Chapter 2

Background and Literature Review

2.1 Introduction

"Porous ceramics" represent a remarkable material amalgamation, harnessing the unique properties of ceramics and the structural advantages of porosity. This captivating material has garnered substantial attention and emerged as a focal point of extensive research efforts. With ceramics contributing inherent traits such as resistance to corrosion and heat, erosion and wear resistance, distinctive electronic properties, favorable bio-affinity, and remarkable specific strength, combined with the porous structures offering attributes like low density, controlled permeability, low dielectric constant, high surface area, and enhanced piezoelectric properties, porous ceramics have become an exceptionally appealing candidate for a diverse array of applications [1,2]. Their multifaceted characteristics, encompassing low density, low specific heat, low permeability, low thermal conductivity, high specific strength, high surface area, and exceptional thermal and chemical stability, along with commendable chemical and mechanical resistance, distinguish porous ceramics from metals, polymers, and even their denser ceramic counterparts [3–5]. These exceptional attributes bestow upon porous ceramics an essential role in driving the advancement of sustainable energy and environmental applications. Moreover, the expansive range of porosity spanning from 2% to 99% and the pore size distribution spanning from nanometre to micro meter position porous ceramics as an exemplary material choice for an extensive range of innovative applications such as efficient filtration for capturing particulate matter, purification of drinking water, catalyst supports for pollutant degradation and hydrogen production, integration into energy storage systems, utilization in advanced micromechanical systems for energy harvesting, electromagnetic interference shielding in wireless communication devices and automobiles, and the creation of construction materials with excellent heat insulation and sound absorption properties [6–8].

Porous materials are categorized into three classes based on pore diameter, following the nomenclature of the International Union of Pure and Applied Chemistry (IUPAC): macroporous ($d > 50$ nm), mesoporous ($50 \text{ nm} > d > 2$ nm), and microporous ($d < 2$ nm) as elaborated in fig 2.1[9,10]. In the case of porous ceramics, their pore structure can be further categorized as open-cell (or reticulated) or closed-cell, which significantly influences the functional properties of the materials [11]. However, a hierarchical pore structure, consisting of a combination of pores with different sizes within a single monolithic matrix, is commonly employed. The synthesis process of porous ceramics plays a crucial role in achieving the desired pore configuration and geometry, ultimately determining the final product's properties, encompassing mechanical properties and advanced functionalities[12,13]. Each synthesis approach exhibits distinct suitability for specific material types, porosity levels, pore sizes, pore connectivity, and pore distribution. Therefore, the precise selection of ceramic types and the meticulous creation of detailed structural features of the pores are critical stages requiring thorough investigations and comprehensive understanding for successful applications in various fields [14,15].

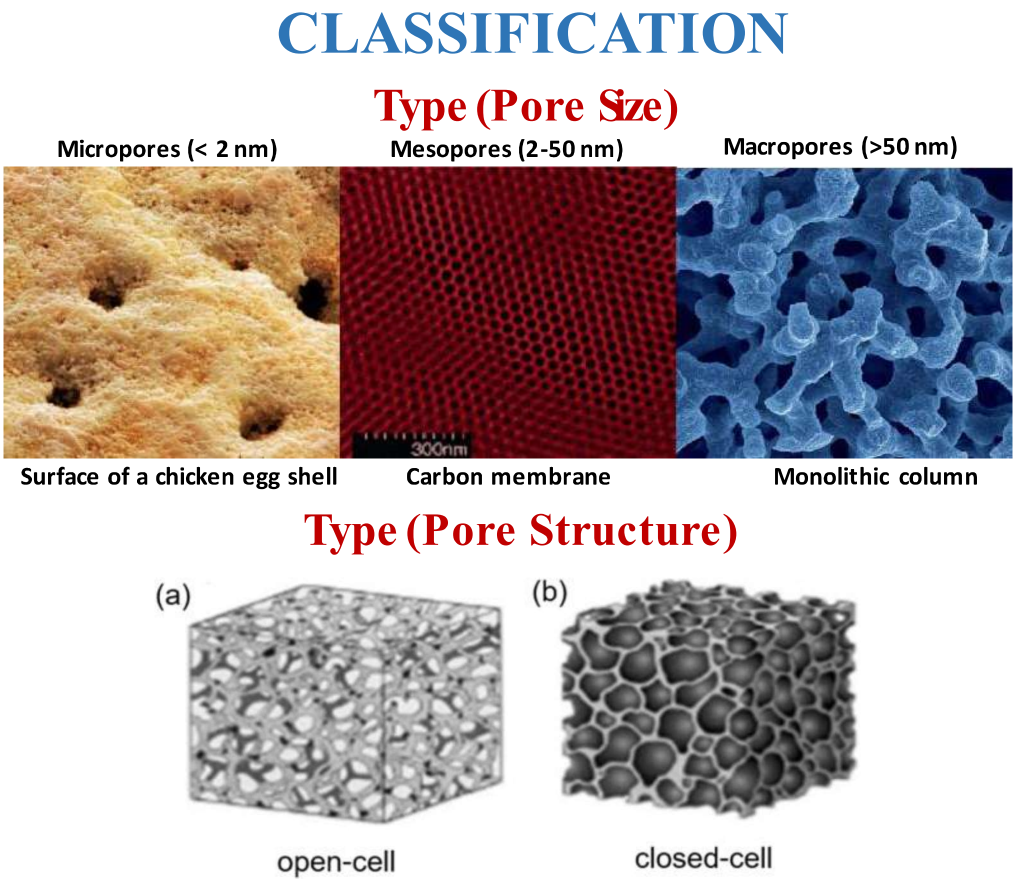

Fig. 2.1 Classification of porous materials [7]

The following section in this chapter provides a comprehensive description of various procedures employed to achieve "Porous Ceramics" and manipulate pore morphology. The underlying principles and challenges associated with each synthesis strategy will be summarized and discussed, along with an exploration of the progress that can be made to meet the requirements of advanced applications. This chapter also highlights the existing gaps and the necessity for a more cost-effective and sustainable approach to porous ceramic fabrication. Furthermore, it offers insights into both traditional and recent ceramic materials utilized in porous ceramic fabrication, with a particular focus on identifying the potential of "Industrial solid waste" as a future raw material for porous fabrication. This paves the way for subsequent chapters to explore economical approaches for porous ceramic fabrication, employing a sustainable "Waste Valorization" approach.

2.2 Applications of Porous Ceramics

Porous ceramics have diverse applications due to their unique properties. They are used in filtration, catalysis, thermal insulation, biomedical fields, energy storage, and aerospace/automotive industries. They serve as efficient filters, catalyst supports, insulating materials, bone scaffolds, and components in batteries and supercapacitors. A visual depiction of potential applications for porous ceramics is presented in Figure 2.2. Ongoing research expands their potential applications.

