most used so far in studies that integrate additive manufacturing and catalysis are presented, based on bibliographic research that includes more than a hundred papers from 1997 to present.

A first look at the statistics in Fig. 4 would suggest that there is an acceptable diversification in the number and types of printing methods used, although DIW, FDM, SLA, SLM and SLS are clearly more used than others are. This is why, information about most used materials and the layer thickness is included for these cases. This last parameter is closely related with the resolution of the obtained 3D objects thus as lower the layer thickness higher the resolution. The greater application of these techniques is mainly due to the fact that there is already a certain maturity in their development (both in printing devices and in printable materials) and this is reflected in the market.

Despite this, the supposed increasing diversification of printing methods reaches a bottleneck when analyzing printing materials, because the properties of the different families of systems that can be used for additive manufacturing set the limits of the applicability of the printing. However, there are not as many satisfactorily-tested alternatives as may be assumed, either on the market, or in the scientific scenario. This makes it clear that expanding the range of printable materials is one of the main areas to be developed in additive manufacturing.

Prior to take a general look at the most relevant groups of printing materials that have been used in printing devices for catalytic applications, it is important to highlight the low, medium or high qualitative estimate, which is presented in Fig. 4 for each family of materials of a series of parameters. The first one is Print Tem, that is, the range of temperatures at which the pieces are manufactured and in this case, low means below 250 °C; medium from 250 to 400 °C and high above 400 °C. The second criterion (Difficulty) estimates the complexity of the printing process. The third parameter (Shrinkage) estimates the shrinkage of the final pieces during post-treatment. The fourth (Soluble) estimates how easily the material can be solubilized, but it does not differ whether in an organic solvent or not and finally, the fifth (Work Temp.) Estimates three temperature ranges in which the final pieces of each material are stable. Again low means below 250 °, medium from 250 to 400 °C and high, above 400 °C.

In all cases, the qualitative estimate was built based on the information reported in technical catalogs of each material, combining it with the data extracted from scientific articles in which the use of these materials has been reported to obtain devices with catalytic applications.

The first group of materials is polymeric ones. These are the group most widely used in additive manufacturing since these can be used in extrusion, light polymerization, power bed, and almost all other mainstream printing technologies as stated by Zhou el al.[17]. These may offer a considerable range of properties based on their plasticity and durability. However, their polymeric nature mainly limits their application in thermal processes above 200 °C and their stability in operating environments where there are certain organic solvents. In addition, these materials present low surface areas and poor surface properties, which hinders their incorporation into catalytic solutions regardless of the strategy. One way to overcome such drawbacks is the incorporation of active ingredients into the polymeric matrix aiming to produce hybrid materials such as TiO_2-ABS (presented in Fig. 3B), and this would extend the use of doped polymers in the printing of systems for catalysis. Nevertheless, additives are required for the preservation of the suitable rheology for an accurate printing process, and controlling the effects of those additives is difficult, especially in the nature of the catalyst if those additives are present during the printing process. In addition, the presence of additives may require further treatments after the printing process with the aim of removing possible contaminants that have influence on the activity of the catalytic phase.

In view of the above, the printing of catalysts or catalyst supports using polymeric materials does not appear to be advantageous at all. However, there are other ways to bring additive manufacturing of polymers to the field of catalysis and it is by printing reaction ware with advanced designs that it is possible to facilitate the catalytic process. For this reason, a series of cases in which additive manufacturing has been applied to obtain useful reaction ware for catalytic processes is included, and which will be seen in detail later when specifically at printed reaction ware for catalytic reactions are looked.

Regarding ceramic materials, the number of examples drawn from our review probably seems high. However, what is actually being considered are more or less complex combinations of oxides such as SiO_2, Al_2O_3, CeO_2, ZrO_2 and TiO_2, some of these containing the presence of doping agents, although in low proportion. There are also aluminosilicates such as clays or zeolites and SiC cases. It is true that these materials are also the most widely used systems as supports for powder catalysts. Nevertheless, there are also

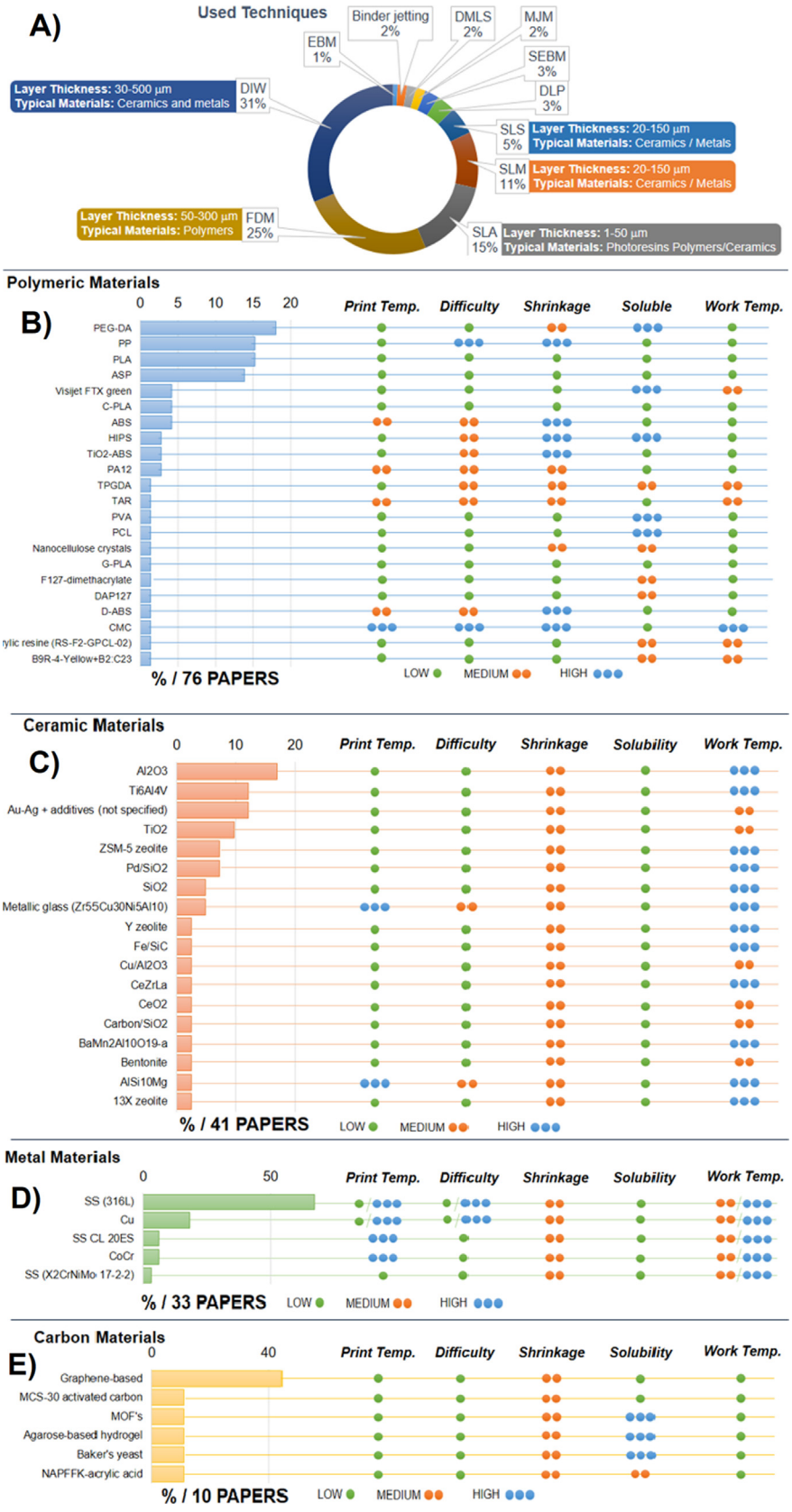

Fig. 4. Additive manufacturing technologies and materials used for the manufacturing of catalytic devices: A) Used technologies; B) Polymeric material including doped formulations, C) Ceramic materials; D) Metal materials; E) Carbon materials, MOF's and bioactive materials.

families of materials such as carbides, nitrides or even oxides of both transition metals and rare earths, which are practically unexplored and which could be studied further to take advantage of their properties in the generation of printed systems with catalytic abilities.

To print with ceramic materials, these must be combined with other organic and inorganic agents (binders) to obtain a printable formulation that meets the appropriate rheological conditions, since reaching the melting temperature of a pure ceramic system (to apply the principle FDM) would require special equipment with injectors capable of working above 1000 °C. Therefore, the prints made of ceramic formulations that include binders, are really raw parts that must be sintered by means of a thermal process. During this type of treatment, the pieces undergo significant changes in their dimensions and their physical and chemical properties can also be altered. Furthermore, these processes make the production of ceramic systems slower and more expensive. In addition, the modification of the dimensions of the prints in the post-treatment of sintering makes the transfer of the digitally designed model not so perfect in reality, generating margins of error in the generation of parts. This is undoubtedly a point that needs improvement when printing with these types of materials.

Although powder-based strategies for ceramic printing are being explored, slurry-based with photopolymerization methods based on the DLP strategy are definitely the most widely used and generate fewer operating costs. However, there are key aspects which still need to be improved, such as the scattering effect of the ceramic material present in the printable formulation that absorbs the incident energy that promotes Photopolymerization, thus decreasing its efficiency and generating heterogeneities in the extension of the printed part. Therefore, the future of this procedure relies on a better understanding of the interaction between the laser and the printing material and how this influences the layer deposition mechanism.

Accordingly, the printing of ceramic systems for catalytic applications with new materials is only a matter of time, given the emerging state of this technological field. In fact, there are already reports of ceramic systems with complex designs and high resolutions, such as those recently reviewed by Chen et al.[30]. In this summary, you can find reports of the additive manufacturing of structured monoliths, scaffolds and parts with materials such as B_4C [31], $CaCO_3$ [32], Al_2O_3 [33], bio-active glass [34,35], Al_2O_3 +-ZrO_2 [32], SiC [36], hydroxyapatite [37], SiO_2 [38], TiO_2 [39], SiCN [40], SiOC [41], Si_3N_4 [42], 3YSZ [43,44], Ti_3SC_2 [45], amongst others. However, the vast majority of these studies focus on the mechanical properties of prints with applications in the engineering field, the generation of biocompatible parts, but not with catalysis. This is, for instance, the case of Al-Ketan et al. [46] that although the title of their work: "additive manufacturing of architected catalytic ceramic substrates" suggests that they deeply analyzed design and production, and studied the mechanical and flow properties of triply periodic minimal surfaces made with ceramic precursors, in fact they omitted to study any catalytic property. This does not mean that the quality of the structured systems obtained is not high. In fact, the high resolution with which they have been able to obtain periodical designs of high complexity (see Fig. 5) is very promising in the field of catalysis with structured systems, since the geometry of the structures plays a crucial role in the transport phenomena during most catalyzed reactions.

There is another way to incorporate additive manufacturing into the generation of ceramic structures and that is to use printed molds with advanced designs, made of polymeric material. The ceramic material is mixed with additives to generate a paste that is embedded within the template and by calcination, the mold material is gasified and the ceramic piece is consolidated. This process is known as indirect printing and has been used in the generation of structured systems for catalytic purposes as in the case of Davo-Quinonero et al.[47] that printed templates of monoliths with a commercial ultraviolet curable polymeric resin (Visijet FTX green), which were subsequently filled by extrusion with a commercial cordierite paste (COR-MIK-MP). The templates were removed by combustion in air at 500 °C for 2 h and then cordierite was sintered in air at 1250 °C for 2 h.

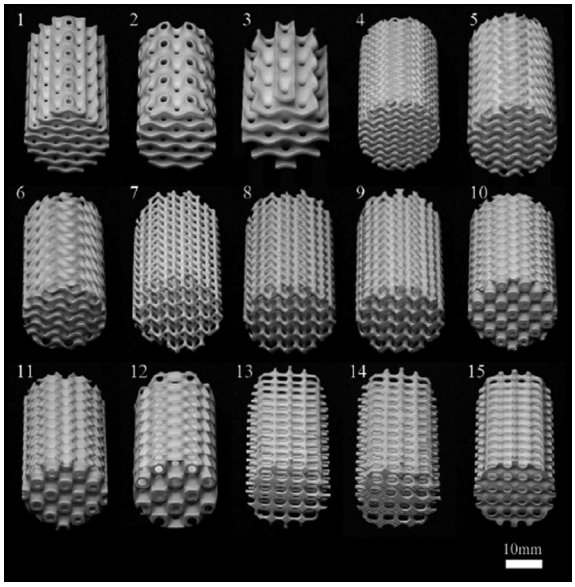

Fig. 5. Additively manufactured ceramic substrates after sintering: 1–3) CLP; 4–6) Gyroid sheet-based with 4, 5, 6 mm cell size and 0.6 mm sheet thickness; 7–9) Gyroid strut-based at different macroporosities; 10–12) Primitive sheet-based with 4, 5, 6 mm cell size and 0.6 mm sheet thickness; 13–15) Primitive strut-based at different macroporosities. Reprinted from reference [46].

As for metals as impression material for catalytic applications, the options found in literature are drastically reduced as can be observed in Fig. 3D. Only some stainless steels (specifically 316L) and copper such as those developed by Danaci et al. [48–50], have been explored in a way to obtain compact catalytic systems and metals such as aluminum, titanium or iron are notable for their absence. This is because metal printing is a major technological challenge due to some disadvantages such as slow build rates, limited component size (restricted by the size of the build chamber), the considerable effort required in application design and for setting process parameters, dimension accuracy, required post-treatment methods such as surface finishing and the stability and quality of the metal used, as summarized by Duda et al. [51]. Up to now, the most widely used approach for printing with metals is the powder-based one. Nevertheless, not all metals (in powder form) behave similarly making some of them not easily printable. Furthermore, the interaction of the laser with the piece may not be homogeneous throughout the process, creating some zones with higher stress than others due to the heterogeneous thermal incidence.

For this reason, alternative routes are being explored such as the development of metal wires to print by means of FDM technologies. However, this implies the mixing of metal with additives, which requires further post-treatment procedures such as those in the case of printing with ceramics. In this case, metal loading is a crucial issue and the main objective is to achieve filaments as rich as possible in metal, in order to minimize the effect of additives on the final finish of the piece. Moreover, new metal printing techniques are also being explored, based on novel principles such as electrochemical 3D metal printing, in which several printing materials can even be combined to generate what is known as

multi-metal 4D printing [52]. The Evolution to 4D occurs by the generation of printed systems capable of changing their shape in response to stimuli such as thermal or acoustic changes, although further developments are required to ensure a mature design and production of 4D objects [53]. The motivation to develop technologies for the printing of metals relies on the fact that in principle, these materials can offer unique functional features, such as high stiffness to weight ratio, heat dissipation and heat transfer control, which could be very useful in catalytic applications, as well as enhanced mechanical energy absorption [54]. Regarding the geometry, although there are some examples of printing structured systems made of metal with complex designs and good resolution [46], systems that have actually been applied in catalysis have basic designs made of stainless steel or copper such as that reported by Danaci et al. [49,50] presented in Fig. 6. Although these exhibited good catalytic performance in reactions such as the CO_2 methanation, the level of resolution and complexity of these sorts of monoliths is clearly improvable, as will be discussed in more detail below.

Carbon materials present inherent advantages such as a high surface area, allotropy, electrical conductivity and chemical stability that make them attractive as catalytic supports and therefore as printing materials [17]. However, given their characteristics, they must be treated in a similar way to ceramic materials because they require additives to generate a matrix with an adequate rheology for the printing process. In this sense, carbon materials are often part of compound matrixes such as that prepared by Regufe et al. [55], which aims to generate a printable material with high CO_2 adsorption/desorption capacity tunable by means of electric field [55]. However, it has to be remarked that the printing of pure carbon-based (graphene-based) structures has also been achieved through the dispersion of the raw material in water or organic solvents to make printing inks for DIW [17,56–58].

Another alternative for obtaining carbon printed materials is the carbonization of thermosetting resins since these materials have a high degree of crosslinking, which can prevent deformation of the prints during the carbonization process. Resorcinol-formaldehyde (R-F) solutions are good example of a pre-polymer solution with the suitable rheological behavior (non-Newtonian fluid with high viscosity) that allows a chain growth reaction that can be controlled in an alkaline medium [17,59]. These pre-polymer solutions can be directly injected through a nozzle following a DIW process, or they could also be embedded in a printed template that determines the shape of the final structure after a carbonization process. This would be achieved using the indirect printing approach described above for the ceramic systems.

Carbon aerogels that have been previously studied as catalytic materials[60], can be also considered for additive manufacturing through a extrusion process. However, special precautions have to be taken to avoid the material drying out during the extrusion as was pointed out by Zhou et al. [17], since the evaporation of the solvent at atmospheric conditions can cause drastic changes in the surface tension of the solvent at the vapor–liquid interface. This may result in the shrinkage of the material and the production of systems with poor mesoporous structure, since mesopores are destroyed during drying. Therefore, the extrusion of the ink directly into a bath of liquid that is immiscible with solvent was proposed by other authors [17]. For instance Zhu et al. [61] reported such a strategy for preparing graphene aerogels with macroscopic architectures where isooctane was used to prevent solvent evaporation during the printing and then, supercritical CO_2 was used to dry the prepared GO gel.

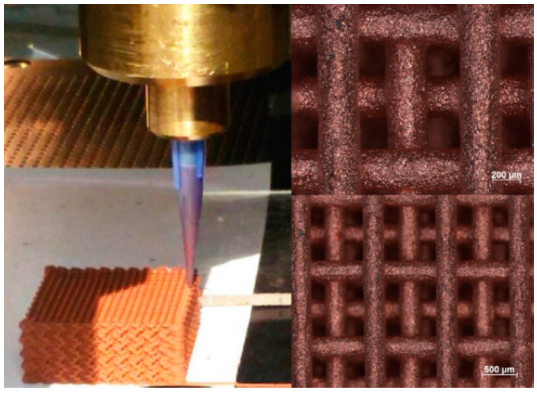

Fig. 6. Additively manufactured structured reactors made with copper for the CO2 methanation. Reprinted from reference [50].

One of the interesting features of carbon is that it can be extracted from renewable sources, such as residual biomass among others. Therefore, the research on the valorization of these raw materials through their transformation into advanced materials is a hot topic. This has motivated, for instance, the use of starch as an interesting material for the production of carbon printed structures. The properties of the starch molecules allow them to be partially dissolved in water, which can be favorable for the extrusion process as was observed by Zhou et al. [17] in a recent study.

Along with carbon materials, bioactive materials have been included in Fig. 3E since there are so few studies in this field. However, the field of printing with bioactive materials (bio-printing) seeks to introduce the advantages of process intensification generating systems with controlled forms to carry out catalytic processes in which the catalysts are enzymes. In this sense, the immobilization of the bio-active species in a structured system, would facilitate their extraction from the reaction medium, which is one of the great challenges in enzymatic processes. Nevertheless, bio-active printing require much more delicate manufacturing and post-treatment conditions than those generated with the materials described so far in order to keep the bio-active agent alive and fully active during the process. Moreover, the resolution of the generated systems is clearly improvable and this will be achieved not only by exploring new printing methods, but also through the use of new additives that allow better control of the printing process without intervening with the properties of the bioactive principle. The most relevant examples of bio-printing for catalytic applications [62,63] will be presented in more detail later.

After discussing the particularities of the families of materials used to print devices with catalytic applications, it can be said that although there are very general aspects that are more or less common for all, additive manufacturing with each of the families of materials should be addressed almost as a separate technology in order to achieve significant breakthroughs in a shorter period of time. This would make it possible to delve into the advances with each type of material more clearly and would broaden the range of printable materials, to focus them specifically on the field of catalysis, where thermal properties, specific area, chemical stability and surface activity are key factors. In this sense, the need to promote the development of new printable materials with fewer restrictions by suppliers, as mentioned above [1], becomes even more important. This does not imply ending the market for printable materials. On the contrary, it could be expanded through greater interaction of 3D technology providers with specialized users so that together they could expand the advanced printable materials that are offered.

Another key aspect to understanding how to integrate catalysis and additive manufacturing is to define which additively manufactured objects can be useful in a catalytic process, both on a laboratory scale and on an industrial scale. Therefore, after a review of what, in our opinion, is everything published to date, not only

different examples will be presented, but also propose their classification into two main groups. The first group is the Catalytic Reaction Ware, which consists of those devices that can aid the catalytic process, but are not necessarily made of or coated with the catalyst. And the second group is that of Structured Catalysts, in which the catalyst can be part of the printing materials of the devices or be integrated with them after printing, through physical and/or chemical processes.

4.1. Printed catalytic reaction ware

There are additively manufactured objects that can aid some catalytic processes, but these objects are not necessarily made or coated with any catalyst [64–84]. Their classification within the family of additively manufactured catalytic reaction ware it is proposed. Within this group it can be found the containers in which the catalytic processes occur are either homogeneous or heterogeneous. These containers can have conventional (generally cylindrical) shapes and serve mainly for batch-type processes. There are also continuous flow reactors with better performance that, if made with typical dimensions of the microreactors (whose characteristics and advantages were previously described), allow the processes to be intensified. However, considering the continuous nature of processes, devices that allow efficient mixing of reagents before the catalytic process occurs are also useful. These are known as mixers and are of interest in both gas and liquid phase processes. There are also mixers on sub-millimeter scales that are studied in the field of microfluidics and their designs can favor the control of the mechanism and the selectivity of some reactions. Moreover, stirrers with special designs are useful, since the mixing regime depends not only on the speed with which they move, but also on the shape they have. Likewise, heat exchangers and / or heaters that are incorporated into a catalytic process are important to guarantee its thermal control.

One of the strongest advantages of additive manufacturing of reaction ware is that it can be done very quickly when compared to the production of laboratory equipment and reactors by conventional methods. In addition, conventional materials for these types of devices such as glass, quartz or steel can be replaced with polymers, ceramics or even printable metals at fairly affordable prices, allowing for the iterative process of design, production, testing, evaluation and redesign to implement improvements with new impressions to be much more agile. This can be decisive in catalytic processes in which the size, shape and material from which the laboratory material is made, can be key to controlling variables such as temperature, pressure, dosage and mixing between reagents, type stirring, phase separation, product separation, and so on. Therefore, it is expected that having laboratory scale 3D printing tools to manufacture laboratory material for catalytic processes will, in the long run, allow advances to be made more quickly, which would allow more complex processes to be tackled more efficiently. One such process is biomass recovery, in which multiple reactions occur simultaneously and it is necessary to seek the promotion of a special way to generate specific products with higher yields.

Another advantage of printed or even partially printed flow reactors, is that they have easier scalability through parallelization as remarked by Parra-Cabrera et al.[2], which cited the case of Adamo et al. [85], who developed a plug-and-play reconfigurable platform to study the continuous-flow Synthesis and formulation of active quantities per day to supply up to thousands of doses, meeting the U.S. Pharmacopeia standards[2,85]. However, Parra-Cabrera et al. highlighted an important fact regarding scale-up reactors, especially in the industrial scenario, because a strategy based only on increasing reactor size and output, will sooner or later encounter the physical problems of transfer of matter and heat that are inherent in the size of the reactors. Therefore the combination of scale-up and scale-out approaches is recom-

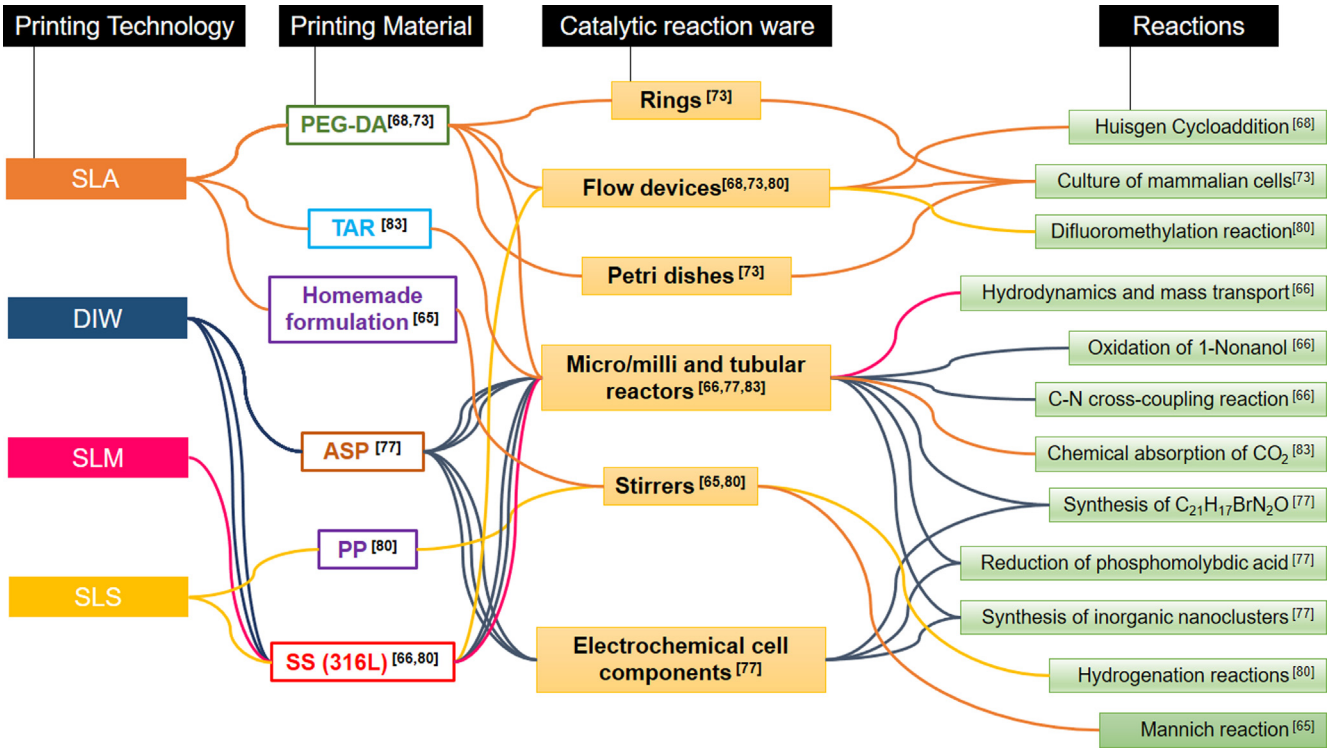

Fig. 7. Graphos diagram that correlates different printing techniques, raw materials, type of catalytic reaction ware and reaction where the devices are used in most cases reported to date.