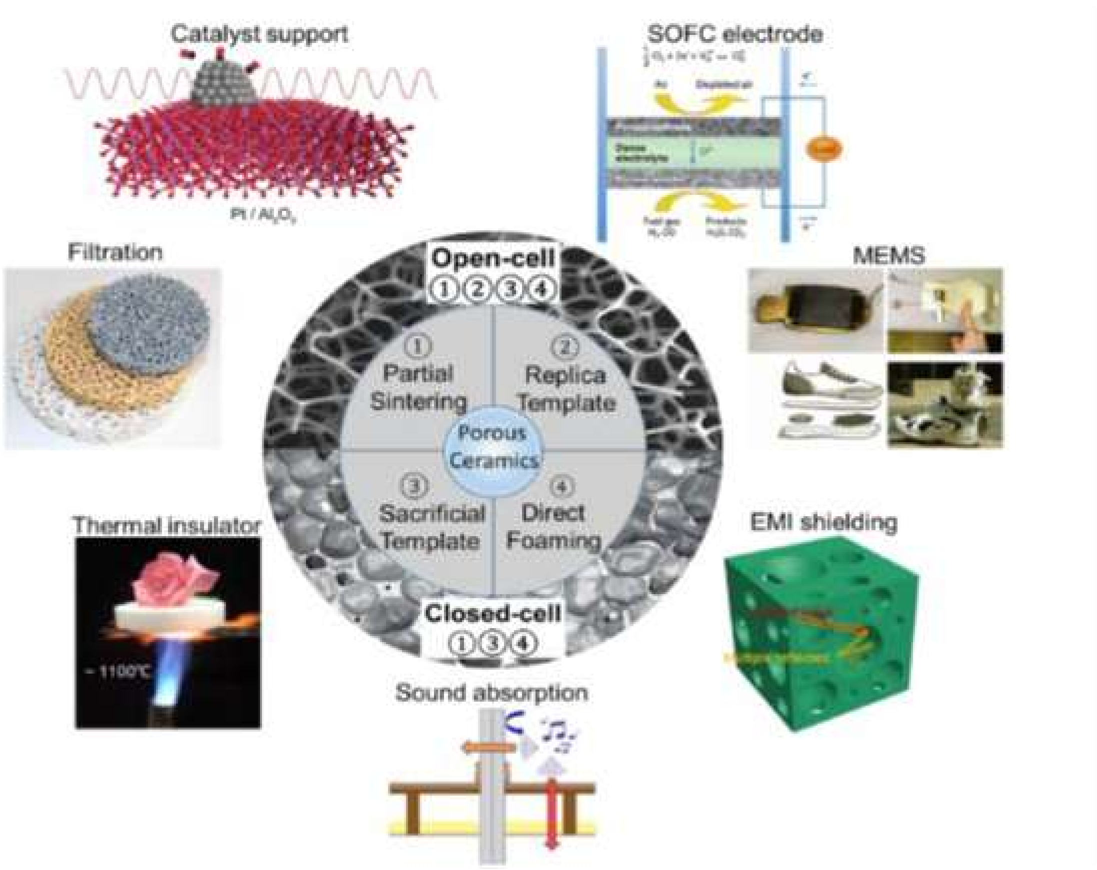

Fig. 2.2 Illustrative representation of various applications of porous materials [7]

2.2.1 Porous Ceramics in Filtration Applications

Filtration plays a vital role in various industries, including chemical, biomedical, environmental, and energy sectors. Compared to metal- and polymer-based materials, porous ceramics offer unique properties such as high temperature stability, thermal shock resistance, corrosion resistance, low thermal expansion, and durability, making them ideal candidates for applications such as hot gas filtration, diesel particulate filters, and water purification [16]. Figure 2.3 illustrates the mechanism of particulate matter filtration through ceramic filters. Ceramic filters typically have around 50% porosity and an average pore diameter of 10 µm, striking a balance between filtration efficiency and mechanical robustness. Filter design depends on controlling porosity and pore size to meet specific requirements. Fine-particle filtration uses filters with pore sizes around 1 µm, while hot gas filtration and diesel particulate filters require larger pore sizes exceeding 10 µm [17].

In hot gas filtration, high collection efficiency and high-temperature durability are crucial for porous ceramics. Materials like multichannel tubular Al_2O_3 are used to remove organic aerosols from furnace flue gas. Filters self-regenerate as the fouling layer falls off under gravity, maintaining the filter structure. Cuo et al. developed a series of highly porous fibrous ceramic membranes with three-dimensional structure and then coated a layer of spherical α-Al_2O_3 on the membrane surface which is used for gas filtration[18]. Dong et al. by combining foaming-sol–gel-tape casting and in-situ mullite reaction has prepared porous mullite-bonded SiC filters with three-dimensional interconnect pore network structure[19].

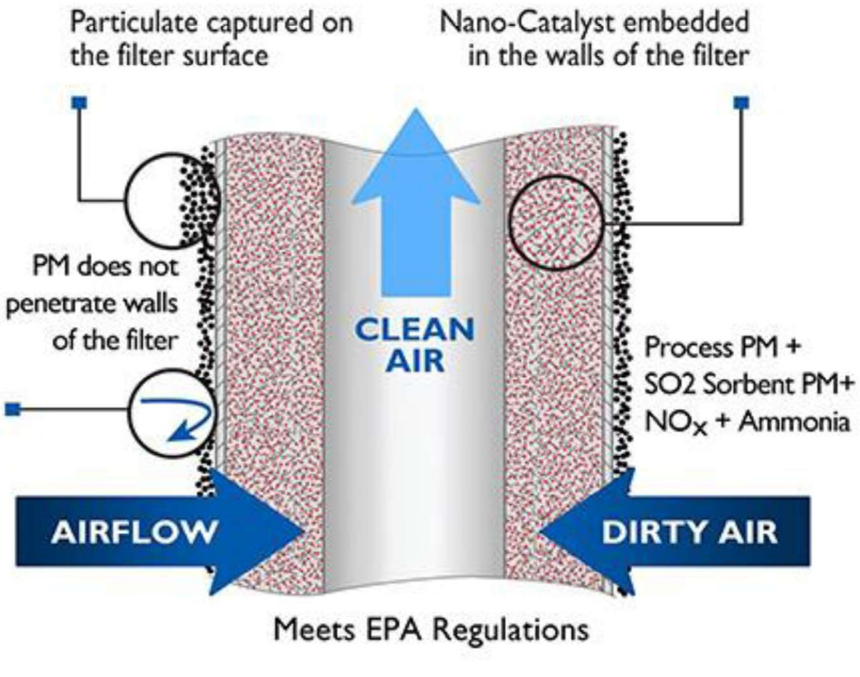

Fig. 2.3 Figure showing mechanism of filtering particulate matter through ceramic filters [7]

Diesel particulate filters (DPFs) trap carbon-based particulate matter in diesel exhaust. Ideal porous ceramics for DPFs have high porosity, narrow pore distribution, good pore connectivity, and large specific surface area. Honeycomb wall filters with millimetre-scale openings are commonly used. Ceramic filters impede soot accumulation and can be regenerated through methods like electrical heating, post-injection of fuel, or continuous catalysis regeneration. Figure 2.4 depicts the characteristic pattern of a ceramic filter employed in the filtration of diesel particulate matter.

Dejneka et al. developed porous niobite ceramics using partial sintering as the porous particulate filter for diesel engines [20]. Park et al. fabricated porous cordierite pellets through direct foaming, and they found that the pressure drop and particle loading rate of their porous pellet filters exhibited superior filtration efficiency to nonporous ones, and small particles were also collected within the pores of the pellet filters [21].

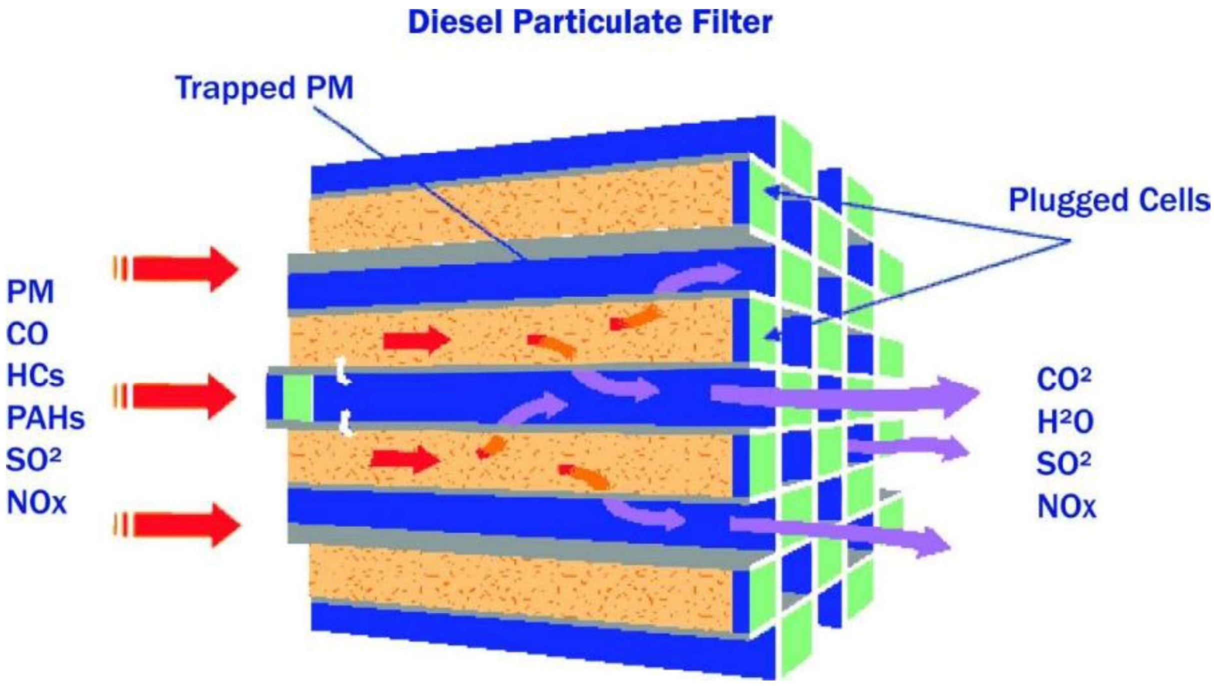

Fig. 2.4 Schematic of diesel particulate through ceramic filter [7]

Porous ceramic filters effectively block bacteria and suspended solids in water treatment. Diatomite or clay-based filters with micrometre-scale pores and 30-40% porosity are used for point-of-use water filtration [22,23]. Combining physical filtration with metallic disinfection mechanisms, such as silver nanoparticles, enhances filtration efficiency and eliminates microorganisms[24]. Silsesquioxane and chitosan are being explored for their antibacterial properties[25,26]. Porous ceramic filters also find applications in wastewater treatment and seawater desalination, removing phosphorus from lake sediment and achieving marine bacteria inactivation and plankton removal in seawater treatment [27–30].

2.2.2 Porous Ceramics as Catalyst Support

Catalysis is vital in academic and industrial settings, with the majority of chemical processes involving catalytic steps. However, traditional catalysts have limitations such as low mechanical strength and complicated recycling processes. To overcome these issues, porous ceramic-based catalyst supports have gained interest due to their advantageous properties. These include simplified loading, lower pressure drops, improved mass transport and dispersion, enhanced heat transfer, and long-term stability in various atmospheres [31,32]. Surface modifications can further enhance catalytic efficiency [33]. Two examples of porous ceramic-supported catalysts are photocatalysts for water treatment and micro-reformers for hydrogen production. These catalysts offer high efficiency, easy handling, and suitability for endothermic processes.

2.2.2.1.1 Photocatalysts for environmental remediation:

TiO_2, a widely studied photocatalyst, can be supported on porous ceramics for water treatment by degrading pollutants. The porous support allows for high photocatalytic efficiency, and the ceramic structure simplifies recycling and handling of the catalyst. Du et al. deposited TiO_2 thin films onto microporous Al_2O_3 (porosity of 60.4−79.5% and pore size of 180−315 μm) by using the sol-gel dip-coating method, for uses as photocatalyst [34].

2.2.2.1.2 Micro-reformer for hydrogenation processes:

Porous ceramic supports, like nanoporous SiC or porous Al_2O_3, offer advantages for hydrogen production via steam reforming or ammonia decomposition. The high surface areas, low pressure drop, large heat transfer capability, and high-temperature stability make them suitable for highly endothermic processes. Kim created porous ceramics (typically composed of 40 % Al_2O_3 and 55 % SiO_2, porosity of 71 %, pore size ranging from a few to ∼100 μm) with large surface areas and good thermal stability, and they further evaluated their performance as the Cu/ZnO catalyst support for steam reforming of methane [35].

2.2.3 Porous Ceramics as Energy storage and conversion media

Energy storage and conversion processes involve complex electrochemical reactions, where porous ceramics have shown potential as components in concentrated solar power (CSP), fuel cells, and batteries.

2.2.3.1 Solar Energy Absorption and Conversion:

Concentrated Solar Power (CSP) plants capture solar energy by concentrating sunlight onto a receiving surface, which converts absorbed heat to mechanical work or electrical energy.

Porous ceramics, such as ceramic honeycombs, have been used as absorber elements in CSP plants [36]. These ceramics can handle high temperatures and efficiently transfer heat to air, which is used for generating steam and power in a Rankine cycle. To increase the storage capacity of solar energy, porous ceramic-based thermochemical storage modules can be integrated into CSP plants. These modules use a thermochemical redox cycle powered by stored heat to split H_2O and CO_2, allowing thermal energy to be recovered during off-sun operation.

2.2.3.2 Components in Fuel Cells and Batteries:

Porous ceramics have shown promise as components in fuel cells and batteries. For example, in Solid Oxide Fuel Cells (SOFCs), porous ceramic electrodes with optimized pore characteristics enable efficient gas diffusion to the active reaction areas [37]. Freeze-casting, a fabrication technique, has been used to create porous ceramic electrodes with straight and parallel pores, promoting electrochemical reactions [38]. Porous ceramics have also been utilized in Photomicrobial Fuel Cells (p-MFCs) and Lithium Metal Batteries (LMBs) [39,40]. Porous ceramic anodes in p-MFCs allow for light scattering and facilitate biofilm growth, resulting in improved power output and stability. In LMBs, nanoporous ceramic membranes have been used to stabilize the anode and inhibit dendrite formation during charge-discharge cycles.

2.2.3.3 Energy Harvesting (MEMS) and Sensing Applications:

Porous ceramics have been explored for energy harvesting in Microelectromechanical Systems (MEMS). Porous ferroelectric ceramics, like lead-zirconia-titanate (PZT) and barium-titanate ($BaTiO_3$), have shown remarkable piezoelectric and pyroelectric properties, enabling them to scavenge energy from mechanical vibrations and temperature fluctuations [41,42]. To enhance energy harvesting capability, pores are introduced into ferroelectric materials to create low permittivity regions [43]. Freeze-casting is a promising technique for manufacturing porous ferroceramics, as it enables good alignment of the porous phase, leading to increased electromechanical coupling and superior mechanical properties [42].

2.2.4 Porous Ceramics in Insulation applications

2.2.4.1 Electromagnetic Wave Shielding:

Electromagnetic waves with wavelengths in the range of $2.4 \times 10^{\wedge -2}$ to $3.7 \times 10^{\wedge -2}$ m are widely used in various electronic equipment, including wireless communication devices, medical facilities, aerospace applications, and flexible electronic devices [44]. To protect instruments and the human body from electromagnetic interference (EMI), materials with high electromagnetic wave shielding effectiveness are required. Traditional metal-based EMI shielding materials have limitations in terms of high mass density and poor corrosion resistance. Polymer-based materials, although lightweight, suffer from low strength and limited operational temperature. Porous ceramics offer unique advantages as EMI shielding materials. Porous SiC foams synthesized using direct foaming and freeze-drying techniques have shown excellent EMI shielding effectiveness [45].

2.2.4.2 Soundproof Applications:

Noise pollution has become a significant problem in modern society, and sound absorption materials that can operate under harsh conditions, such as high temperatures and corrosive environments, are in demand. Porous ceramics with specifically regulated porous microstructures are an excellent choice for sound absorption applications. The loss of sound in porous ceramics occurs through two mechanisms: flexural vibrations within the specimen and dissipation of acoustic energy due to multiple reflections of sound waves within the voids of the structure. Studies have shown that porous alumina/mullite-based ceramics fabricated via freeze casting with sacrificial polystyrene templates exhibited excellent sound absorption performance [46].