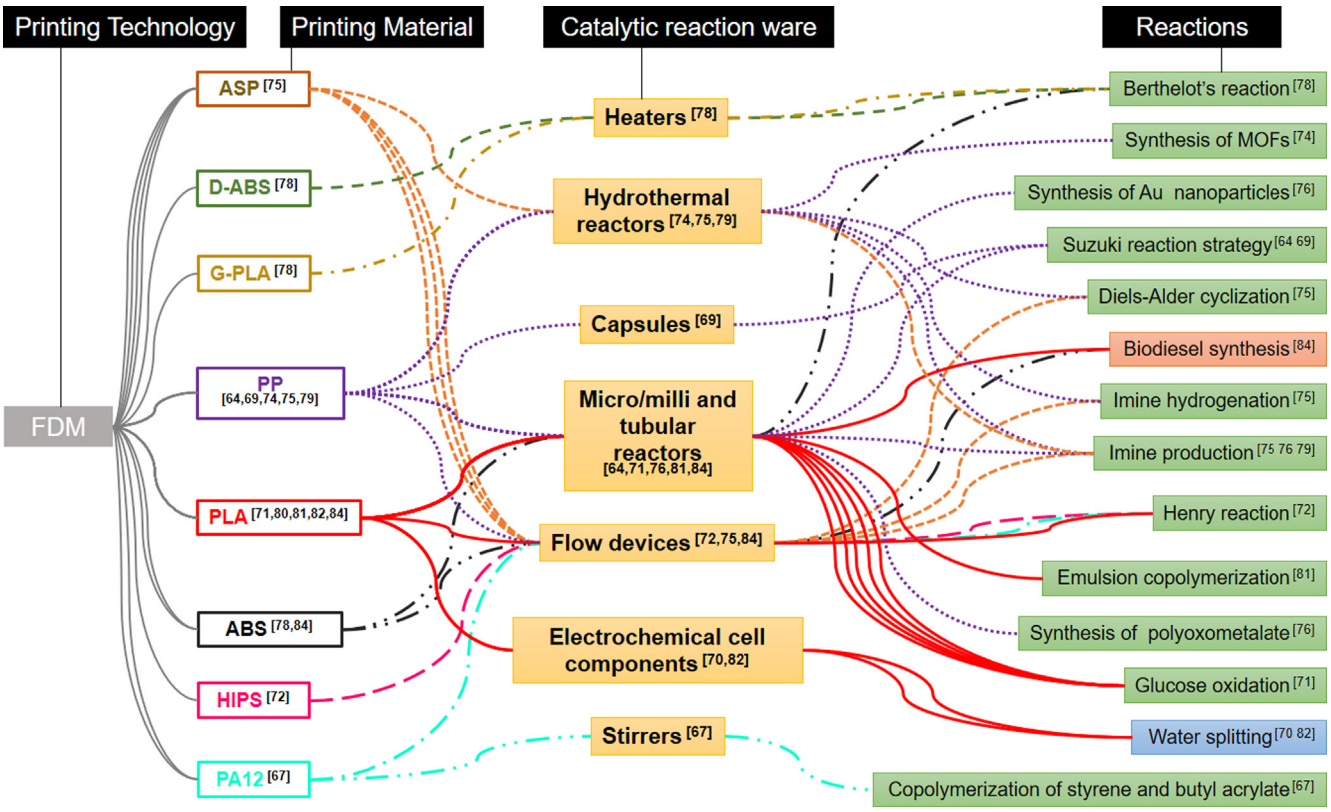

Fig. 8. Graphos diagram that correlates FDM, raw materials, type of catalytic reaction ware and reaction where the devices are used in most cases reported to date.

mended, for instance initially achieving size optimization followed by the numbering up for optimizing the production. This type of procedure can found in additive manufacturing and is the way to implement a greater number of improvements in the prototypes of the reactor to achieve the required optimizations.

Prior to presenting specific examples of catalytic reaction ware classified in the different types of printable devices, it is illustrative to see graphically what type of printing techniques are used and with what materials, as well as what type of reactors are produced and in which reactions they are applied. For this, graphic diagrams are included in Figs. 7 and 8, where the cited variables are correlated simultaneously. Firstly, it is observable that the technology most often used for the production of catalytic reaction ware is FDM. This is why a unique diagram for this printing technique is presented in Fig. 8, since it is the most widely used additive manufacturing technique, thanks to its affordable price, its speed of printing, its considerably wide range of printable materials, its simple maintenance and above all the resolution it achieves in its prints (which varies depending on the materials). In fact, FDM is the technique with which a greater variety of materials have been used (see Fig. 8). The two other most widely-used techniques are DIW and SLA.

Regarding the materials, all the additive manufacturing technologies used up to now are limited to the use of polymeric materials, except in the case of DIW that allows the application of stainless steel, reported in a few examples (see Fig. 7). This implies that the prints are limited to low temperature applications (<180 °C which is usually the limit of some high temperature polymer resins). However, they enjoy the high chemical stability of polymers, which means that they can be used in different reaction environments without great changes in the composition of the impressions. In the graphic diagrams (Figs. 7 and 8) it can be observed that both the PLA and the PP are the most used, which further supports the fact that these materials are in the top 5 of the most used materials in FDM, regardless of the application.

The use of hybrid systems where a typical printing material is doped with other one, as in the case of D-ABS or G-PLA where the common ABS and PLA polymers are combined with diamond or graphene respectively, is remarkable. As was stated above, the introduction of doping agents into the printing materials aims to add further properties or to enhance the existing ones of the bare polymer. Nevertheless, in both cases polymers were the major component of the printing material and therefore what controlled the rheology of the process.

As for the reactions where the catalytic reaction ware is applied, most of them are organic or mixed inorganic–organic reactions that require mild conditions, especially temperature that is in most cases below 200 °C. In addition, the chemical environments they generate do not turn out to be as aggressive with the chemical composition of the printed devices. Nor do they affect (at least not appreciably) their mechanical properties.

Some images of printed catalytic reaction ware, extracted from already published papers are presented in Fig. 9, which allows the identification of the different strategies that researchers are exploring today, and that deal with not only reactors but a series of devices that will be discussed below.

4.1.1. Micro/milli and tubular reactors

Within this group of catalytic reaction ware devices that allow the flow of reactants (liquids or gases) of some catalytic processes are included [64,86]. Such flow can be through holes, channels or inner cavities that existed prior to the printing process of the device, such as the flow reactor made by FDM (with PLA) reported by Su et al. [71] for the online fluorometric monitoring of glucose. One of the first examples of additively manufactured multi-purpose reaction ware was that reported by Symes et al. [77] that

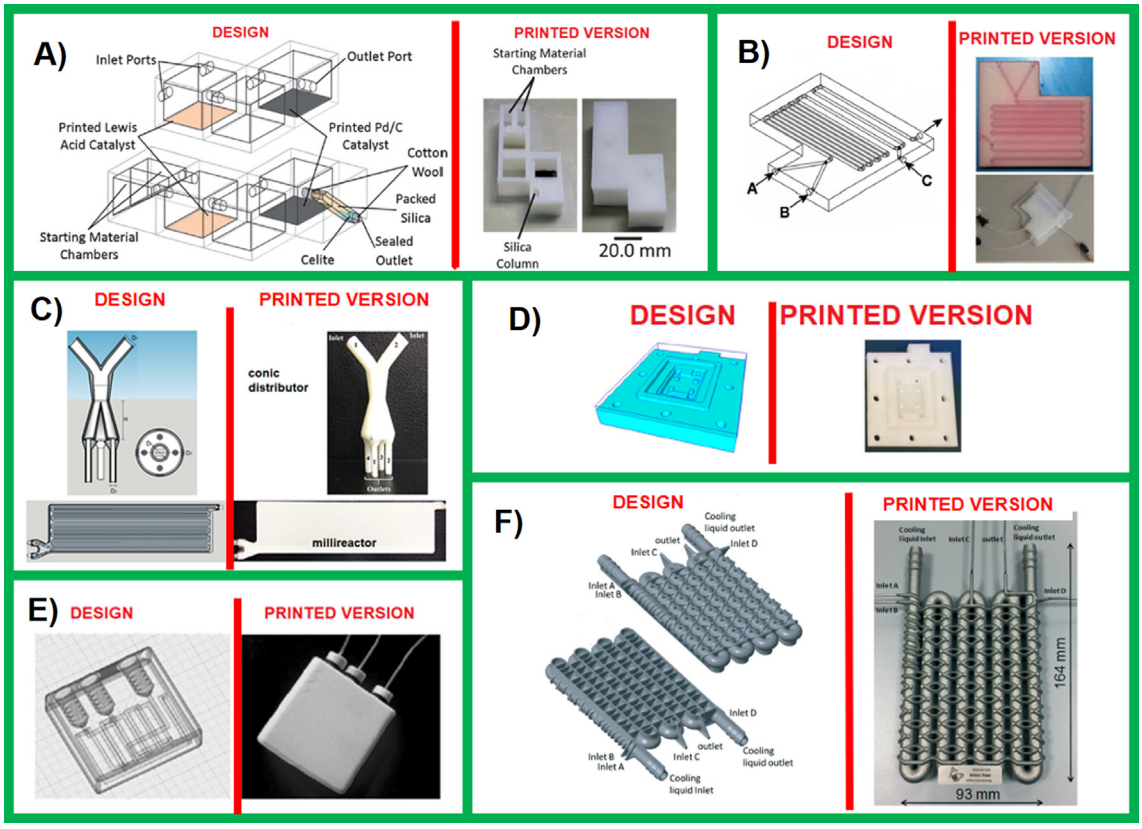

Fig. 9. Catalytic reaction ware: A) Design and final version of a 3D-printed (FDM with PP) sequential reactor for three processes: Diels-Alder cyclization, imine formation and imine hydrogenation. Reproduced from Ref. [75]; B) Design and final version of a 3D-printed (FDM with PP) miniaturized fluidic reaction ware used for three types of processes: organic (reductive amination and alkylation reactions), inorganic (synthesis of large polyoxometalate) and related to materials (synthesis or gold nanoparticles). Reproduced from Ref. [76]; C) Design and final version of 3D-printed conical distributor (FDM with ABS) and a millireactor (FDM with PLA), both integrated and used in the biodiesel synthesis. Reproduced from Ref. [84]; D) Design and final version of a 3D printed (FDM with PLA) electrolyzer cell component for water splitting. Reproduced from Ref. [70]; E) Design and final version of a 3D-printed mesoreactor. (FDM with PLA, HIPS and PA12) for the Cu-catalyzed enantioselective Henry reaction. Reproduced from Ref. [72]; F) Design and final version of a 3D printed (SLM with SS (316L)) flow reactor for difluoromethylation reactions. Reproduced from Ref. [87].

designed and manufactured an integrated system for synthesis and analysis.

Using DIW and ASP as printing material they were able to produce cylindrical reactors for carrying out processes such as: the formation and crystallization of two inorganic nanoclusters ($(C_2H_8N)_mNa_n$ $[W_{19}M_2O_{61}Cl(SeO_3)_2(H_2O)_2]Cl_2{\cdot}xH_2O$ (M = Co(II) or Mn(II)); the synthesis of an heterocyclic compound ($C_{21}H_{17}BrN_2O$) and to conduce real-time in situ spectroelectrochemistry during the reduction of phosphomolybdic acid. Furthermore, one of their more remarkable results was to completely switch the selectivity of the reaction of 4-methoxyaniline with 5-(2-bromoethyl)phenan thridinium bromide simply by means of the modification of the reactor structure that was optimized as the results were analyzed [77]. This is an excellent example of how additive manufacturing can incorporate improvements in a chemical process in a way that is quick and that streamlines the optimization of results. In a similar way, Kitson et al. [75] reported the design of a reactor (made by FDM with PP) that, thanks to its shape, allowed the sequential control of the execution of three processes: Diels-Alder cyclization, imine formation and imine hydrogenation (see Fig. 9A).

Kitson et al.[76] reported the manufacturing of milli- and micro-fluidic reactors for chemical synthesis (see Fig. 9B) by means of FDM using PP as printing material. In this case, the authors highlighted the speed with which custom reactors are obtained and how cheap they are, due to the type of printable material used and the technology selected. Furthermore, they were able to demonstrate how versatile their prototypes are in organic (reductive amination and alkylation reactions), inorganic (large polyoxometalate synthesis) and material synthesis (of gold nanoparticles) processes [76].

Recently, Bettermann et al. [81] reported the successful design, manufacturing and testing of a printed bended reactor made by means of FDM with PLA, which was used in the continuous, redox-initiated emulsion copolymerizations of styrene – butyl acrylate and of vinyl acetate –neodecanoic acid vinyl ester. Amongst the interesting features of this work is the recording of thermal profiles during the copolymerizations. This enables a better understanding of the heat flow, which was made possible thanks to the adaptable design of the reactor. In addition, the inert behaviour of the reactor material against the chemical properties of the reagents was confirmed, and no fouling, clogging or deformation of the reactor was observed.

Regarding advanced designs, Zhang et al. [83] presented a honeycomb fractal reactor for the CO_2-monoethanolamine absorption reaction. In this case, the printed device was manufactured in transparent material (TAR) by means of SLA. This means that along with the improvement of process by the reactor design, the control of the reaction zone through a transparent wall is a further remarkable advantage. Furthermore, numerical models allowed confirmation that the fractal reactor allowed a constant flow pattern as slug flow to be maintained. Moreover, additional information was gained from the interaction of the fluids, both gas and liquid, with the angles and bifurcations of the reactor that were beneficial for the removal of CO_2, thus this work is a clear example of how liquid–gas reactions can be improved by novel reactor designs.

As for the scalability of the processes, which is another aspect that can be favored with additive manufacturing, Potdar et al. [66,88] recently studied the scalability of additively manufactured porous milli-reactors (printed by means of DIW with SS(316L)) in different industrially relevant liquid–liquid processes: the 1-nonanol oxidation, and the C-N cross-coupling reaction. The reactors were built with cylindrical fibers of the material stacked in two types of woodpile-type configurations, and the scale-up approach consisted of increasing the reactor diameter by factors of 1.5 and 2.0 while keeping the fiber dimensions constant. Depending on the flow regime (stratified or Taylor flow), limits were found in which the mass and heat transfer was maximum, and higher values were observed for the systems scaled to a factor of 1.5. What is interesting about this work is that they managed to demonstrate that the addition of eight reactors in series with a scale-up factor of 2 generated a production 6 times faster than a conventional fixed bed reactor. In addition, the problems of pressure drops usual with this type of system were not experienced. Once again, therefore, the ability of printed systems to allow the discovery of efficient ways of intensifying chemical processes, in this case by the sum of subunits that can be studied individually or as part of a larger circuit, can be demonstrated.

Moreover, using PEG-DA and SLA, Manzano et al. [68] reported millifluidic reactors (with two configurations: linear and compact curved) connected for the Huisgen cycloaddition. The main contribution of this work is that it explores the chemical functionality of a commercial polymeric resin that has functionalities such as carboxylic acid, amine and copper carboxylates, which are active in the Mannich, aldol and Huisgen cycloaddition reactions respectively. Therefore, it is one of the few teams that that studies the possible reactivity of the printed structure itself and tries to control it [89].

Finally, perhaps one of the most illustrative examples of the possibility of applying additive manufacturing in the manufacture of various devices (of different materials) that can be integrated to form a personalized reaction system, is presented. This is the case of Mendoça Lopes et al. [84], who manufactured a micro-chemical plant for biodiesel synthesis in millireactors. They not only created a custom reactor but also a distributor for reactant dosing and product separation (see Fig. 9C). They even printed up to a modular support, piece by piece, to integrate the different elements of the plant. In other words, they built not only the reaction ware, but also the structure that would allow the incorporation of more than one reactor into the reaction circuit. Therefore, beyond the positive results of the performance of the distributor and the reactor itself, what is remarkable is that this is a pioneering design in which practically a whole scalable and fully operational reaction unit is printed for production, combining different types of materials. This modular plant allows up to four reactors to be integrated simultaneously to generate 126.4 mL/min of biodiesel. In line with this approach of using additive manufacturing to obtain the different components of a reactor, recently L.M. Gandía [90] and his team presented the obtaining of ABS-based microreactors for photocatalytic applications.

4.1.2. Hydrothermal reactors

This type of catalytic reaction ware allows a reaction to take place internally, similar to that of the systems of micro/milli and tubular reactors. However, in this case it is a differentiating fact that the processes are pressurized. For this type of reaction ware, Kitson / Cronin and their coworkers [74,79] reported the design and production of high-throughput hydrothermal arrays made of PP using FDM for discovery purposes. These devices presented limitation of temperature imposed by the manufacturing material, which means a restriction of the temperatures that are available for the use of this hydrothermal reactor (always < 140 °C), where maintaining the mechanical strength of the device is mandatory. However, their printed hydrothermal reactors do not require the typical steel coatings of conventional ones. This makes them more versatile in terms of the shape and volume they can have, as well as more economical when it comes to manufacturing.

4.1.3. Flow devices

The differentiation between flow devices and micro and millireactors is sometimes not so simple, because in miniaturized reactors, the chemical process is combined with the fluid-dynamic effect of a designed flow path. Therefore, an attempt is made to differentiate flow reactors as those devices that are intended to allow the passage of reagents or products (which may be in the liquid, gas or both phases) of some reactions, which may or may not occur within them [91]. In this kind of laboratory equipment, the design of very specific structures and the miniaturization are more important, because the micro, milli or meso size of the cabins or channels through which the fluids pass and the route they have to take, can determine their reaction behaviour.

As highlighted by Parra-Cabrera et al.[2] additive manufacturing allows the direct integration of active flow control components such as valves before, after or inside the main reactor chamber. For instance, although not within a catalytic process, Sochol et al. [92] developed control operators with multi-jet based additive manufacturing such as fluidic analogues of capacitors, diodes and transistors. In a similar way, Gong et al. developed high density 3D printed microfluidic valves, pumps and multiplexers.

The previously presented cases of Kitson et al. [79] could be also included within flow devices since one of their reactors presents microchannels that allow the passing of reactants during complexation of Cu^{2+} and Ni^{2+} cations with organic ligands[79]. However, it is important to note the evidence of bio-microfluidic devices developed with PEG-DA, whose transparency allows better control of processes. In this case, not only were flow devices developed, but also lens, rings and mixers, and all of them were analyzed in studies of cytocompativility. This type of work therefore opens the window towards applications in which, for example, the enzymes that are living catalysts can be integrated with this type of system.

The last example of a device designed and produced for fluidic purposes is the conic distributor (see Fig. 8C) integrated in the microplant for the production of biodiesel presented above [84]. Specifically, the custom distributor contributed to the improvement of mixing and contact between reagents in order to streamline the process once they entered the reactor. Therefore, this is a clear example of process improvement thanks to a printed catalytic reaction ware which is focused on a fluid control task.

4.1.4. Electrochemical cell components

In this case, the devices that allow the operation of an electrochemical cell other than the electrodes, are put into groups such as housings, supports or tanks for the electrolytes. These components can therefore be integrated with conventional electrodes or also with printed electrodes. For example, Symes et al. [77] reported an electrochemical cell, entirely printed in ASP using DIW as the printing method for the electrochemical reduction of phosphomolybdic acid. The device, despite being experimental, showed considerable benefits that can lead to it being compared with standard devices. However, further development is needed to optimize the performance of this cell.

Recently, Ambrosi and Pumera et al. [70] also reported an entire electrochemical cell for water splitting. In this paper, the authors combine the printing of flat electrodes that were made with steel and that of the electrode holder (in PLA with FDM), which allows contact with the electrolytes (see Fig. 8C) and includes a separator between them. The integration of the different components of the cell was successful, and from the point of integrity of the electrode

holder, it can be said that there was no problem before, during or after the electrochemical reaction. This allowed the cell to be studied in the same way as any standard electrochemical system. These authors, also studied the integration of printed electrodes and the suitable electrochemical cell for the water splitting [82]. In this case, the electrode had a basket shape, so the cell (PLA with FDM) should have a cylindrical shape where the electrode could be inserted. Once again there was a successful integration of the printed electrode and the cell. However, it is important that the cell is able to adapt to the shape of an electrode that is unconventional due to its shape geometry.

4.1.5. Miscellaneous catalytic reaction ware

Finally, there is some reaction ware that can be differentiated from the groups presented above, since they have a less determining role than the reactors themselves despite the fact that they are very useful in different chemical processes. For instance, the printed rotor–stator hydrodynamic cavitation reactor for the acid-catalyzed esterification of crude palm oil [93], or the calorimetric cell for the determination of ammonium in natural water that includes an integrated heater printed on a graphene-doped PLA composite (G-PLA) by means of FDM. Inside the measurement cell, an insulating sheet was included, also printed by FDM on an insulating compound (microdiamond-doped ABS) and this generated a much better insulation than the bare ABS polymer[78]. Moreover, Sanchez Díaz-Marta et al. [69] developed a porous capsule made of PP by FDM. The role of this capsule is similar to that of a tea bag, in which a structured catalyst (Pd-PA12/SiO_2 for the one-pot Chan-Lam azidation/Cu alkyne-azide cycloaddition/Suzuki reaction) is introduced, so that it comes into controlled contact with the reaction medium (liquid). Such contact occurs through the porosity of the capsule, allowing the speed at which the process occurs to be regulated.

Stirrers have also been printed for different purposes [65,89]. For instance, Betterman et al. [67] have printed personalized designs on PA12 by FDM, looking for the device that would favor a more homogeneous and efficient agitation in the process. While Lahtinen et al. [80] designed and printed on PP by SLS a personalized mechanical stirrer to which a structured catalyst for carrying out some hydrogenation reactions (of styrene, cyclohexene, and phenylacetylene) was added.

Desipio et al. [94] studied the photocatalytic and photo-fenton activity of iron-doped carbon nitride using a 3D printed and LED driven photon concentrator. This device presented a successful performance in the photocatalytic degradation of dicamba. It was made on PLA by FDM and has two chips on LEDs boards with visible light spectra and two complex parabolic mirror surfaces.

Finally, developments on alternative additively manufactured devices to work with live cells (mammalian cell cultures) have been reported by Urrios et al. [73], who manufactured personalized systems such as rings or petri dishes made on PEG-DA by means of SLA. This is pioneering work in exploring the biocompatibility of printable resins that can be obtained by modifying commercial formulations or by the total reformulation of the printable matrix.

4.2. Structured catalysts

These devices directly participate in catalytic processes, since they are made of the required catalyst or because they are supports covered by the catalyst. These type of prints were clearly differentiated in the review made by Parra-Cabrera et al. [2] following a similar criterion to that proposed by us, although the integration between these devices and the respective catalysts was dealt with more deeply in the review by Hurt et al. [1] Therefore, to better understand the evolution of synergy between additive manufacturing and catalysis, especially for structured catalysts, it is important to consider several criteria. In this sense, prior to establishing any classification, it is important to see the correlation between common variables extracted from published articles on printed structured catalysts [23,27,48–50,55,62–64,68–70,82,95–142], which includes the 3D printing technique, the printable materials, the produced structured devices, as well as the reactions in which they are studied. For this purpose, diagrams derived from the correlation between the cited variables are presented in Figs. 10 and 11. A special diagram was made for the monolith-type structures, to facilitate their interpretation, because as will be seen in greater depth later, these are the most reported in literature and there are a large number of examples.

Firstly, it is observable that regardless of the type of structured device, the additive manufacturing techniques employed are practically the same to those used to manufacture reaction ware (see Figs. 8 and 9), except for the use of two more techniques (EBM and DMLS). In addition, DIW is the most commonly used technique (Fig. 11), followed by FDM, although what is remarkable is the significant increase in the number of printable materials. In structured catalysts, the palette of materials that has been explored so far is much broader due, in part, to the fact that their direct participation in the reactions requires a series of chemical and physical properties being adapted to the particular conditions of each catalytic process. This requires a wider range of materials capable of working, for example, under higher temperature conditions, in aggressive reaction media and with a certain chemical specificity in their structure and mainly on their surface.

Therefore, in addition to the polymeric materials that have been extensively studied in additive manufacturing (ABS [123], PVA [23] or PEG-DA [68,113]), the joining of additive manufacturing and catalysis has allowed the exploration of metallic materials (including stainless steels), inorganic salts, metallic glasses, metal oxides and materials such as clays or zeolites.

Moreover, carbon-based materials are also found, but the use of composites for combining features of different materials as in the case of ABS-TiO_2 [122] or C-PLA [105] systems, seems to be also attractive. Typical formulation of powder catalysts have been also introduced (Cu/Al_2O_3 [27], CeO_2 [108]), and recently the exploration has been undertaken of printable materials suitable for bio-catalytic processes such as baker's yeast [62] or agarose-based hydrogels [63]. This shows that the variety of materials used for additive manufacturing is gradually expanding, but this trend is expected to continue to increase in the coming years, because the progress achieved so far can be considered to be an exploratory phase.

Regarding the type of catalysts used, it can be said for the moment that this is a variable which should be approached conservatively, since the most widely known catalytic systems have been applied in practically all the processes for which records are available and which are found in the diagrams of Figs. 10 and 11. These demonstrate that the merging of additive manufacturing and catalysis is an emerging topic. For this, the 3D printed structured catalysts are based on typical systems such as noble metals (Pt [95], Cu [97], Rh [108], Pd [109]), alloys (Cu-Mo [97], Au-Ag [119]), metals supported on metal oxides (Pt/IrO_2 [82], Au/TiO_2 [114], Cu/Al_2O_3 [27]), simple oxides (IrO_2 [98], MnOx [102], Al_2O_3 [118]), mixed oxides (CuO/CeO_2 [104], CeO_2/ZrO_2/La_2O_3 [110]), acid materials such as zeolites [55,111,115,124,126], carbon-based materials [117], and some bio-active ones such as enzymes [105,127] or baker's yeast [62].