2.3 Techniques in Porous Ceramics Fabrication

In comparison to the intrinsic properties of ceramics, the control of porosity and microstructure is of paramount importance in tailoring the properties of porous ceramics. The fabrication method employed plays a crucial role in determining the overall porosity range, pore morphology, pore size distribution, and pore connectivity (open and closed porosity). Various techniques are commonly used to create porous ceramics, including partial sintering, sacrificial fugitives, replica templates, and direct foaming methods as shown in fig 2.5. However, recent advancements such as gel casting, freeze casting, and additive manufacturing have opened new pathways to shape complex porous structures with greater control over morphology. This section provides a detailed description of each technique, highlighting their advantages, drawbacks, and future needs, elucidating how they contribute to the advancement of porous ceramics with enhanced properties.

2.3.1 Partial sintering

The underlying principle involved in the production of porous ceramic structures through the partial sintering method revolves around the precise control of microstructure during the consolidation phase of green ceramic bodies. This process entails the cohesive bonding of densely and uniformly packed particles within the powder compact, which are initially loosely aggregated. The bonding is facilitated by various mechanisms such as surface diffusion, evaporation-condensation, or solution-reprecipitation phenomena, which are augmented through controlled heat treatments [7]. By terminating the sintering process before complete densification, a homogeneous porous structure is achieved. This method results in a hierarchical porous arrangement with three interconnected levels of pores: voids between agglomerates, pores within the agglomerates, and pores within the individual particles [47]. Factors such as starting powder size, forming pressure, sintering temperature, and time, as well as additives and specific sintering conditions, allows for control of porosity and pore size [48,49]. Increasing sintering temperature results in increased density and decreased porosity, while higher heating rates and green compaction pressure affect porosity differently. Techniques like mixing particles of different sizes, using sintering additives, partial hot-pressing, and spark plasma sintering can improve mechanical properties [50,51]. In-situ chemical reactions and reaction bonding can also be used [52]. The partial sintering method offers convenient engineering of porous ceramics, but has limitations such as low porosity, difficulties with coarse powders, and limited control over pore morphology [53].

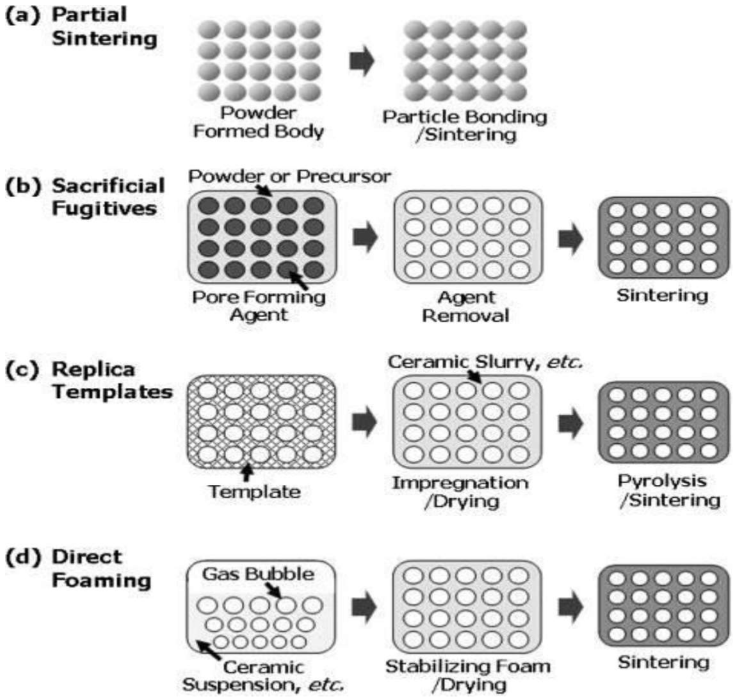

Fig. 2.5 Conventional approaches to fabricate porous ceramics [1]

2.3.2 Replica Template Method

The replica template method is a widely used and effective technique for fabricating open-celled porous ceramics with interconnected pores and large surface areas. This method involves impregnating open-celled porous polymeric foams with a ceramic slurry, followed by thermal treatment. During the heating stage, the organic polymeric substances in the foam decompose while the ceramic material remains, resulting in porous ceramics that replicate the morphology and structure of the original template.

One of the key advantages of the replica method is the ability to control the morphological and microstructural characteristics of the final products. The choice of template material, such as solid foam sponges (polymeric or natural sources like wood, cellulose, and marine sponge), plays a crucial role in achieving high porosities of over 70%. Additionally, the selection of templates and slurry media significantly influences the porosity and mechanical properties of the final ceramics.

The replica method finds applications in various fields, including gas exhaust catalyst devices, burners, scaffolds for bone tissue engineering, catalyst supports, and nanoreactor applications. The process involves coating a reticulated foam with a ceramic slurry, squeezing out excess slurry after each impregnation, and then burning out the organic template during sintering. However, the burning of organics can introduce triangular voids and longitudinal defects in the resulting ceramic struts.

Researchers have successfully utilized different templates and slurry compositions to achieve specific properties in the final ceramics. For example, alumina foams with high porosity ranging from 80% to 95% were fabricated using polyurethane (PU) foam templates. A novel bioactive TiO_2 scaffold with a porosity of 92% and pore sizes ranging from 300 to 700 μm was also created using the replica method.

The selection of the template material is critical for controlling pore geometries and sizes. Polymeric templates, particularly PU foams, are commonly used due to their reliability and structural integrity. Natural sources, such as marine sponges, offer an alternative with better mechanical strength but may exhibit higher shrinkage after sintering. Wood templates have also been investigated, although they present challenges such as low porosity and poor mechanical strength.

The rheological properties of the ceramic suspensions used in the replica method significantly affect the final ceramic structures. Slurries with pseudo-plastic or shear-thinning behavior are required to achieve uniform impregnation of the template. The viscosity of the slurry needs to be carefully controlled during the compression-expansion steps to ensure proper coating and adhesion. Various additives, including binders, dispersants, and thickeners, can be used to improve the rheological behavior and mechanical properties of the slurries.

The use of additives such as binders improves slurry adhesion and protection of the template, while dispersants prevent agglomeration and improve slurry stability. Thickening agents contribute to shear-thinning behavior and promote good coatings. Optimal solid contents in the slurry precursor are crucial for achieving the desired porosity, pore interconnectivity, and mechanical behavior in the final ceramics.

To enhance the mechanical properties of porous ceramics, additional processes can be employed. Techniques like re-infiltration, additional coating, and template surface pre-treatment have been explored. These processes allow for the optimization of the slurry impregnation, resulting in increased thickness, homogeneity, and mechanical strength of the ceramics. The number of coating cycles and the addition of a second phase coating can further improve the mechanical stability and eliminate microcracking.

Further research is needed to develop sustainable template materials and optimize processing parameters for specific applications. The combination of different additives and template materials can lead to near-net-shape ceramic foams with tailorable properties. The understanding and optimization of the replica method hold great potential for advancing the development of porous ceramics in various industries, offering versatile materials with unique properties for a wide range of applications.

2.3.3 Sacrificial Fugitive Method

The sacrificial template technique is a unique method for producing porous ceramics that differs from the template replica approach. While the template replica method involves reproducing the original template's configuration, the sacrificial template method creates a negative copy of the original pore characteristics. This distinctive feature allows the sacrificial template method to generate both open-cell and closed-cell pores. By incorporating sacrificial fugitives and subsequently eliminating them through various means such as evaporation, burn-off, thermal decomposition, etching, or leaching, the sacrificial template process enables the fabrication of porous ceramics with customized porosity and mechanical strength.

Typically, a biphasic composite serves as the initial material for the sacrificial template method, which can exist as a powder mixture, a two-phase suspension, or a template impregnated with preceramic polymer or ceramic slurry. It is crucial to ensure that the matrix materials do not react with the sacrificial materials at high temperatures. Various types of sacrificial fugitives have been utilized, including natural sources like silk and Metroxylon sagu, synthetic organics such as polyethylene (PE) beads, polymethyl methacrylate (PMMA) microbeads, gas-filled expandable polymeric microspheres, and epoxy resin (EP) particles, inorganic substances like graphene sheets and mesocarbon microbeads, as well as frozen liquids such as water and tert-butyl alcohol (TBA). Adjusting the volume fraction of the sacrificial template allows control over the resulting ceramics' porosity.

The selection of the sacrificial template significantly impacts the quality, properties, and potential applications of the porous ceramics. The pore morphology is determined by the structure of the incorporated fugitives. For example, fibrous fillers like Nylon 6,6 and polypropylene fibers have shown better effectiveness in achieving desirable permeability levels compared to spherical template porogens like PMMA beads. Utilizing a combination of preceramic polymer precursor and sacrificial templates offers flexibility in shaping options, enabling the creation of various forms such as monolithic materials, fibers, or coatings. This approach requires low-temperature treatment and yields high-quality porous ceramic structures with minimal shrinkage.

2.3.4 Freeze Casting Method

The sacrificial template method can lead to cracks in the structure during pyrolysis or sintering stages due to the mismatch in thermal expansion coefficients between different phases. However, these drawbacks can be mitigated by utilizing aqueous pore formers that can be easily sublimated. Freeze-casting, a variation of the sacrificial template method, utilizes frozen liquid as templates to create pores. In this process, ceramic suspensions undergo directional cooling, which is a crucial step for subsequently removing the frozen suspension through directional sublimation. This results in the production of macroporous ceramics with unidirectionally aligned pores. The freeze-casting method is a promising approach for fabricating porous ceramics with controlled microstructures and desirable properties.

The freeze-casting method involves four main steps: slurry preparation, solidification of the slurry, sublimation of the frozen solvent, and sintering of the remaining ceramics (fig 2.6). The slurry consists of ceramic powder, solvent, and additives. The directional cooling process during solidification leads to the formation of ceramic walls and the rejection of ceramic particles by the growing solidification front. Subsequent sublimation of the solvent leaves behind a porous structure that can be further sintered. The resulting microstructures and properties of the ceramics depend on various parameters, including slurry formulation, solidification conditions, and the choice of additives and solvent.

Several factors can be manipulated to control the microstructure and properties of freeze-cast porous ceramics. The initial solid loading in the slurry influences the resulting porosity and ceramic wall thickness. Higher solid loadings reduce porosity and suppress pore shrinkage. The choice of solvent and cooling conditions, including cooling rate and temperature gradient, significantly affect the microstructure of the final product. The addition of additives can modify ice crystal growth and lead to different pore morphologies, such as lamellar or dendritic structures. The freeze-casting process allows for the alignment of pores in a unidirectional manner, providing unique opportunities for tailored functional properties.

Porous ceramics fabricated via the freeze-casting method find applications in various fields. With high porosity (>50%) and vertically aligned hierarchical pores, they are suitable for thermal insulation, absorbers, and energy harvesting applications. The porosity of the ceramics directly affects their mechanical strength, thermal conductivity, and dielectric constant. Increasing the solid content and controlling freezing velocities can enhance mechanical properties, while the choice of additives can influence pore morphology and functional properties.

Although freeze-casting offers precise control over the microstructure of porous ceramics, challenges remain. The sublimation of the frozen template can be time-consuming and lead to structural collapse. Cryogenic energy consumption and vacuum conditions pose limitations on mass production. Future research efforts should focus on reducing costs, improving manufacturing ease, and addressing these challenges.

The freeze-casting method provides a versatile approach for fabricating porous ceramics with controlled microstructures and tailored properties. By manipulating various parameters, such as slurry formulation, solidification conditions, and additives, it is possible to achieve unique pore structures and enhance the functional properties of the ceramics. Further advancements in reducing costs and improving manufacturing efficiency will expand the applicability of freeze-cast porous ceramics in diverse industrial sectors.

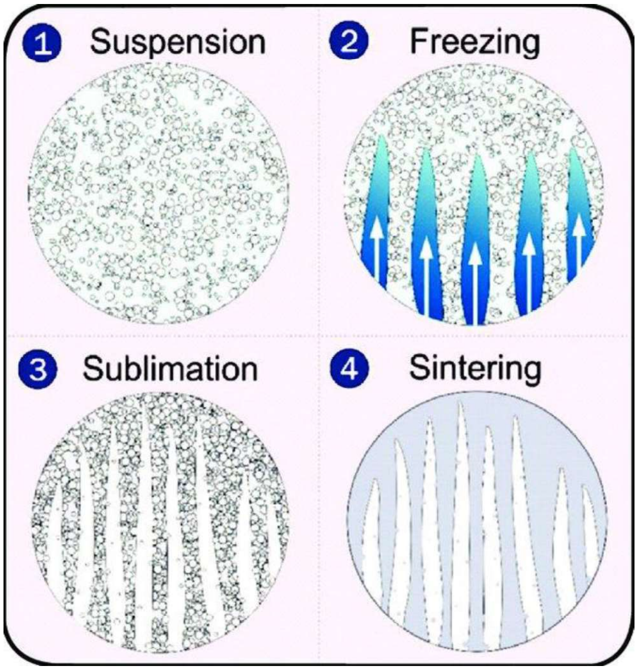

Fig. 2.6 Figure showing mechanism of freeze casting route to fabricate porous ceramics [54]

2.3.5 Direct Foaming Method

The direct foaming technique shows promise for the production of porous ceramics with open and closed pore structures, achieving porosities of up to 97%. This method involves foaming a pre-ceramic suspension containing a surfactant, incorporating gas through mechanical stirring or chemical blowing. The foamed suspension is stabilized and then sintered to obtain the final ceramic product. The direct foaming technique stands out for its simplicity, cost-effectiveness, fast processing, and potential for mass production. Figure 2.7 illustrates the various steps encompassed in the fabrication of porous ceramics through the direct foaming technique.

One of the main challenges in direct foaming is stabilizing the air bubbles within the suspension, particularly when the slurry contains a high bubble content, as the wet foam may collapse and crack. To address this, short-chain amphiphilic molecules are used as surfactants to make the particle surface hydrophobic. These surface-modified particles are absorbed at the gas/liquid interfaces, preventing bubble coalescence and resulting in stable foam with high volume. This leads to successful production of porous ceramics after drying/setting and sintering. Achieving a stable suspension requires careful control of pH value, solid loading, and surfactant concentration in the initial suspension.

Mechanical agitation, often using a household hand mixer, is a common method for foaming the suspension at room temperature. The resulting ceramic's porosity is proportional to the air content in the foamed suspension. Foam stability is critical and is improved by attaching partially hydrophobic particles to the bubble surface with a contact angle $\theta < 90°$. Foam stability can be quantified by measuring volume changes during drying and evaluating the adsorption free energy and Laplace pressure of particles at the air-liquid interface.

Chemical blowing is an alternative foaming technique where gases are generated in-situ from chemical blowing agents during the suspension's chemical reaction and/or thermal decomposition. This method allows for precise control of pore size, ranging from 0.5 to 3 mm, and can achieve higher porosities up to 97.5% after sintering. The choice of surfactants and blowing agents can influence foam structure and morphology. The precursor sol viscosity and curing agent concentration also significantly impact foam structure, porosity, and pore size.