The emerging nature of the studies on structured catalyst printing cited in this review, is also reflected in the fact that there is no particular type of reaction that clearly dominates the research. Therefore, diverse applications are found in several thermochemical processes [48,108,115], as well as in electrochemical [70,82], photocatalytic [101,114] and enzymatic reactions [127], or adsorp-

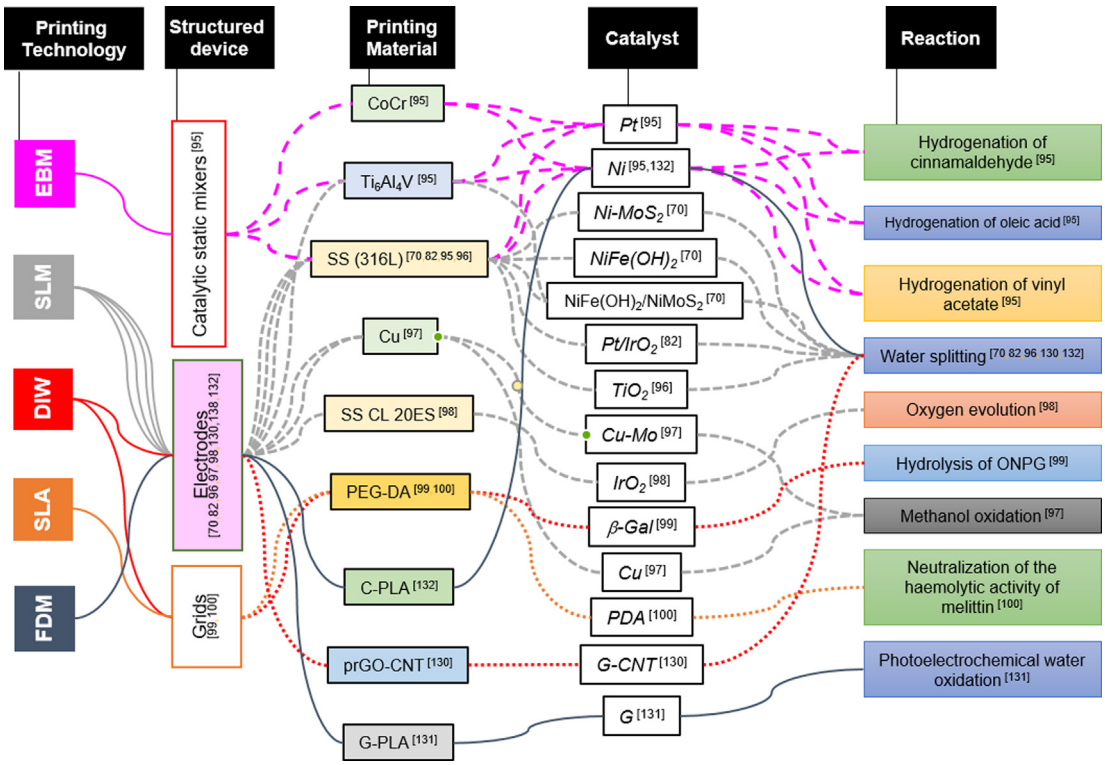

Fig. 10. Graphos diagram that correlates additive manufacturing techniques, printable materials, catalysts and reactions where different types of structured catalysts are applied in most cases reported to date.

tion processes [55,123], which demonstrates a great versatility when generating structured catalysts to operate under different conditions. It is likely that the sectors of thermochemical and electrochemical processes will focus the greatest concentration of studies in the near future, with the seeking for promoting CO_2 recycling projects such as the methane production (nowadays the process with the most reports of use of printed structured catalysts [48–50,107]), or the water splitting for the production of H_2 [70,82,96]. In this sense, many more advances are expected in the development of printed structured catalysts for electrochemical and photocatalytic processes, focused on renewable strategies for the production of H_2, CO_2 recycling and water purification, given that these are topics of high priority in the current global scenario. Nevertheless, this does not rule out that additive manufacturing of structured catalysts will continue to expand to many processes that include catalytic reactions regardless the homogeneous or heterogeneous character. For instance, the challenging upgrading of products derived from residual biomass, which requires advanced designs, not only of catalysts but also of devices that achieve greater efficiency in the field of the biorefinery [143].

Another variable included in the diagrams of Figs. 10 and 11 is the type of structured catalysts that can be printed, and it is observable that although there are several cases, these can be classified into a very small number of types of devices that meet the condition of being made or subsequently coated with a catalyst. On the one hand, the most important ones are monoliths [23,27,48–50,55,62,63,68,69,101–127] and electrodes [70,82,96–98,144–146] (so these will be presented in more detail in the following sections), and on the other hand are the other, alternative devices such as grids [99,100], stir bar covers with porous shell configuration[80] or catalytic static mixers [95,147]. There are also some catalytic reactors that have a hybrid nature between catalytic reaction ware and structured catalysts (not included in Fig. 10 or 11) because part of their structure is coated with a catalyst and perform a double function [148]. They allow contact between the reagents and serve as a reservoir for the process to occur, but they also support the catalyst that modifies the reaction. This is the case of a printed microreactors developed by Mohammad et al., printed by SLM in SS (316L). The devices exhibited a design of plates with microchannels engraved on their surface (presented in Fig. 12).

Three different prints were coated by means of a dip-coating procedure with three types of mesoporous silica supported Co-Ru catalysts (Co-Ru/SiO_2 (KIT-6); Co-Ru/SiO_2 (SBA-15); Co-Ru/SiO_2 (MCM-41)) for the Fischer-Tropsch synthesis. These microreactors, not only allowed the passing and contact between the reactants as well as the releasing of the products, but also regulated the chemical reactions inside the channels thanks to the presence of the catalysts, and although the authors did not delve into the design of the device, it allowed them to effectively compare the performance of the three catalysts.

4.2.1. Monoliths

Recently, Matoh et al. [149] presented a precise definition of what a monolith is: "*Monoliths for reactors are defined as being a single piece of porous material that contains various types of interconnected or separated channels.*" [149]. These devices have been widely applied in several catalytic processes [150], since they "*pose an attractive alternative to conventionally prepared catalysts pellets or powders due to a number of superior properties: good-flow-through properties and permeability, low pressure drop, light weight, and pore size and shape can be easily customized*" [149]. Within the monoliths group, an important subgroup of reticulated foams it can be found that have an open, three-dimensional network structure of interconnected pores (unlike classic honeycomb monoliths) [149].

With the eruption in popularity of additive manufacturing and its enormous advantages in the design and manufacture of structures with complex geometries, as cited above in previous sections,

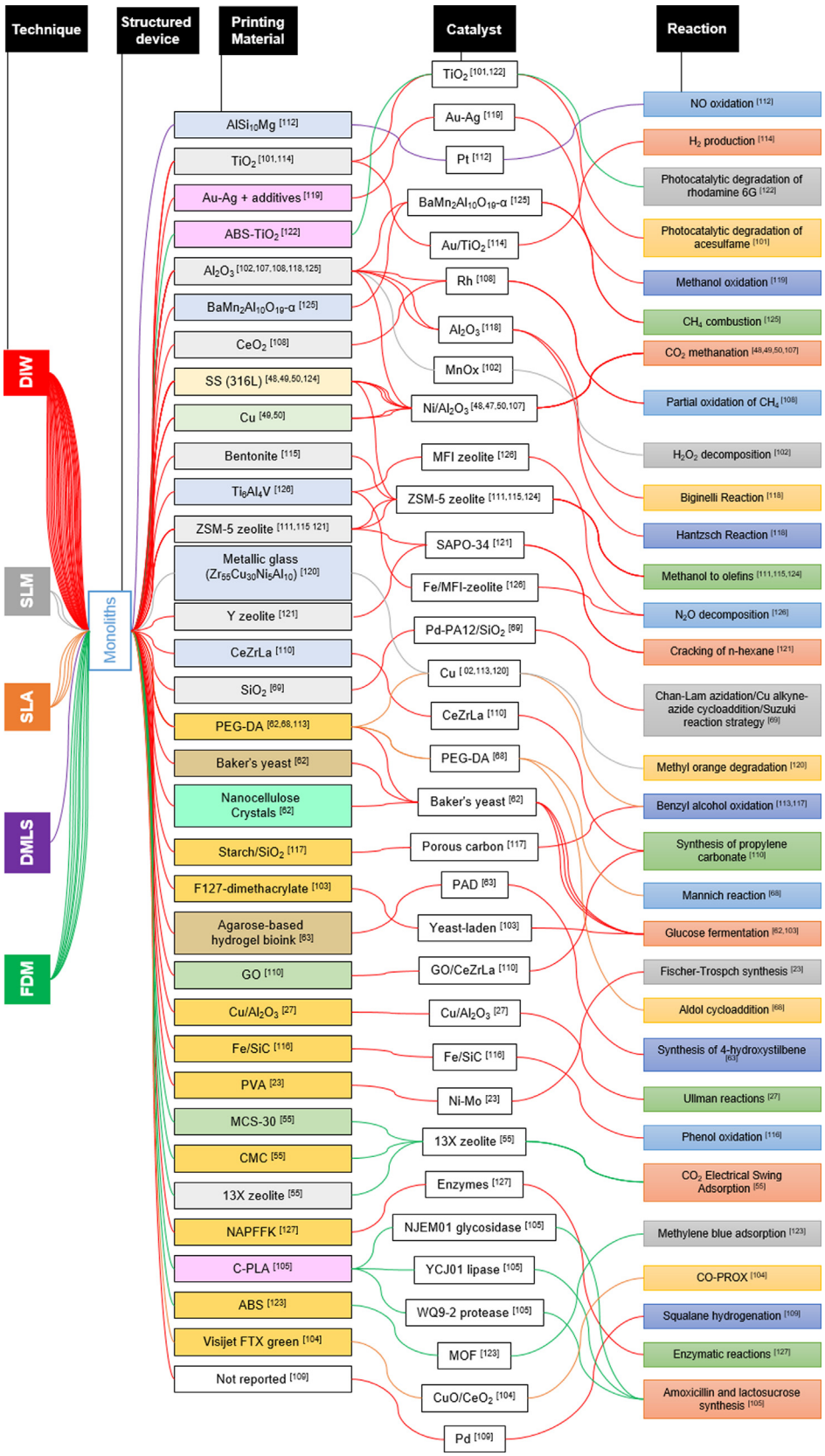

Fig. 11. Graphos diagram that correlates additive manufacturing techniques, printable materials, catalysts and reactions where different monolith type structured catalysts are applied in most cases reported to date.

it is easy to think that these advantages could be transferred to the development of a new generation of monoliths. And yet how much has been achieved in the design of new monoliths with additive manufacturing? The answer is that it is a stage that is still in its exploratory stage. Although there are already several records about printed monoliths with catalytic applications, the complexity of

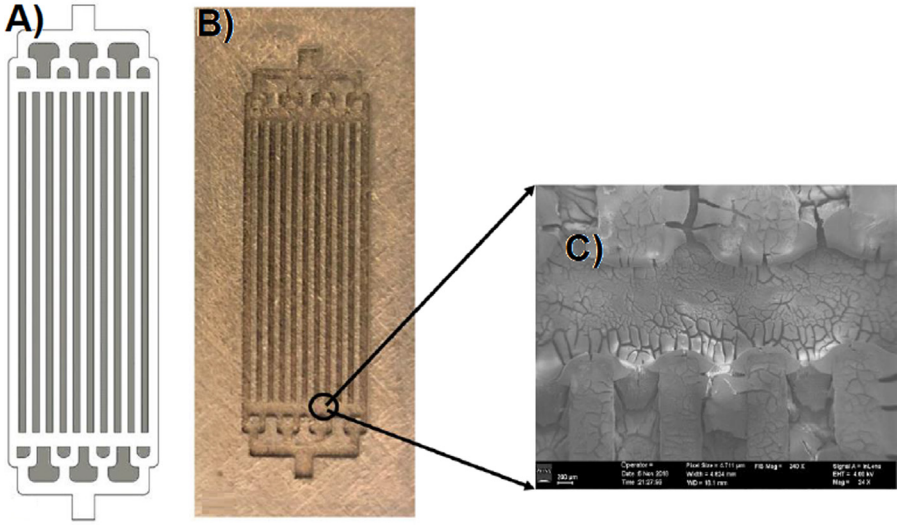

Fig. 12. Printed microreactor for the Fischer-Tropsch synthesis: A) Design of the channels; B) Printed reactor; C) SEM micrograph of the some channels coated with catalyst prior the catalytic reaction. Reproduced from Ref. [106]

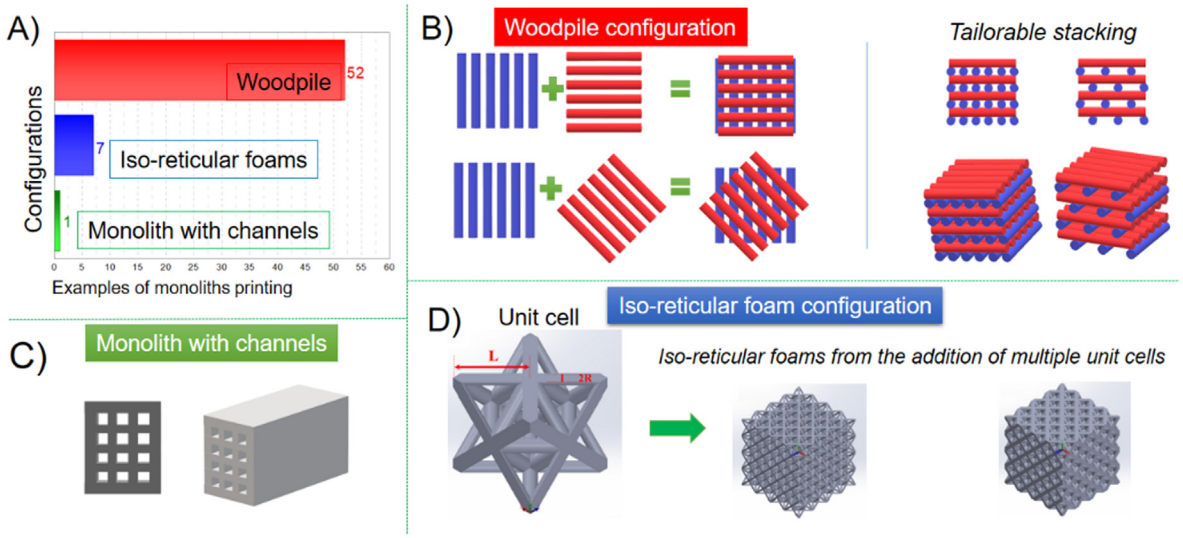

Fig. 13. Configurations used for the design and manufacturing of 3D printed monoliths: A) Amount of papers that apply every specific design; B) Woodpile configuration; C) Monolith with channels configuration D) Iso-reticular foam configuration or POCS.

the structures is still highly unprovable. In fact, for this review it was established that there are around sixty examples in which structured monolith type catalysts were designed and manufactured and three configurations have been identified (woodpile type, *iso*-reticular foam type and monolith with channels type), which are shown in Fig. 13.

In Fig. 13A, the frequency of each configuration is included, thus confirming that most of the cases applied the woodpile configuration (87%), while monolith with channels or *iso*-reticular foam configurations also known as periodic open cell structures (POCS) have been applied just a few times. Woodpile is a simple configuration in which monoliths with different densities of cavities and channels are obtained, playing with variables such as the diameter of the bars with which the scaffold is built. The spacing between the bars can also be modified, which will later mean a different degree of stacking in the final block, or even a variation in the orientation of the bar planes that overlap each other with angles ranging from 45 to 90°. From the woodpile configuration, scaffolding-type monoliths with often cylindrical or cubic shapes are generated.

Therefore, this again confirms the emerging nature of the link between catalysis and additive manufacturing because the advantages of design are not yet reflected in devices with complex shapes. It is particularly important to point out that the simplicity of the geometric models printed and used in catalysis does not mean that it has not been possible to print systems of high geometric complexity. In fact, the number of reports grows progressively [9]. The point is that the implementation of many of them is still yet to come.

Leaving geometric complexity aside, the important thing is that printed monoliths with a woodpile configuration which are used in catalysis, have improved the performance of powder catalysts in most of the cases, and their performance is comparable with or sometimes superior to that of traditional manufacturing devices,

such as ceramic monoliths obtained by extrusion or molding. In this sense, knowledge is already being gathered on the aspects to be improved in all critical aspects (the development of printable materials, more precise and reproducible printing methods with increasingly advanced printers and new post-printing treatments, amongst others).

4.2.1.1. Application examples of monoliths with a woodpile configuration. Regarding the catalytic reactions where printed monoliths are applied, as inferred from Fig. 11, the CO_2 methanation has been the subject of the largest number of reports at present, and all these studies have been led by Danaci et al. [48–50,107]. These authors have produced monoliths with a woodpile configuration by means of DIW, using different printable materials (Cu, Al_2O_3, SS(316L) and a Ni/Al_2O_3 catalyst in all cases, which resist high temperature applications such as the cited reaction that which generally occurs between 150 and 550 °C. The authors have established a comparison of the size and distribution of the channels in the structure systems by the modification of the nozzle size during the printing process and the stacking of the layers. With this, they found that methane productivity depends on the nature and geometry of the structure, since in this reaction heat and mass transport limitations play a crucial role in the total CO_2 conversion and the yield to CH_4. This is why the superior heat transfer ability of monoliths made by Cu or SS(316L) compared to ceramic systems, offers promising results for the manufacturing of metal monoliths. Moreover, the scalability of the process by the addition of different subunits containing printed monoliths was successfully achieved, which is a remarkable result that confirms not only the possibility of intensifying a process by incorporating structured catalysts, but also that of applying this strategy more easily, thanks to additive manufacturing.

Woodpile monoliths like those presented in Fig. 14., have also been studied in processes that aim towards the generation of larger organic molecules from smaller ones such as CO or methanol, by means of the Fischer-Tropsch synthesis [23] or the methanol-to-olefin approach [111,115] respectively. In these kinds of processes, the porosity of the structured catalyst is essential to ensuring a suitable control of the reaction pathways for the generation of the desired products. For instance, Konarova et al. [23] observed that their monoliths made of PVA, that uses Co-Mo alloys as catalysts, presented further microstructural features (structural porosity) useful for the Fischer-Tropsch reaction, thanks to thermal treatments carried out over the printed monoliths. In the case of the methanol-to-olefin reaction, Lefevere et al. [111] related the control of the geometry of the impression (made by DIW) with the design of the porosity of the material (ZSM-5 zeolite), although in their approach, they delved further into the effect of different binders to enrich the material of the structured system with the catalyst that has high porosity and thus favors the methanol-to-olefin reaction. While, Li et al. [115], who also printed monoliths with ZSM-5 zeolite, doped such material with different elements (Zn, Cr, Mg, Cu, La, Ga and Y) and observed a clear difference in the selectivity towards ethylene and propylene, which was higher for the printed monoliths than for the powder catalysts, due to a macro-*meso*-microporous network promoted during the printing process [115].

Oxidation reactions, processes that require relatively high temperatures, have been also carried out with printed monoliths. For instance Leclerc et al. [108] who studied the partial oxidation of CH_4, reported the first printed monolith (by means of DIW) entirely composed of ceria (CeO_2). This device, that was subsequently coated with Rh, presented a superior performance than its alumina manufactured counterpart, thanks to the oxygen exchange that CeO_2 possesses. This highlights the importance of testing new printing materials, with properties that contribute directly to the catalytic process.

Zhu et al. [119] developed different structured catalysts, not only cubic monoliths, but also structures with spiral, honeycomb grid, hollow pillar array, and circular scaffolding shapes. One of the remarkable features of this study is the inclusion of Au and Ag within the printing ink that was used to generate the structured systems by means of DIW. Monoliths have a reasonable performance, but above all, the authors highlight the potential of manufacturing custom designs that minimize the amount of catalyst required to manufacture the device, which in the case of a formulation that includes precious metals, is an important issue from an economic point of view.

Liquid phase oxidation experiments have also been carried out, such as the phenol oxidation (that requires mild conditions: 75 °C

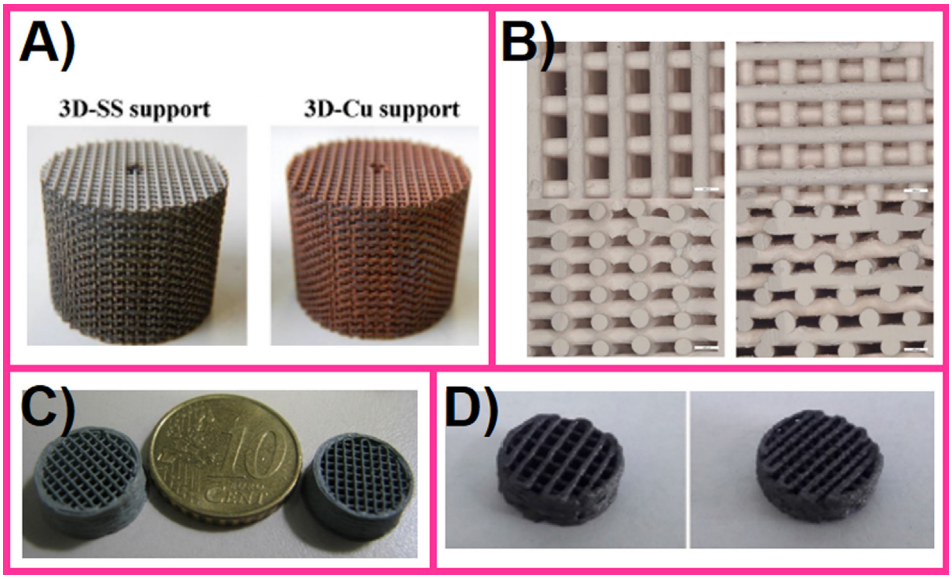

Fig. 14. Examples of monoliths with woodpile configuration: A) 3D-printed (DIW with copper and SS (316L)) monoliths for the CO2 methanation. Reprinted from Ref.[50]; B) 3D-printed (DIW with ZSM-5 zeolite) monoliths for the methanol-to-olefins process. Reprinted from Ref.[111]; C) 3D-printed (DIW with Fe/SiC) monoliths for the oxidation of phenol. Reprinted from Ref.[116]; D) 3D-printed (DIW with carbon materials) monoliths for the oxidation of benzyl alcohol. Reprinted from Ref. [117]

and atmospheric pressure) reported by Quintanilla et al. [116] using monoliths printed with Fe/SiC by means of DIW. The performance of the devices in the reaction seems comparable with that of other structured catalysts used for the same reaction, although in this case, the treatment of the monoliths by means of spark plasma sintering after the printing process decreases the leaching of Fe during the reaction. However, this is generated by a block in the accessibility of the iron available in the material, which implies a reduction in catalytic activity. Therefore, additional studies are required to find a compromise between these two aspects.

Recently, Zhou et al. [117] studied the selective benzyl alcohol oxidation using monoliths printed in structured porous carbon materials. What is interesting in this study is the strategy used to promote meso and macro-porosity in the carbon material, which consisted of adding silica spheres to the carbon matrix and this mixture was used as printing material. Subsequently, by alkaline chemical attack, the silica was removed, thus leaving only the carbonaceous material, but with the porosity left by the silica spheres. In this case, not only the shape of the monoliths was designed, but also their porosity, which resulted in devices with high catalytic activity and that were highly selective towards benzaldehyde production.

The high potential of printed structured catalysts has also been analyzed in enzymatic processes with printed monoliths and has been reported recently, such as the chemoenzymatic synthesis of 4-hydroxystilbene studied by Peng et al. [63], and the glucose fermentation by Qian et al. [62] Similarly, these types of devices have been tested in organic reactions. For instance, Azuje et al. [118] studied the Biginelli and Hantzsch reactions using monoliths made with Al_2O_3 by means of DIW. They observed not only the high catalytic activity of the devices but also remarked on their recyclability and scalability. Furthermore, the authors highlighted the short reaction time and the easy extraction of the catalyst from the reaction medium once the process ends. On the other hand, there was a study carried out by Sánchez Díaz-Marta et al. [69] that printed a monolith, which was then inserted into a catalytic reaction ware also generated by additive manufacturing cited above. The structured monolith was designed for carrying out the Chan-Lam azidation/copper alkyne-azide cycloaddition/Suzuki reaction and is one of the first examples of a successful one-pot approach, where additive manufacturing is applied. This is a remarkable result since the entire design of the monolith assembled with the capsule allows to control of the order in which a series of processes occur.

4.2.1.2. Application example of monolith with channel configuration. So far, only two cases have been found in which the direct manufacture of a monolith with channels is reported. Firstly, Yang et al. [120] printed (by means of SLM) cubic monoliths with hollow channels using metallic glass ($Zr_{55}Cu_{30}Ni_5Al_{10}$) as the printable material. The devices were tested in the degradation of methyl orange and presented a superior performance than a cubic structure without channels, although below that of a printed *iso*-reticular foam structure. These results greatly demonstrated the strong effect of the monolith's shape in the performance during a catalytic process.

Secondly, Chaparro-Garnica et al. [104,151] studied printed devices for the preferential CO oxidation in presence of H_2 (PROX). Their monoliths were printed on a commercial UV curable polymeric resin (VisiJet FTX Green) by means of SLA, and their channels were subsequently coated with a CuO/CeO_2. The fact of using a polymeric resin, greatly limits the operating temperature range of this device. Therefore, temperatures above 180 °C are not used. On the other hand, the low chemical affinity between the polymeric surface of the monolith and the catalyst makes it difficult to anchor it. For this reason, the design of flat channels was changed to one that consisted of channels with cavities so that catalyst deposits were generated. The catalytic results of the device are comparable to those of other structured systems developed with metallic or ceramic materials for this reaction. Therefore, beyond the catalytic performance, this study opens the possibility of expanding the applications of polymeric resins as printing material for useful devices in relatively mild temperature conditions.