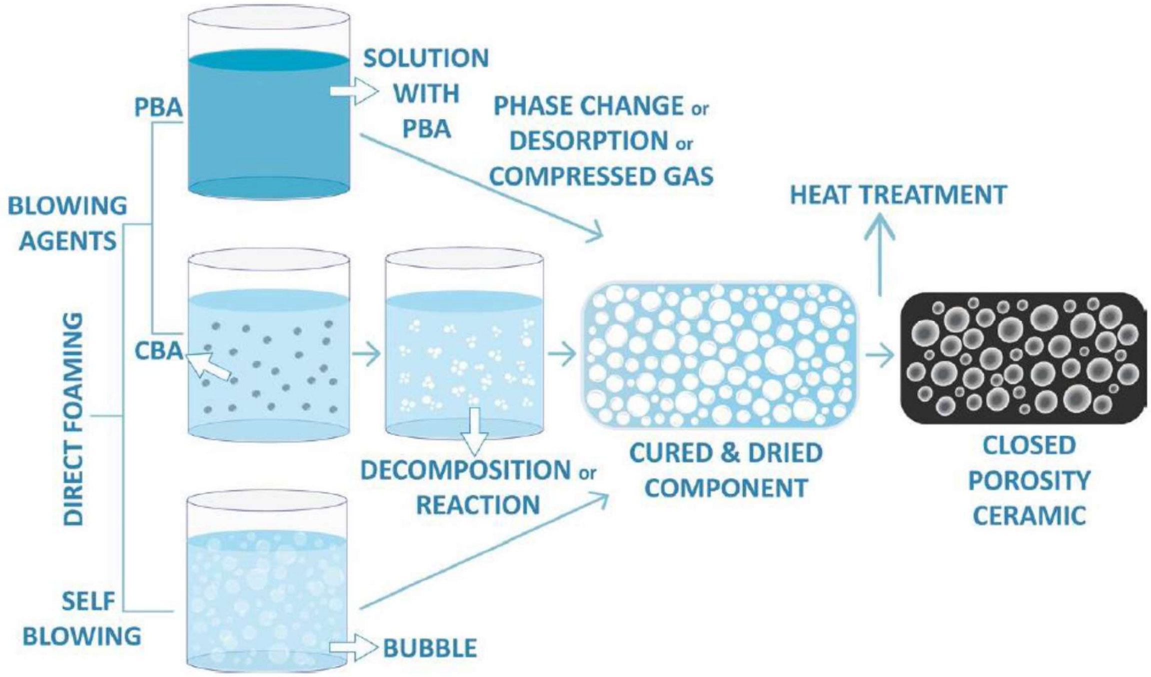

Fig. 2.7 Schematic of porous ceramic fabrication through direct foaming method [55]

In conclusion, the direct foaming technique offers a practical and efficient approach for producing macroporous ceramics with controlled porosities. It has advantages such as cost-effectiveness, rapid processing, and potential for mass production. Optimizing pore structures, including morphology, orientation, and distribution, remains a challenge. With further research and development, direct foaming can become a valuable technique for large-scale production of high-quality porous ceramics.

2.3.6 Gel-Casting Method

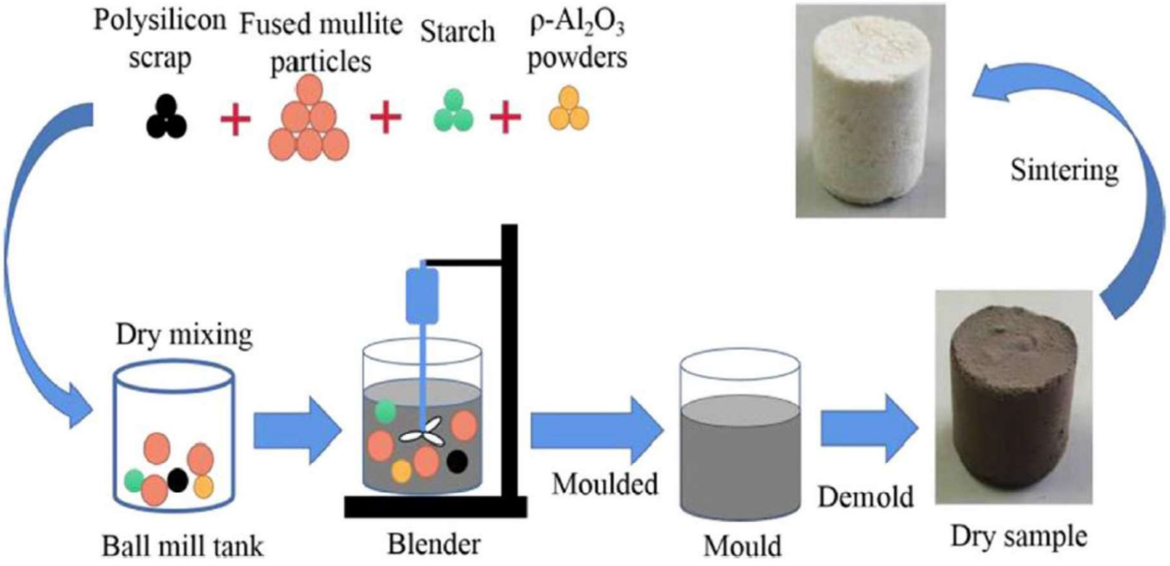

Fig. 2.8 Schematic of porous ceramic fabrication through gel casting method [56]

The gel casting method is a versatile technique employed in the production of porous ceramics. It involves dispersing a polymer into ceramic raw materials such as alumina, silicon carbide, silicon nitride, and zirconium. The process consists of multiple stages, including slurry preparation, gelling addition, degassing, casting, unmolding, drying, and rebinding (fig. 2.8). Success relies on achieving an appropriate powder suspension with desired rheological properties, solid loading, uniformity, and stability. The viscosity of the suspension is influenced by the amount of gelling agent and solid loading, with higher gelling agent content leading to increased viscosity. The gelling agent also acts as a dispersant and affects viscosity. Proper gelation time is crucial for the casting process. Pore formation is achieved by incorporating polymers, commonly starch, into the slurry to create high porosity, which is then targeted during dispersion in water. The pore formation mechanism differs from traditional methods, resulting in non-uniform density and pore arrangement in the ceramic body. Sintering, which removes the polymer, affects the crystal nucleation and growth, impacting properties like crystallinity, porosity, and compressive strength. To address toxicity concerns, low-toxic and non-toxic alternatives, including natural gels, binders, and gums, have been developed. Natural minerals and waste materials can also be utilized, offering advantages such as smaller pore diameters, increased strength, and better chemical stability. The gel casting method can additionally produce fine-pored ceramics with high specific surface area and exposed porosity by employing silica sol and gelling initiators. Overall, the gel casting method necessitates meticulous control of various parameters and has expanded its possibilities through the development of low-toxic and non-toxic methods and the utilization of natural and waste materials.

2.3.7 Additive Manufacturing Method

Porous ceramics with precisely customized architectures and controlled geometrical parameters, such as porosity, pore size, and pore interconnectivity, are highly desirable for advanced energy and environmental applications. Traditional manufacturing techniques have limitations in achieving such intricate designs. Additive Manufacturing (AM) technology, also known as 3D printing, offers a promising solution for fabricating precisely tailored porous ceramic scaffolds with complex shapes. This scientific note explores the basics of ceramic AM, the potential for porous ceramics production, and the challenges and opportunities in this emerging field. The integration of AM techniques with traditional ceramic fabrication methods to produce hierarchical porous ceramics is also discussed. The insights presented in this note pave the way for future advancements and applications of porous ceramics in diverse fields.

Ceramic AM faces unique challenges due to the extremely high melting point of ceramics and limited availability of suitable starting materials. Seven major AM methods have been utilized for ceramics, including Vat Photopolymerization (VP), Binder Jetting (BJ), Material Jetting (MJ), Powder Bed Fusion (PBF), Material Extrusion (ME), Sheet Lamination (SL), and Direct Energy Deposition (DED) (fig. 2.9). These methods are classified into direct and indirect methods based on the state of the starting materials (dry powder, liquid/slurry, or solid-state object).