4.2.1.3. Applications examples of iso-reticular foam configuration or POCS. Nowadays, the formulation of new printing methods and shapes of complex designs are being launched. However, only a few cases of successful printing have been directly related to catalysts and some of them do not present any catalytic result [152,153], beyond the mere establishment of their suitable potential as a structured catalytic system. This does not diminish the contribution of this type of work. It simply shows that it is a developing scenario based on the hypothesis that an *iso*-reticular foam configuration may be highly promising to favor catalytic processes based on the advantages of well controlled shapes.

Iso-reticular foam configurations or POCS are based on a three-dimensional projection of a unit cell to form a superior structure (as seen in the example in Fig. 13D), which, in the case of monoliths, determines the shape of these devices. These are inspired by shapes found in nature, such as the Bravais lattice types or superior structures generated from combinations of these such as those studied by Al-Ketan et al. [54]. The modification of the unit cell dimensions allows generating systems with greater or lesser pore density.

The pore size can be regular throughout the entire length of the structure, but it is also possible to design systems with a variable porosity oriented towards one of the axes in which the structure projects, by means of a progressive modification of the unit cell dimensions, as observed in the example studied by Sheithauer et al. [154] presented in Fig. 15.

Currently, there are very few studies in which experimental results have been obtained from catalytic reactions, using structured catalysts with complex and well controlled designs. The starting designs and the respective prints of said works are presented in Fig. 16.

The first case is that reported by Essa et al. [102], where a nodal diamond-shape lattice design (Fig. 16A) satisfied the requirements of additive manufacturing over-hanging structures, which was established as an optimal configuration by means of CFD simulations. The devices were printed in Al_2O_3 by means of SLM and a surface coating with MnOx was generated afterwards. The devices were tested in the H_2O_2 decomposition reaction and exhibited a better performance when compared with that of alumina pellets coated with MnOx. Furthermore, low drops in pressure were detected.

Then, Chong et al. [120] reported the printing of different structures (not only *iso*-reticular foam configurations) using metallic glass and SLM technology. In this case, the authors established that depending on the designs manufactured, different amorphous phase fractions were achieved after the printing processes, and that the complex structures (Fig. 16B) were suitable to be dealloyed in order to obtain a milli/nano hierarchical porous structure, that exhibited excellent catalytic properties in the degradation of methyl orange.

More recently, Manzano et al. [113] reported a comprehensive study where a commercial printer based on SLA principle (FormLabs® Form 1 was fully adapted in order to test their own printable formulations. For this, the authors modified the build platform and resin tanks with the aim of maximizing the efficiency of the analysis of the different formulations. Several structures printed in PEG-DA-based resins were successfully achieved (Fig. 16C), and some of them that included Cu within the formulation, were tested in the benzyl alcohol oxidation. The experimental results

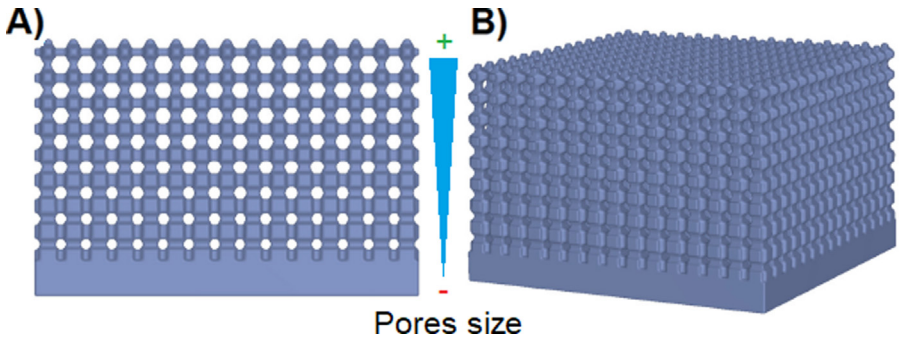

Fig. 15. Graded porous structure of a cuboid where the pores size increases with increasing component height: A) side view; B) perspective view. Reprinted from Ref. [154]

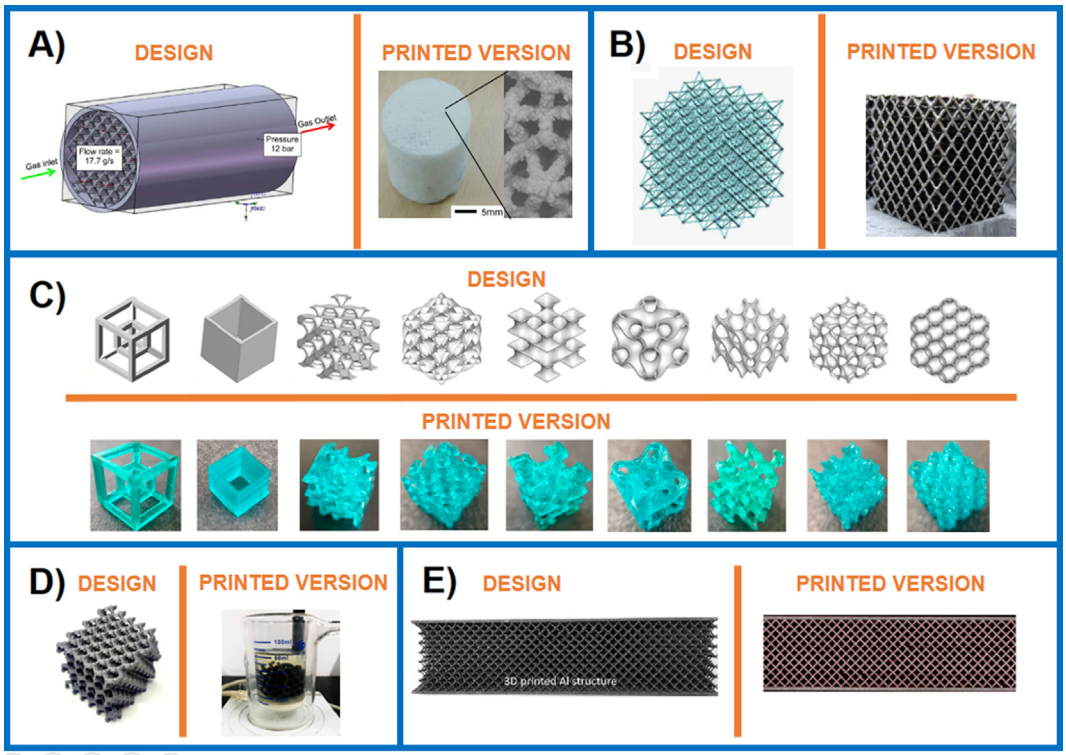

Fig. 16. Examples of monoliths with *iso*-reticular foam configuration already used as structured catalysts: A) 3D-printed (SLM with Al2O3) monolith with nodal diamond-shape lattice. Reprinted from Ref. [102]; B) 3D-printed (SLM with Zr55Cu30Al10Ni5) monolith with lattice structure. Reprinted from Ref. [120]; C) Different 3D-printed (SLA with PEG-DA-based resins) monoliths with scaffolding structures. Reprinted from Ref. [113]; D) 3D-printed (FDM with C-PLA) monoliths with scaffolding structure. Reprinted from Ref. [105]; E) 3D-printed (DMLS with AlSi10Mg) monolith with cubic *iso*-reticular foam configuration. Reprinted from Ref. [112]

allowed linear relationships between 3D printed surface area, surface hydrophobicity, and catalyst performance to be established. Therefore, this is the first case where a strict control of geometry allows the comparison of catalytic activity with other variables that are shape dependent.

Catalytic devices with advanced designs have also been reported for catalytic applications of immobilized enzymes. This is the case of Ye et al. [105] that used C-PLA for producing scaffolds (by means of FDM) with different shapes (Fig. 16D), and after functionalization treatments with piranha solution, peracetic acid and a silane coupling agent, the structures presented high specific surface areas and an abundance of active groups. This surface modification allowed the anchoring of four kinds of enzymes and the modified devices were tested in the amoxicillin and lactosucrose synthesis. From these results, a special scenario called bio-printing is out-lined, confirming that 3D-printed enzyme immobilization carriers offer a promising solution to building a simple platform that is low cost and flexible enough to accommodate various enzymes and reactors for industrial applications. Additionally, the authors highlighted that the next steps would include improving the number of surface-active groups on the scaffolds in order to achieve higher enzyme loading and increasing enzymatic stability by adding protecting agents. Moreover, they remarked that use of 3D bio-printing for the immobilization of thermostable enzymes has a huge potential, especially for the use of cascade reactions tuning the reaction sequence by staking modules with different catalytic activities [105].

Finally, Lind et al. [112] presented a pioneering report on the production of a cubic *iso*-reticular foam (Fig. 16E) by means of DMLS, using $AlSi_{10}Mg$ as printable material and Pt as catalyst. The high chemical stability of such ceramic substrate was suitable for the testing of the monolith in the NO oxidation to NO_2, which implies being submitted to a very corrosive media. The main advantage of the applied methodology is the preparation of a

structured catalyst with hybrid properties. On the one hand, the anodization procedure (carried out after the printing process) allowed the modification of the surface of the printed structure by means of the creation of an alumina layer that reduced spalling problems since it is chemically linked to the support. On the other hand, the created core–shell approach, combined the chemical properties of the surface Al_2O_3 layer with the high thermal conductivity of the core section of the structure.

The examples cited, including two recently published papers with similar design approaches for structured systems applied in other reactions [134,137] show that, so far, the most complex structures are achieved with technologies other than DIW, which until now has been the technique most used to generate monoliths. Therefore, future advances are expected from the exploration of new printing materials and new strategies with alternative techniques, which allow greater resolution and detail in the prints. Probably a bottleneck is being caused by the complication of making printable materials such as metals or ceramics in technologies that do not use such demanding manufacturing conditions, but at the same time achieve high resolutions. Another aspect that exacerbates this bottleneck is access to printing techniques for ceramic, metallic or composite materials that combine the properties of both families of materials. Leading-edge technologies are just taking off and are highly expensive. These two factors mean that it still takes time for them to reach different research centers and thus more strategies are being explored that allow a more efficient union between catalysis and additive manufacturing. However, one of the aspects that can help to overcome these barriers is the easy connection between studies that combine catalysis and additive manufacturing, with simulation models. Thanks to the current computational tools, the development of fluid dynamics models allows to pave the way towards better devices through simulations that consider different variables addressed from theoretical and experimental perspectives, even without catalytic experiments. For instance, the team led by E. Tronconi (from the Politecnico di Milano - Italy), which has a recognized track record in studying structured catalytic systems, is developing studies with printed foams that analyze phenomena such as pressure drop [155,156] or heat transfer [157] in 3D-printed open-cell foams for different reactions [158,159]. These types of studies are extremely important to understanding much more quickly the experimental results in future research, where the combination of catalysis and additive manufacturing is applied in any type of process and will facilitate its scaling-up.

4.2.2. Electrodes

These structured systems can be applied as platforms for different electrochemical devices [145] such as pseudo-capacitors, pH sensors and catalytic setups for the electrogeneration of O_2 and H_2, or the electrochemical degradation of pollutants. In fact, the fastest growing scenario today is the application of additive manufacturing to obtain electrodes as sensors for different species [160,161]. In the design of electrodes, the geometry and the exposed area are determinant since they establish the efficiency of the current flow and consequently the successful achievement of the electrochemical process [28,162]. For this reason, additive manufacturing is a tool that allows, on the one hand, the production of the electrodes to be easier and quicker and, on the other hand, to explore alternative designs, new materials and new treatments in order to improve the performance of these devices. Nowadays, there are not many reports on electrode printing. Additionally, some of these only focus on the manufacturing process and present general characterizations (mass transport, mechanical stability, thermal conduction among others) that show the potential of the printed electrodes to be used in electrocatalytic processes, but without catalytic evaluation results [163,164]. Nevertheless, some recent reports show both manufacturing and catalytic testing of electrodes, such as those exhibited in Fig. 17.

The research team led by Pumera, leaders in the research on printed electrodes [144,145], presented what they named a "breakthrough in on-site prototyping and fabrication of highly tailored electrochemical devices with complex 3D shapes" [98]. In this study, they showed the applicability of metal additive manufacturing as a valid fabrication technique of custom-shaped electrochemical electrode systems (helical shaped – Fig. 17A), that were tested in capacitance measurements, the oxygen evolution reaction and as pH sensors. The electrodes showed excellent capacitive and catalytic properties in alkaline solutions and Nernstian behavior as a pH sensor.

Pumera et al. [70] also reported the printing of an electrode with a flat honeycomb grid configuration (Fig. 17B) by means of SLM with SS(316L), assembled within an electrochemical tested in the water splitting process. One of the relevant features of this study is that it combines in the same device different printed components, not only the electrode but also the other electrolyzer cell components, and this is why this paper was also cited in the section devoted to catalytic reaction ware (Fig. 9D). Consequently, different 3D-printing techniques and printable materials were used, so this is one of the few examples where additive manufacturing is applied in a multi-material project. Regarding the performance of the cell, it was possible to establish not only that it works correctly, but also the improvement in the performance of the electrodes by means of modifying their surface with the deposition of NiFe double-hydroxide film onto the anode and Ni-MoS_2 composite film onto the cathode. Following a similar approach that combines printed monoliths and electrolyzer cell components, Pumera et al. [82] also introduced a new design of basket-shaped electrodes (Fig. 17C), which were also tested in the water splitting process. In this case, the authors focused on the possibility of modifying the catalyst́s surface by coating it with different catalysts (IrO_2, Ni or Pt) by electrodeposition.

More recently, Brown et al. [96] explored a rapid and versatile procedure for the production of tailorable electro-photocatalytic devices. In this case, the printed electrodes made by means of SLM with SS (316L), can be used as is, or modified with post-fabrication processes in photo-electrochemical energy applications. In this study, the atomic deposition layer was used for the first time for the modification of the electrodes with the aim of enhancing their performance in photo-electrochemical water oxidation.

Finally, Zhang et al. [97] presented the design and manufacturing of hierarchical nanoporous structures made with Cu or the alloy Cu-Mn by means of SLM (see Fig. 17D) for the electrochemical methanol oxidation. This work highlights a facile, low-cost, and alternative strategy for the design of structures with complex shapes that can be applied to binary, ternary and quaternary metal alloys for various functional applications. The printed electrodes, which presented structures similar to the *iso*-reticular foam configuration described above for monoliths, exhibited high efficiency during the electro-oxidation of methanol, based on enhanced mass transport properties, thanks to the control of the macro- and nano-scaled porosity from the design itself.

4.3. Integration of the catalyst in printed structured devices

As it has been possible to verify, the large number of variables that can be combined in the development of structured catalysts generates different approaches when classifying this type of device. Up to this point, the printing methods and materials, the type and configuration of the printed devices, as well as their functionality, and also the catalysts and the reactions in which they are applied, have been taken into account. However, the different

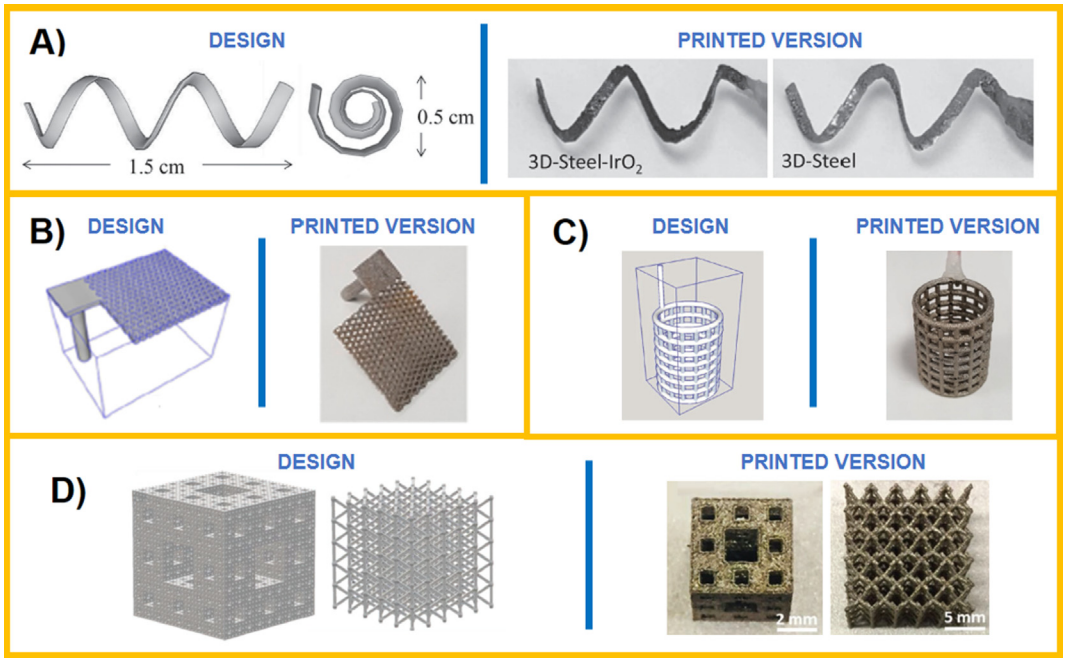

Fig. 17. Examples of 3D-printed electrodes applied in electrocatalytic processes: A) Electrodes with helical strip shape (made by means of SLM with SS CL 20ES) tested in the oxygen evolution reaction. Reprinted from Ref. [98]; B) Electrodes with honeycomb grid shape (made by means of SLM with SS (316L)) tested in the water splitting. Reprinted from Ref. [70]; C) Electrodes with basket shape (made by means of SLM with SS (316L)) tested in the water splitting. Reprinted from Ref. [82]; D) Electrodes with *iso*-reticular foam configurations (made by means of SLM with Cu-Mo alloy) tested in the methanol oxidation. Reprinted from Ref. [97].

examples cited so far lead to infer that there is no single strategy for structuring. Therefore, the question arises as to how and when the catalyst is incorporated in the structured system? Prior to, during or after the printing process?

Amongst the excellent reviews devoted to the analysis of the union between catalysis and additive manufacturing, only that carried out by Hurt et al. [1] considered this question in any depth. In fact, they identified three main groups where the classification of the strategies for the catalyst incorporation followed the different cases reported up to the beginning of 2017. The first group is called "integration strategy" that considers the cases where catalytic phases have been included within an already-valid printable material prior to the printing process, or were used as the building material outright. Secondly, the group called "functionalization strategy" that implies the coating of the printed device during a post-treatment process. Finally, the last group which consisted of a combined approach of integration and functionalization

In principle, these classification results are very useful. However, there are some cases that could be reclassified depending on the criteria applied to decide if the printed device is reaction ware or a structured catalyst. Additionally, new examples with alternative strategies for the use of additive manufacturing in catalysis have appeared and they do not quite fit into any of the cited groups. These are the cases where the printed device is a template into which a colloidal matrix is embedded and then, by means of a thermal and/or chemical treatment, it is transformed into a structured system with a geometry inverse to that of the template. The said template disappears thanks to the thermal and/or chemical treatment, and regarding the structured system, this can be made of the catalyst or not, in which case it would require a subsequent treatment of coating. Therefore, the strategy where the advantages of additive manufacturing are transferred to catalysis by means of the use of a template can be labelled as indirect printing.

Considering this, an alternative classification of the studies devoted to the printing of structured catalysts it is proposed depending on the applied strategy, as presented in Fig. 18. Firstly, the approach labelled *Direct Printing*, where the catalyst constitutes all or an important part of the printable material, and thus the printed object can be subjected almost directly to the catalytic process. Despite this, in most cases activation post-treatments are required, generally of the thermal type in controlled atmospheres. The second one is the *Printing of Support* approach, which is made up of printed objects that are not made of the catalyst, but which will later be coated with it. This means that the incorporation of the catalyst involves additional procedures, apart from the subsequent activation of the catalyst before the reaction, which may involve heat treatments in controlled atmospheres. Finally, the *Indirect Printing* strategy it is proposed, where the printed devices are templates for the manufacturing of structured catalysts. These may or may not be made of materials that contain the catalyst in the colloidal matrix, and in the latter case, an additional process would be needed in which the device is coated with the catalyst.

4.3.1. Direct printing of structured catalysts approach

The inclusion of a catalyst or the precursors that will be subsequently transformed into a catalyst, within the formulation of the printable material, is not simple and the procedure may differ, depending on the catalyst's chemical nature and the printability requirements of the printing techniques used. In most of the cases included, the direct printing approach DIW is the most widely used technique (Fig. 18) and the main products are monolith type structured catalysts. However, electrodes, grids, and stir bar covers have been produced by means of other printing techniques such as SLS, SLM and SLA that provide a superior resolution than DIW.

There are cases in which the printable material is fully developed and this is much easier to do when applying the DIW printing technique, because no photo-curable agents must be added and, in principle, the operating conditions require additives that allow the consolidation of the piece at room temperature without additional treatments. For instance Tubío et al. [27] reported their own printable material for obtaining monoliths with a woodpile

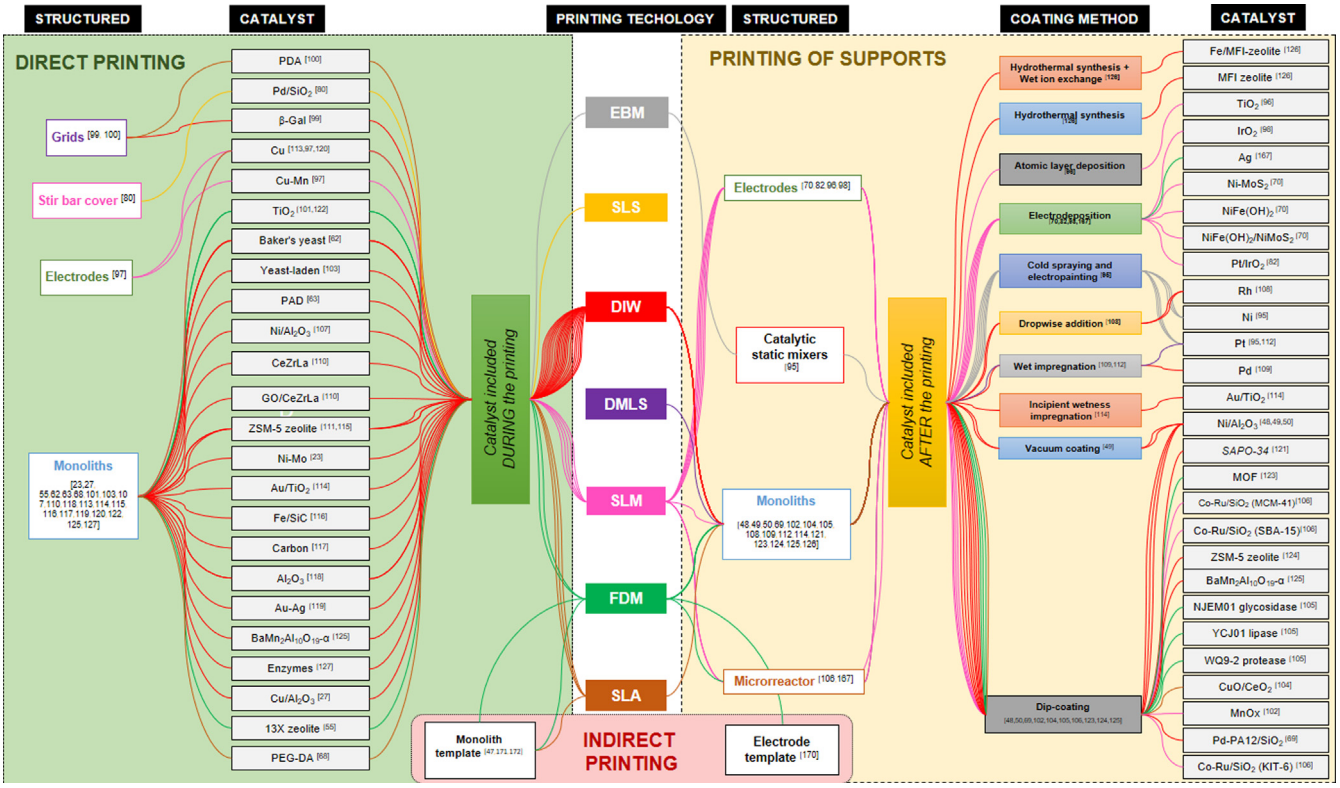

Fig. 18. Classification of the different strategies for the inclusion of the catalyst in most structured systems additively manufactured to date.

configuration by DIW. Their printable material consisted of Al_2O_3 powder dispersed in aqueous $Cu(NO_3)_2$ solution (the precursors of the Cu/Al_2O_3 catalyst) a viscosity modifier (hydroxypropyl methylcellulose) and a chelating agent (cationic polyelectrolyte poly(ethylenimine) to bind the matrix during the printing process. These authors optimized a composition for the printable material that enabled a homogeneous distribution of the catalyst throughout the monolith.

Following a house-produced printable material approach, recently Middelkoop et al. [107] reported the production of monoliths for the CO_2 methanation reaction. In this case, the Ni/Al_2O_3 catalysts were prepared prior to the printable matrix, and bentonite as well as powder Al_2O_3 were included as binders. These authors also reported graphene-supported CeZrLa mixed-oxide catalysts for printing monoliths for the synthesis of propylene carbonate[110]. In this case, the catalysts were previously obtained by continuous hydrothermal flow synthesis, which implies mixing a flow of water-soluble precursors to give rapid, controlled and continuous production (within seconds) of nanomaterials. These powder nanomaterials (42 wt%) were mixed with an aqueous solution of methyl cellulose (54 wt%) and a small portion of lubricant additive (Thinky Mixer ARE-250) to ensure a suitable rheology during the process of printing by DIW.

Wang et al. [165] recently presented the direct production of structured WO_3-based catalysts by additive manufacturing using the DLP method. In this case, structures with complex configurations were printed using suspensions that contained the catalyst precursors in the form of salts dissolved in the medium. This implies that dispersed catalyst particles are not used, but rather that the catalyst is consolidated in the structured itself by calcination after printing. This favors the homogeneous distribution of the catalyst precursors throughout the volume of the printed device and promotes greater control of the resolution of the printing process.

In some cases, catalysts that are part of the printed structured devices, require further treatments for the enhancement of an specific catalytic feature. For example, Quintanilla et al. [116] studied the densification of the printed structures that already contained the catalyst used for the phenol oxidation, using non-pressurized Spark Plasma Sintering, which involves submitting the printed monoliths to temperatures ranging from 1000 to 1500 °C in an argon atmosphere (~6 kPa), and the results obtained create a dilemma. On the one hand, the densification process is effective because it increases the hardness of the monoliths and reduces the leaching of iron. However, the accessibility to the Fe atoms, which are the active sites of the catalyst, decreases. Therefore, a balance must be found between the different properties that are sought in the final structure.

Amongst the novel strategies used to control the properties of printed monoliths that include components with catalytic features, it is interesting to cite the one recently reported by Zhou et al. [117], who presented the manufacturing of monoliths with carbon of tailorable pore size for the benzyl alcohol oxidation. This control of the pore size of carbon was achieved by adding SiO_2 monodisperse spheres within the printable matrix that included starch and gelatin as binder and carbon sources. Once the mixture was completely gelatinized, the printing was carried out and the structures obtained were carbonized at 1100 °C for 2 h with a heating rate of 5 °C/min in an N_2 atmosphere. Afterwards, the monoliths were washed with NaOH (2 M) to remove the SiO_2 spheres resulting in pure carbon replicas with an additional porous structure provided by the no longer present SiO_2 spheres.

The printing of structures that incorporate enzymes is another example that must be highlighted because it involves the creation of a separate branch within the union between additive manufacturing and catalysis, which is the printing of bio-active catalytic systems (bio-printing). This is the case of Wei et al. [127] who prepared supramolecular hydrogel *via* pH triggered molecular

self-assembly in water. Then, dual enzyme-catalyzed reagents, including glucose, among others, were added to the hydrogel until an extrudable rheology was obtained, to be used in the generation of structures through a pseudo DIW process with a syringe as an extruder. In this case, the authors remarked that the hydrogel is cytocompatible and can be used for in situ 3D cell culture, which makes this a promising material for bio-catalysis and tissue engineering.

Another example of the printing of structures for the intensification of bioprocesses is the one reported by Quian et al. [62] that combines nanocellulose crystals and Baker's yeast (Saccaromyces cerevisiae) to obtain different structures through DIW. The authors noted an unprecedented cell loading in the structured system, and it was discovered that the cells exerted a substantial impact on ink rheology, and the cell inks had the shear-tinning behavior desired for extrusion-based printing. Therefore, the living material itself influences the printability. Furthermore, a superior ethanol production was achieved during the glucose fermentation due to the design of the printed lattices compared to bulk counterparts. However, despite the considerable advances in biomaterials printing for catalysis, the immobilization of enzymes within hydrogels supposes mass transfer limitations due to the reduction of access to the active sites of enzymes and thus requiring the increment of the intrinsic enzyme activity. This means that more active systems may overcome the loss of volumetric activity in structured biocatalysts[99].

Regarding the introduction of catalyst on other type of structured catalysts, recently, Zhang et al. [97] presented the production of electrodes by means of SLM using a Cu-Mo alloy. In this case, the active componants are the metal species Cu or the Cu-Mn in the electrode. This is perhaps the easiest way to incorporate a catalyst into a structured system and this is when the printable material is entirely made up of the catalyst. Although in this case, a copper enriched electrode system was also generated on the surface through a pickling process. The absence of additives facilitates the prompt application of the device and reduces the possible effects on the properties of the material due to constant post-printing treatments.

Another relatively simple strategy to include the catalyst is to modify the active component of formulations whose printability has been previously confirmed. For example, Manzano et al. [68,113] analyzed printed devices (made with PEG-DA by means of SLA) for the Mannich reaction and the Aldol and Huisgen cycloaddition reactions. In this case, modified bifunctional molecules were included within the printable formulation, providing accessible carboxylic acid, amine, and copper carboxylate functionalities that were transferred to the printed structured system and exhibited catalytic activity in the cited reactions. Furthermore, an enhancement of the reaction conversion upon increasing the complexity of the additively manufactured objects was observed, highlighting the successful functionalization of commercial resins for anchoring the catalyst prior to the printing process.

4.3.2. Printing of structured supports approach

In this case, the catalyst is coupled with the structures after they have been manufactured, therefore there is a certain freedom in the printing process that is no longer limited by the possible negative effects on the properties of the catalyst. However, the need arises to work with materials that are capable of anchoring the catalyst [166]. In this sense, combining the information in Fig. 7,8,10 and 11, it can be said that a considerable variety of printing materials are beginning to be generated, which include ceramic, metallic and polymeric materials. In the same way, the use of hybrid systems such as TiO_2-ABS, which combines a polymeric part and a ceramic part, is growing. However, regarding the type of catalyst incorporated, it can be observed that the metallic and ceramic structures are related to catalysts of a similar nature, while the polymer-type structures tend to be combined with catalysts based on carbon or bioactive agents such as enzymes. This is an expected result because the coupling between the catalyst and the printed structure is mainly due to chemical affinity.

The incorporation of the catalyst occurs mainly on the surface of the structured system and can be beneficial in two important ways. Firstly, it reduces the amount of catalyst used to manufacture the entire structure, and this becomes highly relevant when it comes to catalysts made up of high-value elements such as precious metals. Furthermore, accessibility to active catalyst phases is improved because the vast majority are exposed on the surface of the framework and there are no catalyst parts hidden within the core of the structured system. Therefore, the phenomena of matter transfer during the catalytic process are much more efficient and the specific activity per mass of catalyst is much higher.

Despite these advantages there are drawbacks. On the one hand the printing of structured supports involves a series of additional stages after the printing process that can increase the cost of this type of structure. On the other hand, achieving a stable anchoring of the catalytic layer to the surface of the catalyst becomes one of the greatest challenges for this type of system because the leaching of the catalyst must be avoided as much as possible during its use in the catalytic process, especially in catalytic reactions occurring in liquid media. This, in principle, would involve not only a suitable procedure to anchor the catalyst to the structured system that acts as support, but also protect the integrity of such structured system during the catalytic process. This is due to the fact that there is evidence in unprinted structured systems coated with catalyst that the structured material itself suffered alterations due to the environment of the working atmosphere, generating a progressive deterioration of the catalytic layer [24].

Until now, the methods used to anchor the catalyst to the printed structures (Fig. 18), have been the same as those commonly used in the coating of non-printed structured systems. The most widely used one is dip-coating [48,50,69,102,104,105,121,123], perhaps because it applies a simple and accessible strategy, in which the surface of the structure is covered with a slurry of the catalyst. It does not require expensive technology, it is reproducible if the rheology of the catalyst suspension can be controlled and it can be carried out under mild conditions, guaranteeing to a great extent the preservation of the integrity of the catalyst. In addition, it is a versatile technology that can be adapted to catalysts of different natures.

In some non-printed structured systems that have been coated with catalyst through the dip-coating process, treatments are usually used on the support to increase the anchorage of the catalyst. For example, in micromonoliths made with FeCrAlloy ®, a heat treatment at 900 °C is usually applied, which allows the evolution of a surface layer of aluminum whiskers, which, thanks to their morphology and ceramic character, protect the metal core of the structure and favor the anchoring of catalysts based on metal oxides. Nevertheless, in most of the cases included in Fig. 18 that reported the use of dip-coating, no pretreatments of the printed structures beyond a mere alcohol and ultrasound cleaning have been reported. This may be due to the fact that, in most cases, the chemical affinity between the support and the catalyst is high, which facilitates its anchoring. However, the case reported by Chaparro-Garnica et al. [104] is special because it poses the challenge of coating the channels of monoliths made of a commercial polymeric resin (Visijet FTX green), with a ceramic catalyst (CuO/CeO_2). In addition to the alternative channel design to promote catalyst build-up pointed out in section 4.2.1.2., the authors proposed the surface be attacked with solvents before or during the active phase incorporation, but this was not entirely effective. What worked better was the incorporation of silica in the resin before printing since the presence of this oxide in the printed monolith

favored the subsequent adhesion of the catalyst. Along the same lines, Ye el al. [105] applied both; the modification of the printing material prior to the generation of the structured ones and the subsequent chemical edging of their surface with piranha solution, paracetic acid, and a silane-coupling agent, resulting in the successful immobilization of enzymes as presented above in Fig. 16D.

With respect to other methods for the incorporation of the catalyst, such as dropwise addition [108], wet impregnation [109,112], electrodeposition [70,82,98,167], atomic layer deposition [96] and cold spraying and electropainting[95], it can be established as a common factor that the catalyst load generated in the structures is less than that usually generated with dip-coating. For this reason, they focus mainly on the incorporation of metallic active phases, since their specific activity is quite high. However, these are also used to deposit some oxide-based catalysts in systems that do not need such a high load in order to achieve adequate catalytic activity results, as in the case of electrodes.

Despite this, it can be said that the use of alternative methods to dip-coating is still in an exploratory phase, and there are no cases that allow the identification of strategies for modifying the printing material, or for the treatment of the printed structures, specifically designed to improve the performance of the catalyst anchorage by means of said methods.

4.3.3. Indirect printing of structured catalysts approach

This is a strategy for the manufacture of structured catalysts that has not been clearly differentiated until today and, although currently there are few articles published on the matter, it clearly differs from the two strategies presented so far. In fact, in other fields where the additive manufacturing is applied, the relevance of this strategy is becoming observable. For instance, Tijing et al. [168] recently presented a review on the use of additive manufacturing for membrane separation, desalination and water treatment, and they included the principles of this strategy within one of the future prospects of this field where additive manufacturing is combined with subtractive manufacturing and formative manufacturing.

In the indirect printing approach, additive manufacturing is used to generate molds that are then sacrificed after chemical and/or thermal treatments [159,169]. This reduces the importance of the chemical affinity between the catalyst and the printed structure because what is sought is that the mold simply drives the consolidation of the final structure through a physical process, which in principle is more practical. However, the template removal stage incorporates other types of factors to be taken into account, such as possible alterations to the final structure, either due to the atmosphere in which the template is removed, or due to diffusion problems during the removal of sacrificial material.

Once the mold is printed, it is filled with a paste that is then cured and consolidated with a thermal or chemical treatment. The release of the material from the mold can occur simultaneously to the consolidation of the paste or afterwards, and in this case, the unit stages of the process would be increased. Taking into account this general operating procedure, two types of structures can be obtained in this way. Firstly, those in which the paste matrix incorporates the catalyst or its precursors and, after consolidation, a structure with catalytic activity is obtained. Once consolidated, these systems are similar to those obtained through the direct printing strategy (section 4.3.1), but to differentiate them, to label them *indirect structured catalysts* it is suggested. Secondly are those in which the matrix that is introduced into the mold does not contain the catalyst. Therefore, in the consolidation process, a structure will be generated that must be subsequently coated with the respective catalyst. This type of structure is similar to that generated by the printing of structured supports (section 4.3.2) and the same coating methods with the suitable catalysts could be applied. However, to differentiate them, naming them *indirect structured supports* it is proposed.

As mentioned above, there are currently few articles that present the application of indirect printing for obtaining structured catalysts[159]. In fact, there are cases such as that of Hereijgers et al. [170] that presented just the manufacturing and characterization without catalytic tests of electrode mixers, which are 3D flow-through structures with mixing properties that at the same time act as electrodes. In this study, printed polymeric templates (made of LimoSolve polymer purchased from Formfutura) were filled with a paste consisting of Ni powder (61.2 wt%), epoxy (14.3 wt%) and glycerol (24.5 wt%). After filling the mold, epoxy was cured for 3 h at 40 °C. The mold was dissolved in toluene and then the structure was sintered by means of a heat treatment, with different stages up to 1000 °C.

The first study that combines the manufacture of an indirect structured catalyst with catalytic activity measurements is that presented by Li et al. [171], whose reported cylinder, tetrahedron, and tetrakaidecahedron phenol–formaldehyde-based hierarchical monoliths coated with Ni/Al_2O_3 catalyst for the CO methanation reaction. The phenol–formaldehyde paste was used for filling the templates (previously printed by means of FDM with PLA), and through a solvothermal polymerization process at 160 °C for 8 h under hypersaline conditions ($ZnCl_2$) [171], subsequently brown monoliths were obtained. The monoliths were then washed with ethanol for removing the residual polymer templates and $ZnCl_2$, dried in vacuum 105 °C, and finally calcined under N_2 atmosphere at 900 °C. These monoliths can be classified as *indirect structured supports*, since they require the subsequent coating with a catalyst. Therefore, with a first impregnation with aluminium isopropoxide and a calcination process at 550 °C, an alumina layer was generated on the surface of the monolith. Afterwards, the system was further impregnated with $Ni(NO_3)_2$ solution and then calcined under nitrogen atmosphere at 550 °C, resulting in the generation of the Ni/Al_2O_3 catalyst. Regarding the catalytic activity measurements, not only was the high performance of the indirectly printed structured catalysts observed, but also a correlation between such performance and the tailored geometry of the devices was noted. Particularly, the control of the tortuosity of macro-channels into the monoliths resulted in high yields towards CH_4 due to the decrease of mass and heat transport limitations.

Another example of *indirect structure support* production is that recently reported by Hędrzak et al. [172] where templates made of a commercial polymeric resin (B9R-4-Yellow) and printed by FDM, were used to obtain monoliths made of α-Al_2O_3. The monoliths were immersed in a hydrothermal reactor with the precursors for the ZSM-5 zeolite synthesis and thus a surface layer was generated with said catalyst (see Fig. 19B). These devices were tested in the gas-phase isomerization of α-pinene. The performance of the device is closely related to the tailoring of the Al/Si molar ratio during the zeolite synthesis over the surface of the monoliths. In general, the success of this work lies in the fact that the monoliths generated by this technique are catalytically active and comparable with other types of structured systems. Furthermore, they can regenerate in oxidizing atmospheres at high temperatures and do not deteriorate. Therefore, it is anticipated that in future studies, it will be possible to delve into the analysis of the influence of geometry on the total conversion and, even more importantly, on the distribution of products.

Davó-Quiñonero et al. [47]obteined printed templates for obtaining monoliths tested in the CO oxidation and the CO-PROX reactions. In this case, templates were made of commercial polymeric resin Visijet FTX Green, and these were filled with a commercial cordierite paste (COR-MIK-MP provided by VICAR S.A.). After the curing process, the template was removed by combustion in static air at 500 °C for 2 h. Subsequently, the resulting monoliths

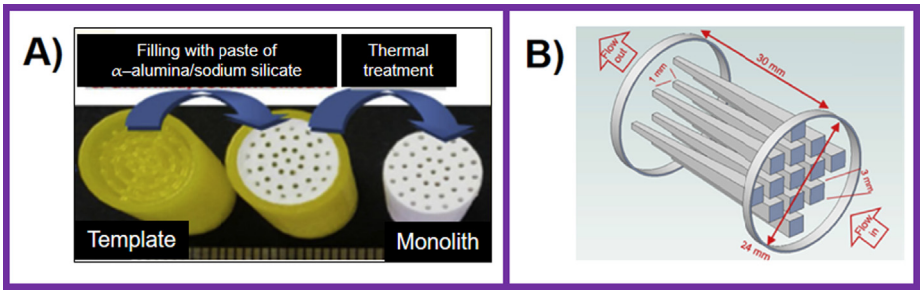

Fig. 19. Examples of indirect printing of structured catalysts: A) Template for obtaining monoliths with straight channels. Reprinted from Ref. [172] B) Scheme of templates for obtaining monoliths with asymmetrical channels. Reprinted from Ref. [47].

were sintered in air at 1250 °C. The authors reported a first coating with α-Al_2O_3 with the aim of avoiding the migration of the active phase into the cordierite body, as well as tohi ensure the anchoring of the catalyst on the surface of the channels. Regarding the catalyst (CuO/CeO2) this was deposited over the surface of the monoliths two times. Firstly, these were immersed in a CeO_2 suspension and further calcined at 600 °C. Then, the CeO_2-coated systems were impregnated with $Cu(NO_3)_2$ and finally calcined at 400 °C for 2 h. The resulting devices demonstrated a good performance in both reactions, although the monoliths which had a design of channels of variable size along the axial axis stand out, because this asymmetry better allows for the thermal control of the processes, which is decisive not only in terms of conversion, but also selectivity. Therefore, as can be seen in this case, the differential factor is the design of the structure and the manufacture of a monolith with channels of variable size, and this is greatly facilitated thanks to the use of additive manufacturing, even if it is governing the structure of the monoliths through templates. More recently, Tronconi et al. [159] obtained copper periodic open cellular structures by means of an indirect printing approach too, and these devices are very promising as supports for heat-transfer limited applications.

5. Patents with applications that merge catalysis and additive manufacturing

Up to now it has been shown that the link between catalysis and additive manufacturing is a recent topic. Therefore, it is to be expected that intellectual property registrations will follow a trend, at least similar to that of scientific articles. After conducting an exhaustive search for patents, using keywords such as structured catalysts, additive manufacturing, monoliths, electrodes, microreactors, 3D printing, printed catalysts, among others, about 60 patents have been found that begin to appear from 2014. Therefore, it can be said that property registrations start about five years behind the mass publication of scientific articles on this topic. Fig. 20 shows a graphic summary of the most relevant trends that can be extracted from the different item, while more detailed information of every registered application up to now is presented in Table 1. In the first place, the change in the increasing trend of the number of patents in 2020 (Fig. 20A) certainly may be influenced by the crisis generated by the pandemic. However, based on the observed behaviour of the scientific papers (see Fig. 3) everything seems to indicate that the registration of patents on this

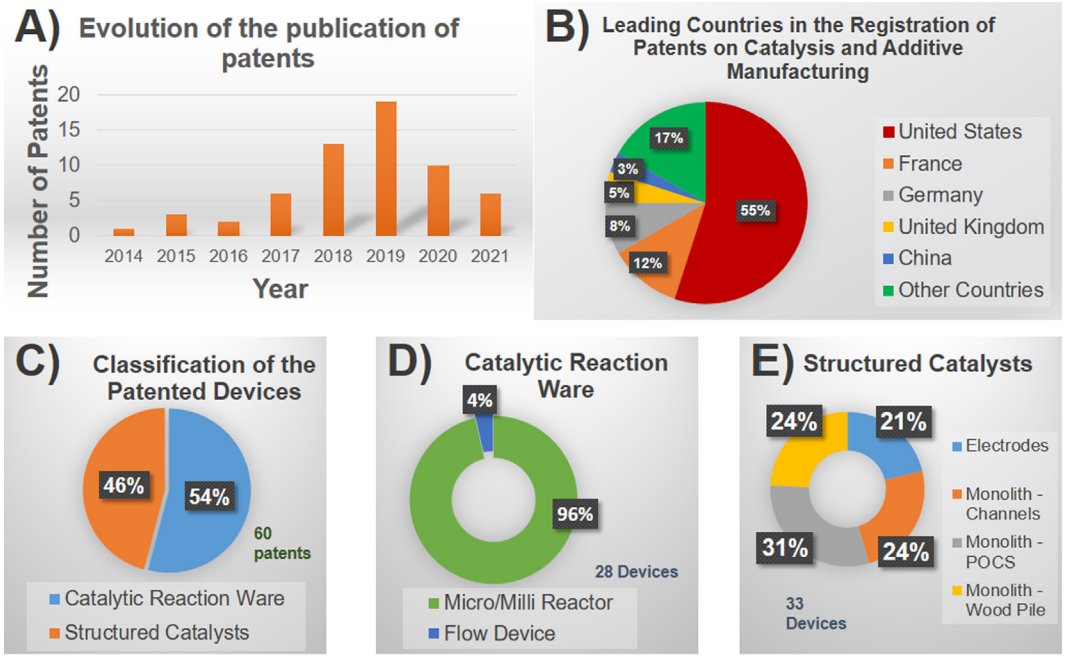

Fig. 20. Summary of the analysis of patents that combine catalysis and additive manufacturing: A) Number of patents per year; B) Leading countries in the registration of patents on this topic; C) Classification of patented devices; D) Types of Catalytic Reaction Ware; E) Types of Structured Catalysts.

Table 1
Registered patents that combine catalysis and additive manufacturing.

Patented Device		Printing Material	Printing Technology	Catalytic Application	Applicants	Country of the Applicants	Ref.	Year
Catalytic Reaction Ware	Flow Device Micro/Milli Reactor	N.S	N.S	N.S	Brunel University	United Kingdom	[173]	2015
		Polymers	N.S	N.S	N.S	Canada	[174]	2015
		Metals, Ceramics and composites	N.S	Catalytic reforming	Watt Fuel Cell Corp	United States	[175]	2016
		Metals, Ceramics, Composites	SLS/SLM	Heat Exchange	L'Air Liquide	France	[176]	2017
		Metals, Cermets	SLS/SLM	Hydrogenation reactions, Carbon-Carbon coupling,	Commonwealth Scientific and Industrial Research Organisation	Australia	[177]	2017
		Polymers	N.S	N.S	The University of Vermont	United States	[178]	2017
		N.S	N.S	Rocket Engine	Airbus DS GMBH	Germany	[179]	2017
		SiO_2	N.S	Methanization	Activated Research Company, LLC	United States	[180]	2017
		Metals	LENS	Low NOx combustion	Utilization Technology Development, NFP	United States	[181]	2018
		Composites	DIW	CO_2 capture and storage	Lawrence Livermore National Security, LLc	United States	[182]	2018
		Metals	SLS/SLM	CH_4 reforming	L'Air Liquide	France	[183] [184]	2018
		N.S	SLS/SLM	Simulation	Sabic Global Technologies, B.V	India	[185]	2018
		Metals	SLS/EBM	Catalytic reforming	Honeywell International INC	United States	[186]	2018
		Metals		Fuel Reforming			[187]	
		Ceramics	SLS	Car Catalytic Converter	Khalifa University of Science and Technology	Arabian Emirates	[188]	2019
		Composites	DIW	CO_2 capture and storage	Lawrence Livermore National Security, LLc	United States	[189]	2019
		Composites					[190]	
		N.S	SLM/SLS/FDM	Fluid Catalytic Cracking	IFP Energies nouvelles	France	[191]	2019
		Metals	SLS/SLM	CO_4 reforming	L'Air Liquide	France	[192]	2019
		N.S	SLS/SLM	Methanol production	Fraunhofer-Gesellschaft Zur Forderung Der Ang. For. E.V.	Germany	[193]	2019
		Metals	SLS/SLM	Thermochemical Processes	Battelle Memorial Institute	United States	[194]	2019
		Ceramics	SLA	NH_3 cracking	Postech Res & Dev Found	Korea	[195]	2020
		Ceramics	N.S	N.S	3D-CAT B.V.	Netherlands	[196]	2020
		N.S	N.S	N.S	Covestro Deutschland AG	Germany	[197]	2021
		Metal	N.S	CO_2 capture and storage	UT-Battelle, LLC	United States	[198]	2021
		SiO_2, ZrO_2, CeO_2, Activated Carbon	DIW	Methanol to olefins	Vlaamse Instelling Voor Tech Onderzoek NV	Belgium	[199]	2017
		Ceramics	N.S	N.S	Fourté International, Sdn. Bhd.	Malaysia	[200]	2018
Structured Catalysts	Monolith - POCS	Al_2O_3, SiO_2, SiN, SiC	SLA/SLS	SCR in vehicles	Johnson Matthey	United Kingdom	[201]	2014
		Zeolites					[202]	2016
		N.S	SLA	Cu-catalyzed azide-alkyne cycloaddition	Lawrence Livermore National Security, LLc	United States	[203]	2018
		PEGDA		CO_2 capture and storage			[204]	2019
		Ceramics	N.S	N.S	Fourté International, Sdn. Bhd.	Malaysia	[200]	2018
		Metals	DIW	N.S	Trustees of Dartmouth College	United States	[205]	2019
		TiO_2	N.S	N.S	West Virginia University	United States	[206]	2019
		Metals	SLA	N.S	California Institute of Technology	United States	[207]	2020
		Ceramics	DIW	Methanol Reforming	East China University of Sci. and Tech.	China	[208]	2020
		Hydrotalcite	DIW	N.S	Beijing University of Chemical Technology	China	[209]	2021
	Monolith - Channels	Metal, Ceramics	N.S	CH_4 reforming	ExxonMobil	United States	[210]	2018
		Ni, Fe, Co– based alloys	DMLS/SLS				[211]	
		TiO_2	DIW	Volatil Organic Compounds Oxidation	N.S	United States	[212]	2019
		Metals	SLS/SLM	Steam Reforming of CH_4	Topsoe Halador	Denmark	[213]	2019
		Bohemite	DIW	N.S	Institut kataliza im. G.K.	Rusia	[214]	2020
		Ceramics	N.S	N.S	Sparks Douglas Ray	United States	[215]	2020
		Polymers	N.S	NH_3 adsorption	Advanced Fuel Research, INC.	United States	[216]	2021
		N.S	FDM	N.S	Xerox Corp.	United States	[217]	2021

(*continued on next page*)

Table 1 (*continued*)

Patented Device	Printing Material	Printing Technology	Catalytic Application	Applicants	Country of the Applicants	Ref.	Year
Monolith - Wood Pile	SiO_2, ZrO_2, CeO_2, Activated Carbon	DIW	Methanol to olefins	Vlaamse Instelling Voor Tech Onderzoek NV	Belgium	[199]	2017
	Hydroxyap.	SLS	Mechanical Properties	University of Bordeaux	France	[218]	2018
	N.S	SLS	N.S	Covestro Deutschland AG	Germany	[219]	2019
	Metals, Ceramics	DIW/SLM	CO_2 Valorisation	Vito NV	France	[220]	2019
	Zeolites	DIW	Fluid Catalytic Cracking	The Curators of the University of Missouri	United States	[221]	2019
	Bentonite	DIW	N.S			[222]	2020
	Carbon	DIW	N.S	Livermore Nat Security LLC	United States	[223]	2020
	Ceramics	DIW	Butyne hydroenation	BASF SE	Germany	[224]	2021
Electrodes	N.S	N.S	Redox processes	Concurrent Tech. Corp.	United States	[225]	2018
	YSZ	Material Jetting/ DIW/SLA	Electricity production	Utility Global, Inc.	United States	[226] [227] [228] [229] [230]	2019
	Ceramics	Material Jetting/ DIW/SLA	Electricity production	Utility Global, Inc.	United States	[231]	2020

subject will continue to increase. What is clear is the leadership of the United States (Fig. 20B) is very marked since they have a little more than half of all the patents registered worldwide.