While ceramics' brittleness demands tight control of the manufacturing process to achieve adequate mechanical strength, this inherent feature is advantageous for producing highly-open porous shapes. AM-fabricated porous ceramic scaffolds are mainly used in non-load or low-load bearing applications. However, the layered structure of AM-produced ceramics can improve compressive strength due to a progressive failure mechanism. Potential applications of porous ceramics in bioengineering, including bone substitutes, implants, and orthopaedic prostheses, are explored.

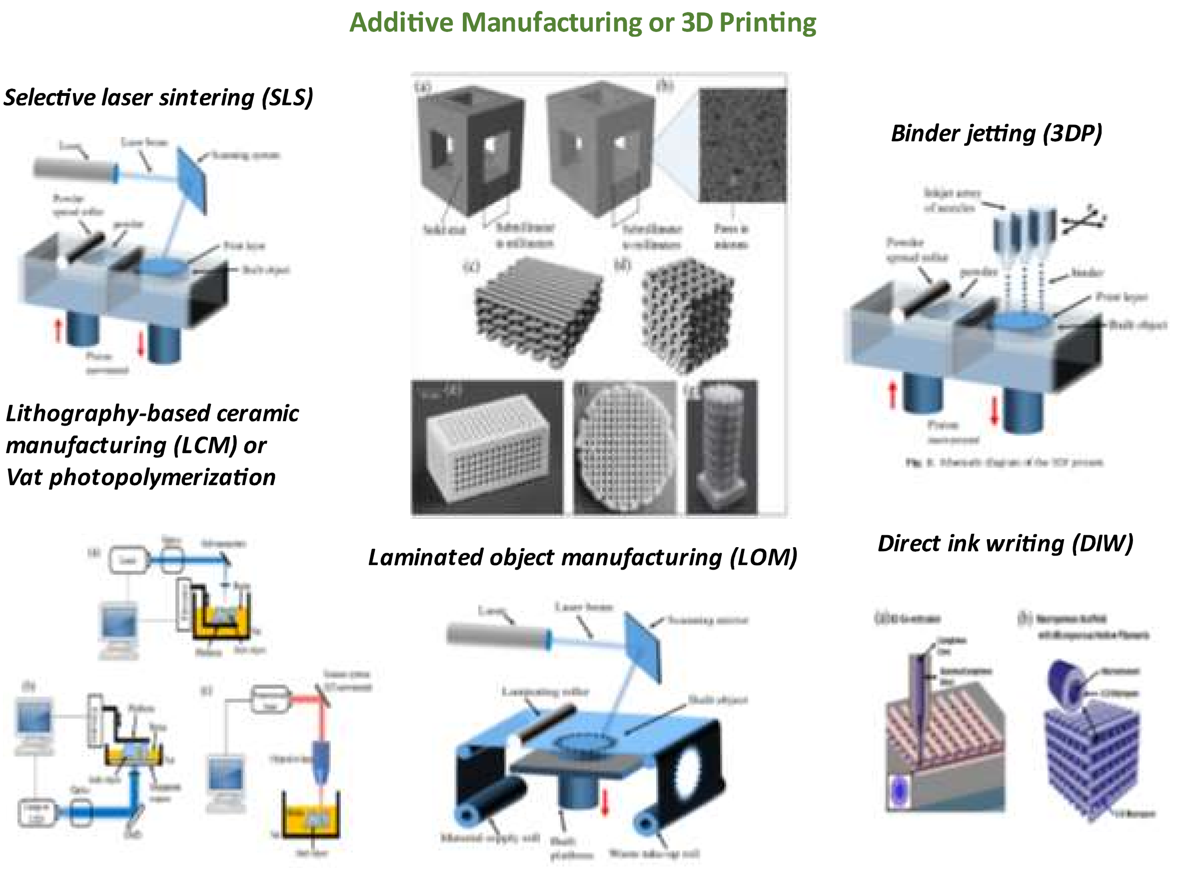

Fig. 2.9 Different additive manufacturing process to fabricate porous ceramics [57]

Despite significant advancements in AM technology for ceramics, challenges persist. These include dimensional accuracy, surface finishing, limited selection of printable materials, and the need to reduce pore size to the nanoscale for specific applications. Additionally, establishing the relationship between porosity, pore geometry, and mechanical properties requires further investigation. Moreover, cost-effectiveness remains a concern for mass production.

2.4 Research Progress in Thermo-Foaming Technique

Section 2.3.5 presented the methods involved in creating porous ceramics using the direct foaming technique. Foaming can be achieved through mechanical agitation or by using blowing agents. Mechanical agitation is typically carried out at room temperature by frothing the ceramic, but it is not discussed in this section. Instead, the focus is on the development of porous ceramics using blowing agents. Blowing agents are substances intentionally added to mixtures (such as polymers or ceramics) to generate gas and create a porous structure. Blowing agents possess specific desirable characteristics, including minimal impact on ozone depletion and global warming, good storage stability, controlled gas release based on time and temperature, low toxicity and odor during decomposition, non-flammability, the ability to create uniform and stable cells, a low-boiling point, and cost-effectiveness [58]. These agents are generally classified into two types: physical blowing agents and chemical blowing agents. Chemical blowing agents generate gas through self-decomposition or reactions with other compounds, while physical blowing agents produce gas through physical transformations like volatilization, desorption of dissolved gases under high pressure, or the direct utilization of compressed gases such as nitrogen (N_2) or carbon dioxide (CO_2). For instance, the utilization of pentane as a blowing agent has been employed to fabricate zirconium carbide (ZrC) ceramics with closed porosity and exceptional thermal stability [59].

The thermo-foaming technique is a widely employed method for producing porous structures, primarily achieved through the use of chemical blowing agents. Throughout history, humans have utilized chemical blowing agents to obtain solid materials with closed or partially closed porosity, as demonstrated in the well-known example of bread-making [60]. During the hydration of wheat flour, yeast and bacteria initiate the fermentation process, generating alcohol, organic acids, and CO_2 gas. These gases become trapped within the viscoelastic gluten network during both fermentation and baking processes [61]. In materials science, chemical blowing agents induce gas formation through thermal decomposition and/or chemical reactions with other components.

2.5 Materials in Porous Ceramic Fabrication

Porous ceramics are fabricated using a variety of materials to achieve specific properties and functionalities. The choice of materials plays a crucial role in determining the performance and characteristics of the resulting porous ceramics. Several materials are commonly used in the fabrication of porous ceramics, each with its unique advantages and applications.

One widely used material is alumina (Al_2O_3), which offers high temperature stability, excellent mechanical strength, and chemical resistance. Alumina-based porous ceramics are often utilized in applications requiring thermal shock resistance and corrosion resistance, such as hot gas filtration and high-temperature catalysis.

Silicon carbide (SiC) is another popular material known for its exceptional mechanical properties, high thermal conductivity, and chemical inertness. Porous ceramics made from SiC find applications in harsh environments, including filtration systems for aggressive chemicals and high-temperature gas filtration.

For specific biomedical and bioengineering applications, bioactive ceramics such as hydroxyapatite (HA) and bioglass are used. These materials have excellent biocompatibility, allowing for bone tissue engineering, dental implants, and drug delivery systems.

Zirconia (ZrO_2) is favored for its high strength, toughness, and resistance to thermal shock. It is commonly employed in applications where mechanical reliability and wear resistance are crucial, such as cutting tools, wear-resistant parts, and membranes for fuel cells.

Other materials used in porous ceramic fabrication include titania (TiO_2), mullite (3Al2O3·2SiO2), and various clay-based ceramics. Each material offers specific properties that are tailored to meet the requirements of different filtration applications.

In recent years, researchers have also focused on developing innovative materials and composites to enhance the performance of porous ceramics. For example, incorporating carbon-based materials or polymers into ceramic matrices can improve filtration efficiency and provide additional functionalities, such as adsorption capabilities.