Regarding the information that can be extracted from patents, it is important to note that this is less detailed than that of scientific articles. Despite this, the different registered applications have been classified following the criteria proposed in this review, where two main groups are distinguished: catalytic reaction ware and structured catalysts.

Unlike scientific articles, in the selected patents there is no marked difference between catalytic reaction ware and structured catalysts. The number of applications of one case or another is very similar (Fig. 20C). Moreover, almost all catalytic reaction ware corresponds to reactors in the milli or micrometer range (Fig. 20D). In some cases, they are heat exchange systems and in others, they fulfil the role of vessels where catalytic reactions occur, with designs that improve the contact between reactants and the active phases. The main manufacturing materials are metals and ceramics, but clearer trends on the types of materials cannot be drawn due to the lack of detailed information. The only thing that can be established is that they are all designed for applications that move in a medium / high temperature range (200–800 °C), according to the catalytic reactions for which they are designed (See Table 1), whose mostly are conceived for reducing emissions in sectors such as the automotive industry, for the CO_2 capture and storage or transformation, or the hydrogen production throughout reforming reactions.

In the case of structured catalysts, about 80% of the devices are monolithic type (Fig. 20E), although there is a widely distributed trend among the configurations of those devices (monoliths with channels, woodpile or *iso*-reticular foams; see Fig. 13). Most of them are applied in processes of automotive industry, CO2 vaorization or the hydrogen production cited above. This means that they are designed for operating temperatures above 200 °C, which justifies the fact that the manufacturing materials are either a metal or a ceramic, which allow an easier integration of the catalytic phase.

From the information in the patents, normalized catalytic performance comparisons cannot be made because there is no standard contrast framework. However, it can be said that the design effect, which is paramount in additive manufacturing, is seen more clearly in catalytic reaction ware than in structured catalysts, because in the first case, the printed reactors have a higher resolution. This resolution is difficult to achieve when printing Milli/Micro monoliths due to their small size and the types of materials being used (ceramic and metal), therefore, most patented printed monoliths have simple geometries or configurations such as the wood-pile. Maybe the POCS configuration may provide advanced effects based on geometry but the cited cases are mainly devoted to the manufacturing and the performance of these devices is not deeply addressed.

In general, the patents show an intensification of positioning by the companies included in Table 1 and which are related, mainly to the energy sector, the automotive industry or the hydrogen production, but more specific trends cannot yet be defined. Additionally, nor these technologies can be considered mature, due to the short time that has passed since these records were published.

6. Perspectives of the union between catalysis and additive manufacturing

Catalysis, as a transversal element and enhancer of the chemical industry, is not unrelated to the boom in additive manufacturing and this is evidenced in the exponential growth of studies in the last decade, in which several additively manufactured objects are used in many catalytic applications. In the union of catalysis and

additive manufacturing, different variables come into play such as the type of role that the printed part performs and under what conditions it operates, what type of printable materials are used, what printing technique is used and how catalysts are incorporated in these types of devices. This implies that the expression "catalytic applications" is a very broad scenario in which these variables are combined in different ways. However, there is already a large body of work that shows that there are strategies for the fusion of catalysis and additive manufacturing that can be clearly differentiated, and this is one of the main tasks that has been carried out in this summary. However, there is already enough information to clearly define the strategies that are being applied for the fusion of catalysis and additive manufacturing, and this is one of the main tasks undertaken in this review.

On the other hand, considering the relevance of design in the production of any object by means of additive manufacturing, the question arises as to where the design of devices with catalytic applications will focus. The answer is not simple because although there are a growing number of examples, the possibilities from a design point of view are enormous and there is a great diversity of reactions still to be studied, of printing materials to be developed and of substantial improvements in manufacturing technologies still to be reached.

Regarding design, the approach of replicating the structures found in nature that act with enormous efficiency, both in their production and in the use of resources, is still very attractive. Therefore, biomimetic will surely have a greater presence in printed devices in the near future. As for the materials, the possible combinations of materials to functionalize the printable matrices is enormous. Nevertheless, a significant amount of growth is expected in the field of metal printing within a short space of time, because the efforts being directed to this task are significant. Another important scenario for the development of printing materials will be that of bio-active systems, because the immobilization of enzymes in structured systems is highly attractive, since they are the catalysts with the highest chemical specificity found in nature and their application can cover many technological scenarios.

Regarding the catalytic processes in which the printed devices will be used, a growth in the diversification of reactions is also expected. However, it is evident that the need to lessen the effects of climate change creates important guidelines that will inspire a huge number of studies. Therefore, everything related to the capture and recovery of CO_2 becomes increasingly decisive, as evidenced by the growing number of studies focused on printed CO_2 adsorbents for purification of closed environments [232–240], which could be combined in the near future with catalytic recovery processes. In the same way, the renewable hydrogen production and obtaining fuels and value-added products from residual biomass, will surely increasingly include examples of printed catalytic applications since are processes that require the advantages of intensified catalytic devices. Similarly, bioactive systems will have a highly significant effect due to their applicability in sectors with a high economic impact, such as pharmaceuticals. Finally, the technological challenges of the future trip to Mars cannot be forgotten, where additive manufacturing is expected to provide a large part of the solutions, where there will surely be more than one catalytic process involved.

On the other hand, after all the discussion generated from the analysis of all the information included in this review, five fields of action have been identified that have great potential to determine an important advance in the union between catalysis and additive manufacturing. They have probably been specifically mentioned throughout the document, but given their innovative nature and taking into account that they are just starting up, it is important to dedicate a special space to them and develop them below.

6.1. Simulation tools for enhancing the union between catalysis and additive manufacturing

The rapid transfer of a computer assisted design (CAD) to a real 3D object achieved by means of additive manufacturing, is a clear opportunity to combine this with computational optimization, as was highlighted by Parra-Cabrera et al. [2]. In their review, these authors presented the most comprehensive analysis on this item within the context of catalysis and additive manufacturing, analysing different studies where computational fluid dynamics (CFD) was introduced to address hydrodynamics and transport phenomena. In addition, they cited the use of multiscale modelling for describing structured catalysts in continuous flow reactors with CFD. However, in that review [2], a classification as strict as that proposed in this document is not assumed and the question arises as to whether the models are being applied for structured catalysts or for catalytic reaction ware.

Bettermann et al. [241] proposed a methodology for the production of 3D-printed reactors based on CAD modelling and CFD simulation. In this study, they presented a scheme that illustrates the role that simulation tools can play in this process. Nevertheless, a modification this scheme is proposed in Fig. 21 since the contribution all CAD modelling, 3D printing, and CFD simulation is asymmetric. Currently, a higher contribution of CAD modelling is observable since the computer tools and the software for design are really powerful. In the second place, 3D printing since further advances are required for the development of new printing technologies and the room for improvement is considerable. Finally, the smallest contribution comes from CFD simulation due to the lack of robust models in practically all the catalytic processes.

From the scheme presented in Fig. 21, it is inferable that the feed-back between the CAD-modelling and the printing process may be enhanced by the inclusion of CFD simulation. CFD simulation can become a tool that makes it possible to estimate the reliability of 3D objects and seek their optimization without the need to manufacture them, because the model itself would rule out unfavourable scenarios based on the trends it can process. However, within this iterative scheme, a relevant fact is revealed and it is that perhaps there are not yet enough iterations in so many catalytic reactions in which 3D printed objects can be included. This means that it is necessary to collect more experimental information generated by the catalytic tests applied to printed devices to generate trends that allow the consolidation and validation of robust CFD models.

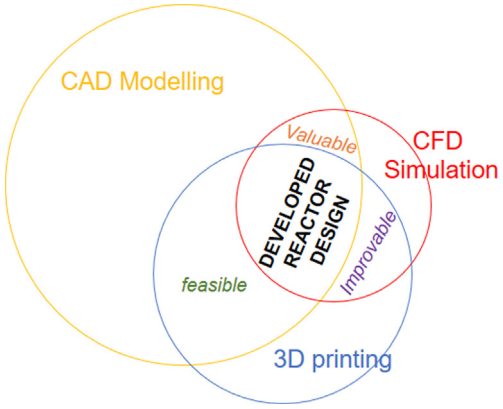

Fig. 21. Adaptation to an asymmetric approach of the overview of the digital and lean development method for tubular reactors as valuable, feasible and improvable combination of CAD modelling, CFD simulation and 3D printing, proposed by Bettermann et al. [241].

Table 2
Recent studies where modelling tools are included for the analysis of printed devices for catalytic applications.

Year	Printed catalytic device	Application	Property analysed with CFD or numerical analysis	Highlights	Ref.
2019	Monolith - POCS	Not specified	- Mechanical properties Pressure drop	Validation of a CFD model that predicts the pressure drop of the structured depending on the cell density.	[46]
2019	Monolith - POCS	Squalene to squalane reaction	- Mass transfer Pressure drop	Geometry optimization of the POCS to minimize pressure drop using CFD	[109]
2019	Monolith - POCS	CH_4 oxidation	- Fluid dynamics Pressure drop	By means of CFD simulation, the geometry of the structured was optimized for enhancing the turbulence during the catalytic reaction.	[133]
2019	Monolith – wood pile	Bio-butanol recovery	- Fluid dynamics Heat exchange	By means of CFD modelling, the cell density of the structured was analysed aiming to maximise the performance	[242]
2019	Micro/milli-reactors	Emulsions polymerization	- Fluid dynamics Heat exchange	By means of CFD, the design of the reactor was optimized aiming to tailor the flow regime within the channels of the catalytic reaction ware.	[241]
2019	Monolith - Foams	Not specified	- Pressure drop	A correlation between geometrical properties of foams and the trends of the pressure drops confirmed by means of CFD simulations.	[155]
2020	Monolith - Foams	Not specified	- Pressure drop	A correlation between geometrical properties of foams and the trends of the pressure drops confirmed by means of numerical simulations.	[156]
2021	Monolith - POCS	Hydrogen oxidation	- Kinetic studies	By means of numerical simulations and kinetic models, it was confirmed that the hydrogen oxidation allows stablishing possible mass transport limitations in printed monoliths (POCS).	[243]

For this reason, the item of modelling is addressed in this review in the perspectives section, because it is a field in full development and much more information compilation of experimental data is still needed, followed by intense processes of modelling and validation. Only in this way, models can more significantly influence the redesign of an application.

As mentioned previously, Parra-Cabrera et al. [2] produced a very comprehensive summary of studies applying CFD tools on printed devices. Based on the classification suggested in this review, most of the cases presented by Parra-Cabrera and co-workers are in the category of catalytic reaction ware. More specifically, these are examples of micro/millireactors in which the design of the channels plays a determining role. Therefore, in order to complement this review, Table 2 includes studies after its publication where interesting advances are observed.

Among the recent studies included in Table 2, those developed by Tronconi and co-workers [155,156,243] stand out because, they show an advanced strategy in the fusion of catalysis and additive manufacturing. In fact, they printed the foams from models created from their own experimentation. In this sense, the last study [243] shows that with a test reaction (hydrogen oxidation) a model can be established to estimate the limitations in the transport of matter of this type of structure. This is precisely the type of study in which the iterative nature of additive manufacturing is used to the maximum since it demonstrates that starting from the analysis of multiple experimental data it is possible to implement models that predict the performance of structured devices based on the geometric information. Therefore, the objective is to be able to implement a *meta*-analysis strategy like the one described by Maconachie et al. [244] for mechanical properties, but in this case, with catalytic parameters.

6.2. Advances in the printing technologies

So far, DIW, SLA and FDM are the most widely used printing techniques and the main groups of materials most widely used, in order of highest to lowest frequency, are those of the polymeric, ceramic and metallic type. However, in the last 5 years there has been a significant diversification in the use of new technologies thanks to the development of new hardware by companies in the additive manufacturing sector, improving the printability of many systems (based on better resolution, speed, and quality of the piece among other aspects). In addition, prints with wider temperature ranges of operation and improved chemical and mechanical stability have been achieved, although the type of printing material marks the roadmap for the development of technologies and without a doubt, metallic materials are the ones of greatest interest today [162]. Therefore, it is expected that the next advances will be related to printing techniques included in the powder bed fusion and direct energy deposition families (see Fig. 1), which include trademarks such as HP, EOS, Stratasys, ExOne, MELTIO and Optomec. Metals have a series of advantages that, focused on the development of catalytic devices, can be very interesting. For instance the superior heat transfer to that of ceramic materials, the electrical conductivity and the thermal and mechanical stability [245].

6.3. Novel and advanced materials

One of the aspects that has been reinforced in this review is that there is no single way to integrate a catalyst into a printed object. The catalyst can be part of the print formulation and incorporated during the manufacturing process itself [246], or it can be incorporated through a series of post-treatment steps. Therefore, it is expected that from existing commercial formulations, new hybrid formulations can be developed which include printable catalysts or

precursors that can be transformed into catalysts in successive stages. The key to such hybrid formulations will be to find a way for the catalysts to preserve their catalytic performance. This type of catalyst development strategy is especially focused on technologies such as DIW, FDM or STL, in which in addition to the printing base material, there are a series of additives that make it printable. Polymeric and organic-based materials will continue to be the most widely used, but the inclusion of inorganic components will expand the palette of printable materials. Therefore, finding the best combination for formulations with catalytic applications is a whole field to explore by harmonizing the properties of the formulation components (maximizing its printability) and those of the final material when it goes through all the post-processing stages.

On the other hand, as mentioned above, there is a high interest in developing metal printing technology and this is due to the attractive qualities of such materials [247]. However, a parallel strategy is to design hybrid composite materials that can achieve benefits similar to those of metals, especially in terms of thermal conductivity, electrical conductivity, mechanical resistance and chemical stability. This type of material can be, for example, cermet-type composites, which combine a metallic material and a ceramic type [248,249]. Cermets have been specially developed in the field of tools making because they are highly resistant materials. However, they have thermal conductivity properties that, combined with their stability against chemically aggressive environments, could place them even above metals as materials for manufacturing structured systems. Furthermore, it has to be considered that the properties of cermets, closer to those of metals and ceramics, mean that their printing can be carried out through techniques included in families of technologies such as binder jetting, powder bed fusion, and direct energy deposition.

6.4. Catalytic bio-printing

Other scenario where important advances are expected is that of catalytic bio-printing, which refers to the printing of objects with catalytic functionalities in biological processes [250,251]. Although there are successful tests for the preparation of frameworks capable of immobilizing enzymes that are later active in biological processes, from a geometric point of view, this type of frameworks present very precarious geometries. This is because most of the printing inks used in this case are gels that fail to preserve a high 3D structural consistency.

Said structural consistency could be achieved by incorporating additives that promote the consolidation of the gel or even that of an alternative material playing the role of dispersant phase, but this works against the living agents that are part of the formulation. Therefore, the challenge is to find a way to control the printable shapes of structured gels in a more refined way, without losing their ability to immobilize and to preserve live catalytic agents, nor their performance in reaction. Finally, it is important to note that all developments in catalytic bio-printing are of special interest in the pharmaceutical and food industries. Therefore, the economic impact of the advancement of this technology will have a relevant economic impact.

6.5. ***4D*** *printing*

The 4D printing concept maximizes the relevance of design in additive manufacturing processes, because it aims to add functionalities to printed objects based on their interaction with certain environments once the object is manufactured . This has very important implications from the selection of the printing material and the manufacturing technique, because the transformation of the material from printable to printed object, will determine its expanded functionality. Consequently, the properties of printing materials must be designed from a nanometric scale to achieve maximum efficiency in preserving their chemical functionality at the end of the manufacturing.

Accordingly, the selection of material palettes for each printing technique will necessarily involve selecting not only macroscopic, but also chemical functionalities at the molecular level that take into account not only the transformations during printing, but also the chemical functionality that the printed object will have.

In this sense, if the functionality is controlled from the manufacturing at the molecular level of the printing material, it is likely that it will tend to reduce the number of post-process stages that today are required to integrate catalysts in many printed devices. However, to achieve this, it is necessary to strengthen the feedback of each of the stages of manufacturing and testing of printed catalytic devices and thus have more information on what type of chemical functionality is required for the largest quantity of possible processes. This will favour a correct selection of the material so that its response to a thermal, electrical, acoustic or chemical stimulus can be controlled with great specificity.

7. Concluding remarks

After the analysis of the enormous amount of information collected for this review, the idea that the union between Catalysis and Additive Manufacturing is a field of future study with a constant growth in the number of reported investigations on this subject is reinforced.

One of the most relevant contributions of this document is to have exhaustively classified the different types of printable devices with applicability in catalysis and two large families stand out: structured catalysts and catalytic reaction ware.

This classification made it possible to establish that there is a significant room for improvement in the application of designs with advanced geometries in all types of printable devices. Despite this, technological scenarios such as 4D printing, modeling, catalytic bio-printing, among others, have been identified, which will mark the roadmap towards an important consolidation of this topic in the future, based on the maximization of the design concept.

Declaration of Competing Interest

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

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References

[1] C. Hurt, M. Brandt, S.S. Priya, T. Bhatelia, J. Patel, P.R. Selvakannan, S. Bhargava, Combining additive manufacturing and catalysis: a review, Catal. Sci. Technol. 7 (2017) 3421–3439.

[2] C. Parra-Cabrera, C. Achille, S. Kuhn, R. Ameloot, 3D printing in chemical engineering and catalytic technology: structured catalysts, mixers and reactors, Chem. Soc. Rev. 47 (2018) 209–230.

[3] I. Gibson, D. Rosen, B. Stuker, Additive Manufacturing Technologies: 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing, 2 ed., Springer-Verlag, New York, 2015.

[4] I. Gibson, D.W. Rosen, B. Stucker, Additive Manufacturing Technologies: Rapid Prototyping to Direct Digital Manufacturing (2010).
[5] The Create Education Project, in, 2020.
[6] 3DGBIRE, in, 2020.
[7] B. Marr, What is Industry 4.0? Here's a super easy explanation for anyone, in: Forbes, Forbes, 2018.
[8] H. Kodama, Automatic method for fabricating a three-dimensional plastic model with photo-hardening polymer, Rev. Sci. Instrum. 52 (1981) 1770–1773.
[9] M.R. Hartings, Z. Ahmed, Chemistry from 3D printed objects, Nat. Rev. Chem. 3 (2019) 305–314.
[10] C.W. Hull, Apparatus for production of three-dimensional objects by stereolithography (US4575330A), in: USPTO (Ed.) USPTO, UVP, Inc. (San Gabriel, CA), United States, 1984.
[11] J.J. Beaman, C.R. Deckard, Selective laser sintering with assisted powder handling (US4938816A), in: USPTO (Ed.) USPTO, United States, 1986, pp. US4938816A.
[12] S.S. Crump, Apparatus and method for creating three-dimensional objects (US5121329A), in: USPTO (Ed.) USPTO, Stratasys, Inc. (Minneapolis, MN), United States, 1992.
[13] B. Redwood, The advantages of 3D printing, in: 3D Hubs: Knowledge Base, 3D Hubs, 2020.
[14] B. Redwood, F. Schöffer, B. Garret, The 3D printing handbook : technologies, design and applications, 3D., Hubs B.V, Amsterdam, 2017.
[15] W. Jarosinksi, J. Zhang, Chapter 2: Additive Manufacturing Process and Equipment, in: J. Zhang, Y.-.G. Jung (Eds.), Additive Manufacturing: Materials, Processes, Quantifications and Applications, Butterworth-Heinemann, 2018.
[16] T.D. Ngo, A. Kashani, G. Imbalzano, K.T.Q. Nguyen, D. Hui, Additive manufacturing (3D printing): A review of materials, methods, applications and challenges, Compos. B Eng. 143 (2018) 172–196.
[17] X. Zhou, C.-J. Liu, Three-dimensional Printing for Catalytic Applications: Current Status and Perspectives, Adv. Funct. Mater. 27 (2017) 1701134.
[18] I. Chorkendorff, J.W. Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, Wiley, 2017.
[19] U.M. Dilberoglu, B. Gharehpapagh, U. Yaman, M. Dolen, The Role of Additive Manufacturing in the Era of Industry 4.0, Procedia Manuf. 11 (2017) 545–554.
[20] C.J. Navarro, A.M. Centeno, H.O. Laguna, A.J. Odriozola, Policies and Motivations for the CO2 Valorization through the Sabatier Reaction Using Structured Catalysts, A Review of the Most Recent Advances, Catalysts 8 (2018).
[21] M. Mazzucato, Missions: Mission-Oriented Research & Innovation in the European Union, in: D.-G.f.R. Innovation (Ed.), European Comission, Brussels, 2018, pp. 1-36.
[22] H.A. Colorado, E.I.G. Velásquez, S.N. Monteiro, Sustainability of additive manufacturing: the circular economy of materials and environmental perspectives, J. Mater. Res. Technol. 9 (2020) 8221–8234.
[23] M. Konarova, W. Aslam, L. Ge, Q. Ma, F. Tang, V. Rudolph, J.N. Beltramini, Enabling Process Intensification by 3D Printing of Catalytic Structures, ChemCatChem 9 (2017) 4132–4138.
[24] O.H. Laguna, M.I. Domínguez, M.A. Centeno, J.A. Odriozola, Forced deactivation and postmortem characterization of a metallic microchannel reactor employed for the preferential oxidation of CO (PROX), Chem. Eng. J. 302 (2016) 650–662.
[25] O.H. Laguna, M. González Castaño, M.A. Centeno, J.A. Odriozola, Microreactors technology for hydrogen purification: Effect of the catalytic layer thickness on CuOx/CeO2-coated microchannel reactors for the PROX reaction, Chem. Eng. J. 275 (2015) 45–52.
[26] H.J. Robota, L.A. Richard, S. Deshmukh, S. LeViness, D. Leonarduzzi, D. Roberts, High Activity and Selective Fischer-Tropsch Catalysts for Use in a Microchannel Reactor, Catal. Surv. Asia 18 (2014) 177–182.
[27] C.R. Tubío, J. Azuaje, L. Escalante, A. Coelho, F. Guitian, E. Sotelo, A. Gil, 3D printing of a heterogeneous copper-based catalyst, J. Catal. 334 (2016) 110–115.
[28] A. Soliman, N. AlAmoodi, G.N. Karanikolos, C.C. Doumanidis, K. Polychronopoulou, A Review on New 3-D Printed Materials' Geometries for Catalysis and Adsorption: Paradigms from Reforming Reactions and CO2 Capture, Nanomaterials 10 (2020).
[29] E. Bogdan, P. Michorczyk, 3D Printing in Heterogeneous Catalysis-The State of the Art, Materials 13 (2020).
[30] Z. Chen, Z. Li, J. Li, C. Liu, C. Lao, Y. Fu, C. Liu, Y. Li, P. Wang, Y. He, 3D printing of ceramics: A review, J. Eur. Ceram. Soc. 39 (2019) 661–687.
[31] S. Eqtesadi, A. Motealleh, F.H. Perera, P. Miranda, A. Pajares, R. Wendelbo, F. Guiberteau, A.L. Ortiz, Fabricating geometrically-complex B4C ceramic components by robocasting and pressureless spark plasma sintering, Scr. Mater. 145 (2018) 14–18.
[32] M.C. Leu, B.K. Deuser, L. Tang, R.G. Landers, G.E. Hilmas, J.L. Watts, Freeze-form extrusion fabrication of functionally graded materials, CIRP Ann. 61 (2012) 223–226.
[33] M. Schwentenwein, J. Homa, Additive Manufacturing of Dense Alumina Ceramics, Int. J. Appl. Ceram. Technol. 12 (2015) 1–7.
[34] R. Felzmann, S. Gruber, G. Mitteramskogler, P. Tesavibul, A.R. Boccaccini, R. Liska, J. Stampfl, Lithography-Based Additive Manufacturing of Cellular Ceramic Structures, Adv. Eng. Mater. 14 (2012) 1052–1058.
[35] R. Gmeiner, G. Mitteramskogler, J. Stampfl, A.R. Boccaccini, Stereolithographic Ceramic Manufacturing of High Strength Bioactive Glass, Int. J. Appl. Ceram. Technol. 12 (2015) 38–45.
[36] Y. de Hazan, D. Penner, SiC and SiOC ceramic articles produced by stereolithography of acrylate modified polycarbosilane systems, J. Eur. Ceram. Soc. 37 (2017) 5205–5212.
[37] J.L. Simon, S. Michna, J.A. Lewis, E.D. Rekow, V.P. Thompson, J.E. Smay, A. Yampolsky, J.R. Parsons, J.L. Ricci, In vivo bone response to 3D periodic hydroxyapatite scaffolds assembled by direct ink writing, J. Biomed. Mater. Res. Part A 83A (2007) 747–758.
[38] Z. Chen, D. Li, W. Zhou, L. Wang, Curing characteristics of ceramic stereolithography for an aqueous-based silica suspension, Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture 224 (2009) 641–651.
[39] M. Lejeune, T. Chartier, C. Dossou-Yovo, R. Noguera, Ink-jet printing of ceramic micro-pillar arrays, J. Eur. Ceram. Soc. 29 (2009) 905–911.
[40] T.A. Pham, D.P. Kim, T.W. Lim, S.H. Park, D.Y. Yang, K.S. Lee, Three-Dimensional SiCN Ceramic Microstructures via Nano-Stereolithography of Inorganic Polymer Photoresists, Adv. Funct. Mater. 16 (2006) 1235–1241.
[41] T. Friedel, N. Travitzky, F. Niebling, M. Scheffler, P. Greil, Fabrication of polymer derived ceramic parts by selective laser curing, J. Eur. Ceram. Soc. 25 (2005) 193–197.
[42] B. Cappi, E. Özkol, J. Ebert, R. Telle, Direct inkjet printing of Si3N4: Characterization of ink, green bodies and microstructure, J. Eur. Ceram. Soc. 28 (2008) 2625–2628.
[43] K. Shahzad, J. Deckers, J.-P. Kruth, J. Vleugels, Additive manufacturing of alumina parts by indirect selective laser sintering and post processing, J. Mater. Process. Technol. 213 (2013) 1484–1494.
[44] A.M. Sukeshini, R. Cummins, T.L. Reitz, R.M. Miller, Inkjet Printing of Anode Supported SOFC: Comparison of Slurry Pasted Cathode and Printed Cathode, Electrochem. Solid-State Lett. 12 (2009) B176.
[45] W. Sun, D.J. Dcosta, F. Lin, T. El-Raghy, Freeform fabrication of Ti3SiC2 powder-based structures: Part I—Integrated fabrication process, J. Mater. Process. Technol. 127 (2002) 343–351.
[46] O. Al-Ketan, M. Pelanconi, A. Ortona, R.K. Abu Al-Rub, Additive manufacturing of architected catalytic ceramic substrates based on triply periodic minimal surfaces, Journal of the American Ceramic Society, 102 (2019) 6176-6193.
[47] A. Davó-Quiñonero, D. Sorolla-Rosario, E. Bailon-Garcia, D. Lozano-Castello, A. Bueno-Lopez, Improved asymmetrical honeycomb monolith catalyst prepared using a 3D printed template, J. Hazard. Mater. 368 (2019) 638–643.
[48] S. Danaci, L. Protasova, J. Lefevere, L. Bedel, R. Guilet, P. Marty, Efficient CO2 methanation over Ni/Al2O3 coated structured catalysts, Catal. Today 273 (2016) 234–243.
[49] S. Danaci, L. Protasova, V. Middelkoop, N. Ray, M. Jouve, A. Bengaouer, P. Marty, Scaling up of 3D printed and Ni/Al2O3 coated reactors for CO2 methanation, React. Chem. Eng. 4 (2019) 1318–1330.
[50] S. Danaci, L. Protasova, F. Snijkers, W. Bouwen, A. Bengaouer, P. Marty, Innovative 3D-manufacture of structured copper supports post-coated with catalytic material for CO2 methanation, Chemical Engineering and Processing-Process Intensification 127 (2018) 168–177.
[51] T. Duda, L.V. Raghavan, 3D Metal Printing Technology, IFAC-PapersOnLine 49 (2016) 103–110.
[52] X. Chen, X. Liu, M. Ouyang, J. Chen, O. Taiwo, Y. Xia, P.R.N. Childs, N.P. Brandon, B. Wu, Multi-metal 4D printing with a desktop electrochemical 3D printer, Sci. Rep. 9 (2019) 3973.
[53] A. Hansen, M. Renner, A.G. Griesbeck, T. Busgen, From 3D to 4D printing: a reactor for photochemical experiments using hybrid polyurethane acrylates for vat-based polymerization and surface functionalization, Chem. Commun. (Camb.) 56 (2020) 15161–15164.
[54] O. Al-Ketan, R. Rowshan, R.K. Abu Al-Rub, Topology-mechanical property relationship of 3D printed strut, skeletal, and sheet based periodic metallic cellular materials, Addit. Manuf. 19 (2018) 167–183.
[55] M.J. Regufe, A.F.P. Ferreira, J.M. Loureiro, A. Rodrigues, A.M. Ribeiro, Electrical conductive 3D-printed monolith adsorbent for CO2 capture, Microporous Mesoporous Mater. 278 (2019) 403–413.
[56] J.H. Kim, W.S. Chang, D. Kim, J.R. Yang, J.T. Han, G.-W. Lee, J.T. Kim, S.K. Seol, 3D Printing of Reduced Graphene Oxide Nanowires, Adv. Mater. 27 (2015) 157–161.
[57] T. Nathan-Walleser, I.-M. Lazar, M. Fabritius, F.J. Toelle, Q. Xia, B. Bruchmann, S.S. Venkataraman, M.G. Schwab, R. Muelhaupt, 3D Micro-Extrusion of Graphene-based Active Electrodes: Towards High-Rate AC Line Filtering Performance Electrochemical Capacitors, Adv. Funct. Mater. 24 (2014) 4706–4716.
[58] Q. Zhang, F. Zhang, S.P. Medarametla, H. Li, C. Zhou, D. Lin, 3D Printing of Graphene Aerogels, Small 12 (2016) 1702–1708.
[59] N. Rodríguez, Y.Y. Agámez-Pertuz, E. Romero, J.d.J. Díaz-Velásquez, J.A. Odriozola, M.Á. Centeno, Effect of starch as binder in carbon aerogel and carbon xerogel preparation, Journal of Non-Crystalline Solids, 522 (2019) 119554.
[60] C. Moreno-Castilla, F.J. Maldonado-Hódar, Carbon aerogels for catalysis applications: An overview, Carbon 43 (2005) 455–465.
[61] C. Zhu, T.Y.-J. Han, E.B. Duoss, A.M. Golobic, J.D. Kuntz, C.M. Spadaccini, M.A. Worsley, Highly compressible 3D periodic graphene aerogel microlattices, Nat. Commun. 6 (2015).
[62] F. Qian, C. Zhu, J.M. Knipe, S. Ruelas, J.K. Stolaroff, J.R. DeOtte, E.B. Duoss, C.M. Spadaccini, C.A. Henard, M.T. Guarnieri, S.E. Baker, Direct Writing of Tunable Living Inks for Bioprocess Intensification, Nano Lett. 19 (2019) 5829–5835.