In conclusion, the selection of materials in porous ceramic fabrication is crucial for achieving the desired properties and performance of the final product. The diverse range of materials available allows for customization and optimization of porous ceramics for various applications, including filtration systems in industries such as environmental, energy, biomedical, and chemical sectors. Ongoing research aims to explore new materials and composites, pushing the boundaries of porous ceramic fabrication and further expanding their applications in filtration and beyond.

2.5.1 Industrial Solid Waste-Rich Source for Ceramic Fabrication

Industrial solid waste, generated by various manufacturing processes, presents an abundant and underutilized resource for ceramic fabrication. The incorporation of industrial solid waste in ceramic production not only offers an eco-friendly approach to waste management but also contributes to the development of sustainable materials.

Numerous industrial solid wastes, such as fly ash, slag, red mud, and rice husk ash, exhibit pozzolanic or ceramic-forming properties that can be harnessed in ceramic fabrication. These waste materials contain valuable components, including silica, alumina, and other oxides, which can serve as raw materials for the production of porous ceramics.

Incorporating industrial solid waste into ceramic formulations offers several advantages. First, it reduces the dependence on traditional raw materials, thereby conserving natural resources and reducing the environmental impact associated with their extraction. Second, the use of waste materials can enhance the properties of ceramic products. For instance, the addition of fly ash can improve the mechanical strength and thermal stability of ceramics.

Moreover, the utilization of industrial solid waste in ceramic fabrication contributes to waste reduction and promotes a circular economy. By converting waste materials into valuable ceramic products, the overall waste generation and disposal burden are reduced. This approach aligns with the principles of sustainable development and resource conservation.

However, the successful incorporation of industrial solid waste in ceramic fabrication requires careful characterization and processing. Proper treatment, including grinding, sieving, and purification, is necessary to ensure the removal of impurities and achieve consistent quality in the final ceramic products. Additionally, the optimization of processing parameters, such as sintering temperature and dwell time, is crucial to achieve the desired properties in the ceramics while maintaining a sustainable approach.

Overall, the utilization of industrial solid waste as a rich source for ceramic fabrication offers a sustainable and cost-effective solution, transforming waste into valuable materials. This approach holds great promise in promoting environmental stewardship and advancing the development of sustainable ceramic products.

2.6 Coal Overburden Waste- A Threat to Ecology & Environment

The ever-growing demand for power generation due to heavy power consumption worldwide leads to severe pressure on available energy resources. Being the world's most abundant fossil fuel, coal is still the most used and low-cost source of power generation. In India, 70 % of total electric production is produced from coal [62]. Considering geo-mining conditions and cost-effectiveness, open-cast is most preferred mining process [63], and in a country like India, it accounts for 80-90% of total coal production, [64]. The waste materials generated during the extraction of coal in an open-cast are a mixture of rock and soil and contain different types of minerals, widely known as MW [65]. It was reported that for 623 Mt of coal production, around 1870 Mt of MW was extracted in 2001-2002 in India (IBM, 2001). It was found that such an amount of coal extraction requires 60 km^2 of land per year and around 75 km^2 of land for dumping the disposal [66,67]. Study reports that 1493 Mt of MW was generated in India in the year 2005-2006, and due to the growing energy demands, this volume is anticipated to increase in further years.

Management of such a massive amount of extracted coal overburden waste (Mining waste; MW) is a difficult task for any coal industry and is not only a challenge to ecology and the environment but also the economy. Dumping MW in a big impoundment in the form of a cone-shaped heap may be the easiest way to handle such a huge amount but also associated with some serious concerns like heap instability which causes dam collapse and eventually affects the environment and ecology [68,69]. Additional noteworthy impacts associated with MW stockpile are acid drainage [70,71], land infertility, contamination of ground and surface water etc., due to material spreading through weathering and erosion. Oxidative weathering and water discharged from active and/or abandoned coal dumping areas of sulphides containing minerals such as pyrite is the major cause of acid drainage. This also increases the bio-availability of metals' ions e.g., Mn, Pb, Cu, Zn, and Fe, leading to ever-increasing health hazards with such dreaded diseases in the form of tumours and cancers. Ground and surface water near mine sites are also contaminated due to presence of mobile element ions such as Mg, Cl, Na, SO_4, and Ca, which salinizes water [72,73]. Effect of acid mine drainage on the soil of rice paddy and their productivity is assessed and found to be declined by 62% compared to non-contaminated land due to excess concentration of sulphur which reduces biomass and, subsequently grain yield [74]. Figure 2.10 visually presents the different environmental threats posed by coal MW.

In this industrialization era, valorization of waste has become the need and demand of the present world due to the reduction in the dumping area and the environmental risks associated with the dumping of waste [75–77]. However, MW management is an expensive and prolonged task which cannot be avoided. The only and best way to tackle this challenge is by adding value to waste management, following the trend of industrial ecology. Industries nowadays are focussing on recycling their waste into valuable products (closed loop cycles) as feed materials for other industries rather than just waste management (open loop systems) so that the overall impact of industrial and urban activities on the environment could be minimized simultaneously [78–80]. MW contains various minerals which are economically feasible, and given the appropriate environment, it could be reutilized [81,82]. This can best be achieved by recycling it as an industrial building material.

Fig. 2.10 Figure showing various threats possessed by coal overburden waste

Over the past several years, efforts have been made to address the challenges posed by MW waste. Banerjee et al. [83] found MW as a potential material for sub-ballast material in railway tracks. Bio-restoration provides another way to restore the productivity of degraded land. Vegetation enhances soil fertility and microbial activity, stabilizes soil erosion and improves the microclimatic conditions. Overburden deposits are recovered by tree species for stabilization, pollution control, and general visual aesthetic enhancement. Use of fly ash has also emerged as an excellent alternative for carrying revegetation along with selective plantations [84]. High acidic nature of MW due to the release of significant amounts of Ca, Mg, Fe and SO_4^{2-} thereby making drinking water unsafe. It has been suggested that use of zeolite and fly ash could be an alternate solution to reduce the acidity of MW, and so is the leachates [85].

According to the literature review, MW can be utilized in a variety of applications, including as filler in hot mix asphalt, underground mine filling material, ceramic and refractories, cement, bricks, concrete, raw geomaterials in construction, lightweight aggregates, paint and enamelling dyes, and many more [86–90]. However, the literature also acknowledges the challenge of dealing with the substantial stockpile of MW waste. To address this issue, there is a need for a concrete and practical solution that enables the mass conversion of MW waste through an economical and straightforward approach.

2.7 Research Gap

The preceding sections of this chapter have discussed diverse techniques for fabricating porous ceramics and ceramic foam composites, each with their own advantages and disadvantages. Among these methods, thermo-foaming has emerged as a versatile, cost-effective, and environmentally friendly process suitable for large-scale production. Despite significant research and advancements in thermo-foaming, there remains a research gap in the production of functionally graded ceramic foams. These foams would offer a one-step processing route and provide operational benefits such as low cost, ease of handling, precise control over material microstructure, and porosity. Additionally, there is a lack of technology that enables green machining of porous ceramics, which are too weak in their green stage to be machined. Green machining is crucial for shaping porous ceramics into complex geometries at a comparatively lower cost. The absence of such a technology further restricts the practical applications of porous ceramics in various industries.

Furthermore, the improper disposal of coal overburden waste poses significant environmental concerns, leading to contamination of water, soil, and air. The limited efforts taken to address this hazardous waste with minimal product formulations exacerbate the negative impact of coal mining. Consequently, there is a pressing need to develop methods that utilize coal overburden waste for the production of value-added products, mitigating its adverse effects on the environment.

Therefore, the research gap lies in exploring novel thermo-foaming techniques to fabricate functionally graded ceramic foams, and devising methods that enable green machining of porous ceramics. Additionally, there is a need to develop innovative approaches to utilize coal overburden waste efficiently, thereby reducing its environmental impact and generating value-added products.