[63] M. Peng, E. Mittmann, L. Wenger, J. Hubbuch, M.K.M. Engqvist, C.M. Niemeyer, K.S. Rabe, 3D-Printed Phenacrylate Decarboxylase Flow Reactors for the Chemoenzymatic Synthesis of 4-Hydroxystilbene, Chemistry-a, European Journal (2019).
[64] A.S. Diaz-Marta, S. Yanez, E. Lasorsa, P. Pacheco, C.R. Tubio, J. Rivas, Y. Pineiro, M.A.G. Gomez, M. Amorin, F. Guitian, A. Coelho, Integrating Reactors and Catalysts through Three-Dimensional Printing: Efficiency and Reusability of an Impregnated Palladium on Silica Monolith in Sonogashira and Suzuki Reactions, ChemCatChem 12 (2020) 1762–1771.
[65] M.R. Penny, S.T. Hilton, Design and development of 3D printed catalytically-active stirrers for chemical synthesis, React. Chem. Eng. 5 (2020) 853–858.
[66] A. Potdar, L.C.J. Thomassen, S. Kuhn, Scalability of 3D printed structured porous milli-scale reactors, Chem. Eng. J. 363 (2019) 337–348.
[67] S. Bettermann, R. Stuhr, H.-U. Moritz, W. Pauer, Customizable 3D-printed stirrers for investigation, optimization and scale-up processes of batch emulsion copolymerizations, Chem. Eng. Sci. 206 (2019) 50–62.
[68] J.S. Manzano, Z.B. Weinstein, A.D. Sadow, I.I. Slowing, Direct 3D Printing of Catalytically Active Structures, ACS Catal. 7 (2017) 7567–7577.
[69] A. Sanchez Díaz-Marta, S. Yáñez, C.R. Tubío, V.L. Barrio, Y. Piñeiro, R. Pedrido, J. Rivas, M. Amorín, F. Guitián, A. Coelho, Multicatalysis Combining 3D-Printed Devices and Magnetic Nanoparticles in One-Pot Reactions: Steps Forward in Compartmentation and Recyclability of Catalysts, ACS Appl. Mater. Interfaces 11 (2019) 25283–25294.
[70] A. Ambrosi, M. Pumera, Multimaterial 3D-Printed Water Electrolyzer with Earth-Abundant Electrodeposited Catalysts, ACS Sustainable Chem. Eng. 6 (2018) 16968–16975.
[71] C.-K. Su, H.-H. Tseng, 3D-printed CuO nanoparticle–functionalized flow reactor enables online fluorometric monitoring of glucose, Microchim. Acta 186 (2019) 404.
[72] S. Rossi, R. Porta, D. Brenna, A. Puglisi, M. Benaglia, Stereoselective Catalytic Synthesis of Active Pharmaceutical Ingredients in Homemade 3D-Printed Mesoreactors, Angewandte Chemie-International Edition 56 (2017) 4290–4294.
[73] A. Urrios, C. Parra-Cabrera, N. Bhattacharjee, A.M. Gonzalez-Suarez, L.G. Rigat-Brugarolas, U. Nallapatti, J. Samitier, C.A. DeForest, F. Posas, J.L. Garcia-Cordero, A. Folch, 3D-printing of transparent bio-microfluidic devices in PEG-DA, Lab Chip 16 (2016) 2287–2294.
[74] 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-International Edition 53 (2014) 12723–12728.
[75] P.J. Kitson, M.D. Symes, V. Dragone, L. Cronin, Combining 3D printing and liquid handling to produce user-friendly reactionware for chemical synthesis and purification, Chem. Sci. 4 (2013) 3099–3103.
[76] P.J. Kitson, M.H. Rosnes, V. Sans, V. Dragone, L. Cronin, Configurable 3D-Printed millifluidic and microfluidic 'lab on a chip' reactionware devices, Lab Chip 12 (2012) 3267–3271.
[77] M.D. Symes, P.J. Kitson, J. Yan, C.J. Richmond, G.J.T. Cooper, R.W. Bowman, T. Vilbrandt, L. Cronin, Integrated 3D-printed reactionware for chemical synthesis and analysis, Nat. Chem. 4 (2012) 349–354.
[78] E. Fornells, E. Murray, S. Waheed, A. Morrin, D. Diamond, B. Paull, M. Breadmore, Integrated 3D printed heaters for microfluidic applications: Ammonium analysis within environmental water, Anal. Chim. Acta 1098 (2020) 94–101.
[79] P.J. Kitson, S. Glatzel, W. Chen, C.-G. Lin, Y.-F. Song, L. Cronin, 3D printing of versatile reactionware for chemical synthesis, Nat. Protoc. 11 (2016) 920–936.
[80] E. Lahtinen, L. Turunen, M.M. Hanninen, K. Kolari, H.M. Tuononen, M. Haukka, Fabrication of Porous Hydrogenation Catalysts by a Selective Laser Sintering 3D Printing Technique, ACS Omega 4 (2019) 12012–12017.
[81] S. Bettermann, B. Schroeter, H.-U. Moritz, W. Pauer, M. Fassbender, G.A. Luinstra, Continuous emulsion copolymerization processes at mild conditions in a 3D-printed tubular bended reactor, Chem. Eng. J. 338 (2018) 311–322.
[82] A. Ambrosi, M. Pumera, Self-Contained Polymer/Metal 3D Printed Electrochemical Platform for Tailored Water Splitting, Adv. Funct. Mater. 28 (2018).
[83] S. Zhang, Y. Lu, Y. Gu, X. Zhang, J. Sun, Z. Tang, The process intensification of CO2 absorption in honeycomb fractal reactor fabricated by 3D printer, Chemical Engineering and Processing-Process Intensification 132 (2018) 42–47.
[84] M.G. Mendonça Lopes, H.S. Santana, V.F. Andolphato, F.N. Russo, J.L. Silva Jr., O.P. Taranto, 3D printed micro-chemical plant for biodiesel synthesis in millireactors, Energy Convers. Manage. 184 (2019) 475–487.
[85] A. Adamo, R.L. Beingessner, M. Behnam, J. Chen, T.F. Jamison, K.F. Jensen, J.-C. M. Monbaliu, A.S. Myerson, E.M. Revalor, D.R. Snead, T. Stelzer, N. Weeranoppanant, S.Y. Wong, P. Zhang, On-demand continuous-flow production of pharmaceuticals in a compact, reconfigurable system, Science 352 (2016) 61.
[86] O.A. Alimi, C.A. Akinnawo, O.R. Onisuru, R. Meijboom, 3-D printed microreactor for continuous flow oxidation of a flavonoid, Journal of Flow Chemistry 10 (2020) 517–531.
[87] B. Gutmann, M. Koeckinger, G. Glotz, T. Ciaglia, E. Slama, M. Zadravec, S. Pfanner, M.C. Maier, H. Gruber-Woelfler, C.O. Kappe, Design and 3D printing of a stainless steel reactor for continuous difluoromethylations using fluoroform, React. Chem. Eng. 2 (2017) 919–927.
[88] A. Potdar, L.N. Protasova, L. Thomassen, S. Kuhn, Designed porous milli-scale reactors with enhanced interfacial mass transfer in two-phase flows, React. Chem. Eng. 2 (2017) 137–148.
[89] J.S. Manzano, H. Wang, L. Qi, I.I. Slowing, Macroscale Control of Reactivity using 3D Printed Materials with Intrinsic Catalytic Properties, Applied Catalysis a-General 605 (2020).
[90] A. Cabrera, I. Pellejero, T. Oroz-Mateo, C. Salazar, A. Navajas, C. Fernández-Acevedo, L.M. Gandía, Three-Dimensional Printing of Acrylonitrile Butadiene Styrene Microreactors for Photocatalytic Applications, Ind. Eng. Chem. Res. 59 (2020) 20686–20692.
[91] M. Debosz, M. Wieczorek, J. Paluch, J. Migdalski, B. Bas, P. Koscielniak, 3D-printed flow manifold based on potentiometric measurements with solid-state ion-selective electrodes and dedicated to multicomponent water analysis, Talanta 217 (2020). 121092 121092.
[92] R.D. Sochol, E. Sweet, C.C. Glick, S. Venkatesh, A. Avetisyan, K.F. Ekman, A. Raulinaitis, A. Tsai, A. Wienkers, K. Korner, K. Hanson, A. Long, B.J. Hightower, G. Slatton, D.C. Burnett, T.L. Massey, K. Iwai, L.P. Lee, K.S.J. Pister, L. Lin, 3D printed microfluidic circuitry via multijet-based additive manufacturing, Lab Chip 16 (2016) 668–678.
[93] Y. Min Oo, G. Prateepchaikul, K. Somnuk, Continuous acid-catalyzed esterification using a 3D printed rotor-stator hydrodynamic cavitation reactor reduces free fatty acid content in mixed crude palm oil, Ultrason. Sonochem. 72 (2020). 105419 105419.
[94] M.M. Desipio, S.E. Van Bramer, R. Thorpe, D. Saha, Photocatalytic and photo-fenton activity of iron oxide-doped carbon nitride in 3D printed and LED driven photon concentrator, J. Hazard. Mater. 376 (2019) 178–187.
[95] A. Avril, C.H. Hornung, A. Urban, D. Fraser, M. Horne, J.P. Veder, J. Tsanaktsidis, T. Rodopoulos, C. Henry, D.R. Gunasegaram, Continuous flow hydrogenations using novel catalytic static mixers inside a tubular reactor, React. Chem. Eng. 2 (2017) 180–188.
[96] M.P. Browne, J. Plutnar, A.M. Pourrahimi, Z. Sofer, M. Pumera, Atomic Layer Deposition as a General Method Turns any 3D-Printed Electrode into a Desired Catalyst: Case Study in Photoelectrochemisty, Adv. Energy Mater. 9 (2019).
[97] Y. Zhang, X. Sun, N. Nomura, T. Fujita, Hierarchical Nanoporous Copper Architectures via 3D Printing Technique for Highly Efficient Catalysts, Small 15 (2019).
[98] A. Ambrosi, J.G.S. Moo, M. Pumera, Helical 3D-Printed Metal Electrodes as Custom-Shaped 3D Platform for Electrochemical Devices, Adv. Funct. Mater. 26 (2016) 698–703.
[99] B. Schmieg, J. Doebber, F. Kirschhoefer, M. Pohl, M. Franzreb, Advantages of Hydrogel-Based 3D-Printed Enzyme Reactors and Their Limitations for Biocatalysis, Front. Bioeng. Biotechnol. 6 (2019).
[100] M. Gou, X. Qu, W. Zhu, M. Xiang, J. Yang, K. Zhang, Y. Wei, S. Chen, Bio-inspired detoxification using 3D-printed hydrogel nanocomposites, Nat. Commun. 5 (2014).
[101] F. Mendez-Arriaga, E.d.l. Calleja, L. Ruiz-Huerta, A. Caballero-Ruiz, R. Almanza, TiO2 3D structures for environmental purposes by additive manufacturing: Photoactivity test and reuse, Materials Science in Semiconductor Processing, 100 (2019) 35-41.
[102] K. Essa, H. Hassanin, M.M. Attallah, N.J. Adkins, A.J. Musker, G.T. Roberts, N. Tenev, M. Smith, Development and testing of an additively manufactured monolithic catalyst bed for HTP thruster applications, Appl. Catal. A 542 (2017) 125–135.
[103] A. Saha, T.G. Johnston, R.T. Shafranek, C.J. Goodman, J.G. Zalatan, D.W. Storti, M.A. Ganter, A. Nelson, Additive Manufacturing of Catalytically Active Living Materials, ACS Appl. Mater. Interfaces 10 (2018) 13373–13380.
[104] C.Y. Chaparro-Garnica, A. Davó-Quiñonero, E. Bailón-García, D. Lozano-Castelló, A. Bueno-López, Design of Monolithic Supports by 3D Printing for Its Application in the Preferential Oxidation of CO (CO-PrOx), ACS Appl. Mater. Interfaces 11 (2019) 36763–36773.
[105] J. Ye, T. Chu, J. Chu, B. Gao, B. He, A Versatile Approach for Enzyme Immobilization Using Chemically Modified 3D-Printed Scaffolds, ACS Sustainable Chem. Eng. 7 (2019) 18048–18054.
[106] N. Mohammad, S. Bepari, S. Aravamudhan, D. Kuila, Kinetics of Fischer-Tropsch Synthesis in a 3-D Printed Stainless Steel Microreactor Using Different Mesoporous Silica Supported Co-Ru Catalysts, Catalysts 9 (2019).
[107] V. Middelkoop, A. Vamvakeros, D. de Wit, S.D.M. Jacques, S. Danaci, C. Jacquot, Y. de Vos, D. Matras, S.W.T. Price, A.M. Beale, 3D printed Ni/Al2O3 based catalysts for CO2 methanation - a comparative and operando XRD-CT study, J. CO2 Util. 33 (2019) 478–487.
[108] C.A. Leclerc, R. Gudgila, Short Contact Time Catalytic Partial Oxidation of Methane over Rhodium Supported on Ceria Based 3-D Printed Supports, Ind. Eng. Chem. Res. 58 (2019) 14632–14637.
[109] S. Garcia, S. Poulston, D. Modeshia, P. Stavarek, M. Ujcic, F. Lali, M.A. Alves, J.D. Araujo, M. Krusche, F. Ullrich, D. Maier, Continuous Production of Squalane Using 3D Printed Catalytic Supports Additive manufacturing confers advantages for catalyst support design, Johnson Matthey Technol. Rev. 63 (2019) 191–204.
[110] V. Middelkoop, T. Slater, M. Florea, F. Neatu, S. Danaci, V. Onyenkeadi, K. Boonen, B. Saha, L.-A. Baragau, S. Kellici, Next frontiers in cleaner synthesis: 3D printed graphene-supported CeZrLa mixed -oxide nanocatalyst for CO2 utilisation and direct propylene carbonate production, J. Cleaner Prod. 214 (2019) 606–614.

[111] J. Lefevere, S. Mullens, V. Meynen, The impact of formulation and 3D-printing on the catalytic properties of ZSM-5 zeolite, Chem. Eng. J. 349 (2018) 260–268.
[112] A. Lind, O. Vistad, M.F. Sunding, K.A. Andreassen, J.H. Cavka, C.A. Grande, Multi-purpose structured catalysts designed and manufactured by 3D printing, Mater. Des. 187 (2020).
[113] J.S. Manzano, H. Wang, I.I. Slowing, High Throughput Screening of 3D Printable Resins: Adjusting the Surface and Catalytic Properties of Multifunctional Architectures, Acs Applied Polymer Materials 1 (2019) 2890–2896.
[114] A. Elkoro, L. Soler, J. Llorca, I. Casanova, 3D printed microstructured Au/TiO2 catalyst for hydrogen photoproduction, Appl. Mater. Today 16 (2019) 265–272.
[115] X. Li, F. Rezaei, A.A. Rownaghi, Methanol-to-olefin conversion on 3D-printed ZSM-5 monolith catalysts: Effects of metal doping, mesoporosity and acid strength, Microporous Mesoporous Mater. 276 (2019) 1–12.
[116] 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.
[117] X. Zhou, C.-J. Liu, Three-dimensional printing of porous carbon structures with tailorable pore sizes, Catal. Today (2018).
[118] J. Azuaje, C.R. Tubío, L. Escalante, M. Gomez, F. Guitian, A. Coelho, O. Caamano, A. Gil, E. Sotelo, An efficient and recyclable 3D printed alpha-Al2O3 catalyst for the multicomponent assembly of bioactive heterocycles, Applied Catalysis a-General 530 (2017) 203–210.
[119] C. Zhu, Z. Qi, V.A. Beck, M. Luneau, J. Lattimer, W. Chen, M.A. Worsley, J. Ye, E. B. Duoss, C.M. Spadaccini, C.M. Friend, J. Biener, Toward digitally controlled catalyst architectures: Hierarchical nanoporous gold via 3D printing, Sci. Adv. 4 (2018).
[120] C. Yang, C. Zhang, W. Xing, L. Liu, 3D printing of Zr-based bulk metallic glasses with complex geometries and enhanced catalytic properties, Intermetallics 94 (2018) 22–28.
[121] X. Li, W. Li, F. Rezaei, A. Rownaghi, Catalytic cracking of n-hexane for producing light olefins on 3D-printed monoliths of MFI and FAU zeolites, Chem. Eng. J. 333 (2018) 545–553.
[122] M.R. Skorski, J.M. Esenther, Z. Ahmed, A.E. Miller, M.R. Hartings, The chemical, mechanical, and physical properties of 3D printed materials composed of TiO2-ABS nanocomposites, Sci. Technol. Adv. Mater. 17 (2016) 89–97.
[123] Z. Wang, J. Wang, M. Li, K. Sun, C.-J. Liu, Three-dimensional Printed Acrylonitrile Butadiene Styrene Framework Coated with Cu-BTC Metal-organic Frameworks for the Removal of Methylene Blue, Sci. Rep. 4 (2014).
[124] J. Lefevere, M. Gysen, S. Mullens, V. Meynen, J. Van Noyen, The benefit of design of support architectures for zeolite coated structured catalysts for methanol-to-olefin conversion, Catal. Today 216 (2013) 18–23.
[125] J.N. Stuecker, J.E. Miller, R.E. Ferrizz, J.E. Mudd, J. Cesarano, Advanced support structures for enhanced catalytic activity, Ind. Eng. Chem. Res. 43 (2004) 51–55.
[126] J. Van Noyen, A. De Wilde, M. Schroeven, S. Mullens, J. Luyten, Ceramic Processing Techniques for Catalyst Design: Formation, Properties, and Catalytic Example of ZSM-5 on 3-Dimensional Fiber Deposition Support Structures, Int. J. Appl. Ceram. Technol. 9 (2012) 902–910.
[127] Q. Wei, M. Xu, C. Liao, Q. Wu, M. Liu, Y. Zhang, C. Wu, L. Cheng, Q. Wang, Printable hybrid hydrogel by dual enzymatic polymerization with superactivity, Chem. Sci. 7 (2016) 2748–2752.
[128] A. Potdar, L.C.J. Thomassen, S. Kuhn, Structured Porous Millireactors for Liquid-Liquid Chemical Reactions, Chem. Ing. Tech. 91 (2019) 592–601.
[129] J.J. Moyano, I. Garcia, J. de Damborenea, D. Perez-Coll, M. Belmonte, P. Miranzo, M.I. Osendi, Remarkable Effects of an Electrodeposited Copper Skin on the Strength and the Electrical and Thermal Conductivities of Reduced Graphene Oxide-Printed Scaffolds, ACS Appl. Mater. Interfaces 12 (2020) 24209–24217.
[130] M. Peng, D. Shi, Y. Sun, J. Cheng, B. Zhao, Y. Xie, J. Zhang, W. Guo, Z. Jia, Z. Liang, L. Jiang, 3D Printed Mechanically Robust Graphene/CNT Electrodes for Highly Efficient Overall Water Splitting, Adv. Mater. (2020).
[131] M.P. Browne, V. Urbanova, J. Plutnar, F. Novotny, M. Pumera, Inherent impurities in 3D-printed electrodes are responsible for catalysis towards water splitting, J. Mater. Chem. A 8 (2020) 1120–1126.
[132] J.C. Bui, J.T. Davis, D.V. Esposito, 3D-Printed electrodes for membraneless water electrolysis, Sustainable Energy Fuels 4 (2020) 213–225.
[133] S. Hajimirzaee, A.M. Doyle, 3D printed catalytic converters with enhanced activity for low-temperature methane oxidation in dual-fuel engines, Fuel 274 (2020).
[134] T. Zheng, W. Zhou, D. Geng, Y. Li, Y. Liu, C. Zhang, Methanol steam reforming microreactor with novel 3D-Printed porous stainless steel support as catalyst support, Int. J. Hydrogen Energy 45 (2020) 14006–14016.
[135] J. Liu, Y. Gao, Y. Fan, W. Zhou, Fabrication of porous metal by selective laser melting as catalyst support for hydrogen production microreactor, Int. J. Hydrogen Energy 45 (2020) 10–22.
[136] M. Casas-Luna, J.A. Torres-Rodríguez, O.U. Valdés-Martínez, N. Obradović, K. Slámečka, K. Maca, J. Kaiser, E.B. Montúfar, L. Čelko, Robocasting of controlled porous CaSiO3–SiO2 structures: Architecture – Strength relationship and material catalytic behavior, Ceram. Int. 46 (2020) 8853–8861.
[137] S. Rossi, A. Puglisi, L.M. Raimondi, M. Benaglia, Stereolithography 3D-Printed Catalytically Active Devices in Organic Synthesis, Catalysts 10 (2020).
[138] B. Zhang, H. Lee, D. Byun, Electrohydrodynamic Jet Printed 3D Metallic Grid: Toward High-Performance Transparent Electrodes, Adv. Eng. Mater. (2020).
[139] S. Hock, M. Rose, 3D-Structured Monoliths of Nanoporous Polymers by Additive Manufacturing, Chem. Ing. Tech. 92 (2020) 525–531.
[140] Y. Jiang, F.-Q. Jiang, X. Liao, S.-L. Lai, S.-B. Wang, X.-Q. Xiong, J. Zheng, Y.-G. Liu, Customized three-dimensional porous catalyst for Knoevenagel reaction, J. Porous Mater. 27 (2020) 779–788.
[141] D. Liu, P. Jiang, X. Li, J. Liu, L. Zhou, X. Wang, F. Zhou, 3D printing of metal-organic frameworks decorated hierarchical porous ceramics for high-efficiency catalytic degradation, Chem. Eng. J. 397 (2020) 125392.
[142] F. Agueniou, H. Vidal, J. de Dios Lopez, J.C. Hernandez-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).
[143] D.M. Alonso, S.H. Hakim, S. Zhou, W. Won, O. Hosseinaei, J. Tao, V. Garcia-Negron, A.H. Motagamwala, M.A. Mellmer, K. Huang, C.J. Houtman, N. Labbé, D.P. Harper, C.T. Maravelias, T. Runge, J.A. Dumesic, Increasing the revenue from lignocellulosic biomass: Maximizing feedstock utilization, Sci. Adv. 3 (2017) e1603301.
[144] C. Iffelsberger, S. Ng, M. Pumera, Catalyst coating of 3D printed structures via electrochemical deposition: Case of the transition metal chalcogenide MoSx for hydrogen evolution reaction, Appl. Mater. Today 20 (2020).
[145] K.P.A. Kumar, K. Ghosh, O. Alduhaish, M. Pumera, Metal-plated 3D-printed electrode for electrochemical detection of carbohydrates, Electrochem. Commun. 120 (2020).
[146] P.J. Zambiazi, A.T.N. de Moraes, R.R. Kogachi, G.O. Aparecido, A.L.B. Formiga, J. A. Bonacin, Performance of Water Oxidation by 3D Printed Electrodes Modified by Prussian Blue Analogues, J. Braz. Chem. Soc. 31 (2020) 2307–2318.
[147] M. Kundra, B.B.M. Sultan, D. Ng, Y. Wang, D.L.J. Alexander, X. Nguyen, Z. Xie, C.H. Hornung, Continuous flow semi-hydrogenation of alkynes using 3D printed catalytic static mixers, Chemical Engineering and Processing-Process Intensification 154 (2020).
[148] S. Bepari, X. Li, R. Abrokwah, N. Mohammad, M. Arslan, D. Kuila, Co-Ru catalysts with different composite oxide supports for Fischer-Tropsch studies in 3D-printed stainless steel microreactors, Applied Catalysis a-General 608 (2020).
[149] L. Matoh, B. Žener, R.C. Korošec, U.L. Štangar, 27 - Photocatalytic water treatment, in: F. Pacheco-Torgal, M.V. Diamanti, A. Nazari, C.G. Granqvist, A. Pruna, S. Amirkhanian (Eds.), Nanotechnology in Eco-efficient Construction (Second Edition), Woodhead Publishing, 2019, pp. 675–702.
[150] O.H. Laguna, M.I. Domínguez, M.A. Centeno, J.A. Odriozola, Chapter 4 - Catalysts on Metallic Surfaces: Monoliths and Microreactors, in: V.I. Parvulescu, E. Kemnitz (Eds.), New Materials for Catalytic Applications, Elsevier, Amsterdam, 2016, pp. 81–120.
[151] 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: Nonchanneled Advanced Monolithic Supports Manufactured by 3D-Printing for Improved Active Phase Coating Performance, ACS Appl. Mater. Interfaces 12 (2020) 54573–54584.
[152] L. Alison, S. Menasce, F. Bouville, E. Tervoort, I. Mattich, A. Ofner, A.R. Studart, 3D printing of sacrificial templates into hierarchical porous materials, Sci. Rep. 9 (2019) 409.
[153] A. Vyatskikh, A. Kudo, S. Delalande, J.R. Greer, Additive manufacturing of polymer-derived titania for one-step solar water purification, Mater. Today Commun. 15 (2018) 288–293.
[154] U. Scheithauer, F. Kerber, A. Füssel, S. Holtzhausen, W. Beckert, E. Schwarzer, S. Weingarten, A. Michaelis, Alternative Process Routes to Manufacture Porous Ceramics—Opportunities and Challenges, Materials 12 (2019) 663.
[155] M. Bracconi, M. Ambrosetti, O. Okafor, V. Sans, X. Zhang, X. Ou, C.P. Da Fonte, X. Fan, M. Maestri, G. Groppi, E. Tronconi, Investigation of pressure drop in 3D replicated open-cell foams: Coupling CFD with experimental data on additively manufactured foams, Chem. Eng. J. 377 (2019).
[156] M. Ambrosetti, M. Bracconi, M. Maestri, G. Groppi, E. Tronconi, Packed foams for the intensification of catalytic processes: assessment of packing efficiency and pressure drop using a combined experimental and numerical approach, Chem. Eng. J. 382 (2020).
[157] P. Aghaei, C.G. Visconti, G. Groppi, E. Tronconi, Development of a heat transport model for open-cell metal foams with high cell densities, Chem. Eng. J. 321 (2017) 432–446.
[158] L. Fratalocchi, G. Groppi, C.G. Visconti, L. Lietti, E. Tronconi, Adoption of 3D printed highly conductive periodic open cellular structures as an effective solution to enhance the heat transfer performances of compact Fischer-Tropsch fixed-bed reactors, Chem. Eng. J. 386 (2020) 123988.
[159] R. Balzarotti, A. Bisaccia, M.C. Tripi, M. Ambrosetti, G. Groppi, E. Tronconi, Production and characterization of copper periodic open cellular structures made by 3D printing-replica technique, Journal of advanced manufacturing and processing 2 (2020). e10068 e10068.
[160] A.L. Squissato, R.A.A. Munoz, C.E. Banks, E.M. Richter, An Overview of Recent Electroanalytical Applications Utilizing Screen-Printed Electrodes Within Flow Systems, ChemElectroChem 7 (2020) 2211–2221.
[161] H. Beitollahi, S.Z. Mohammadi, M. Safaei, S. Tajik, Applications of electrochemical sensors and biosensors based on modified screen-printed electrodes: a review, Anal. Methods 12 (2020) 1547–1560.

[162] Q. Wei, H. Li, G. Liu, Y. He, Y. Wang, Y.E. Tan, D. Wang, X. Peng, G. Yang, N. Tsubaki, Metal 3D printing technology for functional integration of catalytic system, Nat. Commun. 11 (2020).
[163] G. Do, T. Stiegler, M. Fiegl, L. Adler, C. Koerner, A. Boesmann, H. Freund, W. Schwieger, P. Wasserscheid, Electrophoretic Deposition of Boehmite on Additively Manufactured, Interpenetrating Periodic Open Cellular Structures for Catalytic Applications, Ind. Eng. Chem. Res. 56 (2017) 13403–13411.
[164] J. Lölsberg, O. Starck, S. Stiefel, J. Hereijgers, T. Breugelmans, M. Wessling, 3D-Printed Electrodes with Improved Mass Transport Properties, Chemelectrochem 4 (2017) 3309–3313.
[165] X. Wang, W. Guo, R. Abu-Reziq, S. Magdassi, High-Complexity WO3-Based Catalyst with Multi-Catalytic Species via 3D Printing, Catalysts 10 (2020).
[166] D. Liu, P. Jiang, X. Li, J. Liu, L. Zhou, X. Wang, F. Zhou, 3D printing of metal - organic frameworks decorated hierarchical porous ceramics for high -e fficiency catalytic degradation, Chem. Eng. J. 397 (2020).
[167] G. Chisholm, P.J. Kitson, N.D. Kirkaldy, L.G. Bloor, L. Cronin, 3D printed flow plates for the electrolysis of water: an economic and adaptable approach to device manufacture, Energy Environ. Sci. 7 (2014) 3026–3032.
[168] L.D. Tijing, J.R.C. Dizon, I. Ibrahim, A.R.N. Nisay, H.K. Shon, R.C. Advincula, 3D printing for membrane separation, desalination and water treatment, Appl. Mater. Today 18 (2020) 100486.
[169] 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 J. Chem. 44 (2020) 18867–18878.
[170] J. Hereijgers, J. Schalck, J. Loelsberg, M. Wessling, T. Breugelmans, Indirect 3D Printed Electrode Mixers, Chemelectrochem 6 (2019) 378–382.
[171] Y. Li, S. Chen, X. Cai, J. Hong, X. Wu, Y. Xu, J. Zou, B.H. Chen, Rational design and preparation of hierarchical monoliths through 3D printing for syngas methanation, J. Mater. Chem. A 6 (2018) 5695–5702.
[172] E. Hędrzak, A. Wegrzynowicz, R. Rachwalik, B. Sulikowski, P. Michorczyk, Monoliths with MFI zeolite layers prepared with the assistance of 3D printing: Characterization and performance in the gas phase isomerization of alpha-pinene, Applied Catalysis a-General 579 (2019) 75–85.
[173] R. Alsharif, C. Makatsoris, L. Paramonov, Modular flow reactor, USPTO 20150010445 14/349746 (2015) in.
[174] Y. Shanjani, E. Toyserkani, M. Vlasea, Systems and methods for additive manufacturing of heterogeneous porous structures and structures made therefrom, USPTO 20150352639 14/761364 (2015) in.
[175] P. De Wald, C.M. Finnerty, Reformer with perovskite as structural component thereof, USPTO 20160280541 15/033838 (2016) in.
[176] P. Del-Gallo, O. Dubet, M. Flin, L. Frost, M. Wagner, Exchanger and/or reactor-exchanger manufactured in an additive process, USPTO 20170197196 15/324843 (2017) in.
[177] D. Fraser, D.R. Gunasegaram, W. Henry, M.D. Horne, C. Hornung, T. Rodopoulos, J. Tsanaktsidis, A.J. Urban, J.-P. Veder, Static mixers for continuous flow catalytic reactors, WIPO|PCT (CA3008443A1), in, 2017.
[178] K.R. Gagne, D.L. Hitt, M.R. McDevitt, Microfluidic homogeneous catalyzation systems and methods, and apparatuses incorporating same, USPTO 20170138309 15/354508 (2017) in.
[179] U. Gotzig, Catalyst chamber with a catalyst bed embedded therein for a monopropellant thruster of a rocket engine, USPTO 20170037814 15/225438 (2017) in.
[180] A. Jones, C. Spanjers, Catalytic reactor coupled with flame ionization detector for liquid chromatography, USPTO 20170146496 15/356110 (2017) in.
[181] H. Abbasi, S. Alavandi, D. Cygan, D.C. Kalensky, R.J. Kooy, Low NOx combustion devices and methods, USPTO 20180080647 15/713255 (2018).
[182] R.D. Aines, E.B. Baker, W.L. Bourcier, E.B. Duoss, D.T. Nguyen, J.S. Oakdale, M. M. Smith, W.L. Smith, J.K. Stolaroff, C. Ye, Composite 3d-printed reactors for gas absorption, purification, and reaction, USPTO 20180272268 15/468297 (2018).
[183] P. Del-Gallo, O. Dubet, R. Faure, M. Flin, S. Valentin, Heat exchanger and/or heat exchanger-reactor including channels having thin walls between one another, USPTO 20180200690 15/743452 (2018).
[184] P. Del-Gallo, O. Dubet, M. Flin, L. Prost, M. Wagner, Millimeter-scale exchanger-reactor for hydrogen production of less than 10 nm3/h, USPTO 20180170750 15/550618 (2018).
[185] P.V. Gurunath, A.R. Sankar, Chemical process intensification design through modeling and additive manufacturing, WIPO|PCT (WO2018198050A2), in, 2018.
[186] B.F. Hagh, C. Lo, D. Loeffelholz, Cell structures for use in heat exchangers, and methods of producing the same, USPTO 20180297843 15/488724 (2018).
[187] B.F. Hagh, C. Lo, D. Loeffelholz, D. Weng, Hydrogen production system and methods of producing the same, USPTO 20180301725 15/488736 (2018).
[188] R.K. Abu Al-Rub, O. Al-Ketan, Catalytic converter substrates comprising triply periodic minimal surfaces, USPTO 20190145298 16/098314 (2019).
[189] R.D. Aines, S.E. Baker, W.L. Bourcier, E.B. Duoss, D.T. Nguyen, J.S. Oakdale, M. M. Smith, W.L. Smith, J.K. Stolaroff, C. Ye, Composite 3d-printed reactors for gas absorption, purification, USPTO 20190232247 16/380648 (2019).
[190] S.E. Baker, W.L. Bourcier, M.R. Ceron Hernandez, J.M. Knipe, M.R. Murialdo, D. T. Nguyen, J.K. Stolaroff, C. Ye, Composite 3d-printed reactors for gas absorption, purification, and reaction, USPTO 20190240611 16/384520 (2019).
[191] R. Brahem, B. Amblard, A. Cloupet, T. Gauther, L. Raynal, New three dimensional structured packing for improving the contact between a gas phase and a dispersed solid phase following in counter-current, USPTO 20200095507 16/469041 (2019).
[192] B. Croissant, R. Faure, R. Joly, F. Rossignol, Method for depositing a catalyst on the inner surface of the microchannels of a reactor-exchanger, USPTO 20190308160 16/315027 (2019).
[193] C. Hofmann, H. Pennemann, Heat exchanger and reactor, USPO 20190366290 16/484871 (2019).
[194] C.K. Clayton, P.H. Humble, W.E. Tegrotenhuis, T.G. Veldman, R.S. Wegeng, R.F. Zheng, Enhanced microchannel or mesochannel devices and methods of additively manufacturing the same, WIPO|PCT (WO2019246586A1), in, 2019.
[195] K.W. Gyak, D.P. Kim, 3 method of manufacturing 3d ceramic structure using silica nanoparticle and ceramic microreactor for high temeprature chemical process using the same, (KR102117829B1), in, 2020.
[196] G.F. De Scheemaker, A.M. Willemsen Johannes, Modular Additive Manufactured Reactor System, USPTO (US2020346181A1), in, 2020.
[197] D. Achten, T. Büsgen, C. Tomczyk, J. Weikard, F. Richter, R. Wagner, Dual cure method using thermally latent thin catalysts, USPTO 20210087324 16/497562 (2021).
[198] C. Lai, L.J. Love, M. Matuszewski, J.E. Parks II, X. Sun, C. Tsouris, Multifunctional intensified reactor device with integrated heat and mass transfer, USPTO (US2021077978A1), in, 2021.
[199] J. Lefevere, S. Mullens, L. Protasova, Catalytic composition and structures made thereof, WIPO|PCT (WO2017055565A1), in, 2017.
[200] J.J. Farquhar, C.M. Seah, Metal foams and methods of manufacture, USPTO 20180230590 15/954480 (2018).
[201] D.R. Coupland, Catalyst shaped unit and method of its manufacture, EPO (EP2752244A1), in, 2014.
[202] D.R. Coupland, J. Phillips, S. Winfield, Catalyst manufacturing method, WIPO|PCT (WO2016097760A1), in, 2016.
[203] P. Campbell, E. Duoss, J. Oakdale, Click-chemistry compatible structures, click-chemistry functionalized structures, USPTO 20180059541 15/253654 (2018).
[204] P. Campbell, M.C. Hernández, M.A. Worsley, Porous ceramic structure for carbon dioxide capture, USPTO 20190389778 16/482215 (2019).
[205] C. Ke, L. Li, Q. Lin, P. Zhang, Three-dimensional printing with supramolecular templated hydrogels, USPTO 20200131383 16/605651 (2019).
[206] M.A. Torres Arango, K.A. Sierros, Hierarchical cellular mesoporous metal-oxide composites, USPTO 20190375653 16/432306 (2019).
[207] A. Vyatskikh, S. Delalande, J.R. Greer, Additive manufacturing of architectured materials, USPTO 20200073236 16/669379 (2020).
[208] H. Wang, W. P., Q.Q. Wang, H. Zhang, L. Zhang, Method for preparing structured catalyst carrier through photocuring, (CN111760596A), in, 2020.
[209] L. Liu, X. Sun, Z. Yuan, D. Zhou, Hydrotalcite slurry and preparation thereof, and structured catalyst and preparation method thereof, (CN112275271A), in, 2021.
[210] J.W. Allen, J.A. Camisa, M.S. IDE, E.J. O'neal, A.I. Skoulidas, J.J. Wu, Metal monolith for use in a reverse flow reactor, USPTO (20180333703 15/977027), in, 2018.
[211] J.A. Camisa, M.S. Ide, A.I. Skoulidas, J.J. Wu, A method of preparing an activated catalytic metal component, WIPO|PCT (WO2018213111A1), in, 2018.
[212] M.A. Petruska, T.E. James, J.D. Carruthers, P.C. Van Vusick, J.E. Roeder, Monolithic composite photocatalysts, USPTO 20200101440 16/680495 (2019).
[213] F.B. Bendixen, P.M. Mortensen, A. Sorea, P. Valler, Catalyst and system for methane steam reforming by resistance heating; said catalyst's preparation, WIPO|PCT (WO2019228795A1), in, 2019.
[214] D.V. Kuleshov, A.I. Lysikov, N.I. Mashkov, A.G. Okunev, E.V. Parkhomchuk, V. N. Parmon, A.V. Polukhin, Method of producing porous catalytically active material, (RU2730485C1), in, 2020.
[215] D.R. Sparks, Methods Of Making Monolithic Structures And Devices And Monolithic Structures And Devices Made Therefrom, USPTO (20200206972 16/729988), in, 2020.
[216] A.E. Carlson, J.E. Cosgrove, M.A. Serio, M.A. Wójtowicz, Monolithic trace-contaminant sorbents fabricated from 3d-printed polymer precursors, USPTO (US2021001305A1), in, 2021.
[217] C.P. Moorlag, N.-X. Hu, V.M. Farrugia, 3d printing support structures incorporating sacrificial materials, USPTO 20210060867 17/097032 (2021).
[218] A. Largeteau, M. Prakasam, Method for producing a porous monolithic material, USPTO 20180200409 15/743492 (2018).
[219] D. Achten, T. Büsgen, T. Faecke, B. Mettmann, J. Buechner, H.-J. Laas, T. Liu, Method for producing products by means of additive manufacturing methods using reactive powders, and products thereof, USPTO 20200055235 16/609247 (2019).
[220] L. Protosova, F. Snijkers, S. Danaci, A. Bengaouer, Devices for through-flow of fluids comprising graded porous structures, USPTO 20200101435 16/499222 (2019).
[221] A. Rownaghi, X. Li, F. Rezaei, Zeolite monolith compositions and methods for the catalytic cracking of alkanes, USPTO 20200101447 16/585968 (2019).
[222] S. Lawson, F. Rezaei, A. Rownaghi, Additively-manufactured structure for reactionary processes, USPTO (US2020398456A1), in, 2020.
[223] Z. Cheng, E. Duoss, C. Spadaccini, M.A. Worsley, Y. Jianchao, S. Chandraekaran, Base-catalyzed sol-gel inks for direct ink writing of hight resolution hierarchically porous carbon aerogels, USPTO PCT/US2019/023533 16/772627 (2020).
[224] F. Borninkhof, M.O. Kennema, J. Lefevere, B. Michielsen, F. Scharf, C. Walsdorff, Three-dimensional porous catalyst, catalyst carrier or absorbent structure of stacked strands, WIPO|PCT (WO2021013682A1), in, 2021.

[225] P.J. Brezovec, T.A. Kennedy, D.R. Markiewicz, M.J. McCluskey, M.L. Tims, Additive manufactured electrode for flow battery, USPTO 20180205067 15/869676 (2018).
[226] D.R. Hall, M. Dawson, N. Farandos, J. Dawson, Electrochemical reactors with fluid dispersing components, USPTO 20200144653 16/693268 (2019).
[227] D.R. Hall, M. Dawson, N. Farandos, J. Dawson, Method of making electrochemical reactors, USPTO 20200144648 16/684864 (2019).
[228] D.R. Hall, M. Dawson, N. Farandos, J. Dawson, Interconnect with microchannels and method of making, USPTO 20200144633 16/699453 (2019).
[229] D.R. Hall, M. Dawson, N. Farandos, J. Dawson, Method of making channeled electrodes, USPTO 20200144627 16/693271 (2019).
[230] J. Dawson, M. Dawson, N. Farandos, D.R. Hall, Heat Exchanger for an Electrochemical Reactor and Method of Making, USPTO (US2020235410A1), in, 2020.
[231] D.R. Hall, M. Dawson, N. Farandos, J. Dawson, Compact electrochemical reactors, USPTO 20200144654 16/684838 (2020).
[232] S. Lawson, B. Adebayo, C. Robinson, Q. Al-Naddaf, A.A. Rownaghi, F. Rezaei, The effects of cell density and intrinsic porosity on structural properties and adsorption kinetics in 3D-printed zeolite monoliths, Chem. Eng. Sci. 218 (2020).
[233] S. Lawson, M. Snarzyk, D. Hanify, A.A. Rownaghi, F. Rezaei, Development of 3D-Printed Polymer-MOF Monoliths for CO2 Adsorption, Ind. Eng. Chem. Res. 59 (2020) 7151–7160.
[234] S. Lawson, Q. Al-Naddaf, A. Krishnamurthy, M.S. Amour, C. Griffin, A.A. Rownaghi, J.C. Knox, F. Rezaei, UTSA-16 Growth within 3D-Printed Co-Kaolin Monoliths with High Selectivity for CO2/CH4, CO2/N2, and CO2/H2 Separation, ACS Appl. Mater. Interfaces 10 (2018) 19076–19086.
[235] S. Lawson, C. Griffin, K. Rapp, A.A. Rownaghi, F. Rezaei, Amine-Functionalized MIL-101 Monoliths for CO2 Removal from Enclosed Environments, Energy Fuels 33 (2019) 2399–2407.
[236] H. Thakkar, Q. Al-Naddaf, N. Legion, M. Hovis, A. Krishnamurthy, A.A. Rownaghi, F. Rezaei, Adsorption of Ethane and Ethylene over 3D-Printed Ethane-Selective Monoliths, ACS Sustainable Chem. Eng. 6 (2018) 15228–15237.
[237] H. Thakkar, S. Lawson, A.A. Rownaghi, F. Rezaei, Development of 3D-printed polymer-zeolite composite monoliths for gas separation, Chem. Eng. J. 348 (2018) 109–116.
[238] H. Thakkar, S. Eastman, A. Al-Mamoori, A. Hajari, A.A. Rownaghi, F. Rezaei, Formulation of Aminosilica Adsorbents into 3D-Printed Monoliths and Evaluation of Their CO2 Capture Performance, ACS Appl. Mater. Interfaces 9 (2017) 7489–7498.
[239] H. Thakkar, S. Eastman, Q. Al-Naddaf, A.A. Rownaghi, F. Rezaei, 3D-Printed Metal-Organic Framework Monoliths for Gas Adsorption Processes, ACS Appl. Mater. Interfaces 9 (2017) 35908–35916.
[240] H. Thakkar, S. Eastman, A. Hajari, A.A. Rownaghi, J.C. Knox, F. Rezaei, 3D-Printed Zeolite Monoliths for CO2 Removal from Enclosed Environments, ACS Appl. Mater. Interfaces 8 (2016) 27753–27761.
[241] S. Bettermann, F. Kandelhard, H.-U. Moritz, W. Pauer, Digital and lean development method for 3D-printed reactors based on CAD modeling and CFD simulation, Chem. Eng. Res. Des. 152 (2019) 71–84.
[242] B. Claessens, N. Dubois, J. Lefevere, S. Mullens, J. Cousin-Saint-Remi, J.F.M. Denayer, 3D-Printed ZIF-8 Monoliths for Biobutanol Recovery, Ind. Eng. Chem. Res. 59 (2020) 8813–8824.
[243] F.S. Franchi, M. Ambrosetti, R. Balzarotti, M. Bracconi, G. Groppi, E. Tronconi, Rich H2 catalytic oxidation as a novel methodology for the evaluation of mass transport properties of 3D printed catalyst supports, Catal. Today (2021).
[244] T. Maconachie, M. Leary, B. Lozanovski, X. Zhang, M. Qian, O. Faruque, M. Brandt, SLM lattice structures: Properties, performance, applications and challenges, Mater. Des. 183 (2019) 108137.
[245] S. Mooraj, Z. Qi, C. Zhu, J. Ren, S. Peng, L. Liu, S. Zhang, S. Feng, F. Kong, Y. Liu, E.B. Duoss, S. Baker, W. Chen, 3D printing of metal-based materials for renewable energy applications, Nano Res. (2020).
[246] J. Lefevere, L. Protasova, S. Mullens, V. Meynen, 3D-printing of hierarchical porous ZSM-5: The importance of the binder system, Mater. Des. 134 (2017) 331–341.
[247] S. Liu, Y.C. Shin, Additive manufacturing of Ti6Al4V alloy: A review, Mater. Des. 164 (2019) 107552.
[248] S. Chandrasekaran, R. Lu, R. Landingham, J.T. Cahill, L. Thornley, W. Du Frane, M.A. Worsley, J.D. Kuntz, Additive manufacturing of graded B4C-Al cermets with complex shapes, Mater. Des. 188 (2020) 108516.
[249] A. Rajabi, M.J. Ghazali, A.R. Daud, Chemical composition, microstructure and sintering temperature modifications on mechanical properties of TiC-based cermet – A review, Mater. Des. 67 (2015) 95–106.
[250] D. Kong, X. Ni, C. Dong, X. Lei, L. Zhang, C. Man, J. Yao, X. Cheng, X. Li, Bio-functional and anti-corrosive 3D printing 316L stainless steel fabricated by selective laser melting, Mater. Des. 152 (2018) 88–101.
[251] R. Wang, P. Zhu, W. Yang, S. Gao, B. Li, Q. Li, Direct-writing of 3D periodic TiO2 bio-ceramic scaffolds with a sol-gel ink for in vitro cell growth, Mater. Des. 144 (2018) 304–309.